

**RAPID THERMAL PROCESSING FOR PRODUCTION OF
CHALCOPYRITE THIN FILMS FOR SOLAR CELLS: DESIGN,
ANALYSIS, AND EXPERIMENTAL IMPLEMENTATION**

by

Robert J. Lovelett

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

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TABLE OF CONTENTS

LIST OF TABLES	xi
LIST OF FIGURES	xiii
ABSTRACT	xx
 Chapter	
1 INTRODUCTION	1
1.1 Background and Motivation	1
1.1.1 Photovoltaic Industry: History and Current Status	2
1.2 Thin Film and Chalcopyrite Photovoltaics	3
1.2.1 Advantages of Chalcopyrite Photovoltaics	5
1.2.2 Chalcopyrite Deposition	8
1.2.2.1 Elemental Co-evaporation	8
1.2.2.2 Precursor Reaction	9
1.2.2.2.1 Hydride Gas Processes	10
1.2.2.2.2 Elemental Chalcogen Vapor Processes	10
1.2.2.2.3 Chalcogen Pre-Delivery Processes	11
1.2.3 Challenges with Chalcopyrite Photovoltaics	12
1.3 Approach and Outline	12
1.3.1 Rapid Thermal Processing System Design	13
1.3.2 Reaction and Transport Modeling	13
1.3.3 Material and Device Characterization	13
1.3.4 Conclusions	14
1.3.5 Associated Projects and Other Applications	14

2	REACTOR DESIGN AND TEMPERATURE CONTROL	15
2.1	Introduction	15
2.1.1	Project Goals and Approach	15
2.2	Reactor Design Methods	16
2.2.1	Reactor Modeling: Finite Element Analysis	16
2.2.2	Energy Balances and Equipment Sizing	21
2.3	Temperature Control System Design	22
2.3.1	RTP Temperature Control Approaches	23
2.3.2	Control Hardware	24
2.3.3	Process Identification Experiments	25
2.3.3.1	Process Identification for Observer Design	25
2.3.3.2	Process Identification for Controller Design	26
2.3.4	Overview of Control Strategy	26
2.3.5	Heat Transfer Modeling	27
2.3.5.1	Lumped Parameter Temperature Model for Controller Design	28
2.3.5.2	Distributed Parameter Temperature Model for Observer Design	29
2.3.6	Observer Design Approach	32
2.3.7	Controller Design Approach	33
2.3.7.1	Controller Stability	35
2.3.7.2	Controller Monotonicity	36
2.3.8	Temperature Control System Results	37
2.3.8.1	Observer Implementation	37
2.3.8.2	Controller Implementation	38
2.3.8.3	Control System Performance	40
2.4	Reactor Operating Mode	40

2.5	Waste Treatment System Upgrade	44
2.5.1	Column Design Methods	44
2.5.2	Results and Discussion	47
2.6	Summary and Conclusions	48
3	A STOCHASTIC MODEL OF SELENIZATION AND SULFIZATION OF COPPER-INDIUM-GALLIUM PRECURSORS	49
3.1	Introduction	49
3.1.1	Project Goal	49
3.1.2	CuInGaSe ₂ Reaction Modeling	50
3.1.3	Stochastic Model Motivation	53
3.1.4	Stochastic Modeling Background	54
3.2	Model Development and Theory	56
3.2.1	Solution Algorithm	57
3.2.2	Relation to Physical Properties	61
3.2.2.1	Reaction Propensity	61
3.2.2.2	Adsorption Propensity	61
3.2.2.3	Desorption Propensity	62
3.2.2.4	Diffusion Propensity	63
3.3	Application to Cu(InGa)(SeS) ₂ film growth	64
3.3.1	Reaction Mechanism	64
3.3.2	Parameter Reduction	65
3.3.3	Composition Profile Prediction	68
3.3.4	Agglomeration Size Distribution	73
3.4	Summary and Conclusions	76
4	REACTION OF CuInGa PRECURSORS IN H₂Se AND H₂S . .	78
4.1	Introduction	78
4.1.1	Motivation	78
4.1.2	Challenges	78

4.1.3	Project Goals	79
4.2	Experimental Methods	79
4.2.1	Deposition Methods	80
4.2.2	Analytical Methods	80
4.3	Results and Discussion	81
4.3.1	Single Stage Reactions	81
4.3.2	Multistage Reactions	88
4.3.3	Thermal Spike Annealing Reactions	92
4.4	Reaction Modeling	95
4.5	Summary and Conclusions	96
5	REACTION OF SELENIUM-CAPPED PRECURSORS	98
5.1	Introduction	98
5.1.1	Project Goals	98
5.2	Experimental Methods	99
5.2.1	Film Deposition	99
5.2.2	Analytical Methods	99
5.3	Results and Discussion	101
5.3.1	Single Stage Production of $\text{Cu}(\text{InGa})(\text{SeS})_2$ Thin Films	101
5.3.2	Single Stage Production of $(\text{AgCu})(\text{InGa})(\text{SeS})_2$ Thin Films .	109
5.4	Reaction Modeling	118
5.5	Device Fabrication and Analysis	119
5.5.1	Fabrication Process and Cell Testing	122
5.5.2	Device Analysis	122
5.5.3	Empirical Device Optimization	124
5.6	Summary and Conclusions	126

6	SUMMARY, CONCLUSIONS, AND FUTURE WORK	128
6.1	Reactor Design and Effective Temperature Control	128
6.2	Stochastic Model of Thin Film Deposition	129
6.2.1	Future Work	130
6.3	Reaction of Precursors in Hydride Gases	130
6.3.1	Future Work	130
6.4	Reaction of Selenium-Capped Precursors	131
6.4.1	Future Work	131
	BIBLIOGRAPHY	133
	Appendix	
A	PARAMETER ESTIMATION AND VALIDATION FOR AGGLOMERATION DISTRIBUTION	151
B	RESPONSE SURFACE METHODS FOR AGGLOMERATION DISTRIBUTION	154
C	DEPTH PROFILE MEASUREMENT USING ENERGY DISPERSIVE X-RAY SPECTROSCOPY	155
C.1	Introduction and Project Goal	155
C.2	Approach	155
C.3	Results and Discussion	158
D	MODELING OF DOPANT CONCENTRATION IN CADMIUM TELLURIDE VAPOR TRANSPORT DEPOSITION PROCESS	160
D.1	Introduction and Project Goals	160
D.2	Model Development	161
D.3	Model Results and Discussion	163
E	PERMISSIONS	167

LIST OF TABLES

2.1	Composition measurements (in atomic ratios) for sample produced in the flow configuration (image of surface in Figure 2.14a. Substantial compositional nonuniformity is evident, most obvious in the chalcogen uptake fraction, $(\text{Se}+\text{S})/(\text{Cu}+\text{In}+\text{Ga})$	44
3.1	Activation energies from Avrami and parabolic reaction models for varying processes—different selenium sources and different precursor structures.	52
3.2	Reaction mechanism/lattice events for chalcopyrite production with values of baseline propensity constants (p). Propensity constants, as shown in Section 3.2.2, depend on the size of the lattice element, ℓ . In this example, $\ell = 100$ nm. Each reaction takes place between exactly two lattice sites; for accurate stoichiometry, Se and S sites are twice as number-dense, and chalcopyrite sites are half as number-dense as other species; <i>atomic</i> number density is therefore constant across lattice sites. For diffusion events, all pairs of species not shown here have baseline diffusion propensities of zero. Refer to Section 3.3.2 for justification of zero-valued diffusion propensities.	66
4.1	EDX composition measurements for samples produced with 1% H_2Se at 600 °C with varying dwell time.	81
4.2	EDX composition measurements from the back (Mo) side of the films for samples produced with 1% H_2Se at 600 °C with varying dwell time.	81
4.3	EDX spot measurements of composition on the feature and background for sample produced with 1% H_2Se at 600 °C and 5 minute reaction time.	83
4.4	EDX composition measurements for samples produced with 1% H_2Se at 500 °C with varying dwell time.	84

4.5	EDX composition measurements for samples produced using 2-stage process shown in Figure 4.7 with varying argon anneal time.	90
4.6	EDX composition measurements from sample produced using 3-stage process with 1 minute anneal in argon followed by 1.5 minute reaction in H ₂ S.	91
4.7	EDX composition measurements from samples produced using thermal spike process.	93
5.1	EDX measurements of composition from single stage reactions. . . .	102
5.2	Experimental design for analysis of silver incorporation. Block 1 is data from Section 5.3.1; it includes replicates with different ramp rates, found to be insignificant. All experiments were performed at 600 °C and with 10 minute reaction time. Ag represents mole percent Ag in precursor, Se denotes microns Se thickness, and H ₂ S denotes gas concentration.	112
5.3	XRF measurements of composition of films produced with varying selenium layer thickness, H ₂ S concentration, and Ag-content.	113
5.4	Composition ratios from front-side (FS) and back-side (BS) EDX measurements for Ag and Ag-free samples (samples were produced with 8 μm Se and 10% H ₂ S).	116
5.5	New substitution reactions to be included in the stochastic reaction model to account for post-reaction modification of the surface from H ₂ S.	119
5.6	Box-Behnken response surface design used to optimize process variables for device efficiency. The block variable represents precursor batch.	125
A.1	Results from MLE estimates and χ^2 tests of the negative binomial parameters from the agglomeration distribution data. There is no evidence to reject the null hypothesis that the model is adequate in any case. The thickness and composition values were selected to complete a face-centered cubic response surface design. For the “N/A” cases, the sample size was too small for the chi-square test to be valid, but the fit appeared good visually.	152

LIST OF FIGURES

1.1	Learning curve showing the price of modules vs total module shipments. Photovoltaic module prices have dropped more than an order of magnitude since their introduction. Data from [10].	3
1.2	Process flow diagrams for typical (a) silicon photovoltaic manufacturing process and (b) thin film photovoltaic manufacturing process. The thin film process is simpler and possibly lower cost than the silicon process. (Image courtesy of W. N. Shafarman).	4
1.3	Optical absorption vs. thickness for crystalline silicon and CIGS, showing that CIGS devices can be made much thinner than silicon wafers and still absorb nearly all above band gap radiation. (Image courtesy of W. N. Shafarman).	6
1.4	Band gap of a CuInSe_2 alloyed with aluminum, gallium, sulfur, and silver as a function of incorporation of alloyed element. (Image courtesy of W. N. Shafarman).	7
1.5	Typical device structure (substrate configuration) for a Cu(InGa)Se_2 solar cell. (Image courtesy of W. N. Shafarman).	8
2.1	Schematic of the geometry used for the thermal model. Boundary conditions are shown and d was varied using values of R , $2R$, and $3R$	17
2.2	Temperature in $^{\circ}\text{C}$ (a) and velocity in m/s (b) profiles for a cylindrical reactor with sample temperature $T=600^{\circ}\text{C}$ and $d = R$. .	19
2.3	Steady state heat dissipation as a function of temperature and reactor size.	20
2.4	Selenium evaporation rate as a function of surface position.	21
2.5	Photograph of the rapid thermal processing system showing the heat source (1000 W quartz halogen lamp), quartz reactor tube, and short-wavelength pyrometer for temperature measurement.	23

2.6	Schematic of reactor with control hardware and signal descriptions. Note that the thermocouple feedthrough is not available during process runs (which use corrosive gases), but can be used for process identification experiments with only inert gas.	24
2.7	Control block diagram illustrating our approach to surface temperature control.	27
2.8	Schematic showing energy fluxes on the sample and sample holder.	30
2.9	Simplified control block diagram where the hardware and observer dynamics are assumed to be fast enough to be neglected and the lumped parameter model is assumed sufficient to describe the process dynamics.	35
2.10	Lower plot: lamp power. Upper plot: pyrometer data (bottom surface temperature; solid line) and temperature sensitive lacquer data (top surface temperature; stars), with the observer predictions (top surface temperature estimates; dashed line). The “kink” at approximately 2 minutes corresponds to the point at which the measured temperature reaches the minimum of the pyrometer’s operating range (200 °C), and the pyrometer becomes active.	38
2.11	Surface temperature data from thermocouple and fitted lumped parameter model.	39
2.12	Limits of stability (a) and monotonicity (b) for a PII ² controller applied to the nonlinear, lumped parameter model at 480 °C.	41
2.13	Control system performance for: (a) 2 K/s ramp to 500 °C, (b) 2 K/s ramp to 600 °C, (c) 6 K/s ramp to 500 °C, (d) 6 K/s ramp to 600 °C. Temperature ramps start at 200 °C, the minimum of the pyrometers temperature range.	42
2.14	Scanned images of sample surface after reacting in the sample in the flow configuration (a) and the charge-and-react configuration (b). In most cases samples from the charge-and-react are visually more uniform.	43
2.15	Breakthrough curves with and without mass transfer limitations. The x-axis shows time and the y-axis shows normalized concentration at the exit of the tube.	45

2.16	Contour plot showing breakthrough times for varying the column dimensions using Calgon ST I X activated carbon. An operating week is defined as 40 hours. The star denotes the proposed column dimensions.	47
3.1	Ga profile produced from simulation of an H ₂ Se-only process. . . .	68
3.2	Profiles of Ga (a) and S (b) produced from simulation of an H ₂ Se+H ₂ S process.	69
3.3	Profiles of Ga (a) and S (b) produced from simulation of a selenium capped precursor in an H ₂ S atmosphere process, where the initial selenium thickness is four times the precursor thickness (<i>i.e.</i> 40 lattice sites, or four times the stoichiometric amount of selenium required)	71
3.4	Time evolution of composition of the reacting film for the reaction in (a) H ₂ Se only and (b) H ₂ Se and H ₂ S. Fractional composition is the fraction of occupied lattice sites, or volume fraction of the film. The intermediate phases, binary selenides and sulfides, are not shown but exist as a small volume fraction throughout the simulation.	72
3.5	(a)–(d) Agglomeration size distribution for CuGa after 10 s simulation time with no reactions/adsorption allowed, for the following compositions (Ga/(In+Ga)) and lattice thicknesses (in units of lattice sites), respectively: (a) 0.05, 4; (b) 0.05, 10; (c) 0.45, 4; (d) 0.45, 10. (e) MLE estimates (points) and fitted response surface for negative binomial random variable parameter p . (f) MLE estimates (points) and fitted response surface for negative binomial random variable r .	74
4.1	Plan view SEM images of samples produced with 1% H ₂ Se at 600 °C with dwell times of (a) 0 minutes, (b) 2 minutes, (c) 5 minutes, (d) 10 minutes, and (e) 20 minutes.	82
4.2	XRD pattern from a symmetric scan of samples reacted for 10 minutes at 600 °C with 1% H ₂ Se with identified peaks labeled. . . .	84
4.3	Plan view SEM images of samples produced with 1% H ₂ Se at 500 °C with dwell times of (a) 0 minutes, (b) 5 minutes, (c) 10 minutes. . .	85
4.4	XRD pattern from a symmetric scan of samples reacted for 10 minutes at 500 °C with 1% H ₂ Se with identified peaks labeled. . . .	86

4.5	XRD patterns of the chalcopryrite 112 peak from samples produced with 1% H ₂ Se at (a) 600 °C and (b) 500 °C and various reaction times.	87
4.6	Volume of gas, in units of reactor length, required to selenize fully a sample, assuming complete conversion, at ambient temperature and 600 °C.	88
4.7	Time-temperature profile of the 2- and 3-stage reactions using hydride gases. First stage is reaction in H ₂ Se; second is anneal in argon; third is optional reaction in H ₂ S; dashed lines show approximate cooling profiles.	89
4.8	Plan view SEM images of samples produced using 2-stage process shown in Figure 4.7 with (a) 2 minute and (b) 10 minute anneals in argon.	90
4.9	XRD pattern of the chalcopryrite 112 peak from samples produced using 2-stage process shown in Figure 4.7 with different stage 2 annealing time.	91
4.10	Plan view SEM image of film produced using 3-stage process with 1 minute anneal in argon followed by 1.5 minute reaction in H ₂ S. .	92
4.11	Plan view SEM images of films produced using thermal spike reaction process with (a) 0.5 and (b) 1.5 minute reactions.	93
4.12	XRD patterns from a symmetric scan of samples reacted using the thermal spike process for 0.5 and 1.5 minutes. The 0.5 minute sample contains mostly metallic precursor phases; the 1.5 minute samples shows unreacted InSe present in the film. Intensity is shown on a logarithmic scale to show the presence of phases with low concentration (InSe) more clearly.	94
4.13	Gallium profiles (points) resulting from simulation of an H ₂ Se+H ₂ S process using baseline simulation parameters (from Table 3.2) except for sulfur adsorption, which has a varying propensity constant. EDX measurements (horizontal lines, with length corresponding roughly to sampling depth) of Ga/(In+Ga) from samples produced with varying H ₂ S concentration.	96

5.1	Data and linear regression line of XRF-measured selenium thickness versus deposition time. A plot of the residuals vs. fitted values is inset; no structure remains, which, paired with a coefficient of variation approximately equal to unity, suggests the model is sufficient.	100
5.2	Normal probability plot of coded (<i>i.e.</i> , low value for each factor is -1; high values is +1) effects for (a) Ga/(In+Ga) and (b) S/(Se+S) used to determine which effects are significant in the absense of replicated experiments. Significant effects are labeled and Lenth's psuedo standard error is given.	103
5.3	Plan view SEM images of samples produced at high and low temperature and H ₂ S concentration.	104
5.4	XRD patterns from symmetric scans from four samples produced at varying reaction temperature and H ₂ S concentrations.	105
5.5	Time evolution of atomic composition ratios measured by EDX from samples produced at 600 °C with 5% H ₂ S concentration. The film appears to reach a steady state within 5 minutes	107
5.6	Time evolution of XRD patterns of samples produced at 600 °C with 5% H ₂ S concentration.	108
5.7	Time evolution of XRD patterns of the 112 peak of samples produced at 600 °C with 5% H ₂ S concentration. Positions of CuInSe ₂ and CuGaSe ₂ 112 peaks are shown for reference.	109
5.8	Normal probability plots of coded effects for EDX measurements of (a) Ga/(In+Ga), (b) S/(Se+S), and (c) Ag/(Cu+Ag). Significant effects are labeled (for (a) and (b), significance is determined by ANOVA using the 5% significance level and for (c) significance is determined graphically).	111
5.9	Normal probability plots of coded effects for XRF-measured Se/(Ag+Cu+In+Ga). Significant effects, identified by Lenth's method and using the 5% significance level, are labeled.	113
5.10	Plan view SEM images of samples produced at high and low selenium thicknesses and with and without Ag in the precursor (all produced with 10% H ₂ S).	114

5.11	Diffraction patterns of the chalcopyrite 112 peak of samples produced at high and low selenium thicknesses and with and without Ag in the precursor (all produced with 10% H ₂ S).	116
5.12	GI-XRD patterns with varying angles of incidence of chalcopyrite films produced from precursors with with (a) 4 μm Se cap and no Ag, (b) 8 μm Se cap and no Ag, (c) 4 μm Se cap and Ag, and (d) 8 μm Se cap and Ag. Insets show the position of the peak maxima as a function of incident angle (Note that the figures have different y-axis scales; all samples were produced with 10% H ₂ S).	117
5.13	Model predictions for composition profiles using (a-b) low S adsorption and Se layer, (c-d) high S adsorption and low Se layer, (e-f) low S adsorption and high Se layer, and (g-h) high S adsorption and Se layer.	120
5.14	A typical JV curve showing the maximum power point (V_{mp} , J_{mp}), short circuit current (0, J_{sc}), and open circuit voltage (V_{oc} , 0). The fill factor, FF , is the ratio of the area of the rectangle formed by the maximum power point (and shown in the figure) and the area of the rectangle formed by V_{oc} and J_{sc} .	121
5.15	JV curves of devices produced from films reacted with 4 μm Se caps, at 600 °C for 10 minutes and with (a) 1%, (b) 5.5%, and (c) 10% H ₂ S concentrations. Efficiency, V_{oc} , J_{sc} , and FF are shown for each device.	123
5.16	JV curve of the highest efficiency device obtained in this work that was produced using 1% H ₂ S, 4 μm Se and reacted at 587.5 °C.	126
C.1	Intensity of gallium K-L2 x-ray emission as a function of depth in film from Monte Carlo simulations (color curves) and fitted to Equation C.3 (black curves).	159
C.2	EDX-estimated depth profile with actual depth profile measured by a transmission electron microscopy (TEM) cross section. The parameter values fit to Equation C.7 are $z_{min} = 0.59$ μm, $C_{min} = 0.42$ g/cm ³ , $m_1 = -0.33$ g/(cm ³ μm), and $m_2 = 0.08$ g/(cm ³ μm).	159
D.1	Schematic showing single and dual enrichment zones for a CdTe VT deposition system with extrinsic dopants. Dopant is either Cd ₃ P ₂ or Cd ₃ Sb ₂ . Ampoule diameter is 1. cm.	161

D.2	Gas partial pressures (balance is argon) for Cd, Te ₂ and dopant species in a single zone configuration with the temperature profile across the enrichment zone shown. Dopant source is either (a) Cd ₃ P ₂ or (b) Cd ₃ Sb ₂ . The gas velocity is 0.1 m/s.	164
D.3	Gas partial pressures (balance is argon) for Cd, Te ₂ and dopant species in a double zone configuration with the temperature profile across the enrichment zones shown. Dopant source is either (a) Cd ₃ P ₂ or (b) Cd ₃ Sb ₂ . The gas velocities are shown.	165
D.4	Mole fraction of Cd, Te, and dopant atoms as a function of dopant zone temperature for (a) P doping and (b) Sb doping. For (a), CdTe zone temperature is 990 K with gas velocity of 0.05 m/s; dopant zone gas velocity is 0.001 m/s. For (b), CdTe zone temperature is 1100 K with gas velocity of 0.1 m/s; dopant zone gas velocity is 0.001 m/s.	166

ABSTRACT

The direct conversion of solar energy to electricity, or photovoltaic energy conversion, has a number of environmental, social, and economic advantages over conventional electricity generation from fossil fuels. Currently, the most commonly-used material for photovoltaics is crystalline silicon, which is now produced at large scale and silicon-based devices have achieved power conversion efficiencies over 25%. However, alternative materials, such as inorganic thin films, offer a number of advantages including the potential for lower manufacturing costs, higher theoretical efficiencies, and better performance in the field. One of these materials is the chalcopyrite $\text{Cu}(\text{InGa})(\text{SeS})_2$, which has demonstrated module efficiencies over 17% and cell efficiencies over 22%. $\text{Cu}(\text{InGa})(\text{SeS})_2$ is now in the early stages of commercialization using a precursor reaction process referred to as a “selenization/sulfization” reaction. The precursor reaction process is promising because it has demonstrated high efficiency along with the large area (approximately 1 m^2) uniformity that is required for modules. However, some challenges remain that limit the growth of the chalcopyrite solar cell industry including: slow reactions that limit process throughput, a limited understanding of complex reaction kinetics and transport phenomena that affect the through-film composition, and the use of highly toxic H_2Se in the reaction process.

In this work, I approach each of these challenges. First, to improve process throughput, I designed and implemented a rapid thermal processing (RTP) reactor, whereby the samples are heated by a 1000 W quartz-halogen lamp that is capable of fast temperature ramps and high temperature dwells. With the reactor in place, however, achieving effective temperature control in the thin film material system is complicated by two intrinsic process characteristics: (i) the temperature of the $\text{Cu}(\text{InGa})(\text{SeS})_2$

film cannot be measured directly, which leaves the system without complete state feedback; and (ii), the process is significantly nonlinear due to the dominance of radiative heat transfer at high temperatures. Therefore, I developed a novel control system using a first principles-based observer and a specialized temperature controller. Next, to understand the complex kinetics governing the selenization/sulfization processes, a stochastic model of solid state reaction kinetics was developed and applied to the system. The model is capable of predicting several important phenomena observed experimentally, including steep through-film gradients in gallium mole fraction. Furthermore, the model is mathematically general and can be useful for understanding a number of solid state reaction systems. Finally, the RTP system was then used to produce and characterize chalcopyrite films using two general methods: (i) single stage and multi stage reactions in H_2Se and H_2S , and (ii), reaction of a selenium “capped” precursor in H_2S , where selenium was deposited on the precursor by thermal evaporation and the use of toxic H_2Se was avoided. It was found that the processing conditions could be used to control material properties including relative sulfur incorporation, crystallinity, and through-film gallium and sulfur profiles. Films produced using the selenium-capped precursor reaction process were used to fabricate solar cell devices using a $\text{Mo/Cu(InGa)(SeS)}_2/\text{CdS/ZnO/ITO}$ substrate device structure, and the devices were tested by measuring the current-voltage characteristic under standard conditions. Devices with approximately 10% efficiency were obtained over a range of compositions and the best device obtained in this work had an efficiency of 12.7%.

Chapter 1

INTRODUCTION

In 2008, the United States National Academy of Engineering identified 14 “Grand Challenges for Engineering” for the 21st Century [1]. They recognized the key role to be played by engineers in the coming decades to solve complex global challenges. One of the Challenges is to “Make Solar Energy Economical.” Solar energy refers to the use of energy from the sun for human applications and technologies. While such technologies as solar water heaters, passive heating/cooling, and others have been developed for millennia—and are still important today—the largest challenge is to convert solar energy to electricity at low enough cost for widespread distribution and application. While there have been substantial cost reductions in recent years, the Department of Energy has set a goal of 0.06 \$/kWh for solar-produced electricity by the year 2020 [2]. The use of solar energy for electricity eliminates the need to produce electricity via combustion of fossil fuels, which has numerous adverse effects on humans and environments including a substantial contribution to global climate change [3]. The subject of this dissertation is the production of chalcopyrite thin films, in particular, Cu(InGa)(SeS)_2 via rapid thermal processing. Cu(InGa)(SeS)_2 is used as the absorber layer in thin film solar cells, which are promising devices that can be produced at low cost with high energy conversion efficiencies.

1.1 Background and Motivation

A comprehensive discussion of the physics governing the operation of photovoltaic devices is beyond the scope of this dissertation. In this section, however, I will first briefly review the history and current state of photovoltaic science, technology, and industry, which serves as motivation for the present work. Next, thin film

photovoltaic technology and the chalcopyrite absorber material $\text{Cu}(\text{InGa})(\text{SeS})_2$ will be discussed. Finally, while chalcopyrite materials have a number of advantages, including simple processing and high efficiency, I will discuss some of the key challenges that limit the market growth of chalcopyrites, and focus especially on the challenges addressed directly by this work.

1.1.1 Photovoltaic Industry: History and Current Status

The photovoltaic effect was first observed by Alexandre-Edmond Becquerel more than 150 years ago in 1839, where Becquerel observed that if two platinum electrodes were submersed in an acidic solution with silver chloride, separated by a membrane, and illuminated, current and voltage could be generated [4]. There were several incremental improvements in photovoltaic technology, however, until the development of quantum mechanics, there was no available theory to describe the behavior of these devices. These developments led to the first silicon solar cell, reported in 1941 by Russell Ohl [5], and to the first diffused junction solar cell (which remains today the most common device structure) invented at Bell Labs in the 1950s [6].

Since the early silicon solar cells, there have been gradual improvements in device efficiency, leading to the best silicon solar cells exceeding 25% efficiency [6, 7]. Along with these efficiency improvements, the cost of solar-produced electricity has dropped far enough that solar energy is no longer a niche product, but is rapidly becoming a major source of power for millions of people. Specifically, 7.3 GW of solar energy capacity was built in 2015 in the United States, accounting for nearly 30% of new electric capacity, more than any fossil fuel technology and second only to another renewable technology, wind energy, with 39% of new capacity [8]. The increasing rate of installation is enabled by the rapid reduction in module cost—module prices have followed an exponential learning curve as total shipments increase, with a decay exponent of -0.275 (see Figure 1.1). Although historically, the majority of the growth has been in silicon photovoltaics, there are several key challenges that favor alternative methods: the silicon manufacturing process is complex, energy intensive, and expensive

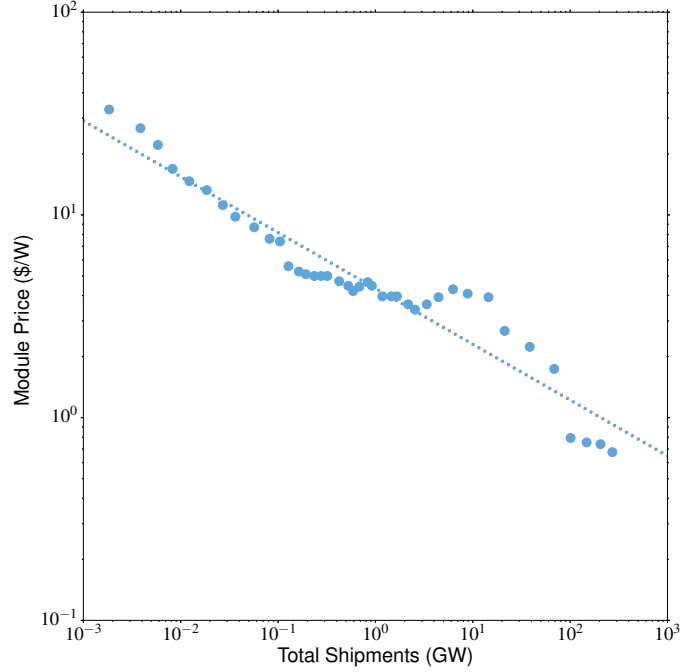


Figure 1.1: Learning curve showing the price of modules vs total module shipments. Photovoltaic module prices have dropped more than an order of magnitude since their introduction. Data from [10].

[9]; recent analysis has found that silicon alone is unlikely to remain competitive for long times [10]; and silicon cells have almost reached their fundamental efficiency limit [11].

1.2 Thin Film and Chalcopyrite Photovoltaics

The past decade has seen very rapid growth in solar energy, particular in silicon photovoltaics. However, silicon is limited by efficiency and a complex manufacturing process. Several alternative technologies have been researched; the second most mature technology (in terms of market penetration) is currently that of inorganic, polycrystalline thin films.

Thin film photovoltaics have some substantial advantages over crystalline silicon that could translate to lower cost solar electricity and allow for learning curve trend shown in Figure 1.1 to continue even as silicon reaches its efficiency limit. Thin

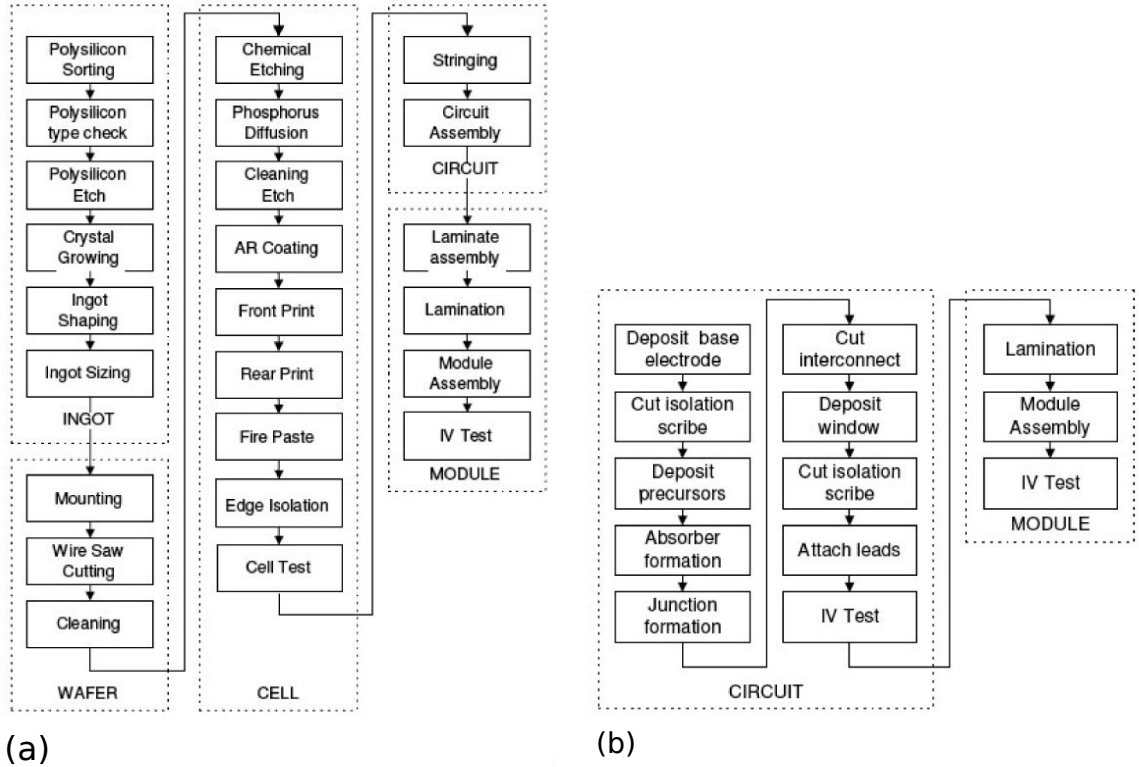


Figure 1.2: Process flow diagrams for typical (a) silicon photovoltaic manufacturing process and (b) thin film photovoltaic manufacturing process. The thin film process is simpler and possibly lower cost than the silicon process. (Image courtesy of W. N. Shafarman).

films are notable for their comparably simple, lower energy manufacturing process. Silicon processing requires a high energy crystal growth method (especially for the single crystals used in the highest efficiency devices), a wafering process with substantial material loss, and high temperature junction formation processes. In contrast, thin films use a series of material depositions at comparatively lower temperatures to fabricate the entire module. For comparison, typical silicon module and thin film module manufacturing processes are shown in Figure 1.2.

The simpler processing has been attractive and led to the study of a number of inorganic, polycrystalline semiconductors that could be used as thin film absorbers.

One of the first thin film solar cells to be studied in detail was a CdS/Cu₂S heterojunction device, with research dating back to the 1970s. Since then, three materials have been investigated most thoroughly and have seen some commercial success: a-Si, CdTe, and CuInSe₂. Now, CdTe is produced at large scale and is the largest component of photovoltaic module production (7% in 2014) except for crystalline silicon [12]. While CdTe has the largest market share, CuInSe₂ and its alloys have seen higher efficiencies and have tunable material properties that make them ideal for solar cell absorbers.

1.2.1 Advantages of Chalcopyrite Photovoltaics

CuInSe₂ is a chalcopyrite material with favorable properties for use in thin film semiconductors. It has been studied since the 1970s and, when alloyed with Ga and S, holds the record for the highest efficiency thin film solar cell with 22.3% [13]. Even very early in its development, chalcopyrite semiconductors showed very good performance and stability; one of the earliest devices (fabricated from a CuInSe₂ single crystal, whereas most modern devices are polycrystalline) from a group at Bell Labs was reported to have an efficiency of approximately 12% in 1975 [14].

Chalcopyrite materials have demonstrated this performance because of their underlying material properties. Several important properties are given below:

- Like other photo-absorbing thin film semiconductors, chalcopyrites are direct band gap absorbers, which results in very high optical absorption coefficients [15] (shown in Figure 1.3).
- Aluminum [16], gallium [17], sulfur [18], and silver [19] have all been alloyed with CuInSe₂ and can be used to tune the electrical properties, including the band gap (see [20] and Figure 1.4 for the relationship between composition and band gap).
- Cu(InGa)Se₂ absorber layers are very robust to composition changes; the Cu/(In+Ga) ratio can be varied from approximately 0.8 to 1.0 and high-quality devices can still be obtained [21].
- While chalcopyrites are usually polycrystalline with micron-sized or smaller grains, the grain boundaries are usually passivated and do not reduce device performance [22].

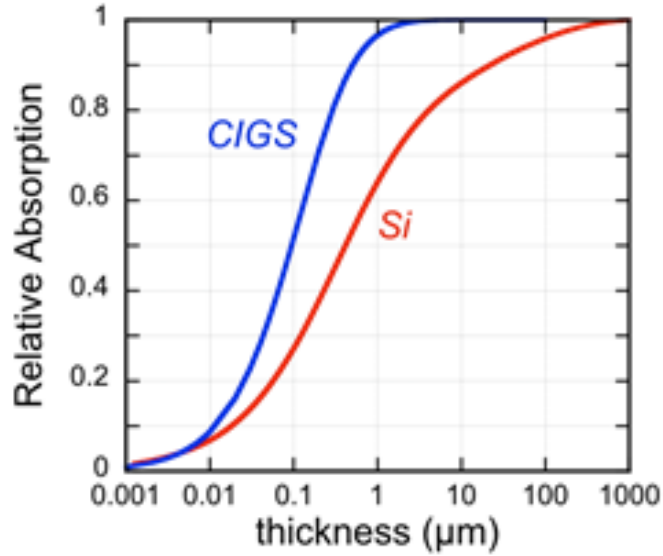


Figure 1.3: Optical absorption vs. thickness for crystalline silicon and CIGS, showing that CIGS devices can be made much thinner than silicon wafers and still absorb nearly all above band gap radiation. (Image courtesy of W. N. Shafarman).

- Inexpensive soda-lime glass (*i.e.*, common window glass) can be used as the substrate for chalcopyrite solar cells; at first, soda-lime glass was chosen to reduce cost [15], but it was discovered that sodium diffusion from the glass can substantially improve device performance [23, 24].
- The chalcopyrites described here show inherent p-type conductivity [25], so no external doping step is necessary to form devices.
- Resulting from lower temperature coefficients (*i.e.*, increasing temperature has a smaller effect on power output), field data has shown that chalcopyrite modules have greater performance ratios (*i.e.*, produce a greater fraction of their nominal capacity) than silicon modules [26].

These properties make chalcopyrites ideal materials for thin film solar cells. Aside from advanced, next-generation structures like tandem cells, most modern chalcopyrite devices use a common device structure, shown in Figure 1.5. The device is usually produced in substrate configuration (though there is some recent work developing superstrate-configured CuInGaSe_2 cells [27]), meaning that the active layers are

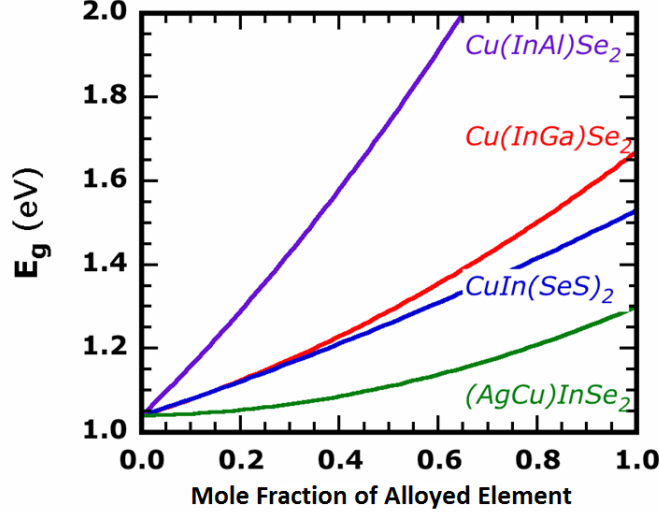


Figure 1.4: Band gap of a CuInSe_2 alloyed with aluminum, gallium, sulfur, and silver as a function of incorporation of alloyed element. (Image courtesy of W. N. Shafarman).

deposited on the substrate and that light enters from above this stack. The most common substrate material is soda lime glass [15], though flexible materials such as metal foils [28] or polyimide [29] have also been used and may be useful for scale-up with roll-to-roll processing [30, 31]. First, a back contact, most commonly molybdenum, and usually using sputtering, is deposited on the substrate. Next, the chalcopyrite absorber is deposited (absorber deposition methods will be reviewed in Section 1.2.2). After the absorber layer is deposited, a heterojunction is formed using an n-type buffer layer, most often CdS by chemical bath deposition [15], but ZnO and other materials have also been investigated to improve device current and eliminate toxic Cd from the device structure [32]. Next, a transparent conductive front contact is deposited, usually aluminum doped ZnO, is deposited [15]; an alternative (used in this work) is indium tin oxide (ITO). Finally, a current collecting grid (for research-scale cells) is deposited (commercial scale modules most often use monolithic integration, which eliminates the need for the grid [33]).

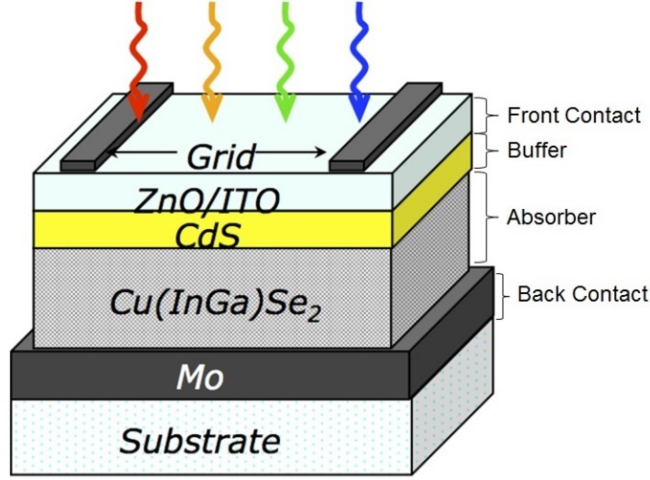


Figure 1.5: Typical device structure (substrate configuration) for a Cu(InGa)Se_2 solar cell. (Image courtesy of W. N. Shafarman).

1.2.2 Chalcopyrite Deposition

Many deposition methods have been studied for chalcopyrite absorbers, but the two most common ones can be classified as elemental co-evaporation or precursor reaction methods. Both of these methods have resulted in devices that have efficiencies exceeding 20% [13, 29, 34, 35, 36]. Materials produced in this work use precursor reaction methods, but both approaches will be briefly described here.

1.2.2.1 Elemental Co-evaporation

Elemental co-evaporation is a vacuum process where the film is grown from elemental sources. In these processes, the substrate is held at high temperature (roughly 450 °C to 600 °C) [15] so that the elements react to form chalcopyrite upon deposition. In its simplest form, each element is deposited simultaneously [37]; however, the best devices are usually fabricated from a multistage process, such as first depositing In, Ga, and Se, and then Cu and Se [38]. Today, the most common approach is a three-stage process, which is commonly used for Cu(InGa)Se_2 [36] and sometimes for $(\text{AgCu})(\text{InGa)Se}_2$ [39, 40] devices. In the typical three stage process, In, Ga, and Se are deposited first, followed by Cu, Ag (if included), and Se, and then In, Ga, and Se

are deposited again. The advantage of this approach is the formation of a “notched” composition gradient, resulting in a film with high band gap near the surface, a minimum band gap at some point in the film, and a positive linear band gap gradient toward the back of the film, which has been shown to produce high efficiency devices [41, 42]. These films with “notched” gradients were used to fabricate the first devices to reach approximately 20% efficiency [41], and their development has inspired much of the research in the precursor reaction method (which, until recently, had substantially lower record efficiencies), where control of composition gradients is more complicated.

1.2.2.2 Precursor Reaction

Today, the precursor reaction method accounts for the large majority of commercially available chalcopyrite solar modules, mostly due to the success of one company that has built over 1 GW of annual manufacturing capacity, Solar Frontier [43]. The precursor reaction method is a two-step growth method that is also referred to as selenization. Formation of chalcopyrites by precursor reaction dates to 1979 [44], where a CuInS_2 was formed by reacting a Cu-In film with H_2S . Now, there are many variations on the precursor reaction process, but they all follow two basic steps: (1) a precursor (usually Cu-In-Ga; though sometimes Se and/or S are included) is deposited at low temperature and (2) the precursor is reacted at higher temperature (450 °C to 600 °C), usually with a source of Se or S, to convert the film to single phase chalcopyrite. Precursor reaction processes can be roughly classified into three categories, or, in some cases, hybrids of these three processes: (1) hydrogen chalcogide (hydride) gas processes, (2) elemental chalcogen vapor processes, and (3) chalcogen pre-delivery processes.¹

¹ “Chalcogens” are defined as group 16 elements. For chalcopyrite photovoltaics, we are interested in selenium and sulfur.

1.2.2.2.1 Hydride Gas Processes

In hydride gas processes, a metal precursor is first deposited and then reacted with H_2Se and/or H_2S . These processes were the first precursor reaction processes studied [44], are the most common in industry today [43], and have yielded the highest efficiency devices among all thin film solar cells [13].

Several variations on this process have been studied, and the material properties of the resulting film, especially the through-film composition profile, depends on the specifics of the process. One common result, first observed by Jensen et al. [45], is that gallium tends to segregate towards the back contact. With the gallium segregated at the back of the film, the device performs much as a CuInSe_2 cell, with only a slight increase in voltage (46 mV from [45]) and nearly identical quantum efficiency curves. While homogenizing the film is possible, it requires a long, high temperature anneal, as shown by Marudachalam et al. [46] who used a 60 minute anneal at 600 °C. An alternative approach for improving the device voltage is to incorporate sulfur into the near surface region by post-treating the film with H_2S [47, 48]. A number of variations on the $\text{H}_2\text{Se}/\text{H}_2\text{S}$ process have been studied, including a three stage process (selenization–inert anneal–sulfization)[49] and a simultaneous $\text{H}_2\text{Se}/\text{H}_2\text{S}$ process [50], both of which produce more homogeneous films. Notice that these multistage processes tend to produce films with similar band gap profiles to the three-stage co-evaporated films described above: high sulfur at the front and high gallium at the back leads to a similarly “notched” band gap gradient.

1.2.2.2.2 Elemental Chalcogen Vapor Processes

An alternative to using H_2Se and H_2S gases is to replace the toxic hydrides with elemental chalcogen (Se and S) gases instead. Processes like this have been studied extensively by academic groups (likely to avoid the use of toxic gases), but because such processes have not produced as efficient devices, they have attracted less interest from industry. However, there has been some work on scale-up of selenium vapor

reaction processes, where forced convection was applied to fabricate devices with large area uniformity [51].

Cabellero and Guillen [52] studied the difference between CuIn and CuGa reactions with Se vapor; they found that the CuIn forms single phase CuInSe₂ at lower temperature and faster rate than CuGa forms CuGaSe₂ (their CuGa films never reached a single phase, though they attributed this to excess Ga). Moon et al. [53] observed the time evolution of the reaction of CuIn with selenium vapor; they observed a multistage process where In–Se phases formed quickly, then Cu–Se phases formed, and then film was converted to single phase CuInSe₂.

1.2.2.2.3 Chalcogen Pre-Delivery Processes

One final approach is to “pre-deliver” chalcogen to the film—in other words, Se or S are already included in the precursor, and the film needs only annealing to convert it to chalcopyrite. Most commonly, these processes use “rapid thermal processing” (RTP) to convert the chalcogen-containing precursor to chalcopyrite, where RTP is a term from the integrated circuit industry that refers to a process with rapid temperature ramps, usually from heat lamps or lasers [54].

One approach that has been studied in detail is the rapid thermal processing of a stack of elemental layers; a series of patents [55, 56, 57, 58, 59] describe the process, and it has been implemented on a commercial scale by Avancis GmbH (previously known as Shell Solar GmbH). In addition to stacked layers of pure elements, several alternative precursor structures have been studied. Some of these include InSe/CuSe bilayers [60], In₂Se₃/CuSe bilayers [61], and CuIn/Ga/Se precursors [62], as well as elemental stacks with S in place of Se [63]. One of the challenges with these methods is the volatility of elemental selenium—the Se layer must be supplied in excess and there is low material utilization.

1.2.3 Challenges with Chalcopyrite Photovoltaics

Chalcopyrite materials have already been shown to produce high efficiency devices, have multiple processing methods available, and, compared to silicon solar cells, are simple to manufacture. However, they still account for only a small fraction of total photovoltaic module production. There are still some key challenges that remain before chalcopyrite materials can be deployed at comparable scale to silicon (which has production capacities of 10s of GW per year [64]). One key limiting factor, should chalcopyrite photovoltaics become a mainstream source of energy, is the scarcity of indium [65]; at some point, more earth-abundant materials will have to be utilized in its place. However, alternative absorber layers are beyond the scope of this dissertation: I will focus on improving the most effective material currently available. Some of these challenges include slow reactions, the difficulty of controlling through-film material gradients, incomplete understanding of reaction kinetics/transport phenomena, and the use of extremely toxic H_2Se . By directly addressing these issues, this dissertation aims to help understand these challenges and offer pathways for overcoming them.

1.3 Approach and Outline

In this work, I will thoroughly investigate rapid thermal processing as a potential method for production of chalcopyrite absorber layers. I will focus primarily on the process design, simulation, and material characterization, and I will demonstrate that device quality films can be fabricated using this method. Here, I will describe the specific aims of this work, each of which correspond to a chapter of this dissertation. First, I will explain the system design and, especially, the temperature control system development. Next, a fundamentally novel reaction modeling method will be presented. Material characterization methods and results will then be reviewed. As the ultimate goal is a high-throughput process that yields high-efficiency devices, the next chapter will discuss device results. Finally, I will discuss two associated projects that, while not directly related to the goal of the dissertation, are important works toward improving thin film photovoltaic technology in general.

1.3.1 Rapid Thermal Processing System Design

To carry out the work required for this dissertation, first, either a commercial RTP system must be purchased, or a custom system designed and deployed. I opted to design and deploy a custom RTP system that was built as an extension to a quartz tube reactor already in use for selenization reactions.

In Chapter 2 of this dissertation, I describe the design process: first simple reactor models were constructed using material and energy balances, as well as finite element analysis methods. Equipment (primarily a quartz halogen heat lamp) was selected and deployed. The remaining challenge, however, was developing effective temperature control for the reactor. I designed a model-based control system using an observer to estimate state feedback and a proportional-integral-double integral controller for effective set point tracking. Finally in Chapter 1, I will discuss some operational details of the reactor, in particular the effect of different reactor configurations (batch vs. semibatch) and hazardous gas treatment.

1.3.2 Reaction and Transport Modeling

In Chapter 3, I present the core theoretical advance of this dissertation—a novel stochastic reaction model for solid state deposition systems—and apply the model to the chalcopyrite system. A description of the model and an efficient solution algorithm will be presented. I will show how transport phenomena and reaction kinetics couple to result in several different through-film composition profiles that are often observed experimentally. Additionally, the underlying stochastic nature of the model will be applied to model the agglomeration size distribution as a function of film thickness and composition.

1.3.3 Material and Device Characterization

In Chapters 4 and 5, I present experimental results and discussion relating to fabrication of chalcopyrite thin films using the RTP reactor described in Chapter 2. First (Chapter 4), I will discuss all-hydride gas processes, including single and multi

stage reactions. Then (Chapter 5), I will discuss a hybrid process: a selenium-capped precursor reacted in the comparatively less toxic H_2S . This selenium-capped process is, in some ways, similar to the industrial process developed by Avancis, GmbH. These films were found to be high-quality and were used to fabricate solar cell devices; device results are also presented in Chapter 5.

1.3.4 Conclusions

Finally, in Chapter 6, I will summarize the results, as well as offer conclusions about what was learned from this research, and suggest possible pathways for future work in the field.

1.3.5 Associated Projects and Other Applications

The work in the dissertation aimed to develop a rapid thermal processing method for production of high-efficiency chalcopyrite solar cells at high throughput. However, the applications of this work extend beyond this narrow scope. In particular, there were two associated projects completed as a component of this dissertation: (1) development of a method for measuring the through-film profile of a thin film using energy dispersive x-ray spectroscopy, and (2) modeling extrinsic dopant incorporation in CdTe deposition using vapor transport. These projects are described in Appendices C and D, respectively.

Chapter 2

REACTOR DESIGN AND TEMPERATURE CONTROL

2.1 Introduction

The overall goal of this dissertation is to design, implement, and analyze a rapid thermal processing (RTP) system for high-throughput production of chalcopyrite thin films. In this chapter, I will focus on the first of these projects: reactor design. An RTP reactor has been designed, implemented, and used to produce chalcopyrite films; here, I will show the design considerations and, importantly, the development of a robust temperature control system for the reactor.

2.1.1 Project Goals and Approach

Towards the development of a rapid thermal processing system for chalcopyrite production, three specific aims will be discussed in this chapter.

First, I will review reactor design considerations and how they were applied to design the RTP system. There are two key operating criteria for the RTP system: (1) the rate of temperature rise must be very rapid, and (2) the resulting films must have across-film uniformity. I will present results from Finite Element Analysis (FEA) models that offer insight into reactor design and I will present simple arguments from energy conservation equations to assist in sizing equipment.

Second, which constitutes the largest section of this chapter, I will design a model based control system that effectively tracks rapid temperature ramps required for this work. As I will show, there are two challenges associated with temperature control in this work: (1) full state feedback (especially the vital controlled variable, film temperature) is not measurable, and (2) the operating mode of the RTP reactor requires linear ramp rates, for which PID control is insufficient. To address these

problems, models with different levels of complexity will be developed and applied for design of an observer that provides the necessary state feedback and a controller that can track linear ramps in set points.

Third, I will discuss two reactor operation challenges that were encountered in this work, and how we overcame them. Specifically, I will examine the effect of two different reactor operating modes: a flow configuration, where hydride and carrier gasses flow continuously across the substrate, or charge-and-react configuration, which is similar to a conventional batch reactor that is charged with a certain concentration of gasses and heated to reaction temperature.

Finally, I will examine a possible future reactor upgrade: a redesigned hydride gas waste treatment method that uses only dry, activated carbon and does not require a large volume of corrosive NaOH solution.

2.2 Reactor Design Methods

2.2.1 Reactor Modeling: Finite Element Analysis

The purpose of the reactor models developed in this section are to understand some design concerns in a system with idealized, simplified geometry. First, I will develop a robust thermal model of a simple reactor; second, we will add mass transfer effects to describe the flow of selenium in the simplified reactor. To solve the PDEs that govern these processes, the COMSOL multiphysics software package is applied, which uses Finite Element Analysis (FEA). The substrate and substrate holder are modeled as a void in the reactor with edges held at constant temperature (although in [Section 2.3](#) we show that temperature is not constant, the assumption is appropriate for a preliminary model).

With the boundary conditions specified in [Figure 2.1](#), COMSOL uses FEM to

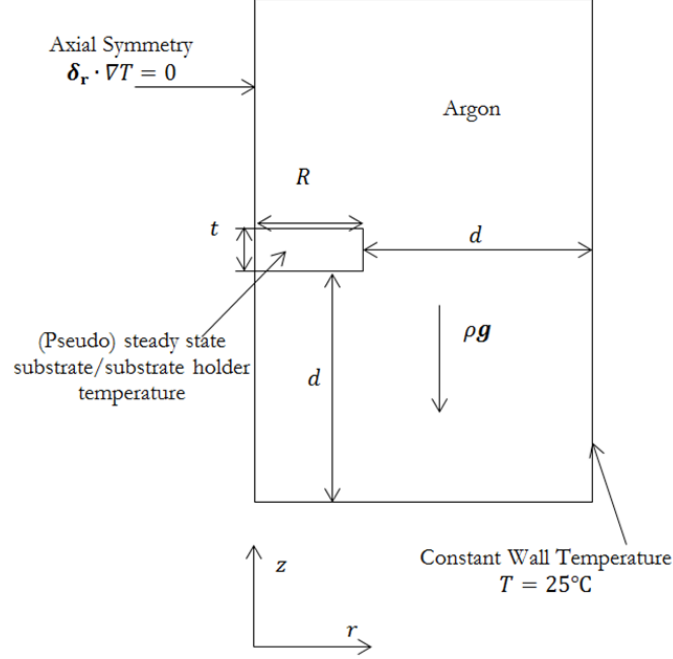


Figure 2.1: Schematic of the geometry used for the thermal model. Boundary conditions are shown and d was varied using values of R , $2R$, and $3R$

solve the steady state continuity, momentum, and energy equations:

$$\begin{aligned}
 \nabla \cdot (\rho u) &= 0 \\
 \rho(u \cdot \nabla)u &= \nabla \cdot [-P\delta + \mu(\nabla u + (\nabla u)^T) - 2/3\mu(\nabla \cdot u)\delta] + \rho g \\
 \rho C_p u \cdot \nabla T &= \nabla \cdot (k \nabla T)
 \end{aligned} \tag{2.1}$$

where u is the velocity, P the pressure, δ the Kronecker delta, μ the fluid viscosity, g the gravitational acceleration (9.81 m/s^2), and T the temperature. From these numerical solutions, temperature and velocity profiles can be generated, and useful properties can be calculated. Heat dissipation, a key system parameter, can be found by applying Fourier's Law for heat conduction and integrating over the surface of the substrate.

Having established a thermal model, it is informative to couple that model with mass transfer effects. In particular, when the reaction process uses a selenium capped precursor (a process that we investigate experimentally in Chapter 5), selenium will evaporate from the sample, and the rate of evaporation will affect the films that

are produced. To include selenium mass transport, the following species balance was coupled with the continuity, momentum, and energy equations above:

$$\nabla \cdot (-D_i \nabla C_i) + u \cdot \nabla C_i = 0 \quad (2.2)$$

where D_i is the diffusivity of selenium in the ambient gas (usually argon), and C_i is the concentration of selenium. Due to a lack of data available, an order of magnitude estimate of $0.01 \text{ cm}^2/\text{s}$ was chosen for the diffusivity. No flux boundary conditions are used on all surfaces except for the top surface of the substrate, for which a constant concentration condition is given. The assumption of local equilibrium, governed by Raoult's Law, was used to find the surface concentration; therefore, the partial pressure of selenium will be equal to its vapor pressure, or 0.297 bar at 600°C . Using this pressure, the ideal gas law gives a surface concentration of 4.145 mol/m^3 . Raoult's Law is valid for ideal gas and liquid mixture phases. While the assumption of an ideal liquid phase is valid—the liquid phase is a pure component—the ideal gas assumption is used with caution and is only reasonable because selenium is a dilute species.

Figure 2.2 shows the temperature and velocity profiles calculated by COMSOL for a reactor with a 600°C substrate temperature and wall distance $d=R$ (the smallest reactor examined). The velocity profile makes it clear that natural convection currents direct flow away from the substrate, meaning gas phase selenium delivery will present a challenge; as shown in Chapter 5, the most effective mechanism for controlling selenium delivery is to adjust the initial thickness of selenium. At lower temperatures and different reactor sizes, the results are qualitatively similar to those in Figure 2.2, the main difference being in the velocity magnitudes—it was found that velocity magnitude is greatest in large, high temperature reactors; suggesting that a small reactor volume would be preferable.

The FEA model can be used to determine the steady state heat dissipation in the reactor, which is important to determine an energy budget and could be important in sizing the equipment (though, as shown later in Section 2.2.2, the temperature ramp rate controls the minimum lamp power). Figure 2.3 shows the steady state heat

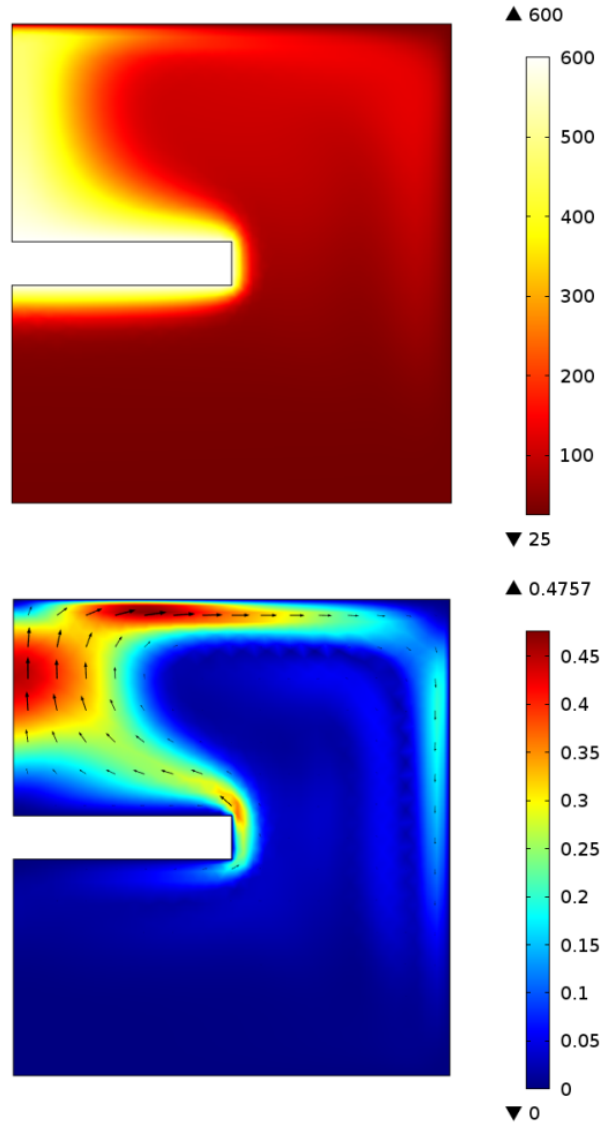


Figure 2.2: Temperature in °C (a) and velocity in m/s (b) profiles for a cylindrical reactor with sample temperature $T=600$ °C and $d = R$.

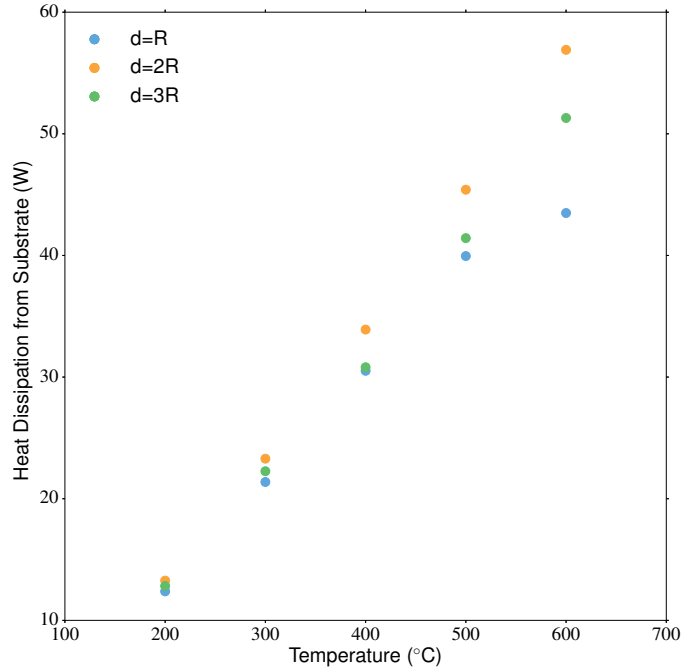


Figure 2.3: Steady state heat dissipation as a function of temperature and reactor size.

dissipation of the substrate as a function of temperature and reactor size, calculated by a surface integral of heat flux over the substrate. Observe that heat dissipation is greater in larger reactors, and that this effect becomes more pronounced at higher temperatures.

The mass transfer model can be used to simulate the *average rate* of selenium evaporation and the *uniformity* of selenium evaporation. The rate of selenium evaporation as a function of position is shown in Figure 2.4, and demonstrates an important consideration: selenium evaporation in this model system is highly non-uniform. The non-uniformity could result in a selenium gradient along the surface of the cell, which would be damaging for device performance. In Chapter 5, we will examine the selenium-capped reaction process experimentally and determine whether non-uniform evaporation presents a challenge.

In this section, I presented an FEA model of a simplified RTP reactor, and discussed some of the challenges associated with reactor design. It was observed that

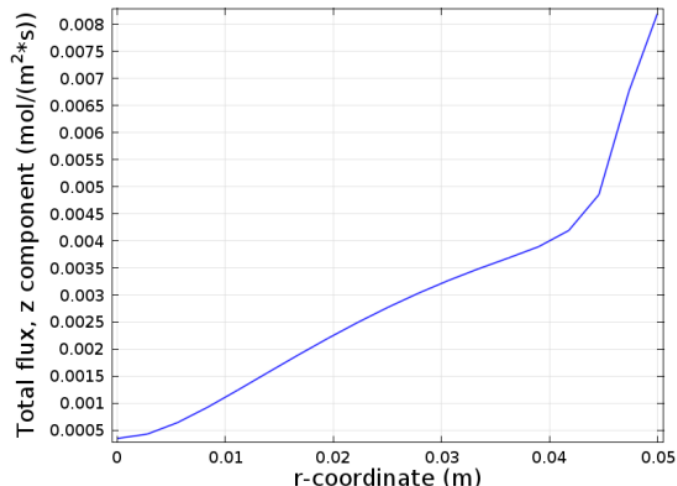


Figure 2.4: Selenium evaporation rate as a function of surface position.

heat dissipation will be relatively low and likely not a concern, but selenium evaporation will be an important consideration. These issues, especially non-uniformity challenges, will be considered throughout this dissertation.

2.2.2 Energy Balances and Equipment Sizing

Ultimately, due to current infrastructure already in place (hydride gas availability, waste treatment system) it was determined that the RTP system would be built as an extension to the existing selenization reactor at the Institute of Energy Conversion. In this section, first, the existing reactor will be described (for a more detailed description, refer to Varrin [66]), and second, energy balances will be used to size the heating equipment for the RTP reactor.

The reactor consists of a 2 inch quartz tube and has inlet gases of argon, hydrogen sulfide, and 16% hydrogen selenide in argon available. At the quartz tube outlet, there is a two stage waste treatment system with a sodium hydroxide gas absorption column followed by a base-impregnated activated carbon filter. The samples are 2.54 cm square pieces of soda lime glass with a thickness of 0.16 cm coated with thin Mo and Cu-In-Ga films (the thin films have negligible thermal masses and will not be

considered to size the equipment). Samples are held using a graphite susceptor with a volume of 0.013 cm³. For the RTP system, a quartz halogen lamp will be used to heat the sample to reaction temperature rapidly and a short-wavelength pyrometer used to measure the temperature.

The required heat lamp power is calculated by finding the total energy required to heat the sample and sample holder and normalizing by the desired ramp time.

$$P_{\text{lamp,min}} = \frac{((\rho C_p V)_{\text{glass}} + (\rho C_p V)_{\text{graphite}})\Delta T}{t_{\text{ramp}}} \quad (2.3)$$

The method is valid if the rate of heat dissipation (from Figure 2.3) is substantially less than the lamp power calculated here. Using a heat capacity 0.88 J/(g °C) for glass and of 0.71 J/(g °C) for graphite density of 2.53 g/cm³ for glass and 2.23 g/cm³ for graphite, a 60 s ramp time and reaction temperature of 600 °C, then considering that up to three samples may be used per reaction, the resulting power is 91.9 W.

In order to assure this performance, even after accounting for heat dissipation from the FEA models (which doesn’t include radiative losses that may be significant), we selected a 1000 W quartz halogen lamp to heat the samples. The lamp was purchased from Research, Inc (Model 5306B) and mounted directly above the quartz tube reactor. For temperature measurement, a short-wavelength pyrometer (Omega OS751, 200–1000 °C range) was purchased and mounted directly below the quartz tube (see photograph in Figure 2.5).

2.3 Temperature Control System Design

To deploy the RTP reactor, an effective temperature control system must be designed and implemented. In this section, I will show why an “off-the-shelf” control system would be inadequate, and how we overcame the particular temperature control challenges in this system. In this work, we will tackle the control problem directly: design a model-based observer and controller to overcome each of these challenges, respectively.

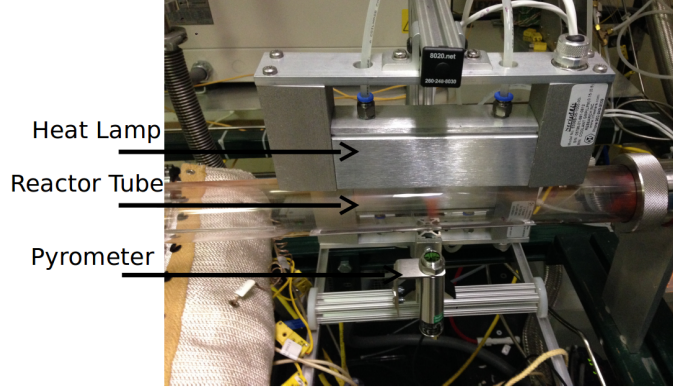


Figure 2.5: Photograph of the rapid thermal processing system showing the heat source (1000 W quartz halogen lamp), quartz reactor tube, and short-wavelength pyrometer for temperature measurement.

2.3.1 RTP Temperature Control Approaches

Rapid thermal processing (RTP) is a method wherein a material is rapidly heated using heat lamps or lasers and is most often used for silicon wafer processing in the integrated circuit industry. When used with silicon wafers, there are often even faster ramp times (several seconds) and higher temperatures ($>1000\text{ }^{\circ}\text{C}$) than are used in Cu(InGa)Se_2 fabrication; however, the premise and the challenges for effective temperature control are similar. Much of the literature concerning RTP temperature control focuses on *advanced instrumentation*, or designing specialized pyrometers that can adequately measure the temperature of interest [54, 67, 68, 69]; we take the alternative approach addressing the control problem *directly*, using conventional instrumentation but *designing advanced, model-based control systems* explicitly to achieve effective temperature control (which is similar in spirit to the approach of Cho et al. [70]).

First, consider the reactor design: a 1000 W quartz halogen lamp that directly irradiates the top surface (*i.e.* the thin film metallic precursor that is converted to chalcopyrite). For practical purposes, we are interested only in the surface temperature; not the temperature of the glass or the sample holder. As seen in Figure 2.5, however, only the bottom surface temperature can be measured directly. Second, consider the

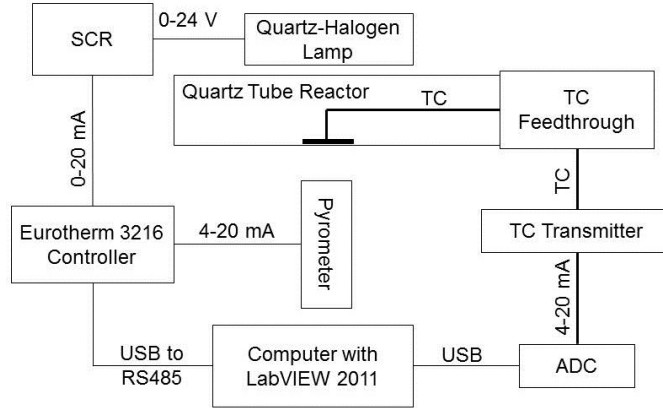


Figure 2.6: Schematic of reactor with control hardware and signal descriptions. Note that the thermocouple feedthrough is not available during process runs (which use corrosive gases), but can be used for process identification experiments with only inert gas.

control problem: in the RTP system, one of the key design variables is the temperature ramp rate. Conventional, proportional-integral-derivative (PID) control, however, cannot track ramp in the set point. At best, in linear systems, there will be a steady state offset; the situation is even worse in rapid thermal processing (whether for convention silicon wafers or for our chalcopyrite reactor), where nonlinearities from radiative heat transfer make the offset time-dependent. To meet these challenges, we propose a technique consisting of two components: (i) a nonlinear, model-based observer to provide real-time estimates of surface temperature, and (ii) a specialized controller with a double integral term that enables effective tracking of linear ramps in set point.

2.3.2 Control Hardware

Figure 2.6 shows a schematic of the quartz tube reactor with associated temperature control hardware. The back surface temperature is measured by an Omega OS-751 short wavelength pyrometer (with a 200–1000 °C operating range), and sent as an analog (4–20 mA) signal to the Eurotherm 3216 controller. Although this controller has built-in PID functionality, it is not used in this work; instead, it serves as a communication link between a Windows 7 computer running LabVIEW 2011 (where

a more complex control algorithm can be implemented) and the process actuator. From the specified desired set-point and the measured temperature transmitted by the Eurotherm controller, the LabVIEW-implemented control algorithm computes the desired lamp power, and transmits this control signal (via the Eurotherm controller) to a silicon controlled rectifier (SCR), which, in turn, actuates the power to the 1000 W quartz-halogen heat lamp (Research Inc., Model 5306B), thus completing the feedback control loop. It is important to note that the LabVIEW program can access and record temperature measurements directly from the process thermocouples *only* during the process identification experiments (as discussed in the following section), never during a process run, because of the corrosive atmosphere.

2.3.3 Process Identification Experiments

In this Section 2.3.4, we develop a physical model-based control strategy to track a linear set point ramp followed by a temperature dwell. However, because high-quality physical property data are not available for the reactor materials, we resorted to estimating model parameters from experimental data. Now, the two model-based control system components—observer and controller—have different operating objectives and hence different data requirements: for the observer, the objective is to provide highly accurate estimates of the surface temperature; for the controller, it is to ensure rapid and stable actuation of the heat lamp power robustly over a wide temperature range. Consequently, we designed two distinct sets of process identification experiments to generate the different data sets needed to design each component effectively.

2.3.3.1 Process Identification for Observer Design

To measure surface temperature accurately, which is vital for generating the data required to design the observer, we used a set of commercially available temperature sensitive lacquers with known melting points. The lacquers were applied with a brush to small regions on the surface of a precursor sample and the precursor sample was loaded into the reactor. The lamp power was then increased linearly from 0 W to 1000 W

at a rate of 100 W/min; pyrometer measurements were recorded each second and the melting times of each of the lacquers were recorded. The linear ramp in lamp power was chosen as the preferred input stimulus over the more conventional step changes in lamp power, in order to reduce the effect of local temperature inhomogeneity: the lacquers have higher absorptivity than the sample and a sudden increase in lamp power can cause it to heat faster than the rest of the sample and melt prematurely. Although the temperature sensitive lacquers provide highly accurate measurements, the data they provide is very sparse—at most, four temperature points during an experiment—which is sufficient for *observer design*, but may be insufficient for *controller design*, where finer resolution information on the process dynamics is crucial. Consequently, we also used thermocouples to provide nearly continuous surface temperature measurements.

2.3.3.2 Process Identification for Controller Design

Thermocouple junctions were formed by arc welding 36-gauge type K thermocouple wire; the junctions were cemented into 1-inch by 1-inch pieces of glass; the glass was loaded in to the reactor in place of the precursor sample. The thermocouple reading was considered as equivalent to the surface temperature measurement, with the caveat that there is systemic bias in the measurement, arising from two sources: (i) the bare glass surface properties (especially adsorption and emission) are different from those of the glass coated with precursor, and (ii) the thermocouple junctions cannot be placed exactly at the surface. A series of step changes of varying magnitudes were performed and the temperature response from the pyrometer and thermocouple measurements was recorded every second.

2.3.4 Overview of Control Strategy

My proposed control system for an RTP reactor is shown in the block diagram in Figure 2.7, where the controlled variable is the surface temperature ($T(L, t)$), and the manipulated variable is the heat lamp power ($u(t)$). The task of designing and implementing an effective controller is complicated by (i) the nonavailability of online

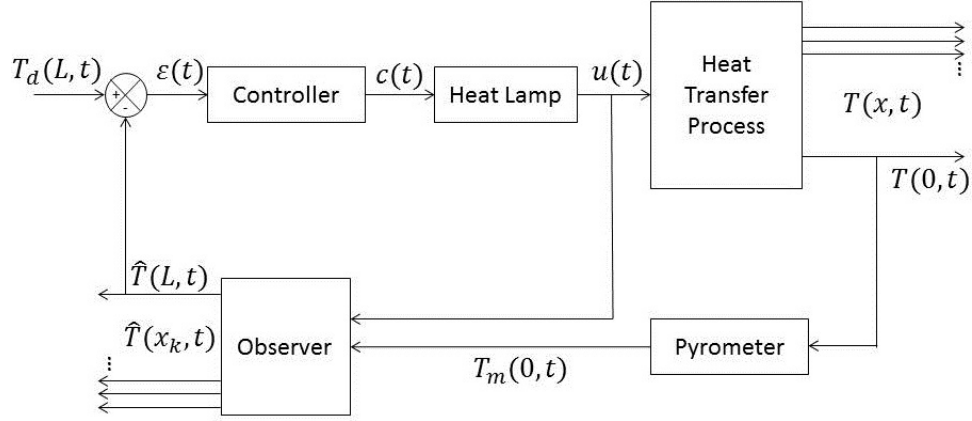


Figure 2.7: Control block diagram illustrating our approach to surface temperature control.

surface temperature measurements, necessitating the implementation of an observer to provide estimates of the desired information and (ii) the difficulty of tracking a linear ramp set point, especially for an intrinsically nonlinear process. In what follows, I describe our approach to modeling the heat transfer process (Section 2.3.5) and designing the observer (Section 2.3.6) and controller (Section 2.3.7). The other blocks in Figure 2.7, the heat lamp and pyrometer (described in Section 2.3.2, are simple hardware components with negligible dynamics.

2.3.5 Heat Transfer Modeling

Model-based controller design (especially in a feedback control configuration) does not require a highly accurate process model, only one that captures the essential dynamics of the relevant aspect of the process in question—in this specific case, the response of the sample surface temperature to changes in heat lamp power. Consequently, I developed a lumped parameter temperature model, treating the substrate and graphite substrate holder as a single control volume. Conversely, to be effective, the observer design requires a higher-fidelity temperature model, since our application requires fairly precise and accurate estimates of the unmeasured surface temperature.

Therefore, for the observer design and implementation, I developed a distributed parameter model, a partial differential equation capable of representing time and spatial variations in temperature explicitly. I describe first the development of the lumped parameter model and subsequently add the complexity of a distributed spatial domain.

2.3.5.1 Lumped Parameter Temperature Model for Controller Design

The lumped parameter temperature model shown in Equation 2.4 arises from a dynamic energy balance over the control volume, which defined in this case as the substrate and substrate holder. The energy input is heat from the lamp and the outputs are convective and radiative heat losses, described by Newton's Law of Cooling and the Stefan-Boltzmann law, respectively:

$$\rho C_P V \frac{dT}{dt} = P(t) \xi \bar{\alpha} A_{lighted} \frac{P_{max}}{100} - h(T - T_{gas}) A_{sample} - \sigma \bar{\epsilon} A_{sample} (T^4 - T_{surr}^4) \quad (2.4)$$

The left hand side represents the rate of change of energy accumulation in the control volume: ρ is average density of the control volume, C_p is the average heat capacity, V is the volume, T is the temperature, and t is the time. The first term on the right hand side is energy input from the lamp, where $P(t)$ is the percent of maximum lamp power, ξ is the lamp efficiency (assumed constant) $\bar{\alpha}$ is the average absorptivity of the surface, $A_{lighted}$ is the ratio of the sample area to the lamp area (thus, I assume that the radiation from the lamp is collimated), and P_{max} is the maximum lamp power (1000 W). The second term is convective heat loss, where h is a heat transfer coefficient, T_{gas} is the temperature of gasses flowing over the substrate, and A_{sample} is the area of the sample. The last term is the radiative heat loss, where σ is the Stefan-Boltzmann constant, $\bar{\epsilon}$ is the average surface emissivity, and T_{surr} is the temperature of the surroundings. The model is a first order, nonlinear ordinary differential equation which, upon straightforward algebraic manipulation, simplifies to:

$$\frac{dT}{dt} = AP(t) - BT - CT^4 + D \quad (2.5)$$

By defining deviation variables $y = T - T_0$ and $u = P - P_0$, where T_0 and P_0 are nominal steady state values of temperature and power, respectively, Equation 2.5 may be linearized using the first order Taylor series approximation of the nonlinear temperature term around the nominal value, to obtain:

$$\frac{dy(t)}{dt} = Au(t) - By - 4CT_0^3y(t) \quad (2.6)$$

Finally, Laplace transforms yield the standard transfer function model form:

$$y(s) = \frac{A/(B + 4CT_0^3)}{s/(B + 4CT_0^3) + 1}u(s) \quad (2.7)$$

Note that in this notation the domains of the variables are specified only through their arguments so that, for example, $y(t)$ is temperature (as a deviation from the nominal value) in the time domain; $y(s)$ is the same variable in the Laplace domain. Although the transfer function is linear, the parameters are *not* constant but depend nonlinearly on the nominal temperature: specifically, steady state gain $K = A/(B + 4CT_0^3)$, and time constant $\tau = 1/(B + 4CT_0^3)$, both decrease with increasing temperature. Consequently, the transfer function is in fact piece-wise linear, with state-dependent gain and time constant.

2.3.5.2 Distributed Parameter Temperature Model for Observer Design

The lumped parameter model from the previous section is coarse because it does not account for spatial variation. While this may be appropriate for controller design, an effective observer demands a higher fidelity distributed parameter model if it is to provide accurate estimates of surface temperature.

The governing partial differential equation (PDE) for the model is the heat equation in one spatial dimension:

$$\frac{\partial T(x, t)}{\partial t} = \alpha \frac{\partial^2 T(x, t)}{\partial x^2} \quad (2.8)$$

Here, $\alpha = k/(\rho C_p)$ is the thermal diffusivity, $x \in [0, L]$ is the spatial coordinate, and $T(x, t)$ is the temperature. (For simplicity, the bivariate argument of T is omitted

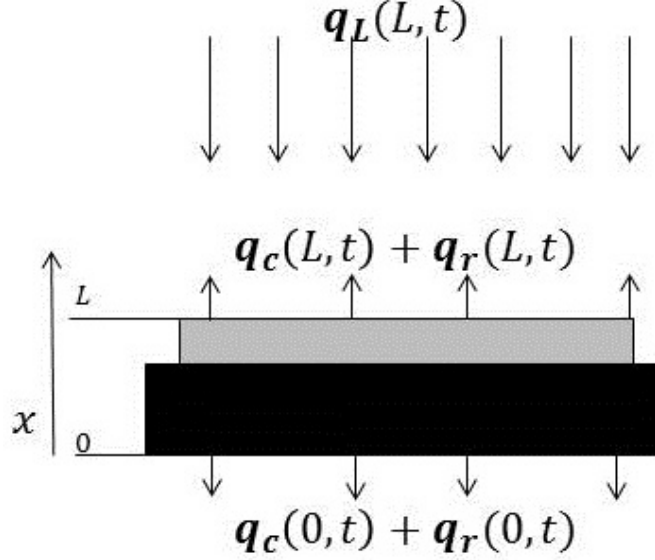


Figure 2.8: Schematic showing energy fluxes on the sample and sample holder.

hereafter). Boundary conditions are determined by writing interfacial energy balances at $x = 0$ and $x = L$, where I will equate the interior and exterior energy fluxes. The interior energy flux is given by Fourier's Law of Heat Conduction, $\mathbf{q} = -k\nabla T$ [71] and the exterior energy fluxes are shown in Figure 2.8, where $\mathbf{q}_L$ is the energy flux from the heat lamp, $\mathbf{q}_c$ is the convective heat flux, and $\mathbf{q}_r$ is the radiative heat flux. Therefore, the boundary condition at $x = L$ becomes:

$$-k \frac{dT}{dx} = q_c + q_r - q_L \quad (2.9)$$

where q_i (for $i = c, r$, or L) is the magnitude of $\mathbf{q}_i$. Substituting in expressions for each heat flux results in the following, at $x = L$:

$$-k \frac{dT}{dx} = h(T - T_{gas}) + \sigma\epsilon(T^4 - T_{surr}^4) - \frac{P_{max}\xi P(t)}{100A_{lighted}} \quad (2.10)$$

Convection is described by Newton's Law of Cooling, radiation by the Stefan-Boltzman Law, and the heat supplied by the lamp is assumed to be directly proportional to the power supplied to the lamp. Similarly, the boundary condition at $x = 0$ is:

$$k \frac{dT}{dx} = h(T - T_{gas}) + \sigma\epsilon(T^4 - T_{surr}^4) \quad (2.11)$$

I linearize the PDE and boundary conditions, which contain T^4 terms yielding, at $x = L$:

$$-k \frac{dT}{dx} = h(T - T_{gas}) + \sigma \epsilon (4T_0^3(T - T_0) - T_{surr}^4) - \frac{P_{max} \xi P(t)}{100 A_{lighted}} \quad (2.12)$$

And at $x = 0$, the boundary condition is:

$$k \frac{dT}{dx} = h(T - T_{gas}) + \sigma \xi (4T_0^3(T - T_0) - T_{surr}^4) \quad (2.13)$$

The PDE and boundary conditions may now be rescaled and non-dimensionalized as follows. First, assuming that the flowing gasses and the surroundings are at the same temperature, let $T_1 = T_{gas} = T_{surr}$. Next, define dimensionless temperature as $\Theta = \frac{T - T_1}{T_2 - T_1}$, where T_2 is a maximum temperature; dimensionless time is defined as $\zeta = tk/L^2 \rho C_p$; and the dimensionless spatial variable is $\eta = x/L$. These variable changes lead to the emergence of two dimensionless groups: (i) the Biot number, $Bi = \frac{hL}{k}$, which describes the ratio of convective to conductive heat transfer and (ii) the Stark number, $St = 4T_0^3 \epsilon \sigma L/k$, which describes the ratio of radiative to conductive heat transfer. The dimensionless form of the linearized distributed parameter model is:

$$\frac{\partial \Theta}{\partial \zeta} = \frac{\partial^2 \Theta}{\partial \eta^2} \quad (2.14)$$

At $\eta = 0$:

$$\frac{\partial \Theta}{\partial \eta} - (Bi + St)\Theta = -C_1 \quad (2.15)$$

At $\eta = 1$:

$$\frac{\partial \Theta}{\partial \eta} + (Bi + St)(\Theta - C_2 P) = C_1 \quad (2.16)$$

Where $C_1 = \sigma \epsilon L/k * (-3T_0^4 + 4T_0^3 T_1 - T_1^4)(T_2 - T_1)$ and $C_2 = \xi L P_{max} [100k A_{lighted}(T_2 - T_1)]$. A final change of variables allows homogeneous boundary conditions to be obtained. If $\Theta^* = \Theta(Bi + St) + C_1$ is defined, then:

$$\frac{\partial \Theta^*}{\partial \zeta} = \frac{\partial^2 \Theta^*}{\partial \eta^2} \quad (2.17)$$

At $\eta = 0$:

$$\frac{\partial \Theta^*}{\partial \eta} - (Bi + St)\Theta^* = 0 \quad (2.18)$$

At $\eta = 1$:

$$\frac{\partial \Theta^*}{\partial \eta} + (Bi + St)(\Theta^* - C_2 P) = 0 \quad (2.19)$$

This PDE with boundary conditions is used to design the observer. T_1 and T_2 will be set to 298.15 K and 873.15 K, respectively. Although the boundary conditions were linearized, the parameters C_1 and St are recalculated at each time point using the pyrometer measurement as T_0 so that they are not constant, but time varying; essentially, a nonlinear time invariant systems is approximated as linear, time variant, state-dependent system.

2.3.6 Observer Design Approach

The purpose of the observer is to provide online estimates of unmeasured process variables based on known measurements and control action [72, 73]. In our system, the controlled variable—the surface temperature—cannot be measured during process runs; what is available for measurement instead is the temperature of the bottom of the graphite sample holder. An observer based on the fundamental physics of the heat transfer process is designed to provide estimates of the surface temperature from the available measurements, using the distributed parameter temperature model described in Section 2.3.5.2. Following the approach presented by Smyshlyaev and Krstic [74] for parabolic PDEs with boundary sensing and boundary control, the following observer equations can be designed using Equations 2.17–2.19, the non-dimensional, linear, time variant PDE that we used to model the system:

$$\frac{\partial \hat{\Theta}^*}{\partial \zeta} = \frac{\partial^2 \hat{\Theta}^*}{\partial \eta^2} + p_1(\eta)(\Theta^*(0, \zeta) - \hat{\Theta}^*(0, \zeta)) \quad (2.20)$$

At $\eta = 0$:

$$\frac{\partial \hat{\Theta}^*}{\partial \eta} - (Bi + St)\hat{\Theta}^* = p_{10}(\Theta^*(0, \zeta) - \hat{\Theta}^*(0, \zeta)) \quad (2.21)$$

At $\eta = 1$:

$$\frac{\partial \hat{\Theta}^*}{\partial \eta} + (Bi + St)(\hat{\Theta}^* - C_2 P) = 0 \quad (2.22)$$

where $\hat{\Theta}^*$ represents the observer estimates of the “true” scaled temperature, Θ^* , $p_1(\eta)$ and p_{10} are observer gains, and $(\Theta^*(0, \zeta) - \hat{\Theta}^*(0, \zeta))$, the so-called “innovation” term,

is the difference between the actual dimensionless pyrometer measurement and its estimate. For this specific application, the observer gains are derived, as indicated by Smyshlyaev and Krstic [74], such that the observer error evolution satisfies a Klein-Gordon type PDE which converges exponentially to zero, ensuring observer stability; the results are:

$$\begin{aligned} p_1(\eta) &= \frac{c(1-\eta)}{\eta(2-\eta)} I_2(\sqrt{c\eta(2-\eta)}) \\ p_{10} &= (-c)/2 \end{aligned} \quad (2.23)$$

Here, c is a tuning parameter affecting the rate of convergence and $I_2(\cdot)$ is the modified Bessel function of the second kind.

The boundary value problem is solved on line by discretizing the PDE and boundary conditions using the method of finite differences to obtain a system of ODEs, yielding an approximate solution to the PDE at N evenly spaced discretization points ($i \in 1, 2, \dots, N$ where $i = 1$ corresponds to $\eta = 0$ and $i = N$ to $\eta = 1$). The ODEs for interior points ($i \in 2, 3, \dots, N-1$) are:

$$\frac{d\hat{\Theta}_i^*}{d\zeta} = \frac{\hat{\Theta}_{i-1}^* - 2\hat{\Theta}_i^* + \hat{\Theta}_{i+1}^*}{(\Delta\eta)^2} + p_1[i](\Theta^*(0, \zeta) - \hat{\Theta}_1^*) \quad (2.24)$$

The ODE at $i = 1$ is:

$$\frac{d\hat{\Theta}_1^*}{d\zeta} = 2 \frac{-\hat{\Theta}_1^* - h((Bi + St)\hat{\Theta}_1^* + p_{10}(\Theta^*(0, \zeta) - \hat{\Theta}_1^*)) + \hat{\Theta}_2^*}{(\Delta\eta)^2} + p_1[1](\Theta^*(0, \zeta) - \hat{\Theta}_1^*) \quad (2.25)$$

And the ODE at $i = N$ is:

$$\frac{d\hat{\Theta}_N^*}{d\zeta} = 2 \frac{-\hat{\Theta}_{N-1}^* - h((Bi + St)(C_2P - \hat{\Theta}_N^*)) + \hat{\Theta}_N^*}{(\Delta\eta)^2} + p_1[N](\Theta^*(0, \zeta) - \hat{\Theta}_1^*) \quad (2.26)$$

2.3.7 Controller Design Approach

The purpose of the controller is to manipulate the lamp power to drive the temperature to the desired set point. In this case, however, the most commonly used controller in industrial practice—the proportional-integral-derivative (PID) controller—is

incapable of tracking temperature ramp set points without offset. Observe from the PID controller equation:

$$c(t) = K_c \left[\varepsilon(t) + 1/\tau_I \int_0^t \varepsilon(t^*) dt^* + \tau_D \frac{d\varepsilon}{dt} \right] + c_s \quad (2.27)$$

(where $c(t)$ is the control action, $\varepsilon(t) = T_d - T$ is the error, K_c is the controller gain, τ_I is the integral time, and τ_D is the derivative time; t^* is a dummy time variable) that, if the desired temperature set point is a ramp, even for a linear first order system, applying the final value theorem to the closed-loop transfer function yields:

$$\lim_{t \rightarrow \infty} \varepsilon(t) = \lim_{s \rightarrow 0} s(T_d(s) - T(s)) = \frac{r\tau_i}{KK_c} \quad (2.28)$$

Therefore feedback error cannot be driven to zero by a PID controller even for a first order linear system if the set point is a ramp. While this is undesirable even in the case of a linear system, recall from Equation 2.7 that for our process $K = \frac{A}{B+CT_0^3}$. Therefore, from Equation 2.28, we see that if PID control is applied to our system, the offset will actually increase (as a function of nominal temperature to the third power) during the temperature ramp, which renders standard PID control entirely untenable.

To handle the steady state offset problem, we propose a proportional-integral-double integral (PII²) controller, defined in the time domain as:

$$c(t) = K_c \left[\varepsilon(t) + \frac{1}{\tau_I} \int_0^t \varepsilon(t^*) dt^* + \frac{1}{\tau_{DI}^2} \int_0^t \int_0^{t_1^*} \varepsilon(t_1^*) dt_1^* dt_2^* \right] + c_s \quad (2.29)$$

Here, τ_{DI} is the double-integral time and t_i^* ($i = 1, 2$) are dummy variables. In the Laplace domain, the controller transfer function is:

$$c(s) = K_c \left(1 + \frac{1}{\tau_I s} + \frac{1}{\tau_{DI}^2 s^2} \right) \quad (2.30)$$

It is easy to show that the presence of the double integral endows this controller with the ability to eliminate any steady state offset in tracking ramped set point.

Unlike PID controllers, for which tuning methods are widely available for controller design, I must now develop techniques for designing and tuning the PII² controller. I propose to base the design on two desirable characteristics: (i) the controller

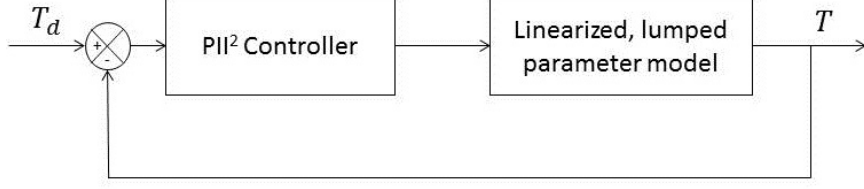


Figure 2.9: Simplified control block diagram where the hardware and observer dynamics are assumed to be fast enough to be neglected and the lumped parameter model is assumed sufficient to describe the process dynamics.

response *must* be stable, and (ii) the response *should* be monotonic. Apart from the process itself and the controller, I will assume that the other control system components are sufficiently fast that their dynamics can be neglected; furthermore, I assume that a linearized lumped parameter model can adequately approximate the essential process dynamics. The resulting block diagram representation of the simplified closed-loop feedback system is shown in Figure 2.9.

2.3.7.1 Controller Stability

From the simplified block diagram in Figure 2.9, the closed loop transfer function is obtained as $\Psi = \frac{GG_c}{1+GG_c}$, where G is the linearized, lumped parameter process model (from Equation 2.7), and G_c is the PII² controller transfer function (from Equation 2.30). Therefore:

$$\Psi = \frac{\frac{K}{\tau s + 1} K_c \left(1 + \frac{1}{\tau_I s} + \frac{1}{\tau_{DI}^2 s^2} \right)}{1 + \frac{K}{\tau s + 1} K_c \left(1 + \frac{1}{\tau_I s} + \frac{1}{\tau_{DI}^2 s^2} \right)} \quad (2.31)$$

Closed loop stability is determined by the roots of the characteristic polynomial obtained from the denominator of Equation 2.31. In this case, the Routh Array [72] is obtained as:

$$\begin{bmatrix} \tau \tau_I \tau_{DI}^2 & K K_c \tau_{DI}^2 & 0 \\ \tau_I \tau_{DI}^2 (1 + K K_c) & K K_c \tau_I & \\ \frac{K K_c \tau_I \tau_{DI}^4 (1 + K K_c) - K K_c \tau \tau_I^2 \tau_{DI}^2}{\tau_I \tau_{DI}^2 (1 + K K_c)} & 0 & \end{bmatrix} \quad (2.32)$$

from where it is easy to show that the Routh stability criterion results in the following algebraic test for stability:

$$\tau_{DI}^2(1 + KK_c) - \tau_I > 0 \quad (2.33)$$

Recalling that K and τ are functions of temperature, it is now straightforward to use Equation 2.33 to test for stability at each temperature value of interest. Assuming that the model is sufficiently representative of the process, Lyapunov stability can be guaranteed if and only if the controller is stable at each temperature value, *i.e.*, the inequality in Equation 2.33 is satisfied for each K and τ in the temperature range of interest

Once the condition in Equation 2.33 is satisfied, then in conjunction with the earlier discussion of observer design, we will have established the individual stability of each component in our entire closed loop system—the controller, the observer, and the process. Unfortunately, this does not guarantee input-to-state stability, because our system is intrinsically nonlinear, in which the separation principle no longer applies. Nevertheless, *point-wise* Lyapunov stability is still assured, and will be assumed sufficient for this work.

2.3.7.2 Controller Monotonicity

In addition to stability, it is desired that the controller response be monotonic. A monotonic response is guaranteed when the poles of the system transfer function are purely real numbers (with no imaginary parts). The simplest way to test whether roots of a polynomial are real, without calculating the roots explicitly, is via discriminants. If a , b , c , and d are the coefficients (in descending order) of a cubic polynomial, then it can be shown that the cubic discriminant, Δ is given by:

$$\Delta = 18abcd - 4b^3d + b^2c^2 - 4ac^3 - 27a^2d^2 \quad (2.34)$$

The roots of a cubic polynomial will be strictly real numbers if and only if $\Delta \geq 0$. Consequently, the response of the control system with the closed loop transfer function

in Equation 2.31 will be monotonic when the roots of the characteristic polynomial (derived from the denominator in Equation 2.31 are real, *i.e.*:

$$18\tau_I^3\tau_{DI}^6KK_C(1+KK_C) - 4KK_C\tau_I^4\tau_{DI}^6(1+KK_C)^3 + K^3K_C^2\tau_I^2\tau_{DI}^8(1+KK_C)^2 - 4KK_C\tau_I\tau_{DI}^8 - 27(K^2K_C^2\tau_I^4\tau_{DI}^4) \geq 0 \quad (2.35)$$

Analogous to the test for stability from Inequality 2.33, Inequality 2.35 is a simple algebraic test that can be applied to ensure a monotonic response for each temperature value in the range of interest. Controller design may now be carried out by selecting controller parameters to satisfy Equations 2.33 and 2.35.

2.3.8 Temperature Control System Results

2.3.8.1 Observer Implementation

The parameters needed to implement the observer derived in Section 2.3.6 are determined from data generated by the process identification experiments described in Section 2.3.3.1. The experimental apparatus is configured such that the pyrometer generates nearly continuous measurements of the bottom surface temperature, but the temperature sensitive lacquers only provide measurements of the top surface temperatures at certain specified temperatures, specifically, at the melting points of the lacquers. By representing the parameters in Equations 2.24–2.26 as $\theta_D = [Bi \ St \ C_1^+ \ C_2]$ (where $C_1^+ = \sigma\epsilon L/(k(T_2 - T_1))$, the constant term of C_1), appropriate estimates are obtained by minimizing the sum of squares of the residuals defined by:

$$\mathbf{R}(\theta_D) = \mathbf{T}_{\text{measured}} - \mathbf{T}_{\text{predicted}}(\theta_D), \quad (2.36)$$

where $\mathbf{T}_{\text{measured}}$ is the vector of temperature measurements available from the temperature sensitive lacquers, and $\mathbf{T}_{\text{predicted}}$ is the corresponding temperature predicted from Equations 2.24–2.26; *i.e.*, “least squares estimates”, $\hat{\theta}_D$ is the solution to the following optimization problem:

$$F(\hat{\theta}_D) = \min_{\theta_D} |\mathbf{R}(\theta_D)|_{L_2} \quad (2.37)$$

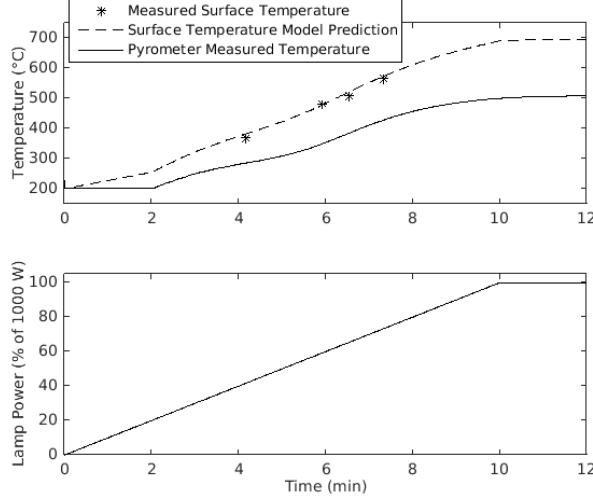


Figure 2.10: Lower plot: lamp power. Upper plot: pyrometer data (bottom surface temperature; solid line) and temperature sensitive lacquer data (top surface temperature; stars), with the observer predictions (top surface temperature estimates; dashed line). The “kink” at approximately 2 minutes corresponds to the point at which the measured temperature reaches the minimum of the pyrometer’s operating range (200 °C), and the pyrometer becomes active.

I solved this nonlinear optimization problem using the Nelder-Mead simplex method (the MATLAB built-in *fminsearch* function) with the initial guess:

$$\hat{\theta}_{D,0} = [(8.8571 * 10^{-13}) (2.0371 * 10^{-9}) (0.1891) (3.2611 * 10^{-4})], \quad (2.38)$$

determined from approximate physical property data and order of magnitude estimates.

Figure 2.10 shows raw data and the observer estimates using the parameters: $\hat{\theta}_D = [(4.0288 * 10^{-13}) (7.3638 * 10^{-10}) (0.3354) (8.0183 * 10^{-3})]$.

2.3.8.2 Controller Implementation

Implementing the model-based controller described in Section 2.3.7 requires the determination of appropriate values for the process parameters in the lumped parameter model of Section 2.3.5.1. As in the previous section, I obtain these parameters using data from the specifically designed process identification experiment described in

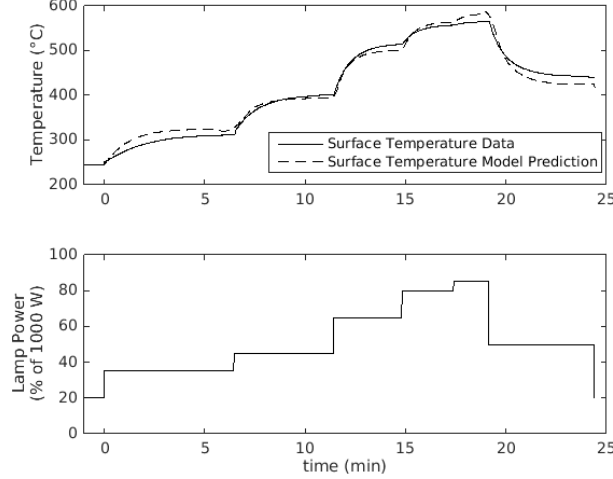


Figure 2.11: Surface temperature data from thermocouple and fitted lumped parameter model.

Section 2.3.3.2, in conjunction with the same least squares optimization procedure. By defining the parameters from Equation 2.4 as $\theta_L = [A \ B \ C \ D]$, along with an initial guess, $\theta_{L,0} = [10^{-1} \ 10^{-2} \ 10^{-11} \ 1]$, determined from order of magnitude estimates, the optimization procedure yields the result $\hat{\theta}_0 = [(1.1611 * 10^{-1}) \ (0.6567 * 10^{-2}) \ (1.0077 * 10^{-11}) \ (1.1535)]$.

Figure 2.11 shows a comparison of the measured surface temperature (solid line) and the corresponding lumped parameter temperature model prediction (dashed line) in response to the indicated changes in lamp power. The indicated fit is seen to be more than good enough for controller design, since the important process dynamics are captured quite well.

With these process parameter estimates, appropriate values for the PII² controller's tuning parameters (see Section 2.3.7) such that the conditions given in Inequalities 2.33 and 2.35 are satisfied simultaneously may now be obtained. Specifically, I am able to determine the region in the three-dimensional space of the PII² controller parameters where stability (Equation 2.33) and monotonicity (Equation 2.35) are achieved; any parameter combination in this region will therefore be eligible for selection. Note

that as a result of system nonlinearity, these regions are temperature dependent. Figure 2.12 shows an example of such surfaces delineating the boundaries of stability and monotonicity for a temperature of 480 °C. In each case, the stable/monotonic region lies above the surface. From such considerations, the following tuning parameters were selected:

$$\begin{aligned} K_C &= 20\%/K \\ \tau_I &= 5s \\ \tau_{DI} &= 40s \end{aligned} \tag{2.39}$$

2.3.8.3 Control System Performance

The entire control system was implemented in LabVIEW 2011 and tested experimentally on the RTP system. Pyrometer measurements are sampled every 1 s and are made continuous with a zero-order hold. The lamp power was actuated every 1 s by the SCR with negligible internal dynamics.

Figure 2.13 shows the real control system performance under 4 experimental conditions (a combination of two different desired temperature ramp rates and two different terminal temperatures): 2 °C/s and 6 °C/s ramp rates to 500 °C and 600 °C. Aside from small oscillations in lamp power at the beginning of the temperature ramp (caused by the zero-order hold), the control system is robust and able to control temperature ramps virtually perfectly in 3 of the 4 experimental cases. Even then, for the only exception, the high ramp rate, high temperature sequence (Figure 2.13d) the *slight* deviation between the actual surface temperature and the desired value occurred over a short interval of time (about 1 minute) during which the lamp power saturated at 100%; otherwise, the desired set-point was tracked effectively here as well.

2.4 Reactor Operating Mode

With the reactor and its temperature control system in place, the system can be used for reacting Cu-In-Ga precursors with hydride gases. However, the reactor may be operated in different operating modes, which have not yet been considered in the

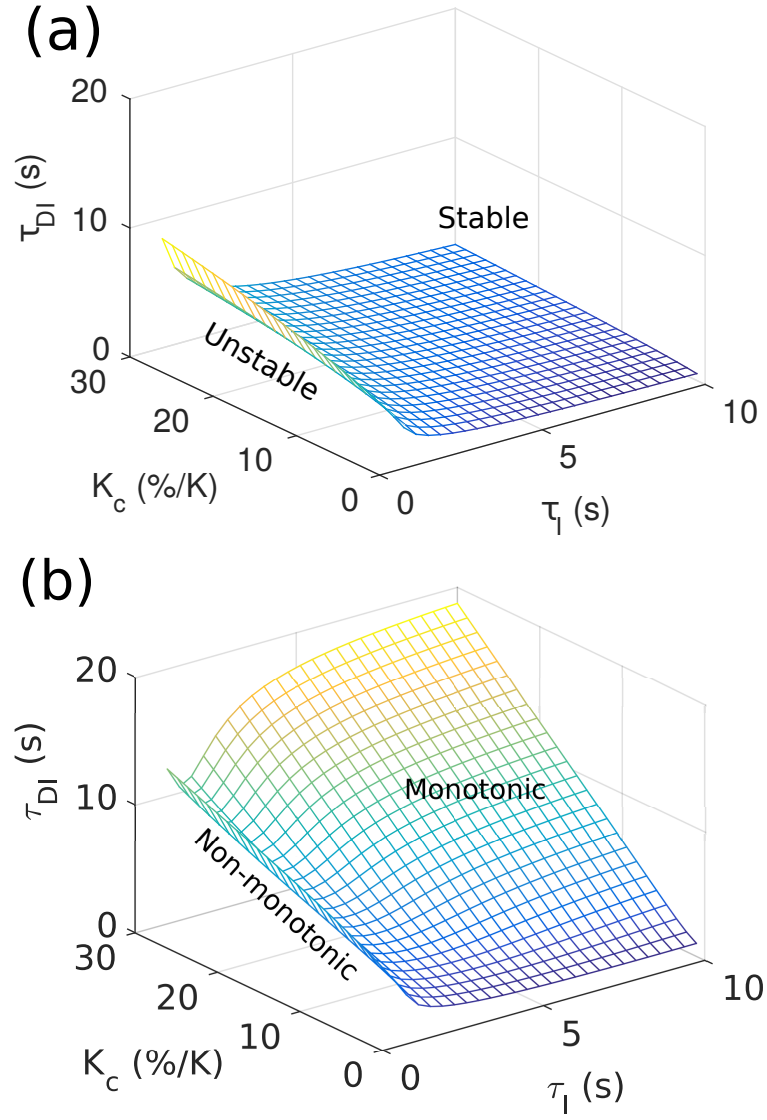


Figure 2.12: Limits of stability (a) and monotonicity (b) for a PII² controller applied to the nonlinear, lumped parameter model at 480 °C.

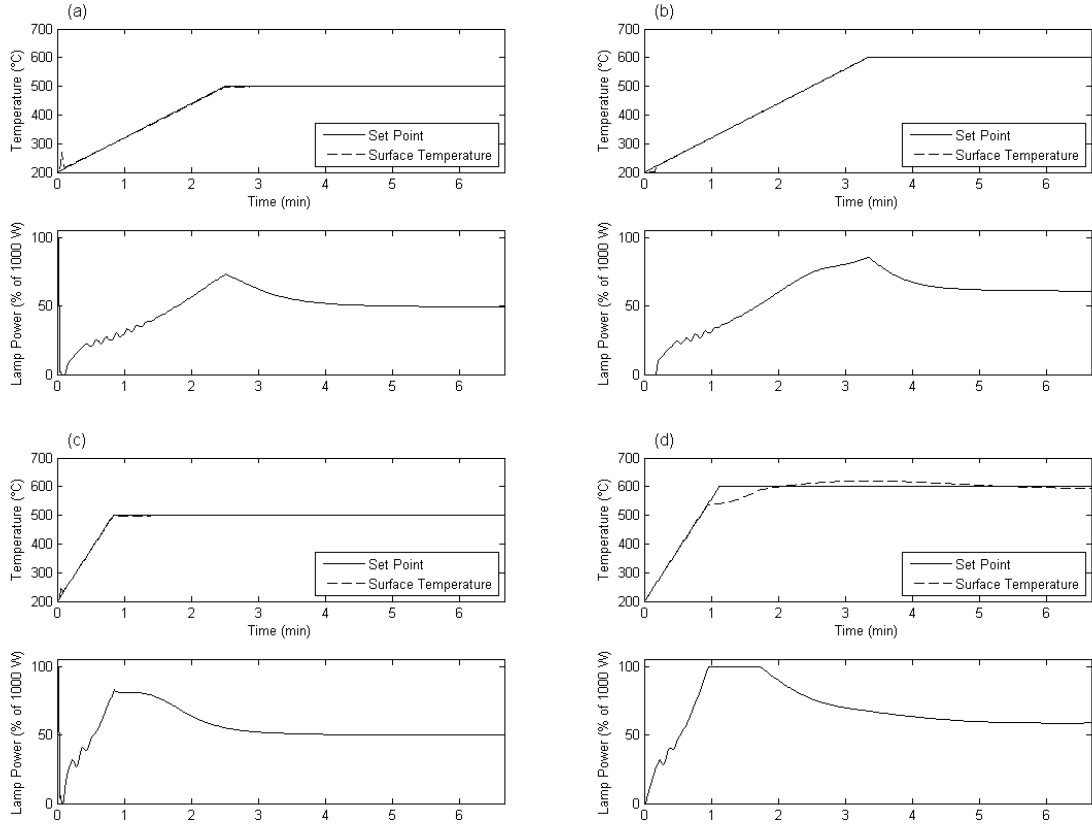


Figure 2.13: Control system performance for: (a) 2 K/s ramp to 500 °C, (b) 2 K/s ramp to 600 °C, (c) 6 K/s ramp to 500 °C, (d) 6 K/s ramp to 600 °C. Temperature ramps start at 200 °C, the minimum of the pyrometers temperature range.

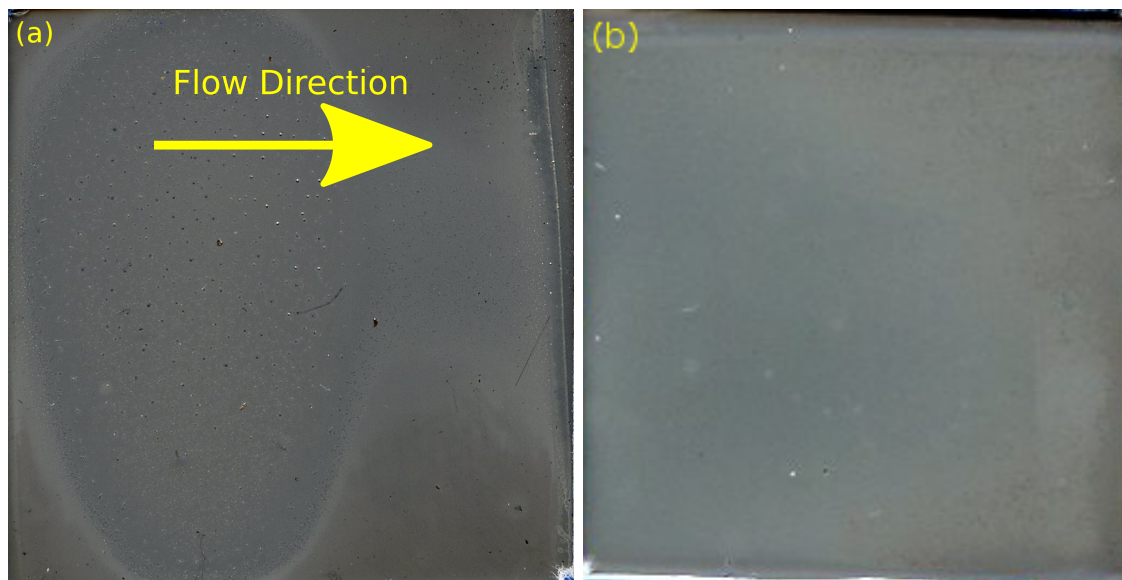


Figure 2.14: Scanned images of sample surface after reacting in the sample in the flow configuration (a) and the charge-and-react configuration (b). In most cases samples from the charge-and-react are visually more uniform.

reactor design procedure. The reactor may be operating in the following two modes: (1) the carrier gas (Ar) with H_2S and/or H_2Se flows across the substrate, and exits to the waste treatment system, called the *flow configuration* or (2) the reactor is charged with a certain concentration of gases (as measured by the mass flow controllers) to just above atmospheric pressure, and then the inlet valves are closed and the waste valves is opened (to prevent overpressure upon heating), called the *charge-and-react* configuration. Changing the reactor configuration could affect the uniformity across the samples either through asymmetric delivery of chalcogen or through asymmetric heat transfer, which would cause temperature non-uniformity. Samples were prepared using each of these configurations; scanned images of the sample surface are shown in Figure 2.14; it is easy to observe that substantial non-uniformity is present in the sample produced from the flow configuration. This is further confirmed by energy dispersive x-ray spectroscopy measurements Table 2.1 showing substantial nonuniformity across the flow direction; therefore, samples prepared for this work were reacted using the *charge-and-react* configuration.

Table 2.1: Composition measurements (in atomic ratios) for sample produced in the flow configuration (image of surface in Figure 2.14a. Substantial compositional nonuniformity is evident, most obvious in the chalcogen uptake fraction, $(\text{Se}+\text{S})/(\text{Cu}+\text{In}+\text{Ga})$)

Position	Cu/(In+Ga)	Ga/(In+Ga)	S/(Se+S)	(Se+S)/(Cu+In+Ga)
Center	1.02	0.29	0.25	0.99
Outside “Ring”	0.88	0.27	0.18	0.82

2.5 Waste Treatment System Upgrade

The selenization reactor at the Institute of Energy Conversion requires an effective waste treatment system in order to use H_2S and H_2Se safely. Currently, the waste treatment system is a 2-stage system wherein the gas flows through an countercurrent NaOH scrubber column, and then (as a failsafe) through a base-impregnated activated carbon filter. For details of the current waste treatment system design, refer to Varrin [66]. However, it would be desirable to avoid the use of large volumes of NaOH solution, which is itself highly corrosive and prone to failure because it requires constant operation of a pump. Further, replacement of the activated carbon is much simpler than the NaOH liquid. Therefore, I examined replacing the current NaOH scrubber with an all-activated carbon waste treatment system.

2.5.1 Column Design Methods

To design the all-activated carbon hydride gas scrubber, both equilibrium column capacity and mass transfer limitations must be considered. Essentially, equilibrium capacity is the maximum amount (in moles, kg, etc.) of chalcogen ($\text{Se}+\text{S}$) that can be adsorbed by the column before the hydride passes through in its unreacted, toxic form. Mass transfer limitations refers to diffusive limitations that allow some unreacted chalcogen to pass through a particular point in the column (and, eventually, through the entire column).

Equilibrium limitations are governed by the *adsorption isotherm*, *i.e.*, the function: $n^* = f(C|\theta)$, where n^* is the equilibrium loading, C is a fluid phase concentration,

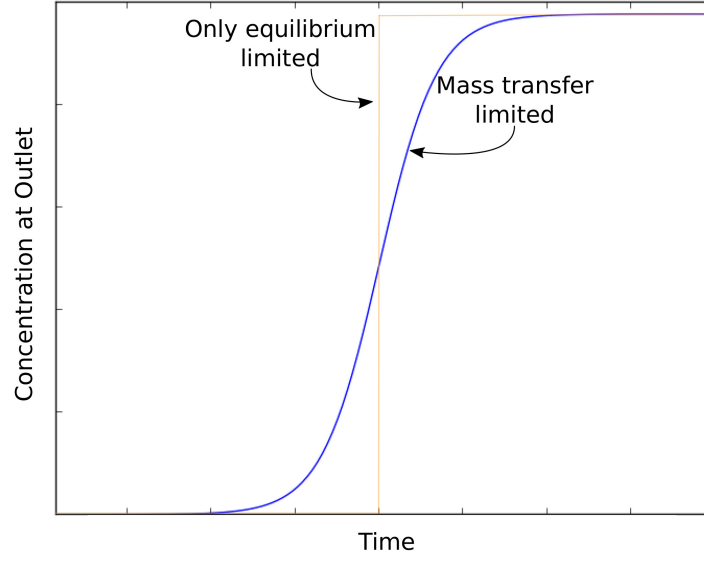


Figure 2.15: Breakthrough curves with and without mass transfer limitations. The x-axis shows time and the y-axis shows normalized concentration at the exit of the tube.

and θ is the vector of parameters. Three commonly used isotherms are:

$$\begin{aligned}
 n^* &= \theta_0 C \\
 n^* &= \frac{\theta_0 C}{1 + \theta_1 C} \\
 n^* &= \theta_0 C^{\theta_1}
 \end{aligned} \tag{2.40}$$

called the Henry, Langmuir, and Freundlich isotherms, respectively [75]. The parameters are, except for very simple systems, usually fit to data.

For an arbitrarily low flow rate, at which the system is known to reach equilibrium, the isotherm is the only necessary data to determine when the column will fail (*i.e.*, the breakthrough time). However, in real systems, mass transfer or kinetic limitations prevent the system from reaching equilibrium; instead of an instantaneous breakthrough time, there will be a sigmoidal breakthrough curve (see Figure 2.15). Ultimately, describing the shape of the breakthrough curve requires an overall mass transfer coefficient, k , which is best obtained from empirical correlations that depend

on the particular flow regime. Two methods were used to obtain k : (1) Kiel et al. [76] have adapted the Ranz-Marshall equation [77] for adsorption problems, or (2) correlations based on the Chilton-Colburn j-factor [78, 79] may be used (either from Yoshida et al. [80] or from Sherwood et al. [81], each of which is valid in a different flow regime).

First, the Ranz-Marshall equation is:

$$Sh = 2 + 0.6Sc^{\frac{1}{3}}Re^{\frac{1}{5}} \quad (2.41)$$

which uses Sh , the Sherwood number, or *dimensionless* mass transfer coefficient; $Sc = \frac{\mu}{\rho D}$ is the Schmidt number that describes the ratio the rates of viscous diffusion to molecular diffusion, where μ and ρ are the gas viscosity and density, respectively, and D is the diffusion coefficient of the hydride gas in argon, and $Re = \frac{\rho v_s \ell}{\mu}$ is the Reynolds number, where ℓ is particle diameter and v_s the superficial velocity (ratio of flow rate to column cross sectional area). Therefore, k , is recovered from the definition of the Sherwood number:

$$Sh = \frac{k\ell}{D} \quad (2.42)$$

For the j-factor method, Yoshida's correlation is:

$$j_d = 0.91\Psi Re_m^{-.51} \quad \text{for } Re < 50 \quad (2.43)$$

where Ψ is a shape factor (in this work, 0.91 for pellets) and Re_m is a modified Reynold's number, $Re_m = \frac{\rho v_s}{\mu \Psi \ell a_i}$, where a_i the interfacial area. The correlation from Sherwood et al. [81] is:

$$j_d = 1.15Re^{-0.415} \quad \text{for } 50 < Re < 2500 \quad (2.44)$$

Then k is found from the definition of the j-factor,

$$j_d = \frac{k}{v_s / Sc^{\frac{2}{3}}}. \quad (2.45)$$

With an adsorption isotherm and mass transfer coefficient, it is possible to construct breakthrough curves, like those shown in Figure 2.15. An explicit expression for concentration of adsorbed species at was derived by Thomas [82] that relates the output concentration to column variables (length, diameter, porosity), inlet variables (flow rate, concentration of hydride), and equilibrium and mass transfer limitations.

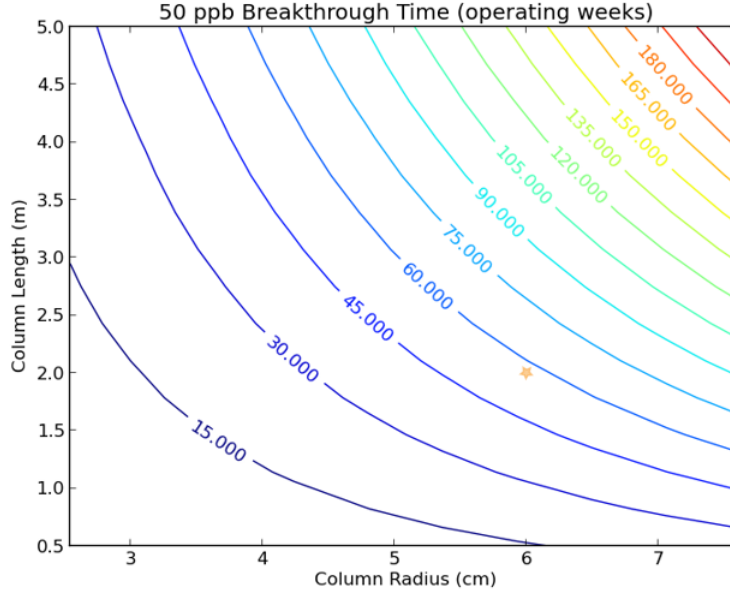


Figure 2.16: Contour plot showing breakthrough times for varying the column dimensions using Calgon ST I X activated carbon. An operating week is defined as 40 hours. The star denotes the proposed column dimensions.

2.5.2 Results and Discussion

These methods were applied to size a column using activated carbon purchased from Calgon Carbon (model ST I X) with properties measured using ASTM D6646-03 [83]. Due to the lack of data, some properties are based on H_2S instead of the more toxic H_2Se , and experimental measurements of H_2Se would be necessary before using the system on line. Python code to perform the calculations is available at www.bitbucket.org/rlovelett/column_design. Figure 2.16 shows a contour plot of breakthrough times (defined as time until 50 ppb of H_2Se will exit the column) as a function of column dimensions using the Ranz-Marshall method to obtain k (the alternative correlations give nearly the same results; this is because in our case mass transfer limitations affect breakthrough times on the order of hours, not weeks).

Based on the results from Figure 2.16, a reasonably sized column could have 6 cm diameter and 2 m length; the activated carbon should be refreshed approximately

once per year.

2.6 Summary and Conclusions

In this chapter I discussed the design, implementation, and operation of the rapid thermal processing system used for this work. The RTP system was designed with considerations taken for heat transfer limitations that were investigated using FEA. I determined that a 1000 W quartz halogen lamp should be sufficient to power the system. With the RTP system in place, a robust temperature control system needed to be developed. I used two operating objectives as the basis for control system design: (i) the unmeasured *top surface temperature* must be adequately controlled, and (ii) fast, linear set point ramps must be achievable with little to no offset. I carefully modeled heat transfer in the system, using lumped and distributed parameter models, designed experiments specifically to obtain the necessary data for each objective, obtained model parameters from this data, and designed control system components—an *observer* and a *PII² controller*—that achieve these objectives. With the reactor control system in place, I examined operational challenges that arose during this work. I determined that compositional uniformity is substantially improved by using a charge-and-react configuration instead of a flow configuration. Finally, in response to several disadvantages of the current hydride gas waste treatment system, I modeled and designed an all-activated carbon, liquid free waste treatment system.

The work presented in this chapter can be applied to several other systems. Most impactful is the temperature control system design, for which a novel approach was taken for a previously unsolved problem—the problem controlling of a distributed parameter system with boundary sensing and actuation *and* nonlinear (radiative) boundary conditions. Given the ubiquitous need for accurate temperature sensing and effective control in advanced manufacturing processes, such as those in thin film photovoltaics, optoelectronics, and other industries, this strategy has the potential to become an important component of the overall control strategy for several industries.

Chapter 3

A STOCHASTIC MODEL OF SELENIZATION AND SULFIZATION OF COPPER-INDIUM-GALLIUM PRECURSORS

3.1 Introduction

The selenization reaction method used to fabricate chalcopyrite thin films is very complex and contains multiple competing processes occurring simultaneously. There is a multiphase, polycrystalline film undergoing a multistage reaction; diffusion of atomic species through the film, either through the bulk or along the grain boundaries; the film interacts with its atmosphere via adsorption and desorption. Although thermodynamics dictates that a single phase, homogeneous chalcopyrite film is the endpoint of the process, the reaction pathway can be very complex and inhibited by mass transfer or kinetic limitations. Because of these complications, there have been many efforts to systematically model the selenization process for improving process design and to develop fundamental understanding of the process. However, while some approaches have been useful in describing specific processes, a more general description of the system is still unavailable.

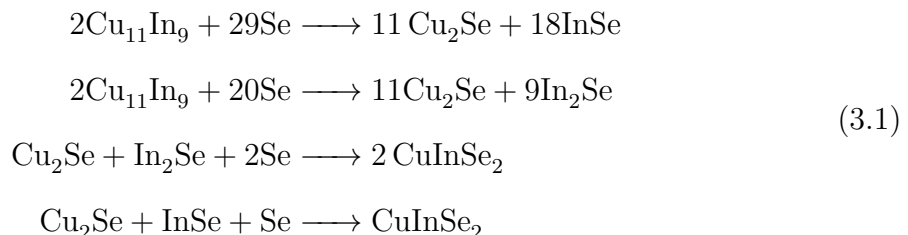
3.1.1 Project Goal

One of the goals of this dissertation is to develop a more thorough understanding of the selenization reaction through modeling and computational methods. In this chapter, I will discuss my approach for modeling this system: a *novel, stochastic solid state reaction and diffusion model* that applies to the precursor reaction/selenization process. The approach should be versatile and grounded in theory, such that it can be applied to other selenization processes as well as to entirely different material systems. Further, the model should be predictive, especially, it should be capable of predicting

the through-film composition of chalcopyrites produced by selenization. The ability to predict and tune through-film composition will be an especially important advance for the field, where the device properties rely on material properties that are mostly tuned on an *ad-hoc* basis.

3.1.2 CuInGaSe₂ Reaction Modeling

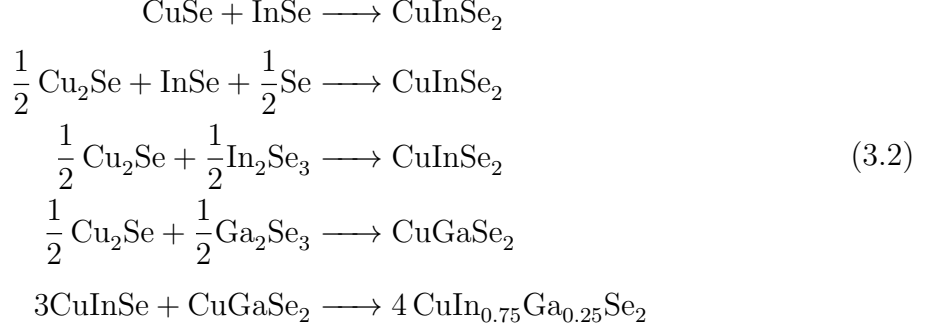
This work is not the first attempt to model the reaction kinetics or the film growth mechanism for Cu(InGa)(SeS)₂ thin films; however, it does represent a departure from previous approaches. The first kinetic models for selenization were developed by Verma et al. [84] and Orbey et al. [85] and only concern CuInSe₂ (*i.e.*, no gallium or sulfur was included in the process); they used simple mass action equations to describe the reaction. They postulated a multistage reaction mechanism where first selenide species were formed, and then the selenides reacted to form CuInSe₂. The reaction mechanism from Verma et al. [84] is:



Even in the comparably simple Cu–In–Se system, there are still at least four reactions that occur. Verma et al. [84] was able to develop rate expressions using mass action equations and fit these to data; molar concentrations (except for selenium, which was assumed constant) were determined from x-ray diffraction patterns after quenching the reaction.

The system becomes substantially more complex with the addition of gallium and sulfur. Most models of these precursor reaction systems are either qualitative or only include a single, lumped reaction coordinate instead of individual reactions. For

an RTP process where the precursor is a stack of elemental layers, Hergert et al. [86] proposed the following reaction mechanism:



where each of the reactions was observed by *in situ* x-ray diffraction. However, a model based on mass action is not an effective description of the observed kinetics in this system, most likely because of diffusion limitations.

In order to develop quantitative models of the selenization reaction, most authors have used classical solid state reaction methods, such as those pioneered by Avrami [87, 88] and Johnson and Mehl [89], and fit these models to data from *in situ* x-ray diffraction (XRD) patterns or differential scanning calorimetry. In models like these, there is typically a single, monotonically increasing reaction coordinate used to represent a possibly multistage reaction with diffusion limitations. For example, several studies using *in situ* XRD have determined the activation energy of the selenization reaction using different precursor structures and selenium sources, and fitting the data to the Avrami model (nucleation and growth) or parabolic model (1-dimensional diffusion limited) [61, 60, 90, 91, 92]; the results are summarized in Table 3.1. From Table 3.1, it is clear that both the composition (Ga versus In) and structure of the precursor affect the selenization reaction kinetics. The lowest activation energy is obtained with an InSe/CuSe bilayer, and the largest from a In₂Se₃/CuSe bilayer. Comparing the Cu-Ga vs Cu-In precursors reacted with Se gas, there is not a significant difference in activation energies, suggesting that the rate of reaction with gallium could be substantially increased at higher temperature, allowing for fabrication of a more homogeneous film.

Table 3.1: Activation energies from Avrami and parabolic reaction models for varying processes—different selenium sources and different precursor structures.

Process	E_a Avrami (kJ/mol)	E_a Parabolic (kJ/mol)	Reference
In ₂ Se ₃ /CuSe bilayer	Poor Model Fit	162	[61]
InSe/CuSe bilayer	66	65	[60]
Cu-In + Se (g)	124	100	[90]
GaSe/CuSe bilayer	124	115	[92]
Cu-Ga + Se (g)	109	N/A	[91]

Purwins et al. [93] uses solid state reaction models in conjunction with DSC data to study the reactions to produce CuInSe₂ and CuGaSe₂ independently. They prepared precursors that were bilayer stacks of InSe and CuSe and bilayer stacks of Ga₂Se₃ and Cu₂Se. For the gallium-containing precursors, two exothermic reactions were identified, and Kissinger analysis [94] and methods from Opfermann [95] were applied to obtain activation energies—159 kJ/mol for the first reaction and 140 kJ/mol for the second. For the indium-containing precursors, they assumed that growth was diffusion limited in 1 spatial dimension and used the DSC data to obtain kinetic parameters. They transformed the signal (heat flow, or $\frac{dH}{dt}$) to a temperature dependent product thickening rate ($\frac{dx}{dT}$) and then fit the transformed signal to the following equation:

$$\frac{dx}{dT} = \left(\frac{AE_a}{2R\beta} \right)^{1/2} \frac{1}{T} \exp \left(-\frac{E_a}{2RT} \right), \quad (3.3)$$

which is straightforward to derive from the Arrhenius equation (See Michaelsen et al. [96]): x is the thickness of a product layer (that increases monotonically), T is temperature, A is the pre-exponential factor, E_a is activation energy, R is the gas constant, and β is the heating rate. This analysis resulted in an activation energy of 128 kJ/mol.

There have been fewer studies of the sulfization reaction than the selenization reaction, and few quantitative modeling results. Von Klopmann et al. [97] studied the sulfization of stoichiometric and Cu-poor CuIn precursors under vacuum with an elemental sulfur source. They identified a stress-induced growth mechanism that requires

a dynamic temperature (to induce stress gradients). However, the mechanism of reaction with elemental sulfur may be very different than with H_2S because H_2S is a very stable gas that will require substantially higher temperatures for reaction. Kim et al. [50] examined simultaneous selenization and sulfization with hydride gases and found, at 550 °C, that Ga preferentially incorporates in the film when sulfur is present.

The studies summarized here show the diversity of reaction models and experimental methods that have been used to examine the kinetics of this system. Some key points are: (i) the reaction kinetics are process dependent; while in all cases chalcopyrite is the preferred phase, the precursor structure and chalcogen source has a substantial effect on the reaction mechanism and reaction rate, (ii) the reaction is usually multistage, where metal selenides are formed and then converted to chalcopyrites (of course, the first step is not necessary when the precursor consists of metal selenides), and (iii) in most cases, indium preferentially reacts with selenium and gallium with sulfur, which can lead to through-film variation in composition.

3.1.3 Stochastic Model Motivation

While several of the previous efforts at modeling the $\text{Cu}(\text{InGa})(\text{SeS})_2$ thin film system are time-resolved, there was no previous attempt to develop a model that is both time resolved and *spatially resolved*. This is despite widespread acknowledgment that the composition depth profile is an important property that affects the performance of the device¹ and that the precursor reaction methods often yield films with significant composition gradients. In this work, I derive a new modeling approach for solid state reactions that includes spatial information explicitly. As I will show, some of the details of crystallography and *exact* reaction mechanisms are sacrificed in this approach, but the addition of spatial information into the model makes the work compelling.

In order to model the selenization/sulfization reaction, I developed a novel

¹ For example Marudachalam et al. [46] shows a 100 mV increase in voltage with a homogeneous film instead of a graded film with, on average $\text{Ga}/(\text{In}+\text{Ga})=0.25$

stochastic reaction model. At first, this may seem unnecessary; there are not obvious macroscopic effects of microscopic fluctuations that stochastic models are usually designed to obtain. However, there are both practical and technical motivations for a stochastic model. First, while effects of fluctuations are not observed in the time domain or in the through-film composition, they are observed in the *lateral* domain. For example, Hanket et al. [98] and Liao et al. [99] observed agglomerations of Ga-rich species after partial reactions. Second, there are practical advantages to a stochastic model; in particular, rigorous continuum treatment of multicomponent diffusion is challenging and would require data that is unavailable, whereas, as I will show, the stochastic approach allows the problem to be simplified to binary interactions.

3.1.4 Stochastic Modeling Background

There have been several approaches to the stochastic modeling of chemical reactions. The overall goal of a stochastic model of a chemical system is to obtain a solution to the *chemical master equation*, or an approximation thereof. The chemical master equation is an equation that gives, at any time point, the probability that a chemical system occupies any particular state [100]. For a well-mixed chemical system, the state is defined as the number of molecules of each particular type; for a system that is not well-mixed, the state is the position and type of each molecule in the system (for the second case, because position is a continuous variable, the master equation is instead defined to give the probability density). In principle, it is possible to obtain the chemical master equation explicitly (at least for well-mixed system), but for most practical problems, it is intractable due to the enormous number of possible system states.

While obtaining the master equation explicitly is intractable, in many cases it is possible to *sample from* the master equation. Therefore, if one can sample from a probability distribution, then it is straightforward to obtain an empirical approximation of that distribution by collecting multiple samples.²

² This approach is the basis of the popular Markov Chain Monte Carlo (MCMC) that

The first (accurate) method for sampling from the chemical master equation was developed by Gillespie [102], and is now commonly referred to as the Gillespie algorithm. The method is based on the observation that an individual chemical reaction between two molecules is a Poisson process, with Poisson intensity (called the reaction propensity) proportional to the rate constant. Therefore, the time until a reaction occurs is exponentially distributed, with mean waiting time equal to the sum of all reaction propensities. The algorithm advances by individual steps, where a step is an individual chemical reaction.

Gillespie’s method has recently been extended to include diffusion, mostly used for micro-scale modeling of biomolecular systems. Erban and Chapman [103] discuss two general approaches: on-lattice methods and off-lattice methods. On-lattice approaches restrict the position of molecules to discrete locations or compartments where each compartment contains multiple occupant species, while off-lattice methods allow movement on a continuous domain, usually through Brownian motion. However, these approaches are designed for fluid systems where species density may vary.

In the method presented here, I apply similar concepts and expand the capability of stochastic models for reactions in the solid state. The approach, discussed in Section 3.2, is similar to on-lattice methods, but with the additional restriction that lattice occupancy is always exactly one. Instead of interacting with co-occupants, species interact with adjacent lattice points. I show how this approach allows stochastic simulation of mesoscale systems of solid, crystalline species, where unit-cell level (1 Å) simulation would be impractical for complete thin film (1–10 µm) systems. Although I assume the lattice is square, with a coordination number of four, this approach is easily generalized to allow for simulation of advanced, non-isotropic materials such as graphene, carbon nanotubes, and other materials with complex microstructure.

is used in, among other fields, Bayesian inference [101]; not surprisingly, there are many mathematical parallels between MCMC and stochastic simulation of chemical reactions.

3.2 Model Development and Theory

In the polycrystalline $\text{Cu}(\text{InGa})(\text{SeS})_2$ system, solid state reactions occur, species interdiffuse, and the film interacts with its environment by adsorption and desorption of volatile species. For this section, I generalize to any thin solid film in a deposition system where these processes occur. The film is represented as a two-dimensional square lattice, where each point contains a species or a vacancy. The model is mesoscopic; so that each lattice point does not represent an individual atom, molecule, or unit cell, otherwise the lattice would be too large to be computationally tractable. The lattice is therefore a coarse-grained approximation of the actual film; each lattice point is a finite volume element small enough such that it is accurately approximated as phase-pure.

The approach is to recast Gillespie’s stochastic simulation algorithm [102] for spatially heterogeneous solid state systems with approximately constant mass density and number density. In Gillespie’s method, a random number is selected at each time step to determine which reaction occurs. Here, we generalize reaction events to “lattice” events, which take place at interfaces between lattice points and are classified as reaction, diffusion, adsorption, or desorption events. The probability and the rate of occurrence of each lattice event are governed by an intrinsic parameter called the propensity constant. The propensity of a given event is the product of its propensity constant and the number of interfaces at which the event can occur.

The modeling approach is as follows:

1. A square lattice is initialized with the starting species. If adsorption/desorption events are included, the lattice should contain vacancy points above the species. If the lattice is represented as an $N \times M$ array, row 0 and row N are considered boundaries with no interactions above row 0 points or below row N points. Column 0 is considered adjacent with column M (*cf.*, periodic boundary conditions in a boundary value problem involving a partial differential equation).
2. Propensity of each lattice event is calculated as: $a_i = p_i N_i$, where p_i is the propensity constant and N_i the number of interfaces associated with lattice event i .
3. Probability of each lattice event is proportional to the propensity of an event; a random number is generated to determine which lattice event occurs.

4. The time, τ , until the next time step is selected from an exponentially distributed random variable.
5. The reaction chosen in Step 3 occurs at one possible interface. For example, if a reaction takes place between species A and B, then one of the A—B interfaces is selected at random and updated accordingly. For reaction events, the final orientation (that is, the relative position of the product species) is random; it is fixed for adsorption, and diffusion events.
6. The lattice is updated and steps 2–5 are repeated until an exit condition is met.

3.2.1 Solution Algorithm

The conceptually simplest algorithm for implementing this modeling approach is to store the lattice in a 2D array that is updated at each time step. Although straightforward, this method is inefficient and will be computationally tractable only for relatively small lattice sizes. There are two possible bottlenecks that can lead to very slow solutions: (1) counting the number of interfaces of each kind, and (2) choosing one of these interfaces at random for a reaction event. To address these issues, the lattice itself is not stored and updated at each time step; instead each interface and its position is tracked an array. First, I define the simple 2D representation of the lattice; then I demonstrate how to convert this to the 1D representation that is used in the algorithm.

Consider a film discretized to a lattice and represented by the 2D array: $\mathbf{L} \in \mathbb{N}_0^{(N \times M)}$ with elements $l_{(i,j)}$. The indices of each element in $\mathbf{L}$ represent the position of each lattice point (*i.e.*, volume element) in physical space, and the value of that element represents its occupant species. If there are S unique species, including vacant elements, and the value of each array element corresponds to its occupant species, then the domain of $l_{(i,j)}$ is given as: $\{l_{(i,j)} | l_{(i,j)} \in \mathbb{N}_0, l_{(i,j)} < S\}$. Now, consider the set of adjacent points in $\mathbf{L}$. For this model, the set of adjacent elements is defined as:

$$(l_{\text{adj}}^1, l_{\text{adj}}^2) | (l_{\text{adj}}^1, l_{\text{adj}}^2) \in \begin{cases} (l_{(i,j)}, l_{(i,j-1)}) \forall j > 0, \\ (l_{(i,j)}, l_{(i-1,j)}) \forall i > 0, \\ (l_{(i,0)}, l_{(i,M-1)}) \end{cases} \quad (3.4)$$

where the first two cases are trivially adjacent points and the third is analogous to applying periodic boundary conditions to a PDE to reduce edge effects. The periodic boundary condition is applied only to the columns of $\mathbf{L}$, as the rows represent the full thickness of the thin film. Next, I convert the 2D representation, $\mathbf{L}$, to a 1D representation $\mathbf{X}$, with elements x_k by: (1) defining a mapping from *species pairs* to *interface kinds*, or, $x = f(l_{\text{adj}}^1, l_{\text{adj}}^2)$, and (2) define a mapping from indices in $\mathbf{L}$ to index in $\mathbf{X}$, or $k = g((i_1, j_1), (i_2, j_2))$, where $((i_1, j_1), (i_2, j_2))$ are the indices of $(l_{\text{adj}}^1, l_{\text{adj}}^2)$.

Each adjacent pair of lattice elements constitutes an interface, which can be represented by a single value $\{x | x \in \mathbb{N}_0, x < S^2\}$, where there are S^2 “kinds” of interfaces (observe that interfaces of different orientation are considered distinct). *Pairs of species* can then be mapped to *interface kinds*:

$$x = l_{\text{adj}}^1 S + l_{\text{adj}}^2 \quad (3.5)$$

where x is the interface kind.

Next, I define a mapping for the indices for interface location in $\mathbf{L}$ to the index for interface location in $\mathbf{X}$. Here, I assume that the number of columns, M , is an even number (a similar procedure applies if M were odd-valued). With $((i_1, j_1), (i_2, j_2))$ as indices of adjacent elements in $\mathbf{L}$ and k as the index of $\mathbf{X}$:

$$k = \begin{cases} j_1 & \text{if } i_1 = i_2 = 0 \\ M + 2M(i_1 - 1) + 2j_1 & \text{if } i_1 = i_2 \neq 0 \\ M + 2M(i_1 - 1) + 2j_1 + 1 & \text{if } j_1 = j_2 \end{cases} \quad (3.6)$$

Using the mappings defined in Equations 3.5 and 3.6 to translate $\mathbf{L} \rightarrow \mathbf{X}$, the simulation algorithm may now be written as follows:

1. Define a set of allowable species, $\{0, 1, 2, \dots, (S - 1)\}$.
2. Define a set of directional lattice events, $\mathbf{D}$. Directional events will preserve the orientation of the interface and are used to represent diffusion, adsorption, and desorption events. $\mathbf{D}$ is a $(N_D \times 3)$ matrix, where N_D is the number of directional lattice events. The columns of $\mathbf{D}$ correspond to $\{p, x_0, x_f\}$ for the propensity constant, initial interface kind, and final interface kind, respectively

(interface kind is the unique identifier for a pair of species defined in Equation 3.5).

3. Define a set of non-directional lattice events, $\mathbf{N}$. Non-directional events will not preserve the orientation of the interface and are used to represent reaction events. $\mathbf{N}$ is a $(3 \times N_N)$ matrix, where N_N is the number of non-directional lattice events. The columns of $\mathbf{N}$ correspond to $\{p, x_0, x_f\}$ for the propensity constant, initial interface kind, and final interface kind, respectively. Directionality refers to the orientation of the *products*, not the reactants. For example, if there are species A, B, C, and D, then the reaction $A+B \longrightarrow C+D$ is distinct from $B+A \longrightarrow C+D$.
4. Define an initial condition $\mathbf{L}_0$.
5. Use Equations 3.5 and 3.6 to map $\mathbf{L}_0 \rightarrow \mathbf{X}$.
6. Count the number of interfaces of each kind in array $\mathbf{X}$, saving the results in array $\mathbf{Y}$, referred to as the “interface count array”:

$$y_m = \sum_{m \in \mathbf{X}} 1, \text{ for } m \in \mathbb{N}_0, m < S^2 \quad (3.7)$$

7. Calculate the total propensity array, $\mathbf{A} \in \mathbb{R}^{((\text{rows}(\mathbf{D})+\text{rows}(\mathbf{N})) \times 1)}$ from each event in $\mathbf{D}$ and $\mathbf{N}$, which has the elements:

$$\begin{aligned} a_i &= \{p \in \mathbf{D}_i\} y_{x_0 \in \mathbf{D}_i} \text{ and} \\ a_{i+\text{rows}(\mathbf{D})} &= \{p \in \mathbf{N}_i\} y_{x_0 \in \mathbf{N}_i} \end{aligned} \quad (3.8)$$

8. Determine the time step, τ , drawn from the probability density function:

$$f(\tau|\mathbf{A}) = \sum a_i \exp(-\tau \sum a_i) \quad (3.9)$$

9. Determine which lattice event occurs using probabilities:

$$P_i = \frac{a_i}{\sum a_j} \quad (3.10)$$

10. From a uniformly random distribution, choose the reactive interface, *i.e.*, the allowable interface at which the reaction takes place.
11. Update $\mathbf{X}$ and $\mathbf{Y}$. The reactive interface (an element in $\mathbf{X}$) and the interfaces adjacent to the reactive interface will be updated. The interface count array $\mathbf{Y}$ is updated by subtracting the previous the values of $\mathbf{X}$ and adding the new values of $\mathbf{X}$ to their corresponding elements in $\mathbf{Y}$. (Refer to the code at the URL below for a complete definition of adjacent elements in $\mathbf{X}$).

12. Check if exit condition is reached. If yes: continue; else: return to Step 7. The exit condition should be determined on a case-by-case basis. In this work, a specified simulation time is used and alternatives include a specified number of time steps or composition (though specifying a composition as an exit condition will not ensure that the composition will ever be reached).
13. Using the inverses of Equations 3.5 and 3.6, calculate $\mathbf{L}$. End.

It should now be clear that the solution of the model is equivalent to sampling from a Markov chain where the elements of $\mathbf{X}$ define the system state; further, each step of the Markov chain will be assigned a step time in continuous time by assuming that each step is a Poisson process with intensity equal to the sum of all event propensities. The algorithm has been written in Python using NumPy [104] and the code is available at www.bitbucket.org/rlovelett/stochastic_solid_state. Moderately sized simulations (about 1000 elements in $\mathbf{L}$, 100 elements in $\mathbf{D}$ and $\mathbf{N}$, and 10^7 time steps) run in several minutes on a typical personal computer.

Determining the appropriate lattice size (*i.e.*, the dimensions of $\mathbf{L}$) requires a trade-off between the computational cost (reduced by using small lattices) and the variance of the model predictions (reduced by using large lattices). With the exception of edge effects that are present when simulating very small lattices, the dimensions do not affect the average model predictions (*i.e.*, the model “accuracy”). However, changing the dimensions of $\mathbf{L}$ might inadvertently change the *physical system that the model describes*. For example, adding rows to $\mathbf{L}$, without changing the other model parameters, would model a film with a greater thickness. Therefore, in the subsequent section, I show how physical properties are functions of both the propensity constants and the *size of an individual lattice site*. To ensure that model accuracy is not sacrificed when the number of *rows* in $\mathbf{L}$ is changed, the propensity constants must be rescaled using the functions that we derive in the next section (however, if the number of *columns* is changed, no other changes are necessary).

3.2.2 Relation to Physical Properties

One of the advantages of a spatially distributed model is its ability to decouple the rates of different processes—reactions, adsorption, desorption, and diffusion. The physical properties that govern these rates can be related to the propensity constants used to advance the model and to the dimensions of the lattice. I now show how to derive physical property values from the value of the propensity constants and the size of lattice sites.

3.2.2.1 Reaction Propensity

In its original implementation, the Gillespie algorithm's propensity constant, c_i , is related to the macroscopic reaction rate constant, k_i according to $k_i = V^{b-1}c_i$, where V is the reactor volume and b is the reaction order. Solid state reaction systems are analogous, except that these reactions occur at surfaces. I assume that every formula unit on a lattice site is available for reaction at the surface, *i.e.*, that diffusion within a lattice site is rapid. The characteristic surface area for reaction is ℓ^2 , where ℓ is the length of a lattice site. Therefore, the rate constant can be written as:

$$k_i = \ell^2 \rho_{n,s} p_i \quad (3.11)$$

where $\rho_{n,s}$ is the area specific number density (units of inverse area) of formula units. With enough data at varying temperature, activation energies of the reactions can be estimated using the Arrhenius equation.

3.2.2.2 Adsorption Propensity

The rate of adsorption can be described by the product of the rate of collisions between a surface and a gas, and a sticking coefficient, S_i , or the probability that the species will stay on the surface. In some cases, such as in reactions with hydride gases, the probability of dissociation of a gas phase species should also be included. For simplicity, however, probability of hydride gas dissociation will be lumped with the sticking coefficient. First, from kinetic theory, we can determine the rate of collisions

with the surface per area, $F_{i,a} = P_i/\sqrt{2\pi M_i k_b T}$, where $F_{i,a}$ is the adsorptive flux of species i ($\text{m}^{-2}\text{s}^{-1}$); P_i , the partial pressure; M_i , the molecular weight; k_b , Boltzmann's constant; and T , the absolute temperature. Therefore, the rate of adsorption on a single lattice site can be determined using the area of that lattice site: $r_{ads} = F_{i,a} S \ell^2$. However, this rate is in *molecules* per time, not *lattice sites* per time; thus, it should be scaled by the number of molecules in a lattice site, or $\rho_n \ell^3$, where ρ_n is the number density of the species. Since $1/p_i$ is the average time until an adsorption event occurs on a single site, p_i is the stochastic equivalent of the rate of adsorption on a single lattice site. If the propensity constant is known, then S_i can be written as:

$$S_i = \frac{p_i \sqrt{2\pi M_i k_b T}}{\rho_n \ell^5 P_i} \quad (3.12)$$

The adsorption propensity is an important adjustable parameter that can be used to model several common situations. First, adsorption may be “selective”, that is, an adsorbent is more likely to adsorb on one particular substrate than on others. Selective adsorption can be modeled by adjusting the adsorption propensity for each pair of possible adsorbent and substrate species. Second, the concentration and/or flux of adsorbing species may be time-dependent for some manufacturing processes. The adsorption propensity can be made a function of time in order to model these dynamic deposition processes.

3.2.2.3 Desorption Propensity

Desorption is physically equivalent to evaporation. Unlike other lattice events, however, the rate of evaporation is not a function of thermodynamic properties only; it depends also on system-specific parameters such as gas flow rate and reactor geometry. Therefore, the rate of evaporation is best captured by a mass transfer coefficient, $k_{m,i} = F_{i,e}/\Delta f_i$, where $F_{i,e}$ is the evaporative flux, and Δf_i is the difference in the species i fugacity between the adsorbed phase and gas phase. Assuming that the gas phase is ideal, the fugacity difference reduces to $(P_{vap,i} - P_i)$. Similar to the adsorption case, the rate of evaporation from a single lattice site can be determined, $r_{evap} = F_{i,e} \ell^2$,

scaled by the number of molecules in a lattice site, and set equal to the propensity constant. Solving for $k_{m,i}$ yields:

$$k_{m,i} = \frac{p_i}{\rho_n \ell^5 (P_{vap,i} - P_i)} \quad (3.13)$$

3.2.2.4 Diffusion Propensity

Multicomponent systems with significant diffusion limitations can be challenging to model appropriately. However, because the modeling approach involves binary interactions between species, the propensity constants for diffusion events can be related to binary diffusivities, using a well-known result from statistical physics:

$$D_{s_1,s_2} = \int_t^\infty R(t') dt' \quad (3.14)$$

Here D_{s_1,s_2} is the diffusivity and $R(t')$ is the velocity autocorrelation function of species s_1 surrounded by species s_2 , defined as $R(t') = \langle \mathbf{v}(t) \cdot \mathbf{v}(t + t') \rangle$, denoting the inner product of $\mathbf{v}(t)$ and $\mathbf{v}(t + t')$. For the model presented here, consider a single lattice point with value s_1 surrounded by an infinite lattice species s_2 . In this case, because there are four s_1, s_2 interfaces, the propensity for diffusion is $a_{s_1,s_2} = 4p_{s_1,s_2}$, which means that the average time until the occurrence of a diffusion event is:

$$\overline{\Delta t_k} = \frac{1}{4p_{s_1,s_2}} \quad (3.15)$$

Therefore, the velocity magnitude of species i is $4p_{s_1,s_2}\ell$. Choosing the current time to be immediately before a diffusion event, and recognizing that this model consists of discrete time steps, Equation 3.14 can be rewritten as:

$$D_{s_1,s_2} = \langle \mathbf{v}_0 \cdot \mathbf{v}_0 \rangle \Delta t_0 + \sum_{k=1}^{\infty} \langle \mathbf{v}_0 \cdot \mathbf{v}_k \rangle \Delta t_k \quad (3.16)$$

where $\mathbf{v}_k$ is the velocity of species s_1 during time step k , Δt_k is the duration of time step k , and initial element of the series ($k = 0$) is moved outside the summation. Considering that the direction of the velocity vector $\mathbf{v}_k$ will be chosen randomly from two orthogonal unit vectors and their inverses at each time step, I conclude that the sum will converge to zero, and that only the average value of the first term should be

retained. Therefore, by using the average velocity magnitude and average time until the occurrence of an event given in Equation 3.15, the binary diffusivity is obtained as:

$$D_{s_1,s_2} = 4p_{s_1,s_2}\ell^2 \quad (3.17)$$

Finally, I should note that the approach presented here is unconventional for describing diffusion in solids. Typically, the crystallinity of the material should be taken into account explicitly and non-isotropic effects should be considered. This analysis, however, does not include non-isotropic effects or explicitly consider the presence of discrete crystalline grains. Therefore, the approach will strictly only be valid if (1) the crystal does not show preferential orientation *and* (2) grain interior diffusion (such as interstitial or vacancy-mediated diffusion) occurs at a rate similar to or greater than grain boundary diffusion. The second condition could be very restrictive, as grain boundary diffusion usually dominates in polycrystalline films. However, if this assumption were to be violated, the result would be that the diffusion propensities in the model would correspond to *effective* diffusion coefficients (via Equation 3.17). In this case, the diffusion coefficient would not correspond to the energy of a fundamental reaction step or obey the Arrhenius relation that is typical of solid state diffusivities. However, in cases where defect-mediated diffusion *is* the dominant mechanism of mass transfer, information about the defect concentration can be incorporated into the model for more accurate estimation of the diffusion propensity.

3.3 Application to Cu(InGa)(SeS)₂ film growth

3.3.1 Reaction Mechanism

To apply the model to the reaction of Cu-In-Ga precursor with H₂S and H₂Se, a reaction mechanism must be specified. As discussed in Section 3.1.2, the specific phases or species involved vary somewhat among groups, suggesting that the reaction pathway may be process dependent. However, some elements are common to each mechanism. First, there are at least two stages to the reaction: (1) metal chalcogenide formation (e.g., InSe, InS, Ga₂Se₃), and (2) chalcopyrite formation (CuInSe₂, CuInS₂,

etc.). Second, although reaction rates are often not determined quantitatively, it is suggested that the reaction of Se and In is faster than the reaction of Se and Ga. This asymmetry in reaction rates leads to mostly CuInSe₂ near the front and Ga-containing species accumulated at the back. Finally, for the initial condition, I assume that a mixture of CuIn and CuGa binary species is an adequate simplified representation of an actual metal precursor, which typically contains more complex Cu-Ga-In alloys and elemental In [105]. Consequently, I propose that the system can be modeled using the mechanism in Table 3.2.

3.3.2 Parameter Reduction

The reaction mechanism presented in Table 3.2 involves 12 reaction propensities, 4 adsorption/desorption propensities, and, in principle, $\binom{14}{2} = 91$ unique diffusion propensities (though many are neglected). Furthermore, the lattice size may affect the model results (see Section 3.2.2) and will greatly affect the computation time. With such a large parameter set and a computationally intensive model, conventional parameter fitting is impractical. I present three simplifying assumptions and heuristics and show how they can be used as a guide in determining physically meaningful estimates for the model parameters.

1. **Parabolic Film Growth:** Results from the literature [61, 93] suggest that Cu(InGa)(SeS)₂ films produced via reaction of metal precursors follow a parabolic growth mechanism, referring to a solid state reaction process where there is a planar, advancing reaction front, rather than a nucleation and growth mechanism. Invoking this mechanism suggests that the gas phase reactants, Se and S, can diffuse through reacted species, but not through the original CuIn and CuGa species. Therefore, diffusion propensities are set such that no species can diffuse with precursors—except for precursors themselves (CuIn and CuGa), which may diffuse with each other.

Recognizing that the diffusion of Se and S are rate limiting in the parabolic mechanism, the magnitude of the diffusion coefficients can be estimated using the characteristic diffusion time:

$$\tau_D = \frac{L^2}{D_{s_1, s_2}} \quad (3.18)$$

Since the reaction takes place on the order of minutes and the film thickness is approximately 2 μm , a reasonable estimate for the diffusivity of Se is $6.7 \times$

Table 3.2: Reaction mechanism/lattice events for chalcopyrite production with values of baseline propensity constants (p). Propensity constants, as shown in Section 3.2.2, depend on the size of the lattice element, ℓ . In this example, $\ell = 100$ nm. Each reaction takes place between exactly two lattice sites; for accurate stoichiometry, Se and S sites are twice as number-dense, and chalcopyrite sites are half as number-dense as other species; *atomic* number density is therefore constant across lattice sites. For diffusion events, all pairs of species not shown here have baseline diffusion propensities of zero. Refer to Section 3.3.2 for justification of zero-valued diffusion propensities.

Event Class	Event	p
Adsorption/ Desorption	Selenium Adsorption	0.20
	Sulfur Adsorption	0.01
	Selenium Desorption	5.00
	Sulfur Desorption	5.00
Binary Selenide/ Sulfide Formation	$\text{CuIn} + 2 \text{Se} \longrightarrow \text{CuSe} + \text{InSe}$	50.00
	$\text{CuGa} + 2 \text{Se} \longrightarrow \text{CuSe} + \text{GaSe}$	1.00
	$\text{CuIn} + 2 \text{S} \longrightarrow \text{CuS} + \text{InS}$	1.00
	$\text{CuGa} + 2 \text{S} \longrightarrow \text{CuS} + \text{GaS}$	25.00
Chalcopyrite Formation	$\text{CuSe} + \text{InSe} \longrightarrow \text{CuInSe}_2$	0.10
	$\text{CuSe} + \text{GaSe} \longrightarrow \text{CuGaSe}_2$	0.10
	$\text{CuS} + \text{InS} \longrightarrow \text{CuInS}_2$	0.10
	$\text{CuS} + \text{GaS} \longrightarrow \text{CuGaS}_2$	0.10
	$\text{CuS} + \text{InSe} \longrightarrow 0.5 \text{CuInSe}_2 + 0.5 \text{CuInS}_2$	0.10
	$\text{CuS} + \text{GaSe} \longrightarrow 0.5 \text{CuGaSe}_2 + 0.5 \text{CuGaS}_2$	0.10
	$\text{CuSe} + \text{InS} \longrightarrow 0.5 \text{CuInSe}_2 + 0.5 \text{CuInS}_2$	0.10
	$\text{CuSe} + \text{GaS} \longrightarrow 0.5 \text{CuGaSe}_2 + 0.5 \text{CuGaS}_2$	0.10
Diffusion	$\text{CuIn} \longleftrightarrow \text{CuGa}$	20.00
	$2 \text{Se} \longleftrightarrow \text{CuInSe}_2$	1.00
	$2 \text{Se} \longleftrightarrow \text{CuGaSe}_2$	1.00
	$2 \text{Se} \longleftrightarrow \text{CuInS}_2$	1.00
	$2 \text{Se} \longleftrightarrow \text{CuGaS}_2$	1.00
	$2 \text{S} \longleftrightarrow \text{CuInSe}_2$	10.00
	$2 \text{S} \longleftrightarrow \text{CuGaSe}_2$	10.00
	$2 \text{S} \longleftrightarrow \text{CuInS}_2$	10.00
	$2 \text{S} \longleftrightarrow \text{CuGaS}_2$	10.00

$10^{-14} \text{ m}^2\text{s}^{-1}$. After selecting a lattice size, the diffusion coefficients can be used to estimate the propensity constant for diffusion from Equation 3.17. In the simulations presented below, the lattice size is 100 nm, suggesting 1.7 (which is truncated to 1.0) is a reasonable estimate of selenium diffusion propensity.

2. **Slow Chalcopyrite Interdiffusion:** One feature commonly observed in chalcopyrite films produced by reaction of metal precursors is a persistent gradient in gallium. That is, a gallium gradient forms and does not quickly anneal out to yield a uniform film [42, 45, 49, 106, 107]. However, because $\text{Cu}(\text{InGa})(\text{SeS})_2$ is a continuous solid solution, the gradient is not a thermodynamic limitation, but must be limited by mass transfer. Therefore, I set the diffusion propensities of fully reacted species with each other to be zero, as their diffusion time is longer than the time scale of a typical reaction.
3. **Fast Precursor Interdiffusion:** In contrast to fully reacted chalcopyrite species, the unreacted species must interdiffuse relatively quickly. The fast interdiffusion of CuIn and CuGa (at least faster than the time scale of the diffusion and reaction of Se) is required for the reaction asymmetry to cause composition gradients.

The three heuristics presented above were used to guide parameter selection, especially the diffusion propensities for all sulfur-free lattice events (sulfur-containing lattice events are discussed in the next section when sulfur-containing models are presented). From the first heuristic, to ensure a reasonable time scale, the diffusion propensities of selenium with chalcogenides and chalcopyrites were set to 1.0. Based on the second heuristic, most of the remaining diffusion propensities were set to zero, except for interdiffusion of precursor species (CuIn and CuGa). The third heuristic compels us to select a diffusion propensity for CuIn and CuGa that is larger than that of selenium and reacted phases; therefore I selected 20.0 for the baseline. As discussed earlier, the rate of reaction of Se and In species is much faster than Se and Ga, therefore a baseline estimate for the propensity constant is 50.0 for InSe formation and 1.0 for GaSe formation. The remaining reaction propensities (chalcopyrite formation reactions) did not have a substantial effect on the composition profile and were set to 0.1. One possible approach for estimating adsorption and desorption propensities would be to use first principles and the equations derived in Section 3.2.2. However, unless reasonable estimates for sticking coefficient are available (in many cases, its order of magnitude is much less than 1), I recommend choosing a value of similar order to the propensity

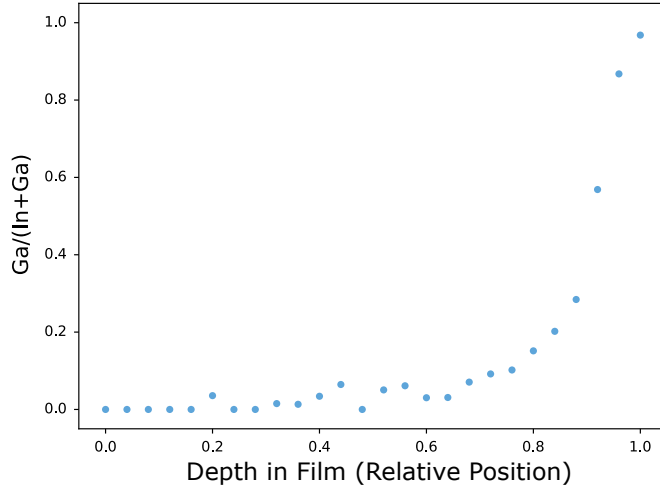


Figure 3.1: Ga profile produced from simulation of an H_2Se -only process.

constants of the other processes to reduce the computational burden. For this case, because significant accumulation of selenium *in its elemental form* is not expected (due to its high vapor pressure and the stability of H_2Se molecules), the propensity of adsorption should be less than propensity for desorption. Therefore, for selenium, adsorption propensity is set to 0.1 and desorption propensity to 5.0. These propensities were used for the baseline simulations presented in the next section and are shown in Table 3.2.

3.3.3 Composition Profile Prediction

The simulation algorithm from Section 3.2 was applied to the chalcopyrite growth model in Table 3.2. The initial lattice, $\mathbf{L}_0$, is 23 rows $\times$ 100 columns, with rows 0 to 11 specified as vacancy elements, and rows 12 to 22 specified as a 0.25:0.75 mixture of CuGa and CuIn elements (this ratio was chosen for industrial relevance). Because $\text{Cu}(\text{InGa})(\text{SeS})_2$ films for photovoltaic cells are typically about 2 μm thick, the 23 rows result in lattice length $\ell \approx 100$ nm. The algorithm was applied to advance the lattice until 40 minutes simulation time elapsed. A useful way to visualize the results from the simulations is to plot the $\text{Ga}/(\text{In}+\text{Ga})$ and $\text{S}/(\text{S}+\text{Se})$ ratios as functions of

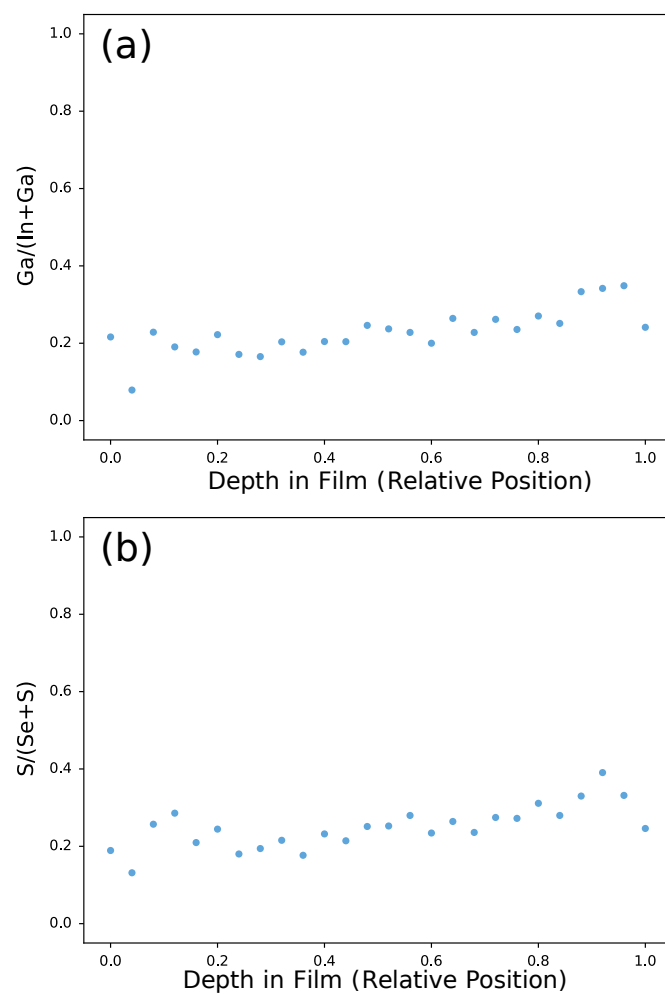


Figure 3.2: Profiles of Ga (a) and S (b) produced from simulation of an $\text{H}_2\text{Se}+\text{H}_2\text{S}$ process.

depth.

For a first case, I considered a process with only H_2Se , for which the propensity for adsorption of H_2S was therefore set to zero. The results are shown in Figure 3.1, where a large amount of gallium accumulates near the back of the film, which is a feature that has been well-documented experimentally [45, 49, 98].

For a second case, the precursors are reacted simultaneously in equal concentrations of H_2Se and H_2S . The simultaneous reaction process is modeled by setting adsorption of sulfur lower than adsorption of selenium, but diffusion of sulfur faster than diffusion of selenium. Through-film profiles of gallium and sulfur are shown in Figure 3.2. Consistent with experimental results from Kim et al. [50], gallium is distributed more homogeneously than in a process with H_2Se only.

A third case is that of a selenium-capped precursor (*i.e.* a layer of elemental selenium is deposited on the metal precursor) reacted in H_2S . Experimental results for reactions with selenium-capped precursors are presented in Chapter 5. The simulated through-film gallium and sulfur profiles are shown in Figure 3.3. Similar to the $\text{H}_2\text{Se}/\text{H}_2\text{S}$ process, the gallium gradient is much more homogeneous than in a H_2Se only process.

The gallium and sulfur profiles in Figures 3.1, 3.2, and 3.3 result from complex interactions of the different propensity constants. One way to understand how these profiles arise is to examine the dynamics of the process. A simplified representation of the dynamics is shown in Figure 5.5, where composition is spatially averaged through the entire film and shown as a function of time. In the first case, because the propensity for reaction with CuIn is much faster than with CuGa , most CuGa remains in its precursor form until nearly all of the CuIn is converted to chalcopyrite. During this time, CuGa diffuses toward the back contact leading to the profile in Figure 3.1. For the second case, with H_2Se and H_2S , there is first a rapid increase in CuInSe_2 because of the relatively faster adsorption of Se compared to S; however, the faster diffusion of sulfur, combined with its preference to react with CuGa , leads to more incorporation of CuGa earlier in the process than if there were H_2Se alone.

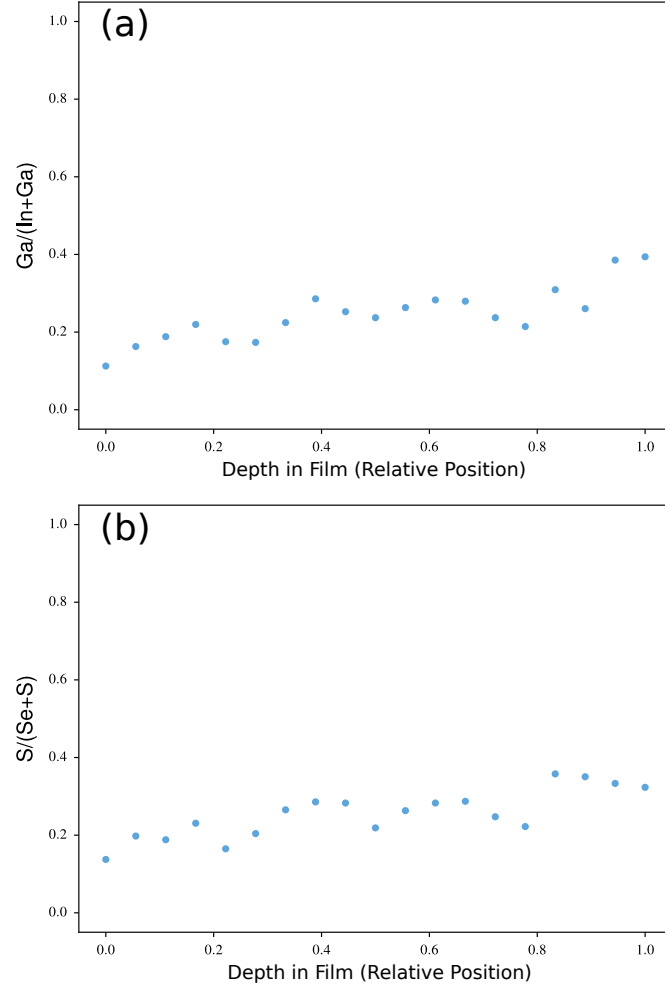


Figure 3.3: Profiles of Ga (a) and S (b) produced from simulation of a selenium capped precursor in an H_2S atmosphere process, where the initial selenium thickness is four times the precursor thickness (*i.e.* 40 lattice sites, or four times the stoichiometric amount of selenium required)

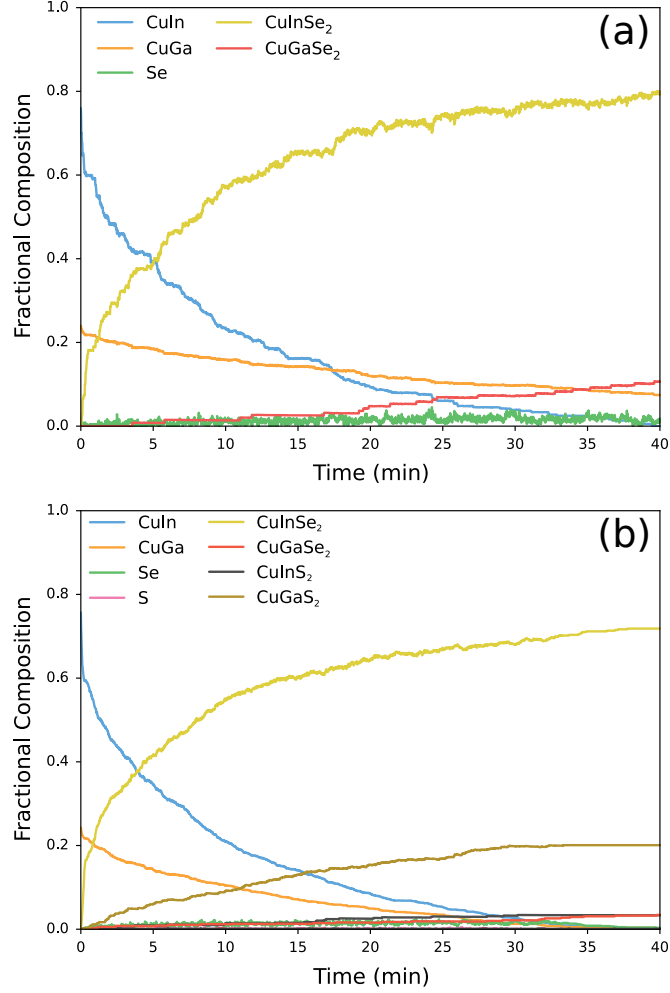


Figure 3.4: Time evolution of composition of the reacting film for the reaction in (a) H_2Se only and (b) H_2Se and H_2S . Fractional composition is the fraction of occupied lattice sites, or volume fraction of the film. The intermediate phases, binary selenides and sulfides, are not shown but exist as a small volume fraction throughout the simulation.

3.3.4 Agglomeration Size Distribution

One of the advantages of applying stochastic simulation at the mesoscopic scale is that it allows one to study fluctuations in local composition explicitly. The fluctuations result in some spatially confined features that can be described statistically in the example system, $\text{Cu}(\text{InGa})(\text{SeS})_2$. One of the important features observed experimentally is agglomerations of Ga-rich species at the back contact [98]. In principle, there are two causes of these agglomerations: thermodynamic phase separation, and random fluctuations in species positions (*i.e.* entropy-driven agglomerations). The modeling approach cannot account for thermodynamic phase separations, but can be used to examine the effect of random fluctuations. Although thermodynamic driving forces are likely important in $\text{Cu}(\text{InGa})(\text{SeS})_2$ films (evidenced by formation of Cu_9Ga_4 phase near the back contact [49, 98]), the model results are still presented to demonstrate the approach for characterizing agglomeration size distribution.

For this purpose, simulations with large lattice sizes (2500 columns) were run with no adsorption or reaction events allowed and with precursors (*i.e.*, $\mathbf{L}_0$ matrices) of varying composition and thickness. *Any* isolated collection of CuGa elements is defined to be an agglomeration, regardless of size. Thus, a single, isolated CuGa element is considered a size-1 agglomeration. Figs. 3.5a–d show histograms of the size distribution of agglomerations for different film thicknesses and compositions (which models later stages of the reaction, where the precursor film gets thinner as the front of the film is converted to chalcopyrite).

The negative binomial probability distribution function is considered as an appropriate model for quantifying the effects of composition fluctuations on agglomeration formation for the following reasons: The negative binomial random variable is, by definition, the number of Bernoulli trials with probability p until r “successes” are reached. Further, r can be thought of as a “waiting time” parameter and need not be integer-valued. More generally, the negative binomial random variable is an overdispersed form of a Poisson random variable with mean $\mu = \frac{pr}{1-p} + 1$, but with gamma-distributed intensity. In this form, the r parameter is often referred to as an

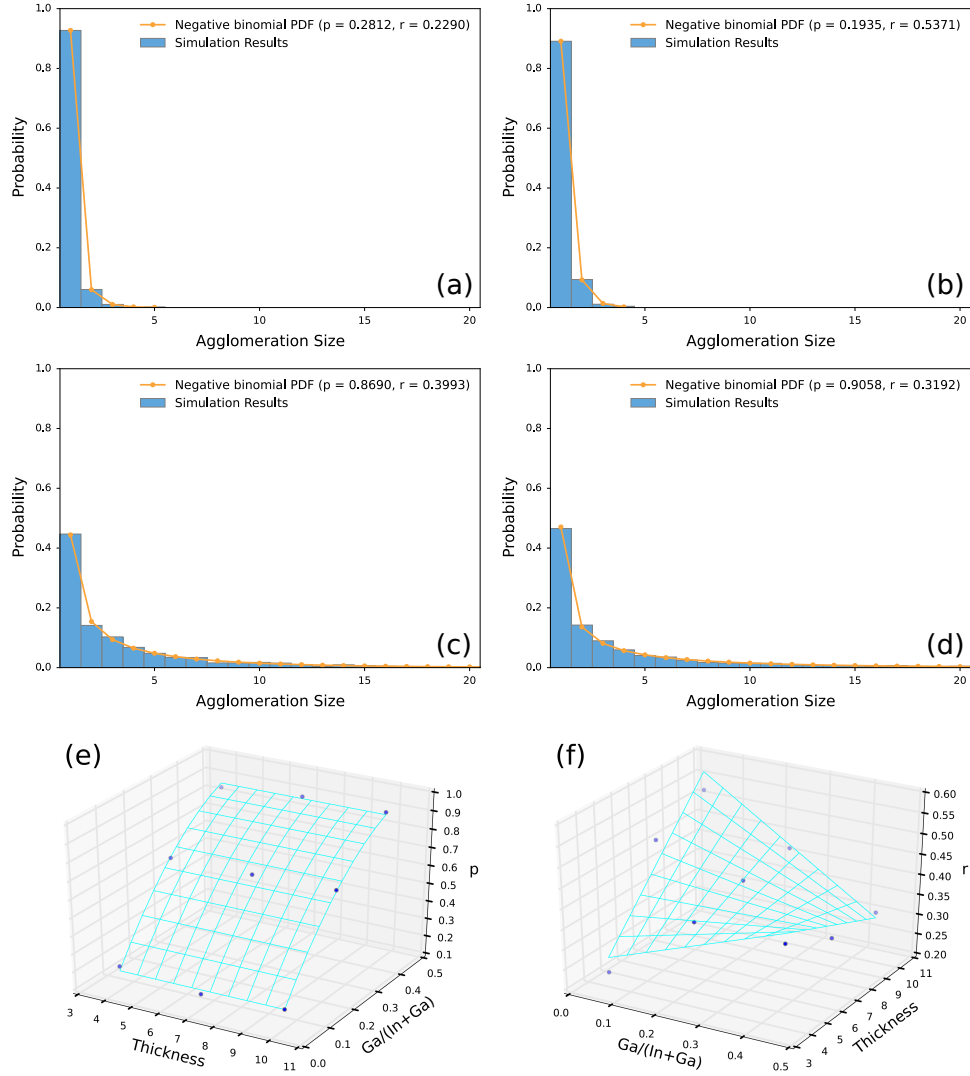


Figure 3.5: (a)–(d) Agglomeration size distribution for CuGa after 10 s simulation time with no reactions/adsorption allowed, for the following compositions ($Ga/(In+Ga)$) and lattice thicknesses (in units of lattice sites), respectively: (a) 0.05, 4; (b) 0.05, 10; (c) 0.45, 4; (d) 0.45, 10. (e) MLE estimates (points) and fitted response surface for negative binomial random variable parameter p . (f) MLE estimates (points) and fitted response surface for negative binomial random variable r .

“aggregation” or inverse dispersion parameter, where as $r \rightarrow 0$, $\sigma^2 \rightarrow \infty$, where σ^2 is variance [108, 109, 110]. Now, if the formation of an agglomeration can be considered as a series of trials, where p is the probability of adding another species to the agglomeration, then the agglomeration size should follow a negative binomial distribution with $r = 1$ (*i.e.*, a geometric distribution). However, because of its improved handling of highly dispersed data, we use the more general negative binomial form allowing both p and r to be estimated. Intuitively, an increasing p or increasing r , will move the distribution rightward, toward a tendency for larger agglomerations.

The expression for the negative binomial probability distribution,

$$f(x|r, p) = \frac{\Gamma(x - 1 + r)}{(x - 1)! \Gamma(r)} p^x (1 - p)^r, \text{ for } x = 1, 2, 3... \quad (3.19)$$

is used to characterize agglomeration size distribution by estimating the two parameters, p and r , using Maximum Likelihood Estimation (MLE) (see Appendix A) from the simulation data.

In order to uncover the effects of geometry (*i.e.*, film thickness) and composition (Ga/(In+Ga)) on the parameters, (p, r) , a face-centered cubic response surface design was constructed, and used it to develop an empirical model. In the response surface model, geometry and composition are considered factors that affect the response variables, p and r . Nine simulations were run with varying lattice thickness and Ga/(In+Ga) ratios; p and r were estimated with MLE; and the estimates were used to fit 2nd order polynomial models of p and r as a function of lattice thickness and composition (see Appendix B). The fitted response surfaces, *i.e.*, the polynomial models, are shown in Figs. 3.5e–f, from which I conclude that the probability of success parameter, p , is a function of only composition. Thus, all else being equal, when the fraction of CuGa sites increases, the agglomerations of CuGa tend to grow larger. The waiting time/aggregation parameter, r , has a more complicated response surface that is strongly affected by the interaction of geometry and composition. Specifically, from the partial derivative of the response surface ($\frac{\partial r}{\partial x_1}$ of Equation B.2), films with a gallium

fraction less than 0.33 form larger agglomerations (due to larger r) when thickness is greater; the inverse is true for films with a gallium fraction greater than 0.33.

3.4 Summary and Conclusions

In this chapter, I have reviewed the previous models that describe the kinetics of the precursor reaction process, reviewed stochastic modeling of chemical systems in general, and developed and presented a novel method for modeling thin film growth using a stochastic simulation method and an algorithm that makes the model computationally tractable for a typical desktop PC. The model was used to simulate the selenization and sulfization processes used to produce Cu(InGa)(SeS)_2 films from metallic precursors. The model explains how the complicated, experimentally observed through-film profiles in Ga and S arise from complex interactions of reaction rates, adsorption rates, and diffusion limitations. Further, I showed how because the model is stochastic, it can be used to understand lateral inhomogeneities, in particular agglomerations, that would otherwise be ignored or averaged out in continuum approaches. In Chapters 4 and 5, the utility of the model will be demonstrated by comparing the model predictions with the results of experiments performed using the RTP selenization reactor described in Chapter 2 for a series of different operating conditions and different precursor structures.

This modeling approach will find wide application in a number of thin film or other solid state material systems. In particular, this approach will be especially useful for vacuum-deposited Cu(InGa)Se_2 , for $\text{Cu}_2\text{ZnSnS}_4$, and for silicon systems with impurities because of similarities to the selenization and sulfization reaction systems, including the potential for composition profiles and lateral heterogeneity. Furthermore, because of the method’s emphasis on material adjacency, it can be applied to systems with complex geometry, such as graphene or carbon nanotubes. More fundamentally, however, the stochastic simulation that was developed is a new approach that could be generalized for any system where system evolution is governed by network connectivity

(in this case, material adjacency) instead of bulk composition, and may be applied in entirely unrelated fields.

Chapter 4

REACTION OF CuInGa PRECURSORS IN H_2Se AND H_2S

4.1 Introduction

The most common method to produce chalcopyrite thin films for solar cells is a reaction of metallic precursors in hydrogen selenide (H_2Se) and hydrogen sulfide (H_2S). Over 1.5 GW annual manufacturing capacity is currently in place and devices fabricated with this method have achieved 22.3% efficiency [13], higher than any other thin film technology. Despite moderate of commercial success, there are still challenges associated with using this method as a fabrication approach including slow reaction kinetics, toxic gas handling, through-film composition gradients, and poor film adhesion. In this chapter, I will present results from the production of $\text{Cu}(\text{InGa})(\text{SeS})_2$ thin films with the hydride gases H_2Se and H_2S using the RTP reactor described in Chapter 2.

4.1.1 Motivation

There are several advantages of using hydride gases for the production of chalcopyrite films for thin film absorber layers. Unlike the other two selenium delivery methods (gas phase Se or S or incorporation of chalcogen in the precursor), hydride gases are stable and easily stored and delivered in the gas phase due to subambient boiling points. Unlike the selenium-capped precursor reaction process (presented in Chapter 5), no additional process step is required for selenium deposition, resulting in a process that has potentially higher throughput and lower capital expenses.

4.1.2 Challenges

Despite the ease-of-delivery, there are some challenges associated with reactions in hydride gases. The most salient challenge is the extremely high toxicity of H_2Se , with

a time-weighted exposure limit of only 50 ppb [111]. The safety challenges required careful design of the reactor and a waste treatment system, which for this work was discussed in Chapter 2. Additionally, while no separate selenium deposition process is required when using H_2Se , the throughput may be limited because film adhesion at the Mo/CuInGaSe_2 interface if the reaction temperature is too high [112], and lower temperature reactions lead to slower conversion and lower throughput.

4.1.3 Project Goals

The goal of the work presented in this chapter is to examine the production of chalcopyrite thin films using the RTP reactor developed in Chapter 2 and to determine if high-quality films can be produced via RTP of precursors in hydride gases. I will examine three rapid processes for the production of chalcopyrite films, including high-temperature single stage reactions, multistage reactions inspired by results from literature, such as from Kim et al. [49], and a “thermal spike anneal” process designed to maximize throughput by controlling input power instead of film temperature. I will present material properties and reaction kinetics results showing that, while single-phase chalcopyrite films can be produced using this method, this method is *not* appropriate for large scale production of absorbers due to poor adhesion and lower quality material. Therefore, in Chapter 5, I will present an alternative process using selenium-capped precursors instead of H_2Se that can yield device quality materials using short reactions.

4.2 Experimental Methods

A series of Cu(InGa)Se_2 and Cu(InGa)(SeS)_2 thin films were prepared using one of three processes: (1) single stage reactions with varying temperature and gas concentration, (2) two- or three-stage reactions with Stage 1 reaction in H_2Se followed by Stage 2 anneal in inert atmosphere, and (optional) Stage 3 reaction with H_2S , and (3) “thermal spike” reaction in H_2Se , where lamp power is set to 100% with varying dwell time to minimize reaction time.

4.2.1 Deposition Methods

Films were deposited on commercially available soda lime glass substrates. First, the glass substrates were thoroughly cleaned using a Crest glass cleaning system with high temperature acidic and basic washes. Next a ~ 700 nm layer of Mo was deposited using DC magnetron sputtering in a commercial system from Lesker. In the same sputtering system, without breaking vacuum, the metallic precursors were deposited by rotationally sputtering from $\text{Cu}_{0.8}\text{Ga}_{0.2}$ and In sputter targets to yield precursors a final Ga/(In+Ga) ratio of approximately 0.25 and Cu/(In+Ga) ratio of approximately 0.9 and a film thickness of approximately 800 nm.

The films were reacted in the RTP system with varying temperature profiles and gas concentrations, always using the charge-and-react configuration described in Chapter 2 unless otherwise noted.

4.2.2 Analytical Methods

The morphology of the samples was examined using an Amray 1810 scanning electron microscope in plan-view and the atomic compositions were measured using an Oxford Instruments PentaFET 6900 energy dispersive x-ray (EDX) spectroscopy detector. The microscope acceleration potential was set to 20 kV, which corresponds to an EDX sampling depth of approximately 0.8 μm , or one half of the total film thickness. For some samples, EDX measurements from the back side, at the CIGS/Mo interface were also obtained. To obtain back side measurements, a second piece of soda lime glass was glued using epoxy or Gorilla[®] glue to the front of the sample, allowed to set, and then peeled off; in most cases, the weakest interface is between Mo and $\text{Cu}(\text{InGa})(\text{SeS})_2$; when the glass was peeled from the sample, the back of the chalcopyrite film was exposed and measured.

The phase composition and crystallinity was examined using x-ray diffraction (XRD) in either a Phillips/Norelco or a Rigaku x-ray diffractometer, both using $\text{Cu K}\alpha$ x-ray sources. In some samples, grazing incidence (GI-)XRD patterns were also measured using angles of incidence from 0.05° to 8° .

Table 4.1: EDX composition measurements for samples produced with 1% H₂Se at 600 °C with varying dwell time.

Dwell time (min)	Cu	In	Ga	Se	$\frac{\text{Cu}}{\text{In+Ga}}$	$\frac{\text{Ga}}{\text{In+Ga}}$	$\frac{\text{Se}}{\text{Cu+In+Ga}}$
0	42.99	48.45	11.27	10.29	0.92	0.24	0.11
2	24.35	26.72	0.86	48.07	0.88	0.03	0.93
5	26.42	25.48	0.78	47.32	1.01	0.03	0.90
10	26.24	25.30	0.94	47.41	1.00	0.04	0.91
20	26.64	24.88	0.96	47.52	1.03	0.04	0.91

Table 4.2: EDX composition measurements from the back (Mo) side of the films for samples produced with 1% H₂Se at 600 °C with varying dwell time.

Dwell time (min)	Cu	In	Ga	Se	$\frac{\text{Cu}}{\text{In+Ga}}$	$\frac{\text{Ga}}{\text{In+Ga}}$	$\frac{\text{Se}}{\text{Cu+In+Ga}}$
5	23.86	9.93	15.74	50.38	0.92	0.61	1.02
10	22.58	10.61	14.92	52.09	0.88	0.58	1.08

4.3 Results and Discussion

4.3.1 Single Stage Reactions

A series of films were produced using a 30 s ramp to 500 °C or a 70 s ramp to 600 °C with 1% H₂Se and varying reaction times. Figure 4.1 shows plan-view SEM images of the samples produced at high temperature, Tables 4.1 and 4.2 show EDX measurements of composition from the front side and back side of the films. Based on morphology alone, it appears that the samples reach a steady-state very quickly, after only a 2 minute reaction. From the SEM images it is evident that “features” form on the surface early in the reaction and that they remain for at least 20 minutes.

From the EDX measurements in Table 4.1, the composition follows a commonly observed trend, first described by Jensen et al. [45] and modeled in Chapter 3, where the reaction of a Cu-In-Ga precursor in H₂Se leads to low gallium near the front of the film, in the EDX sampling volume, with nearly all of the gallium segregated at the back contact. Measurements of the composition from the back side of the film, shown in Table 4.2, confirm that gallium accumulated near the back contact. The gallium

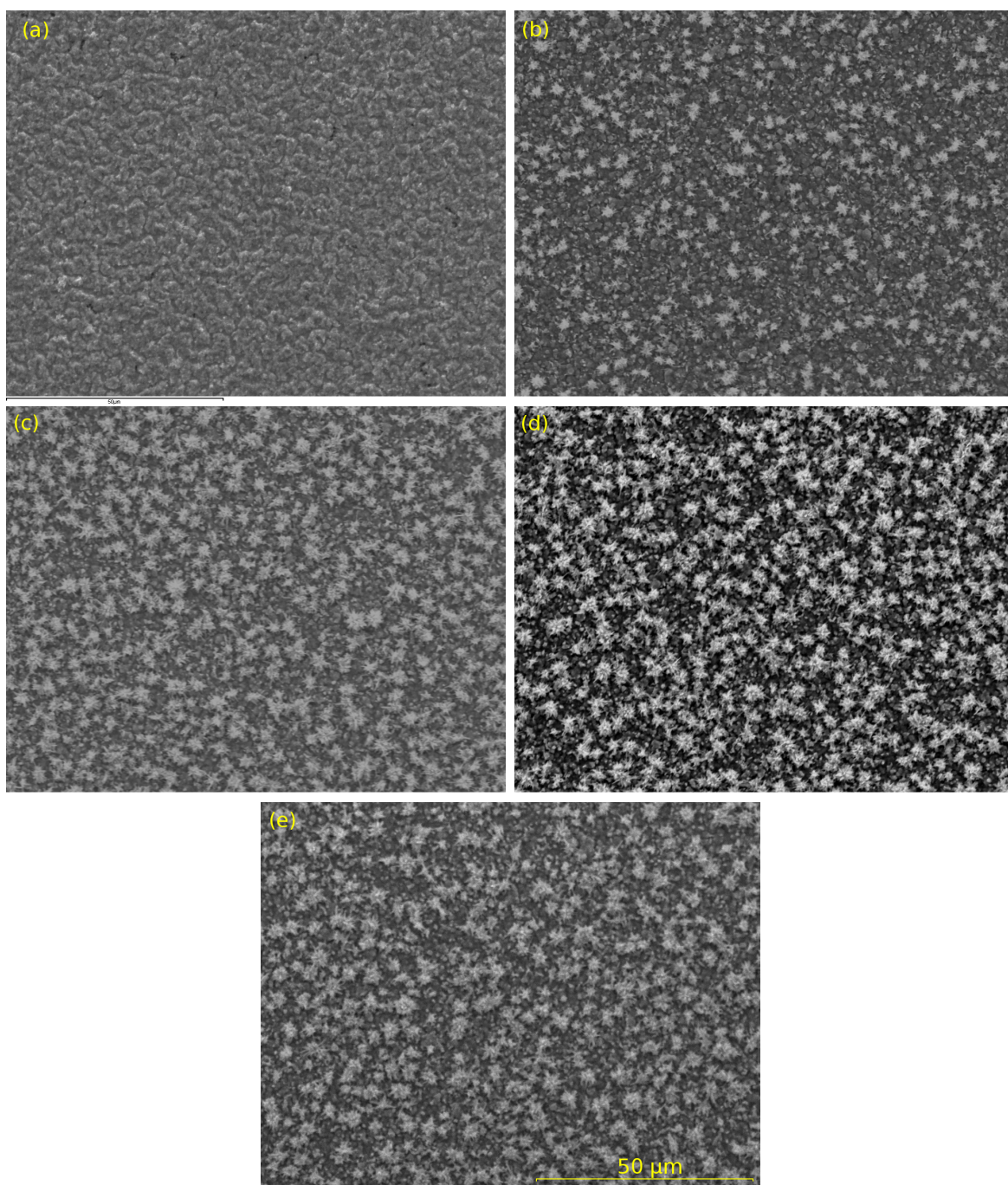


Figure 4.1: Plan view SEM images of samples produced with 1% H₂Se at 600 °C with dwell times of (a) 0 minutes, (b) 2 minutes, (c) 5 minutes, (d) 10 minutes, and (e) 20 minutes.

Table 4.3: EDX spot measurements of composition on the feature and background for sample produced with 1% H₂Se at 600 °C and 5 minute reaction time.

Location	Cu	In	Ga	Se	$\frac{\text{Cu}}{\text{In}+\text{Ga}}$	$\frac{\text{Ga}}{\text{In}+\text{Ga}}$	$\frac{\text{Se}}{\text{Cu}+\text{In}+\text{Ga}}$
Feature	21.49	24.62	0.25	53.64	0.86	0.01	1.16
Background	24.13	25.21	0.91	49.75	0.92	0.03	0.99

segregation occurs very early in the reaction, as all of the atomic fractions and ratios reach an approximate steady state within 2 minutes.

EDX spot measurements can be obtained to understand the composition of the surface features. From the results in Table 4.3, the features are relatively rich in selenium and indium, compared with the background. It is therefore likely that an indium selenide compound forms very rapidly on the surface. Because the films are grown in a selenium-rich environment, the most plausible compound, based on the In-Se phase diagram from Okamoto [113] is In₂Se₃; this is the same phase that Kim et al. [61] identified as having a high activation energy for conversion to chalcopyrite, which may, along with its apparent physical segregation at the surface (which limits mass transfer), explain its persistence.

To examine the phase composition of the film, and test whether the In₂Se₃ phase is present, an XRD pattern was obtained using a symmetric scan for the sample with 10 minute reaction time and is shown in Figure 4.2. As expected, the chalcopyrite, CuInSe₂, the back contact, Mo, and the surface feature, In₂Se₃, are observed in the diffraction pattern.

For the samples prepared at 500 °C, reaction times of 0, 5, and 10 minutes were examined. SEM images are shown in Figure 4.3 and composition data in Table 4.4. Unlike the samples produced at higher temperature, these appear to be fully selenized within 5 minutes. The persistent In₂Se₃ features on the surface are not observed, nor does In₂Se₃ appear in the diffraction pattern in Figure 4.4. Similarly, though, they still have gallium segregated near the back contact, as evidenced by the low Ga/(In+Ga) ratios in Table 4.4

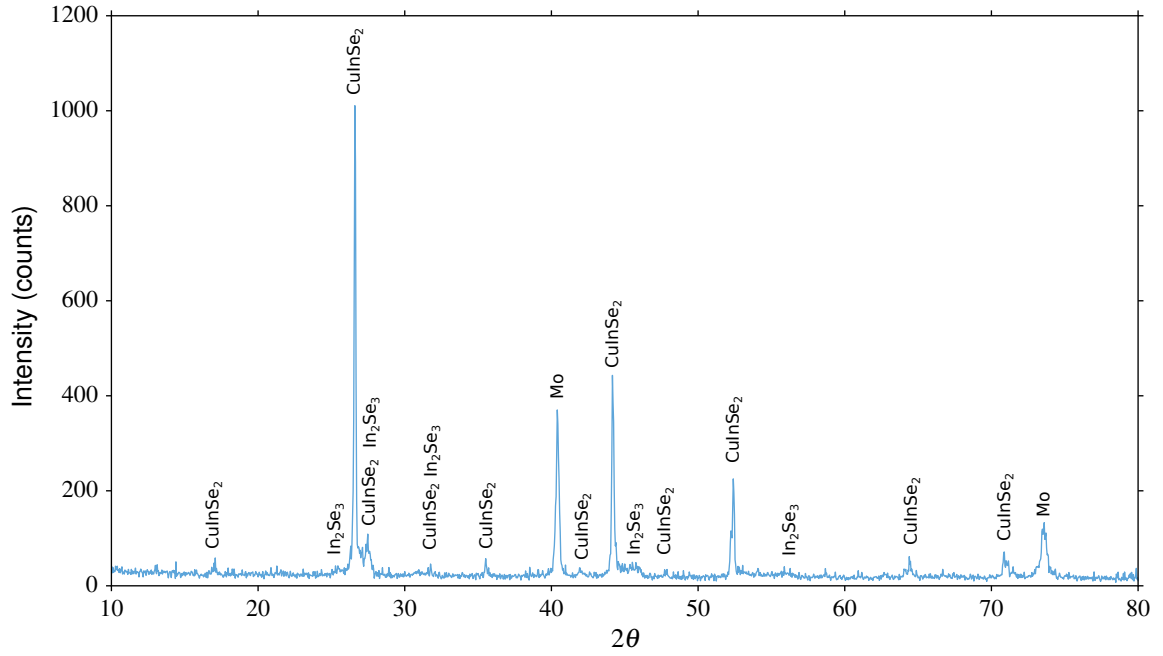


Figure 4.2: XRD pattern from a symmetric scan of samples reacted for 10 minutes at 600 °C with 1% H₂Se with identified peaks labeled.

Table 4.4: EDX composition measurements for samples produced with 1% H₂Se at 500 °C with varying dwell time.

Dwell time (min)	Cu	In	Ga	Se	$\frac{\text{Cu}}{\text{In+Ga}}$	$\frac{\text{Ga}}{\text{In+Ga}}$	$\frac{\text{Se}}{\text{Cu+In+Ga}}$
0	47.05	37.67	12.86	2.49	0.93	0.25	0.03
5	25.33	25.38	0.59	48.70	0.97	0.02	0.95
10	24.33	25.69	0.58	49.40	0.93	0.02	0.98

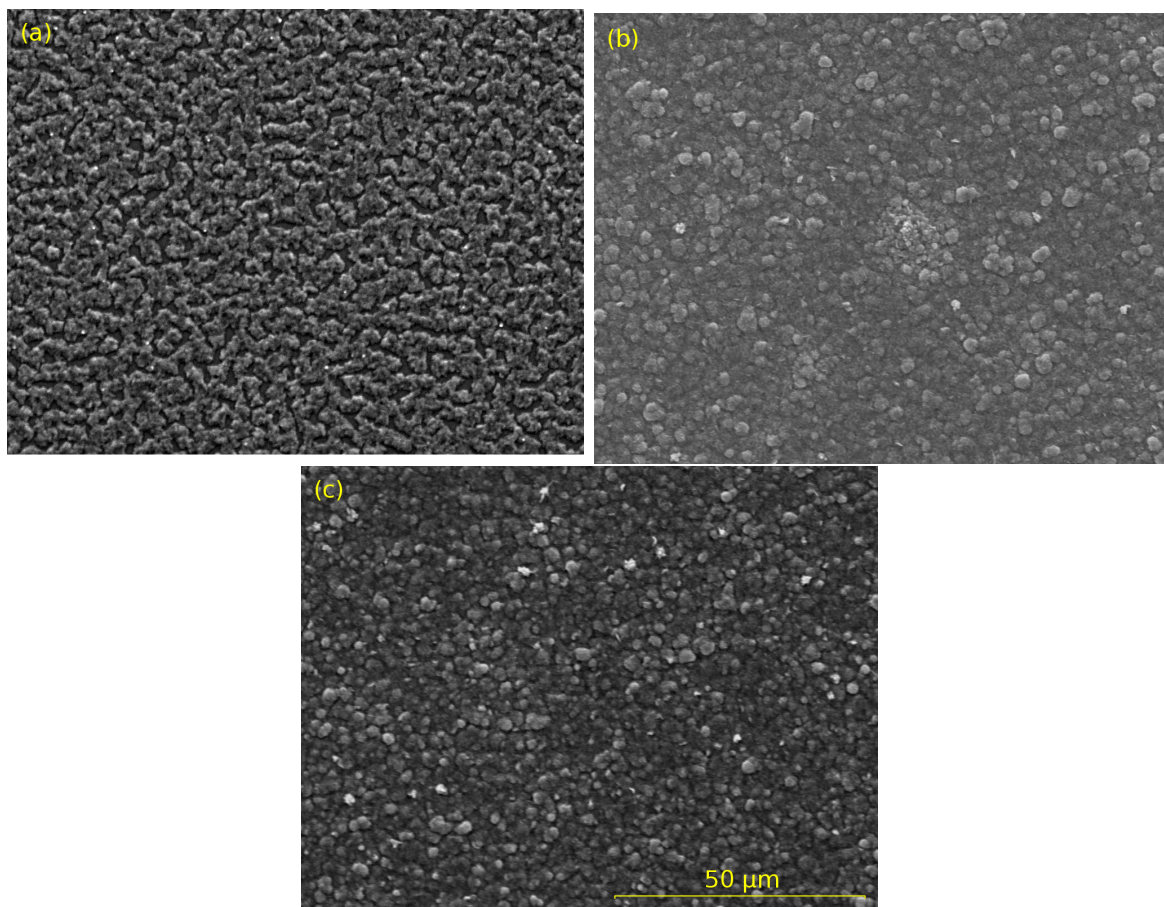


Figure 4.3: Plan view SEM images of samples produced with 1% H_2Se at 500 °C with dwell times of (a) 0 minutes, (b) 5 minutes, (c) 10 minutes.

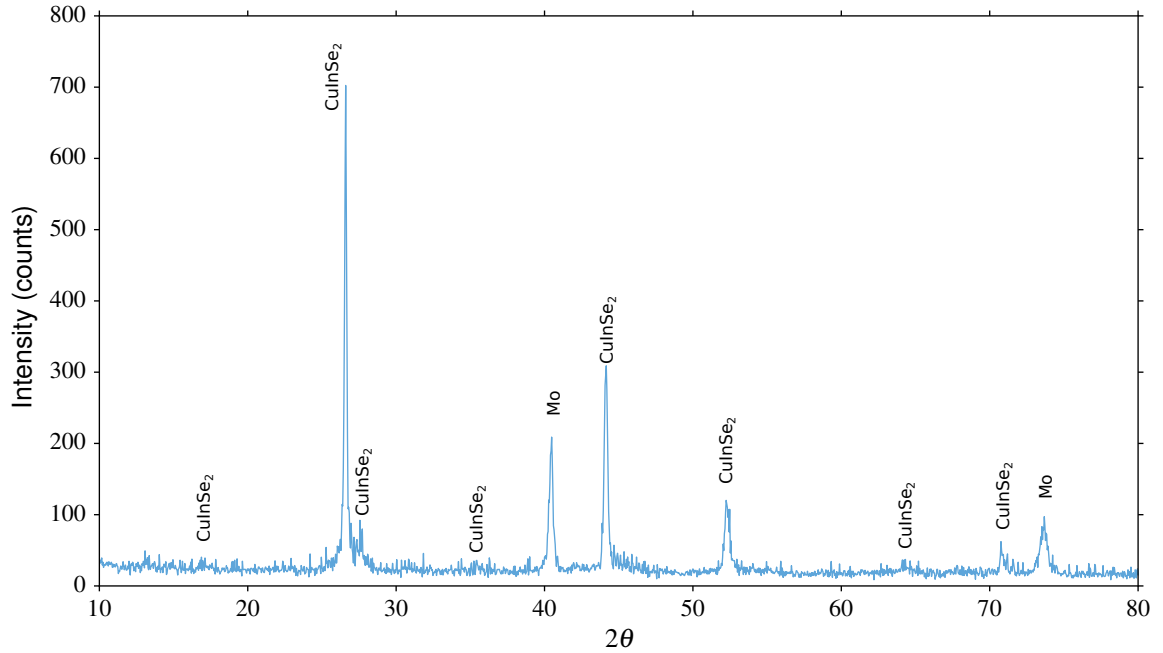


Figure 4.4: XRD pattern from a symmetric scan of samples reacted for 10 minutes at 500 °C with 1% H₂Se with identified peaks labeled.

The results from the high and low temperature processes can be compared directly. Specifically, high resolution XRD patterns of the dominant chalcopyrite peak, the 112 peak at $2\theta \approx 27^\circ$, were measured from each of the samples and are shown in Figure 4.5. As expected from the composition measurements, the films appear to reach a steady state within 5 minutes for both temperatures. However, for the samples produced at 600 °C, the 20 minute reaction appears to have started to homogenize, as the secondary peak, which could be a high-gallium chalcopyrite phase, shifts toward lower 2θ , toward a more homogeneous phase. This shift may be expected based on results from Marudachalam et al. [46], who observed that a 600 °C anneal will eventually result in a homogenous film.

Based on the composition measurements presented in Tables 4.1 and 4.4, it may appear that all of the films are slightly under-selenized. Stoichiometric concentration of selenium would result in a Se/(Cu+In+Ga) ratio of 1.0, but all of these measurements are slightly below 1.0 (though, still within the single phase region). This may be

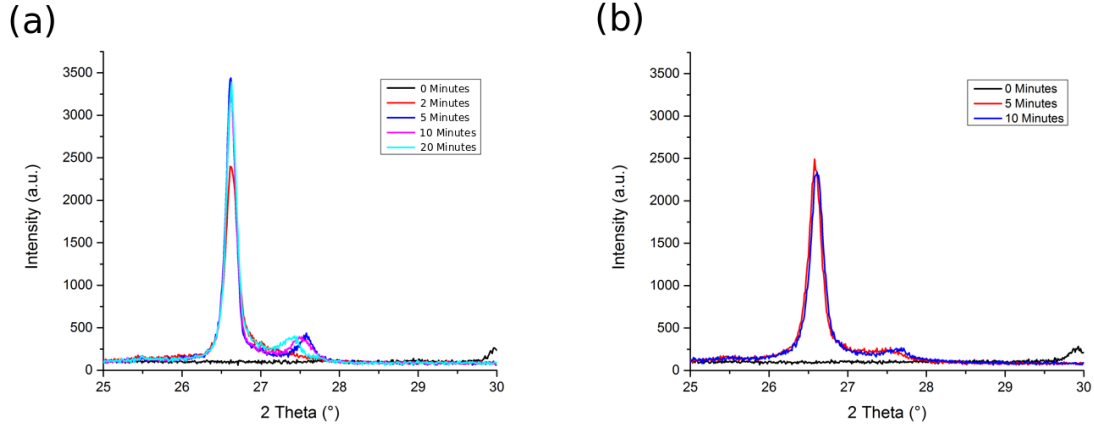


Figure 4.5: XRD patterns of the chalcopyrite 112 peak from samples produced with 1% H_2Se at (a) 600 °C and (b) 500 °C and various reaction times.

explained, in part, by reactor design issues. As shown in Figure 4.6, the volume of gas required to selenize fully a film with 1% H_2Se is slightly larger than the heated area of the reactor; diffusion limitations in the gas phase could be preventing complete reaction. The simplest method for correcting this problem is increasing the concentration of H_2Se ; even 1.5% H_2Se should be sufficient. Unfortunately, film adhesion is affected by gas concentration, and films with a higher concentration of H_2Se flaked off immediately after removing them from the reactor at both 500 °C and 600 °C. Rather than use a lower temperature process, which would require a longer reaction and be contrary to the project motivation, multistage reaction processes were investigated and are presented in Section 4.3.2.

The single stage process with H_2Se is not likely to yield high-quality devices. At high temperature, In_2Se_4 forms on the surface, which will at least increase resistive losses, if not short the junction and result in unusable devices. Even the samples produced at lower temperature are not ideal; the large gradients in gallium would probably result in low voltage devices. Furthermore, all samples were under-selenized, which means that there are likely residual intermetallic phases with concentrations lower than the detection limit of the XRD patterns; these residual intermetallic phases could result in resistive losses. However, a larger problem is very poor adhesion at

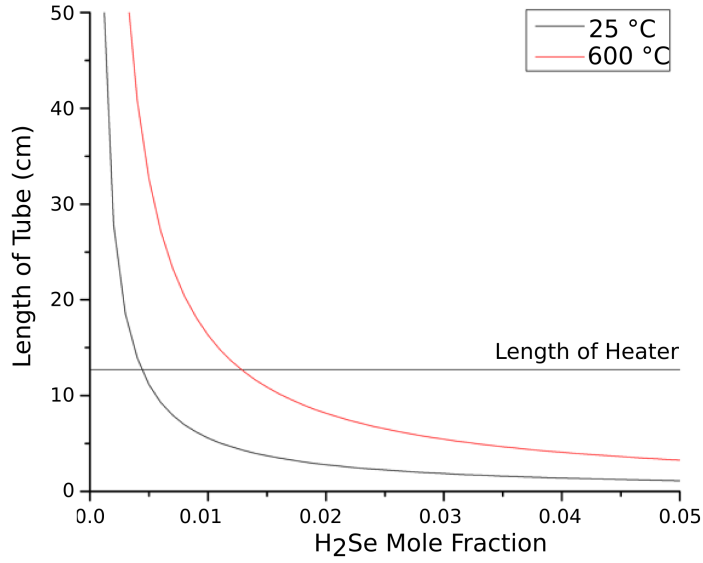


Figure 4.6: Volume of gas, in units of reactor length, required to selenize fully a sample, assuming complete conversion, at ambient temperature and 600 °C.

the chalcopyrite/Mo interface. All films delaminated in the chemical bath that is used to form the junction (see Chapter 5 for device fabrication details), rendering device fabrication impossible.

4.3.2 Multistage Reactions

Most precursor reaction processes used in industry use a multistage reaction process in order to achieve the desired material properties. However, conventional multistage precursor reaction processes require long residence times that limit process throughput. In this section, I describe the results from short 2- or 3-stage reaction processes.

The time-temperature profile for the multistage reactions is shown in Figure 4.7; it is inspired by the 3-stage process presented by Kim et al. [49]. In that work, the authors observed that an incomplete reaction with H₂Se in the first stage will result in CuInSe₂ at the front of the film, and Cu-Ga inter metallic phases at the back

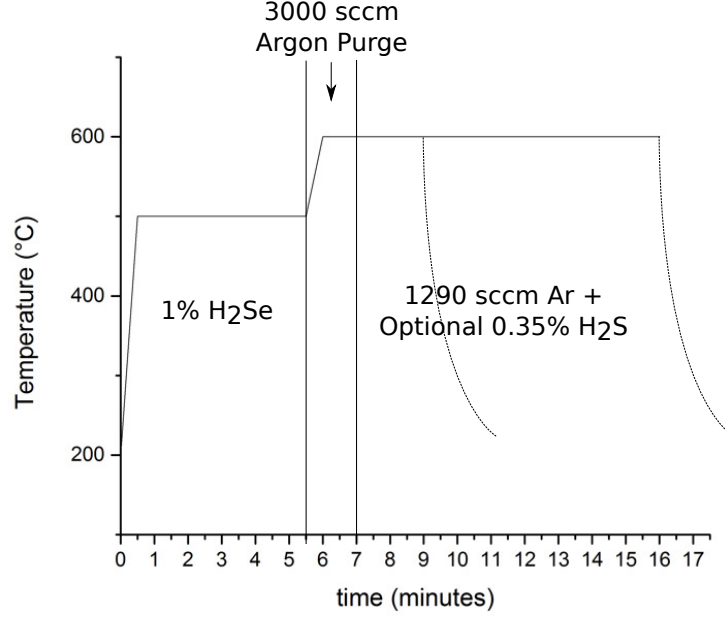


Figure 4.7: Time-temperature profile of the 2- and 3-stage reactions using hydride gases. First stage is reaction in H_2Se ; second is anneal in argon; third is optional reaction in H_2S ; dashed lines show approximate cooling profiles.

contact. Next, in the second stage, an inert anneal will cause a recrystallization where the gallium diffuses toward the front of the film and a more homogeneous gallium distribution is observed. Finally, the third stage is a short reaction in H_2S that increases the band gap at the front of the film to increase device voltage. The process shown in Figure 4.7 follows those same steps (with third stage optional) at higher temperatures to attempt to replicate the process with a shorter reaction time. Instead of the rate-limited Stage 1 from Kim et al. [49], the first stage in this process would be limited by selenium delivery, due to the insufficient supply of H_2Se in the gas phase, shown in Figure 4.6. Notice that only the first stage of the reaction is run in the charge-and-react configuration; after that stage, an argon purge followed by an anneal or second reaction occurs in flowing gas.

Figure 4.8 shows SEM images of samples with 2 and 10 minute anneals in argon (*i.e.* samples following each of the cooling profiles in Figure 4.7) and Table 4.5 shows

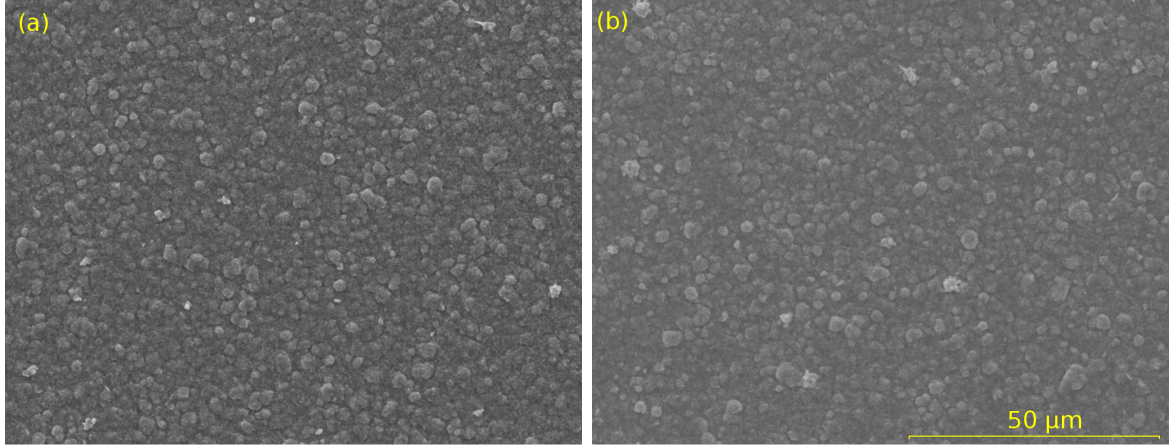


Figure 4.8: Plan view SEM images of samples produced using 2-stage process shown in Figure 4.7 with (a) 2 minute and (b) 10 minute anneals in argon.

Table 4.5: EDX composition measurements for samples produced using 2-stage process shown in Figure 4.7 with varying argon anneal time.

Stage 2 Time (min)	Cu	In	Ga	Se	$\frac{\text{Cu}}{\text{In}+\text{Ga}}$	$\frac{\text{Ga}}{\text{In}+\text{Ga}}$	$\frac{\text{Se}}{\text{Cu}+\text{In}+\text{Ga}}$
0	25.33	25.38	0.59	48.70	0.97	0.02	0.95
2	24.73	25.38	0.57	49.32	0.95	0.02	0.97
10	24.02	25.02	1.23	49.73	0.92	0.05	0.99

EDX composition measurements from 0, 2, and 10 minute argon anneals (the 0 minute anneal data is from the same sample as the 5 minute single stage reaction sample from Section 4.3.1 above).

There are no substantial changes in surface morphology during the argon anneal and no large change in the measured compositions, though the 10 minute anneal shows a small increase in gallium near the front. This increase in gallium is also suggested by the XRD patterns of the 112 peaks from the 0, 2, and 10 minute anneals, shown in Figure 4.9. In addition to the substantially increased crystallinity (seen from sharper peaks), a secondary, gallium rich phase appears to shift to lower values of 2θ , indicating more incorporation of indium, when the argon anneal is longer.

A short 3-stage reaction with a 5 minute reaction in H_2Se at 500 °C, 1 minute

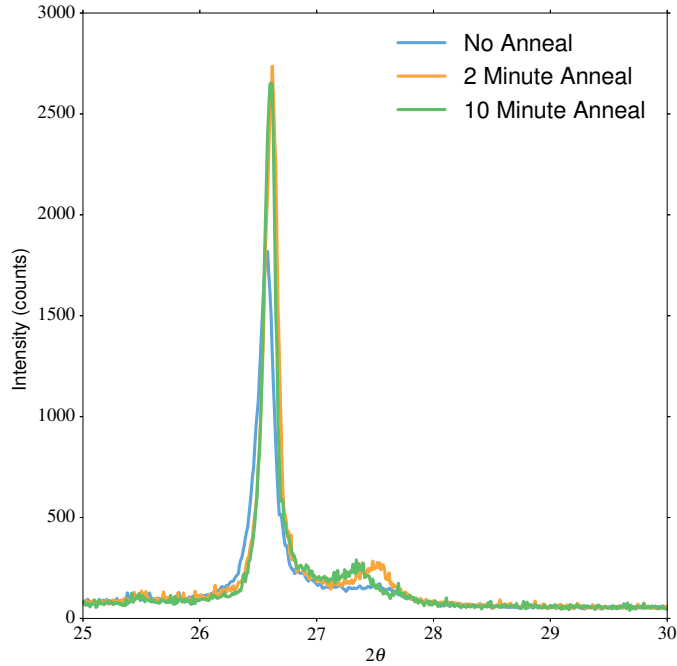


Figure 4.9: XRD pattern of the chalcopyrite 112 peak from samples produced using 2-stage process shown in Figure 4.7 with different stage 2 annealing time.

Table 4.6: EDX composition measurements from sample produced using 3-stage process with 1 minute anneal in argon followed by 1.5 minute reaction in H_2S .

Cu	In	Ga	Se	$\frac{\text{Cu}}{\text{In}+\text{Ga}}$	$\frac{\text{Ga}}{\text{In}+\text{Ga}}$	$\frac{\text{Se}}{\text{Cu}+\text{In}+\text{Ga}}$
24.27	25.50	0.71	50.52	0.93	0.03	1.00

anneal in argon at 600 °C, and 1.5 minute reaction in 0.35% H_2S at 600 °C was also examined. SEM images and composition measurements are in Figure 4.10 and Table 4.6, respectively. No measureable (by EDX) sulfur uptake occurred during the 3-stage process and the film had similar properties to the 2-stage process, suggesting that either the sulfur reaction was limited by kinetics, or the concentration of H_2S in the gas phase (0.35%) was too low to result in significant reaction with sulfur.

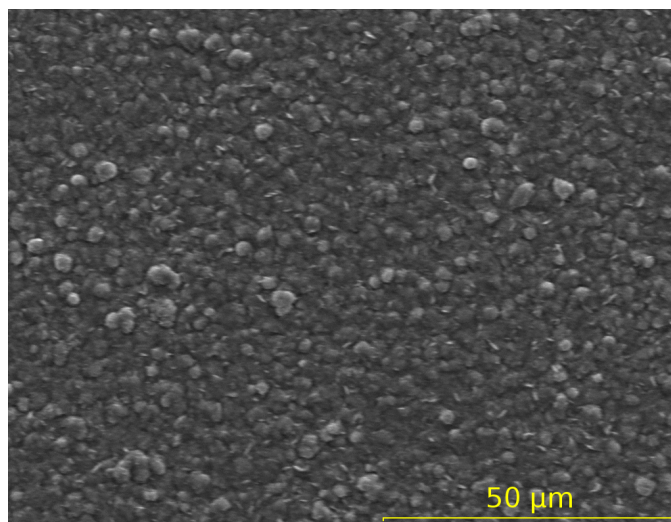


Figure 4.10: Plan view SEM image of film produced using 3-stage process with 1 minute anneal in argon followed by 1.5 minute reaction in H_2S .

4.3.3 Thermal Spike Annealing Reactions

The last reaction method presented here is referred to as a “thermal spike” anneal. Instead of controlled temperature, in the process, the lamp power is fixed at 100%, with the goal of maximizing reaction rate and, therefore, process throughput. To ensure sufficient H_2Se is present for complete reactions, the reactor is charged with 3% H_2Se in Ar.

Films were produced using 0.5, 1.5, 2.0, and 3.0 minute reactions, however, the films flaked off due to poor adhesion for the 2.0 and 3.0 minute samples and could not be analyzed. Figure 4.11 shows SEM images and Table 4.7 shows the compositions measured by EDX for the remaining samples. Similar to the other reaction methods presented here, substantial gallium segregation occurred during these reactions, as indicated by the low measured gallium fraction. From the morphology and composition data, it is apparent that the 0.5 minute reaction was insufficient to react fully the sample. Furthermore, XRD patterns (see Figure 4.12) show that the reaction does not go to completion even for the 1.5 minute reaction, as there unreacted InSe is present, which would likely result in low quality devices.

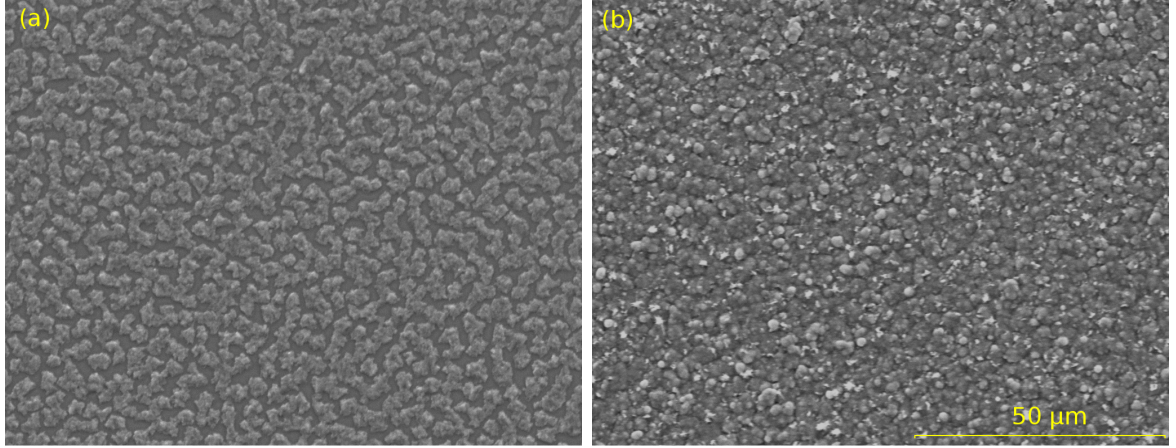


Figure 4.11: Plan view SEM images of films produced using thermal spike reaction process with (a) 0.5 and (b) 1.5 minute reactions.

Table 4.7: EDX composition measurements from samples produced using thermal spike process.

Reaction Time (min)	Cu	In	Ga	Se	$\frac{\text{Cu}}{\text{In}+\text{Ga}}$	$\frac{\text{Ga}}{\text{In}+\text{Ga}}$	$\frac{\text{Se}}{\text{Cu}+\text{In}+\text{Ga}}$
0.5	48.47	83.86	13.23	2.44	0.93	0.25	0.02
1.5	23.79	25.90	1.31	49.00	0.97	0.05	0.96

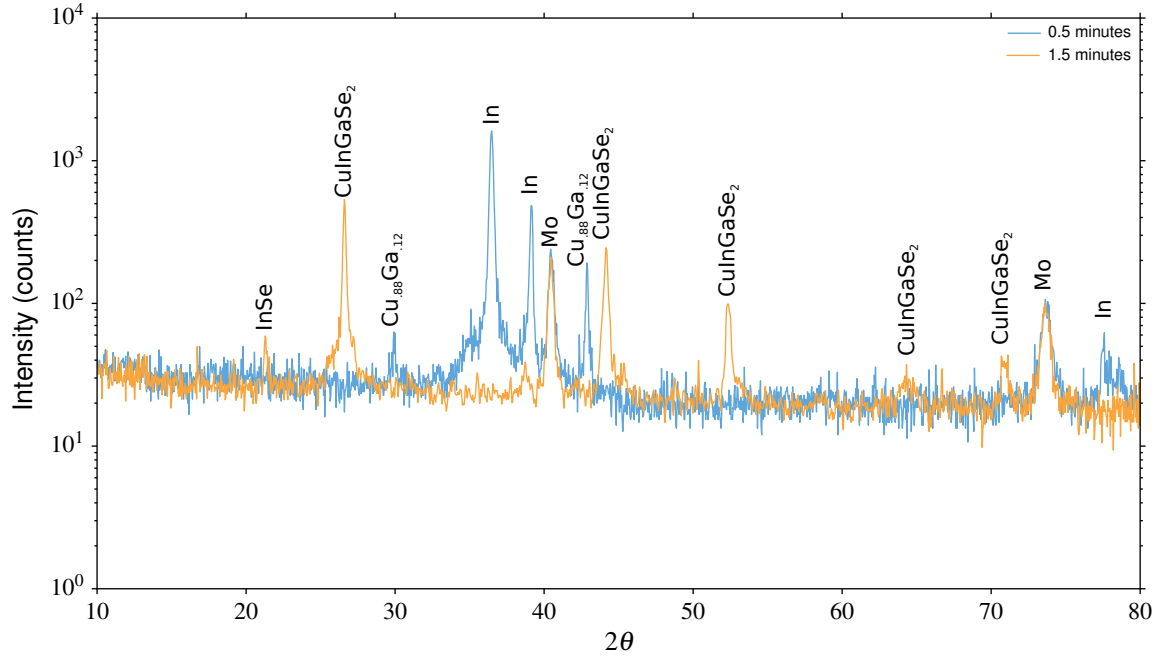


Figure 4.12: XRD patterns from a symmetric scan of samples reacted using the thermal spike process for 0.5 and 1.5 minutes. The 0.5 minute sample contains mostly metallic precursor phases; the 1.5 minute samples shows unreacted InSe present in the film. Intensity is shown on a logarithmic scale to show the presence of phases with low concentration (InSe) more clearly.

4.4 Reaction Modeling

The model presented in Chapter 3 was used to compare model predictions to experimental data; we produced a series of samples in the laboratory using single stage reactions with the following process conditions: reaction temperature of 550 °C, H_2Se concentration of 1%, and varying H_2S concentration in Ar gas. Sample compositions were measured EDX with results for $\text{Ga}/(\text{In}+\text{Ga})$ shown in Figure 4.13. While sulfur was detected in each sample, the composition was too low (less than 1 atom percent) for accurate quantitative measurement.

Here, we compare the effect of varying H_2S concentration in the gas phase to the equivalent change in the model, that is, changing the propensity for adsorption of sulfur. We expect that varying H_2S concentration will affect the through-film gallium profile, and that this effect will be captured in experimental results and by the model. However, rather than absolute convergence (which would require more precise parameter estimates), similar trends should be observed in experiments and simulations.

Figure 4.13 shows the through-film gallium profiles from the model using the baseline simulation parameters, except for adsorption of sulfur, which varies between simulations. Also displayed in the figure is the measured gallium ratio of the films produced with varying H_2S concentration in the gas phase. In both simulation and experiment, when the sulfur (propensity in simulations or concentration in experiments) is low, gallium fraction increases near the front surface with increasing sulfur, but the effect is diminished as sulfur increases further. However, the simulation overestimates the effect of sulfur on gallium fraction. Several mechanisms may explain the discrepancy; for example, the reaction between selenium and indium or the adsorption rate of selenium may be faster than the estimate, which limits the tendency of sulfur to increase gallium homogenization. Kim et al. [50] reported more substantial gallium homogenization than is observed here, which may be explained by the lower H_2Se concentration (0.35%) in their experiments. However, because the reactor is operated in the charge-and-react configuration, lower concentrations of H_2Se could not be used (see Figure 4.6).

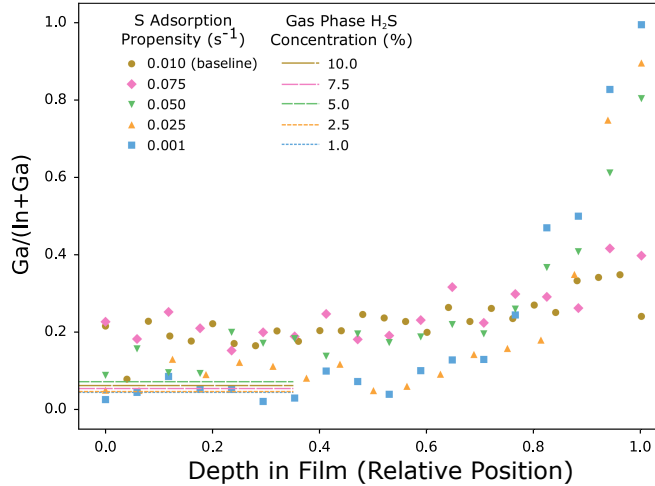


Figure 4.13: Gallium profiles (points) resulting from simulation of an $\text{H}_2\text{Se}+\text{H}_2\text{S}$ process using baseline simulation parameters (from Table 3.2) except for sulfur adsorption, which has a varying propensity constant. EDX measurements (horizontal lines, with length corresponding roughly to sampling depth) of $\text{Ga}/(\text{In}+\text{Ga})$ from samples produced with varying H_2S concentration.

4.5 Summary and Conclusions

Several reaction methods were presented in this chapter including single stage, multistage, and thermal spike reactions. Based on composition measurements and diffraction patterns, all of the reactions presented here resulted in films with large gradients in gallium, with most of the gallium segregated near the back of the film. Device results were not presented here; the films from the section had very poor adhesion that would usually delaminate in a chemical bath (the next step in device fabrication), which makes device fabrication impossible.

In addition to experimental results, the single stage reaction process was simulated using the method described in Chapter 3. The model results showed a more homogeneous gallium distribution¹ than was observed experimentally, but the trend

¹ Because the average $\text{Ga}/(\text{In}+\text{Ga})$ ratio is known *a priori* to be approximately 0.25, the low measured $\text{Ga}/(\text{In}+\text{Ga})$ ratio near the front surface indicates that composition is highly nonuniform due to gallium near the back contact.

of increasing gallium near the front of the film with increasing H_2S concentration was observed in both simulation and experiment.

In part because the processes presented here did not result in high-quality chalcopyrite films, an alternative approach will be investigated in the next chapter. Chapter 5 focuses on the reaction of selenium-capped precursors, where selenium is not supplied as a hydride gas, but instead as an elemental “capping” layer deposited directly on the precursor.

Chapter 5

REACTION OF SELENIUM-CAPPED PRECURSORS

5.1 Introduction

Chalcopyrite thin films for solar cells are commonly fabricated by depositing Cu-In-Ga precursors and then reacting the precursors in H_2Se and H_2S . However, H_2Se is extremely toxic with a time-weighted average exposure limit of only 50 ppb [111]. One method to eliminate the use of hydrogen selenide from the process is to include selenium in the precursor. Several different approaches to incorporating selenium in the precursor have been investigated and were reviewed in Chapter 1. In this work, we study chalcopyrite films produced from precursors with “selenium caps,” that is, a layer of elemental selenium has been deposited on top of a sputtered Cu-In-Ga precursor using thermal evaporation. The process studied in this chapter is similar to that used by the company Avancis, GmbH [55, 56, 57, 58, 59], where they produce chalcopyrite films by annealing “stacked elemental layers” in H_2S , rather than the compound precursors used in this work. We characterize the chalcopyrite films produced with varying operating conditions, paying particular attention to the through-film elemental composition and crystallinity.

5.1.1 Project Goals

The goal of the work presented here is to examine a selenium-capped precursor reaction process as a method for rapid production of chalcopyrite thin films. I will examine the effects of several process variables, including precursor composition, selenium layer thickness, temperature, and process gas composition (H_2S concentration). I will show that high-quality chalcopyrite material can be produced using this process, with material properties tuneable by process variables. Finally, the films produced

using this process will be used to fabricate complete solar cell devices, which will be tested to demonstrate that the process results in a high-quality photovoltaic material. I will show results from the current best devices that have been obtained in this work and how the processing conditions for the absorber layer affect the device properties.

5.2 Experimental Methods

A series of Cu(InGa)(SeS)_2 thin films were prepared using varying operating conditions and varying precursor conditions in order to determine which process variables affect relevant material properties and ultimately, the device properties. The overall approach is to use designed experiments to ascertain the significant effects of each process variable, including possible interactions.

5.2.1 Film Deposition

The same method as in Chapter 4 was used to produce Cu-In-Ga precursors films. Alternatively, Ag-Cu-In-Ga precursors were sequentially sputtered from CuGa, In, and AgGa sputter targets (See Soltanmohammad et al. [114]) to yield films with Ag ratios, $\text{Ag}/(\text{Cu}+\text{Ag})$, of approximately 0.25, gallium ratios, $\text{Ga}/(\text{In}+\text{Ga})$, of approximately 0.25, and thicknesses of approximately 800 nm.

Next, selenium “caps” were deposited in a vacuum bell jar. The selenium source was heated to 300 °C and the substrates kept at ambient temperature. Thickness was controlled by deposition time, which was calibrated against x-ray fluorescence spectroscopic thickness measurements (see Figure 5.1).

The selenium-capped precursors were then loaded in the selenization reactor (see Chapter 2), which was charged with hydrogen sulfide, heated to reaction temperature at varying ramp rates; held for 10 minutes (unless stated otherwise below), and cooled under flowing argon.

5.2.2 Analytical Methods

The material properties from each of the films were measured using several techniques. Bulk composition was measured using x-ray fluorescence spectroscopy

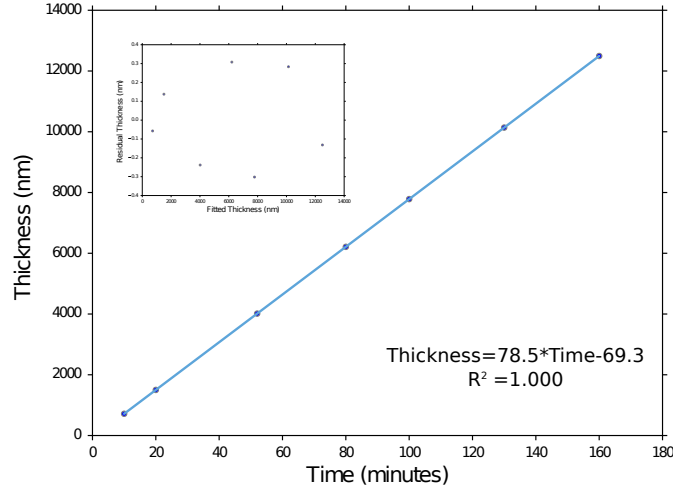


Figure 5.1: Data and linear regression line of XRF-measured selenium thickness versus deposition time. A plot of the residuals vs. fitted values is inset; no structure remains, which, paired with a coefficient of variation approximately equal to unity, suggests the model is sufficient.

(XRF); however, sulfur composition could not be measured via XRF due to overlap of spectral lines with those of the molybdenum back contact. Composition was also measured using energy dispersive x-ray (EDX) spectroscopy in a scanning electron microscope (SEM) in plan view using an acceleration voltage of 20 keV. The depth sensitivity of these measurements is approximately 0.75 μm , or slightly less than one half of the total film thickness. Therefore, comparing XRF measurements to EDX measurements gives information about the variation of the composition through the film depth. In addition to typical front, plan view measurements, EDX composition measurements were collected on the back side of some films. To obtain back side measurements, a second piece of soda lime glass was glued (using epoxy or Gorilla[®] glue) to the front of the sample, allowed to set, and then peeled off; in most cases, the weakest interface is between Mo and Cu(InGa)(SeS)_2 ; when the samples peeled, the back of the film was exposed and measured.

The phase composition and crystallinity was measured using x-ray diffraction (XRD). Symmetric x-ray patterns were collected from all samples using $\text{Cu } k\alpha$ radiation

in either a Rigaku or Phillips x-ray diffractometer. In some samples, grazing incidence (GI-)XRD patterns were also measured using angles of incidence from 0.05° to 8° . Whereas symmetric scans sample the entire film thickness, when a grazing incidence angle is used, only a small fraction of the thickness is sampled, which increases with increasing angle of incidence.

5.3 Results and Discussion

First, a study of a single stage, rapid (10 minute reaction) process to produce Cu(InGa)(SeS)_2 thin films will be presented and the effects of several process variables will be examined. Next, the effect of introducing silver in the precursor, which yields $(\text{AgCu})(\text{InGa})(\text{SeS})_2$ thin films, will be examined, and the implications that this may have for process/device design will be discussed.

5.3.1 Single Stage Production of Cu(InGa)(SeS)_2 Thin Films

A set of samples was prepared using the procedure described in Section 5.2.1. Specifically, a 2^3 factorial design was used to study the effects of temperature ramp rate (2°C/s and 6°C/s), reaction temperature (500°C and 600°C), and H_2S (1% and 10%) concentration, resulting in eight total films that were produced and analyzed. Atomic composition and XRD patterns were measured as outputs, where in addition to raw EDX composition data, the relevant atomic composition ratios ($\text{Cu}/(\text{In}+\text{Ga})$, $\text{Ga}/(\text{In}+\text{Ga})$, $\text{S}/(\text{Se}+\text{S})$ and $(\text{Se}+\text{S})/(\text{Cu}+\text{In}+\text{Ga})$) were calculated. A response surface model was postulated to predict model outputs from factors:

$$\mathbf{Y} = \mathbf{x}\boldsymbol{\theta} \quad (5.1)$$

where $\mathbf{Y}$ is an output vector; $\mathbf{x}$ is a matrix with columns representing each factor (temperature, ramp rate, H_2S concentration), their 2- and 3-way interactions, and a constant; $\boldsymbol{\theta}$ is the vector of coefficients that will be estimated from data. In order to identify which effects were significant, without replicated experiments, we fit the full-rank model, plotted the effects on a normal probability plot (quantile-quantile plot),

and used Lenth’s psuedo standard error method [115]; results for Ga/(In+Ga) and S/(Se+S) responses are shown in Figure 5.2.

For each output variable, the ramp rate was found to be insignificant, and is therefore not included in further analysis. Eliminating ramp rate as a factor allows for estimating standard errors and effect significance, as replicates at each data point are now available.

Plan view images of four samples (corresponding to high and low reaction temperatures and H₂S concentrations) are shown in Figure 5.3; there are no obvious effects of the process variables on the morphology of the films.

Table 5.1: EDX measurements of composition from single stage reactions.

Temperature (°C)	Ramp Rate (°C/s)	H ₂ S (%)	$\frac{\text{Cu}}{\text{In+Ga}}$	$\frac{\text{Ga}}{\text{In+Ga}}$	$\frac{\text{Se}}{\text{Se+S}}$	$\frac{\text{Se+S}}{\text{Cu+In+Ga}}$
500	2	1	0.92	0.09	0.19	0.95
500	2	10	0.96	0.06	0.46	0.89
500	6	1	0.90	0.09	0.18	0.93
500	6	10	0.95	0.08	0.45	0.91
600	2	1	0.91	0.21	0.29	0.94
600	2	10	0.94	0.17	0.45	0.90
600	6	1	0.95	0.20	0.27	0.93
600	6	10	0.94	0.17	0.46	0.93

The composition data for varying process conditions is shown in Table 5.1. First, the most prominent effect is that gas phase H₂S concentration has a large effect on the measured sulfur ratio in the film. The second prominent effect is that increasing temperature increases the measured gallium ratio. Of course, the total gallium ratio is unchanged between samples because gallium species are not being deposited and are not volatile during reaction, but the reaction temperature strongly affects the distribution of gallium through the film. A gallium fraction closer to 0.25 (the bulk value) indicates less through-film grading; therefore, the samples produced at higher temperature have more evenly distributed gallium.

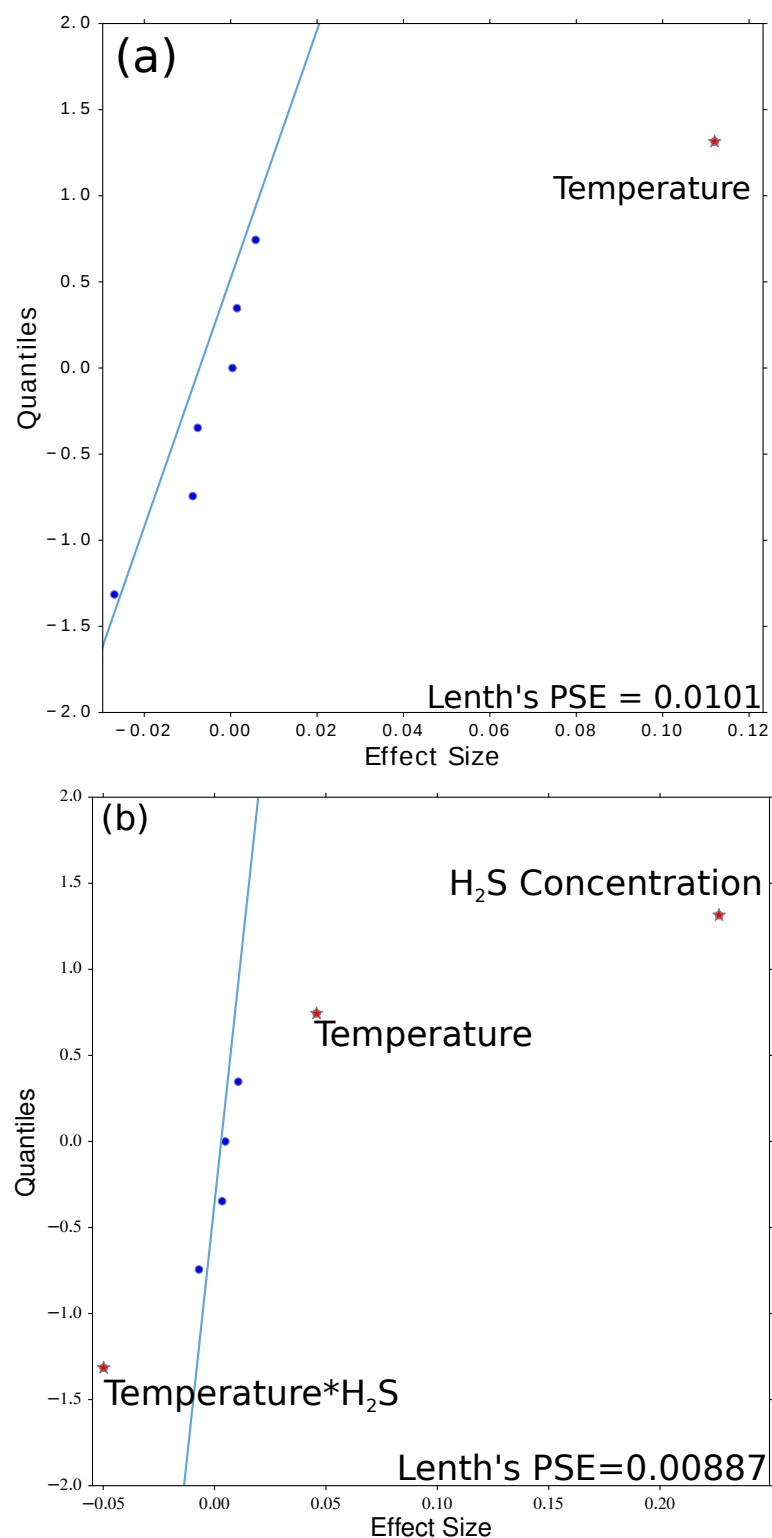


Figure 5.2: Normal probability plot of coded (*i.e.*, low value for each factor is -1; high values is +1) effects for (a) Ga/(In+Ga) and (b) S/(Se+S) used to determine which effects are significant in the absense of replicated experiments. Significant effects are labeled and Lenth's psuedo standard error is given.

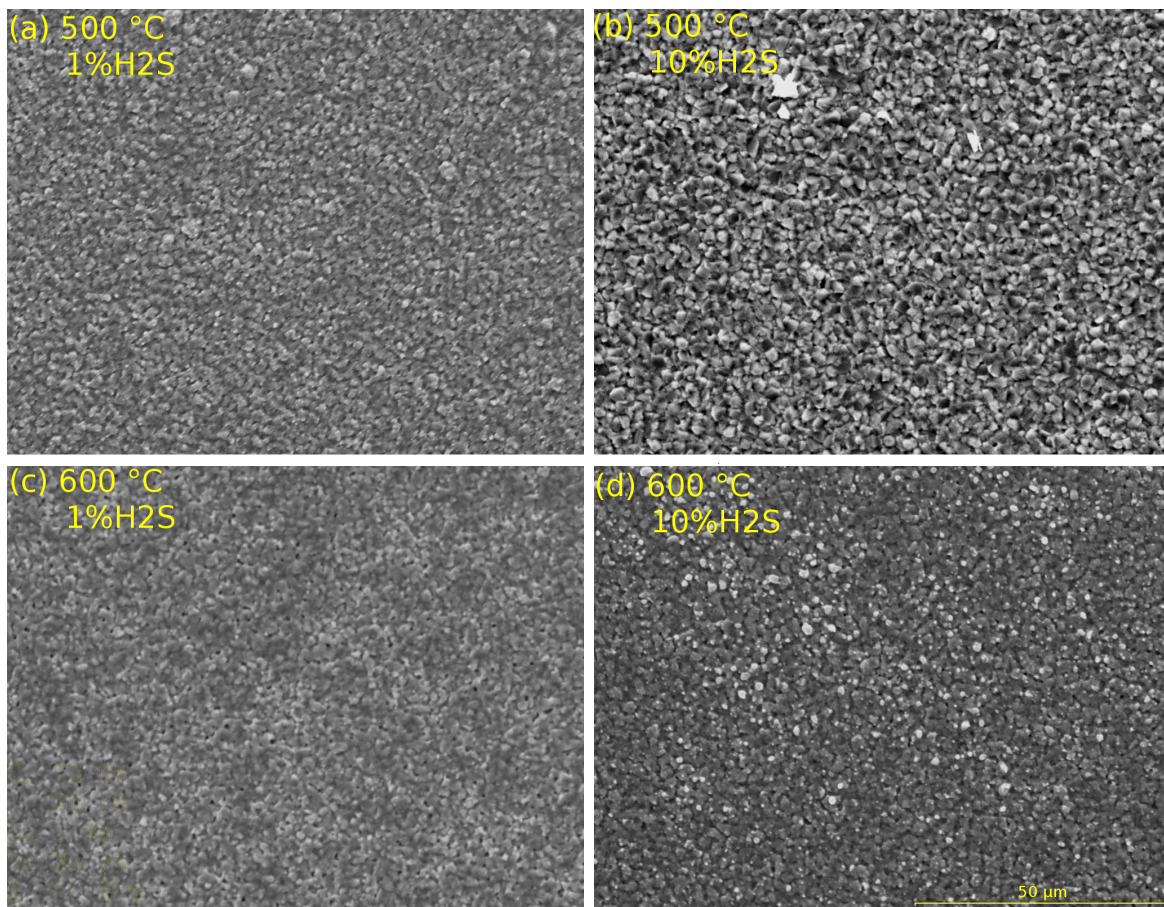


Figure 5.3: Plan view SEM images of samples produced at high and low temperature and H₂S concentration.

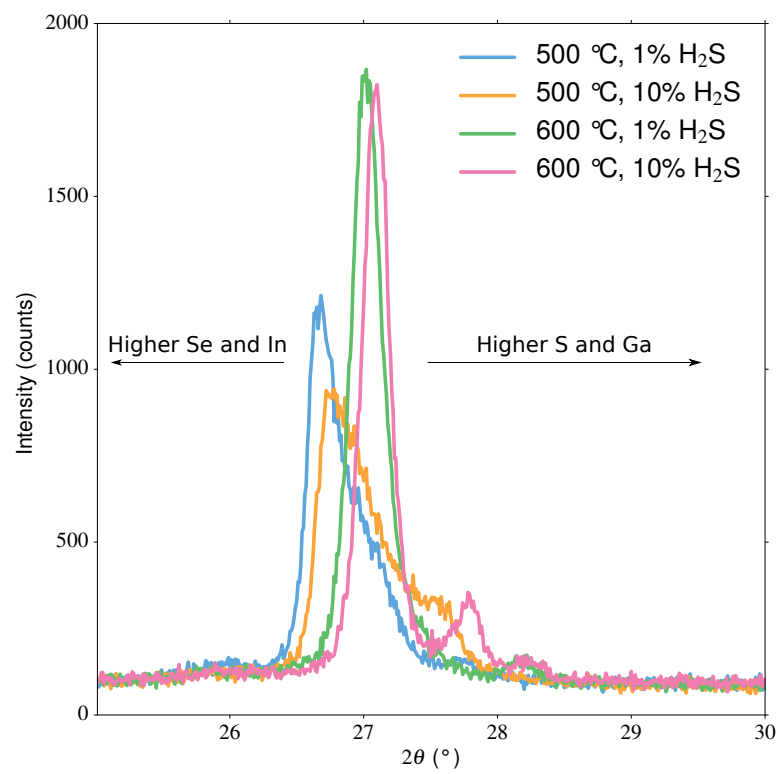


Figure 5.4: XRD patterns from symmetric scans from four samples produced at varying reaction temperature and H_2S concentrations.

In addition to composition, XRD patterns were measured for each of the samples. In all samples, only peaks for chalcopyrite (Cu(InGa)(SeS)_2) and Mo were observed, suggesting that the reaction went to completion for all samples. Figure 5.4 shows XRD patterns from symmetric scans from 2θ values of 25 to 29—the region of the 112 peak. Here, several effects may be observed: first at higher temperature, the peaks are much sharper, indicating more crystallinity with less compositional nonuniformity; second, when H_2S concentration is higher, a second peak is present at higher 2θ that might indicate a separate, high sulfur phase forming near the surface; finally, at lower temperatures, the peaks are significantly more asymmetric, indicating a larger gradient in film composition.

A 10 minute reaction time was chosen for practical reasons—longer reaction times decrease process throughput, whereas shorter reactions may not ensure complete conversion. Therefore, the time evolution of composition was also studied to understand whether the sample has reached a steady state within the 10 minute reaction time. To study the time evolution, we produced a series of samples using a fast ($6\text{ }^\circ\text{C/s}$) ramp rate, $600\text{ }^\circ\text{C}$ reaction temperature, and 5% H_2S concentration, but varying reaction time from 0 minutes to 10 minutes, where reaction time refers to time at $600\text{ }^\circ\text{C}$ and does not include the ramp time; the 0 minute sample was heated and immediately quenched.

The time evolution of the EDX-measured composition ratios is shown in Figure 5.5; because the Se layers had not yet evaporated, the composition of the 0 minute sample could not be measured. By 5 minutes, each of the composition variables appears to have reached a steady state, suggesting a complete reaction.

To further examine time evolution of the film during reaction, XRD patterns were collected from each of these samples as well and are shown in Figure 5.6. At 0 minutes, the Se layer is still visible on the surface and only a small, very broad peak indicates the presence of Cu(InGa)(SeS)_2 ; additionally, an intermetallic phase (identified as Cu_4In) is still present in the film. After that point, the film converts rapidly to single phase chalcopyrite, with the only additional peaks attributed to Mo,

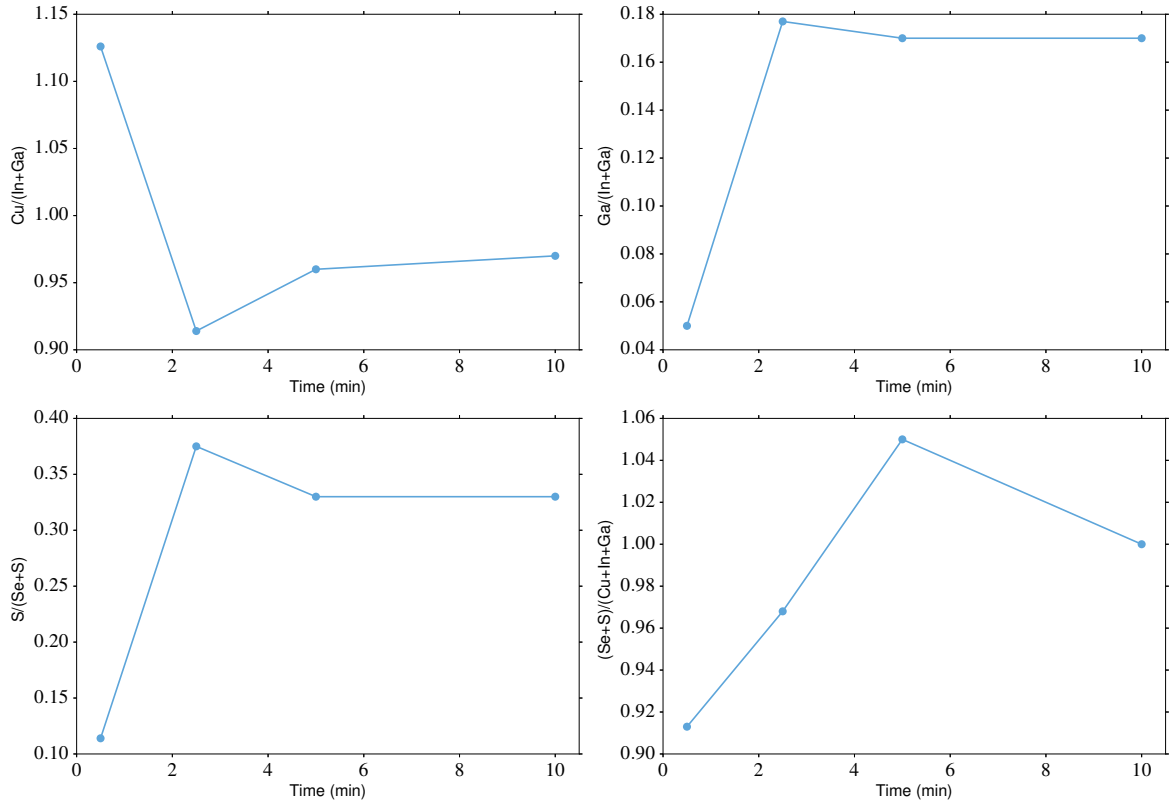


Figure 5.5: Time evolution of atomic composition ratios measured by EDX from samples produced at 600 °C with 5% H₂S concentration. The film appears to reach a steady state within 5 minutes

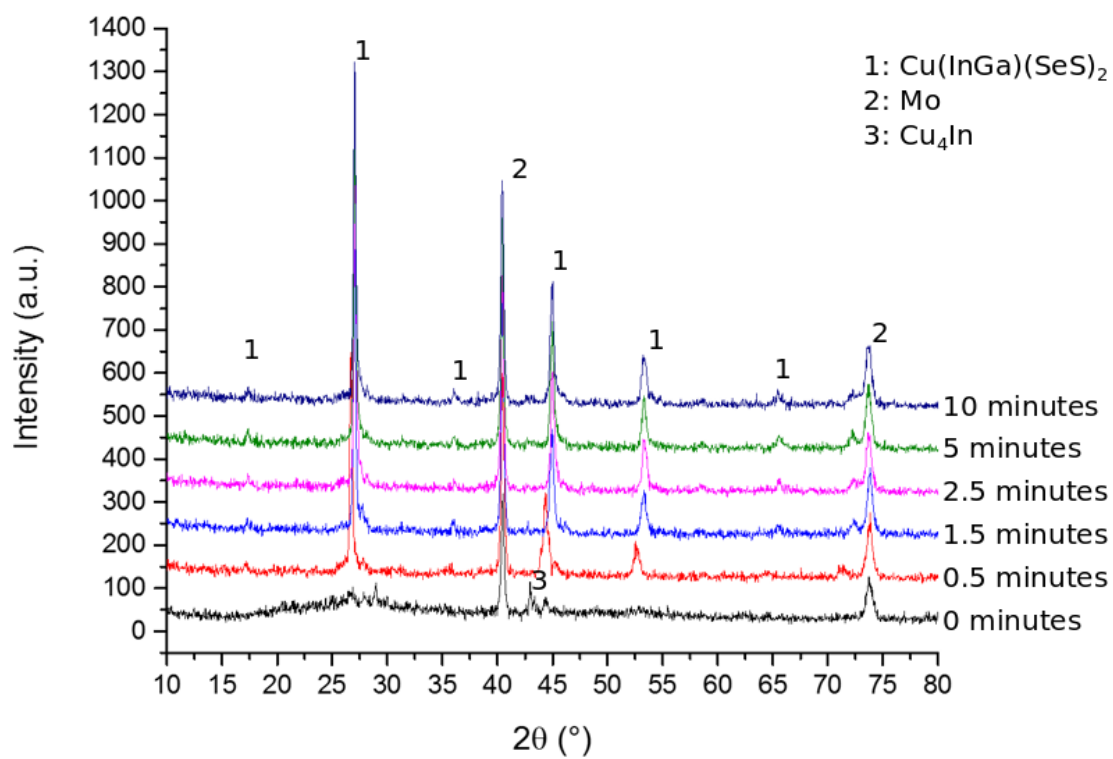


Figure 5.6: Time evolution of XRD patterns of samples produced at 600 °C with 5% H_2S concentration.

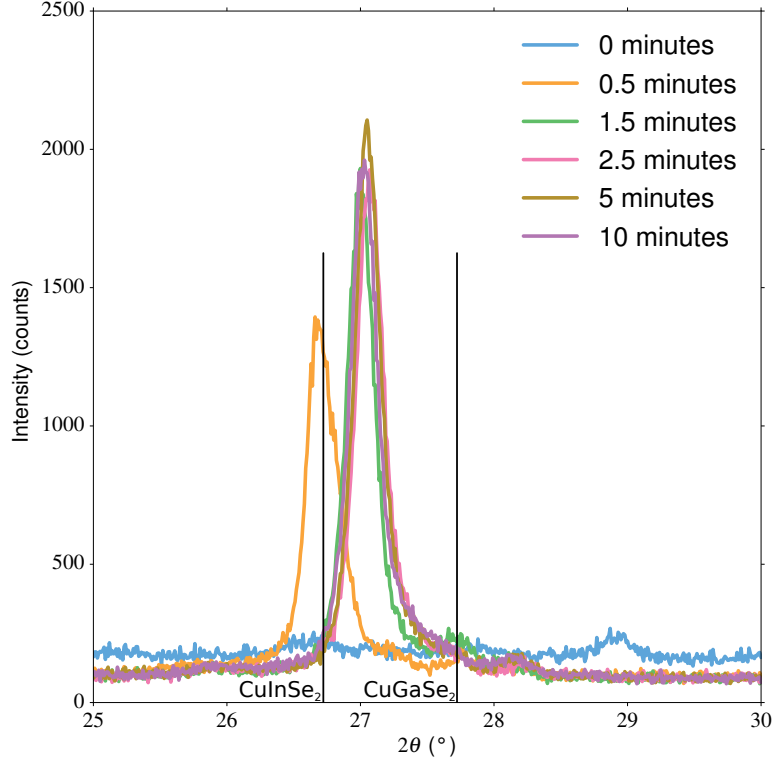


Figure 5.7: Time evolution of XRD patterns of the 112 peak of samples produced at 600 °C with 5% H₂S concentration. Positions of CuInSe₂ and CuGaSe₂ 112 peaks are shown for reference.

the back contact.

Focusing on the 112 peak evolution, shown in Figure 5.7, within 0.5 minutes chalcopyrite becomes the dominant phase; however, mostly CuInSe₂ is present, with little incorporation of sulfur or gallium into the chalcopyrite. After 1.5 minutes, the XRD pattern appears to reach a steady state, with the peak no longer shifting position in time, which is consistent with the results in Figure 5.5 that show no additional incorporation of sulfur or gallium intermixing.

5.3.2 Single Stage Production of (AgCu)(InGa)(SeS)₂ Thin Films

Alloying chalcopyrite materials with silver has a number of favorable properties including the potential for higher voltage devices due to fewer defects in the material [19]. In this section, I explore the effect of alloying silver in the precursor and using

the single stage selenium-capped reaction process. Another 2^3 factorial design was completed; in this case, the three factors were, H_2S concentration (1%, 10%), selenium thickness (4 μm , 8 μm), and silver incorporation in precursor (0%, 12.5%); reaction temperature was 600 °C and was not varied.

To analyze the effect of silver incorporation, the experiments must be designed carefully because the effect of batch-to-batch precursor variation must also be considered. Silver-containing and silver-free precursors cannot, of course, be produced in the same batch and, therefore, it is impossible in principle to determine whether the addition of silver or the precursor batch affects the responses. However, this can be mitigated by including the previous data from Section 5.3.1 as second block. The experimental design and relevant composition ratios are shown in Table 5.2. Because replicates are included in the design, significant effects can be identified using Analysis of Variance, which is a more powerful method than Lenth’s method used previously, and are shown for gallium and sulfur ratios in Figure 5.8. To identify the effects of each factor on silver ratio, $\text{Ag}/(\text{Cu}+\text{Ag})$, however, because no replicates of Ag-containing precursors are available, ANOVA is unfeasible. From the normal probability plot of the effects, though, it is apparent that silver content in the precursor is the only significant factor and that other factors have, at most, a small effect on the distribution of Ag in the film.

Figure 5.8b shows the effects of each of the factors on the $\text{S}/(\text{Se}+\text{S})$ ratio; surprisingly, the main effect of selenium layer thickness does not appear to be significant, but its interaction with Ag content is significant. It is possible that the reaction with sulfur at the surface prevents the effect from being detectable by EDX. Therefore, XRF measurements, which average over the entire film thickness were also obtained and are shown in Table 5.3. Unfortunately, due to the x-ray emission peak overlapping with Mo, S cannot be measured by XRF; however, comparison of the other species allows for an indirect measurement of sulfur incorporation. Figure 5.9 shows the coded effects of each factor on the $\text{Se}/(\text{Ag}+\text{Cu}+\text{In}+\text{Ga})$ ratio; since $(\text{Se}+\text{S})/(\text{Ag}+\text{Cu}+\text{In}+\text{Ga})$ is approximately constant (because the films are approximately stoichiometric), a larger

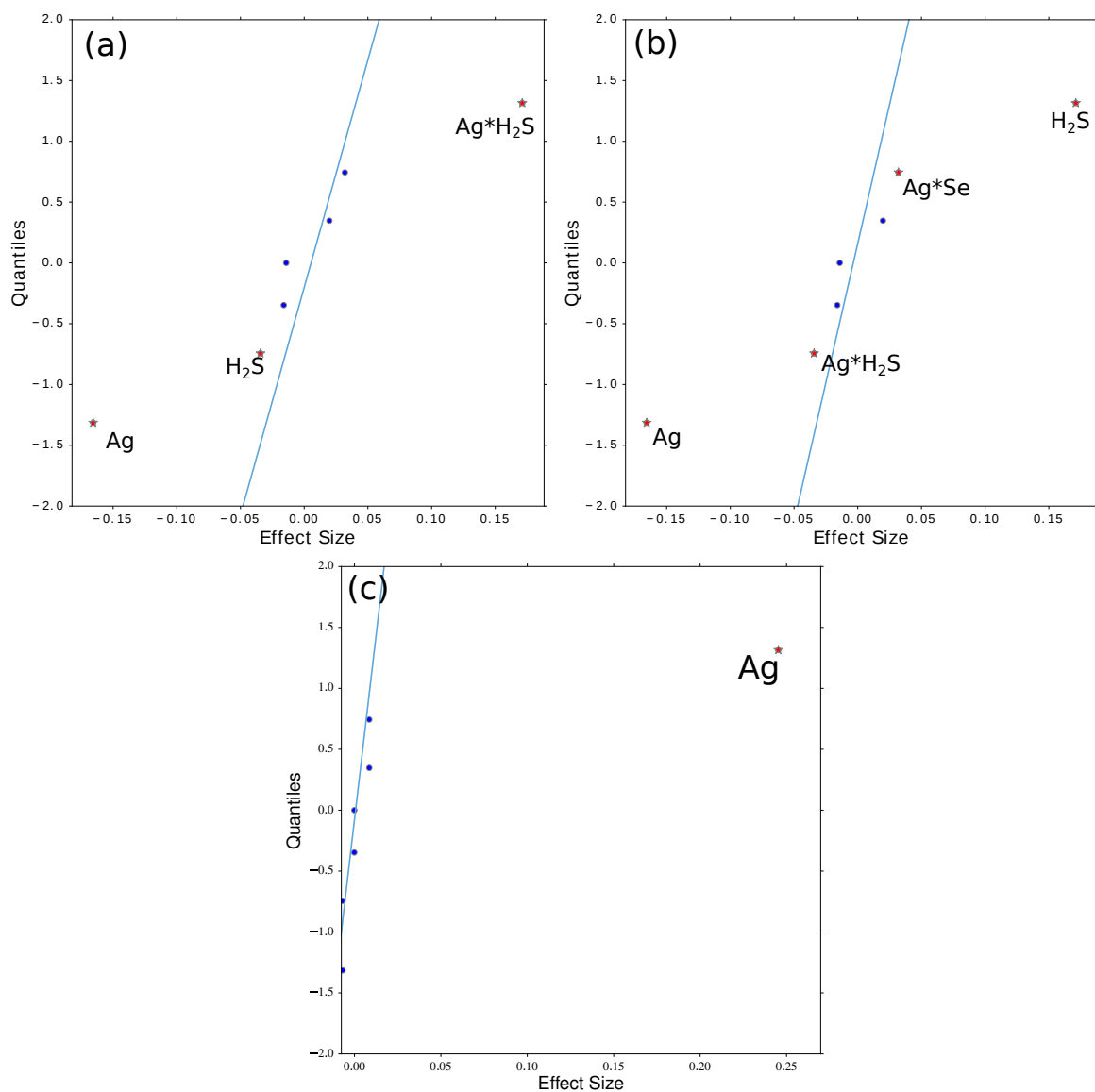


Figure 5.8: Normal probability plots of coded effects for EDX measurements of (a) Ga/(In+Ga), (b) S/(Se+S), and (c) Ag/(Cu+Ag). Significant effects are labeled (for (a) and (b), significance is determined by ANOVA using the 5% significance level and for (c) significance is determined graphically).

Table 5.2: Experimental design for analysis of silver incorporation. Block 1 is data from Section 5.3.1; it includes replicates with different ramp rates, found to be insignificant. All experiments were performed at 600 °C and with 10 minute reaction time. Ag represents mole percent Ag in precursor, Se denotes microns Se thickness, and H₂S denotes gas concentration.

Ag (%)	Se (μm)	H ₂ S (%)	Block	$\frac{\text{Cu+Ag}}{\text{In+Ga}}$	$\frac{\text{Ag}}{\text{Cu+Ag}}$	$\frac{\text{Ga}}{\text{In+Ga}}$	$\frac{\text{S}}{\text{Se+S}}$	$\frac{\text{Se+S}}{\text{Ag+Cu+In+Ga}}$
0	4	1	1	0.95	0	0.20	0.27	0.93
0	4	1	1	0.91	0	0.21	0.29	0.94
0	4	10	1	0.94	0	0.17	0.45	0.90
0	4	10	1	0.94	0	0.17	0.46	0.93
0	4	1	2	0.89	0	0.22	0.29	1.00
0	4	10	2	0.95	0	0.17	0.45	0.94
0	8	1	2	0.89	0	0.21	0.20	0.98
0	8	10	2	0.92	0	0.17	0.44	0.94
12.5	4	1	2	0.87	0.24	0.13	0.10	1.05
12.5	4	10	2	0.84	0.26	0.11	0.24	1.03
12.5	8	1	2	0.85	0.23	0.09	0.12	1.01
12.5	8	10	2	0.86	0.25	0.13	0.26	1.10

ratio of $\text{Se}/(\text{Ag}+\text{Cu}+\text{In}+\text{Ga})$ indicates less sulfur incorporation in the film.

From Figures 5.8 and 5.9, several salient effects can be identified. First, Ag has a significant effect on all of the composition variables; adding silver tends to decrease the incorporation of sulfur and the measured gallium, which means gallium is more segregated near the back. Selenium thickness affects the total $\text{S}/(\text{Se}+\text{S})$ ratio (see Figure 5.9), but has, at most, a weak effect on the composition near the surface. The concentration of H₂S in the gas phase strongly affects both the bulk and surface incorporation of sulfur, as well as the distribution of gallium.

Figure 5.10 shows SEM images of samples with and without silver included in the precursor and with varying selenium layer thicknesses. The Ag-containing and Ag-free samples have different morphologies, where Ag-containing films have larger, but more variable grain sizes; selenium layer thickness does not appear to affect morphology.

Next, it is informative to compare the diffraction patterns for different selenium layer thicknesses and silver content. Broad scans (not shown) indicate that no residual

Table 5.3: XRF measurements of composition of films produced with varying selenium layer thickness, H₂S concentration, and Ag-content.

Se (μm)	H ₂ S (%)	Ag (precursor %)	Ag (%)	Cu (%)	In (%)	Ga (%)	Se (%)
4	1	0	0	26.07	24.02	7.48	42.43
4	10	0	0	27.46	25.04	7.81	39.69
8	1	0	0	24.15	22.08	6.99	46.78
8	10	0	0	25.61	23.37	7.38	43.65
4	1	12.5	5.52	17.15	23.12	5.82	48.39
4	10	12.5	6.27	17.78	24.67	5.95	45.33
8	1	12.5	5.06	16.96	21.53	5.74	50.70
8	10	12.5	5.77	17.62	23.50	5.93	47.19

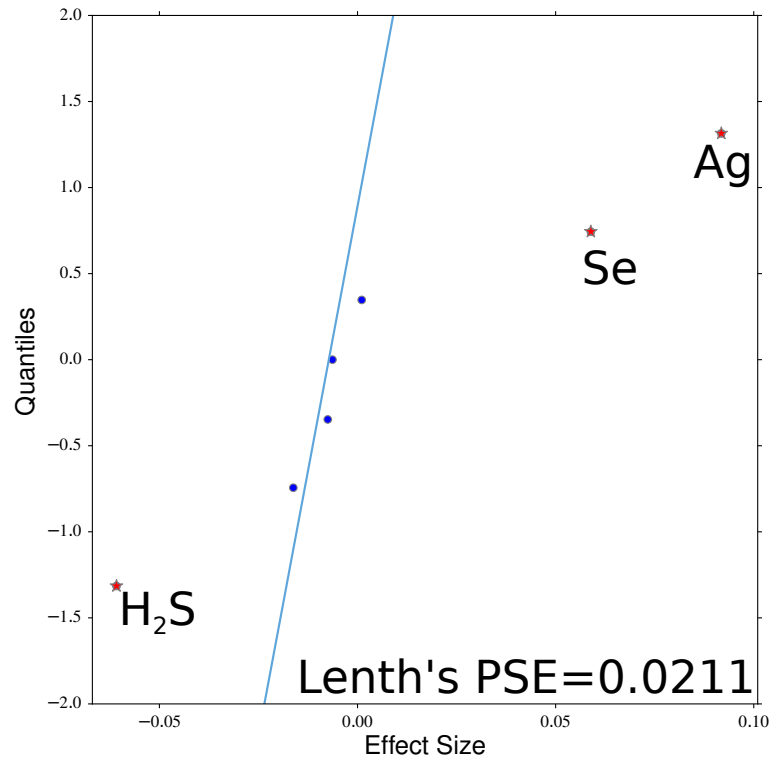


Figure 5.9: Normal probability plots of coded effects for XRF-measured Se/(Ag+Cu+In+Ga). Significant effects, identified by Lenth's method and using the 5% significance level, are labeled.

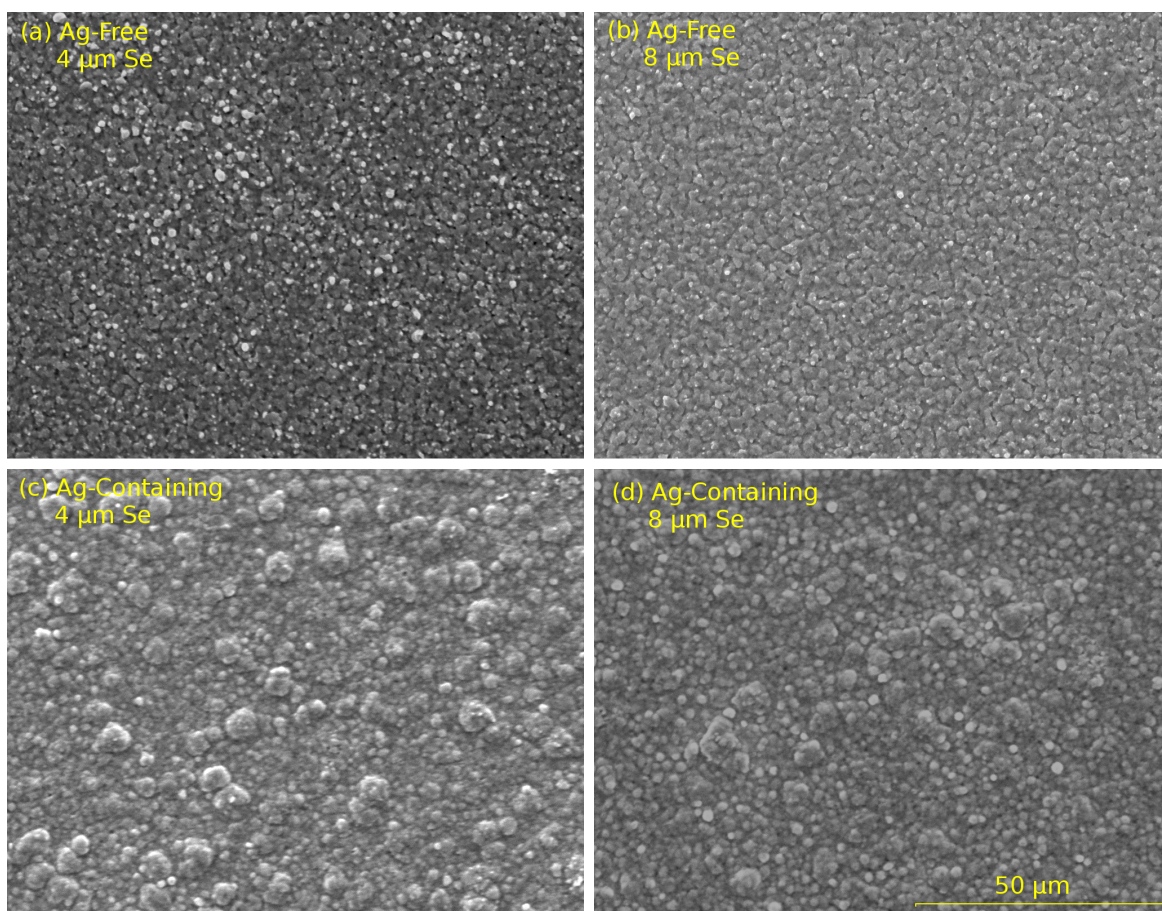


Figure 5.10: Plan view SEM images of samples produced at high and low selenium thicknesses and with and without Ag in the precursor (all produced with 10% H₂S).

intermetallic or binary selenide phases remain in any of the samples. XRD patterns from symmetric scans of the 112 peak for samples with varying selenium thickness and Ag content are shown in Figure 5.11 and GI-XRD patterns are shown in Figure 5.12. From the symmetric scans, it is clear that Ag-containing precursors yield films with much broader and less symmetric diffraction patterns, which are indicative of less crystallinity and compositional nonuniformity that results from gallium grading. For Ag-free films, thicker selenium layers also result in sharper peaks, but the opposite is true for Ag-containing films. Finally, as expected, the Ag-containing films have diffraction peaks shifted to lower values of 2θ , resulting from the larger Ag atoms substituting for Cu atoms.

The GI-XRD patterns from each of the films show similar trends as the patterns from symmetric scans. In addition, the varying incident angles allow for more close examination of through-film variation. The samples show little variation in position of the peak maxima as incident angle changes (see insets from Figure 5.12). However, for the Ag-containing samples, the peaks become more asymmetric at increasing angle of incidence, indicating more substantial grading in gallium farther from the front surface.

These hypotheses can be supported by comparison of front-side and back side EDX measurements, shown in Table 5.4. Here, for Ag-free films, there is low S near the back of the film, but Ga is approximately constant throughout. Further, because the average gallium ratio is about 0.25, and the measured gallium ratio is below this value at the front and back of the film, the gallium fraction must reach a maximum near the middle of the film. The Ag-containing precursors have a much steeper gradient in gallium, though not as steep a gradient as would result from the H_2Se reactions that were examined in Chapter 4.

The relationships discussed here and in Section 5.3.1 have important implications for designing a process for device fabrication. Whereas a typical industrial reaction process takes place on the order of hours [15], the ability to reduce reaction time to less than 10 minutes may substantially increase process throughput. Further,

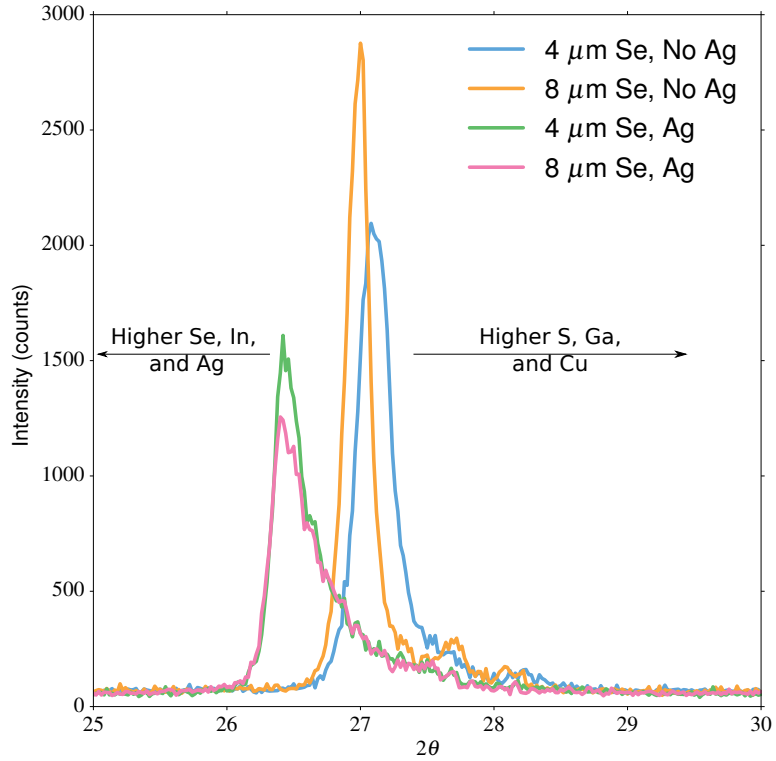


Figure 5.11: Diffraction patterns of the chalcopyrite 112 peak of samples produced at high and low selenium thicknesses and with and without Ag in the precursor (all produced with 10% H₂S).

Table 5.4: Composition ratios from front-side (FS) and back-side (BS) EDX measurements for Ag and Ag-free samples (samples were produced with 8 μm Se and 10% H₂S).

Ag (%)	FS $\frac{\text{Ag}}{\text{Cu+Ag}}$	BS $\frac{\text{Ag}}{\text{Cu+Ag}}$	FS $\frac{\text{Ga}}{\text{In+Ga}}$	BS $\frac{\text{Ga}}{\text{In+Ga}}$	FS $\frac{\text{S}}{\text{Se+S}}$	BS $\frac{\text{S}}{\text{Se+S}}$
0	0.	0.	0.17	0.17	0.44	0.14
12.5	0.25	0.27	0.13	0.26	0.26	0.23

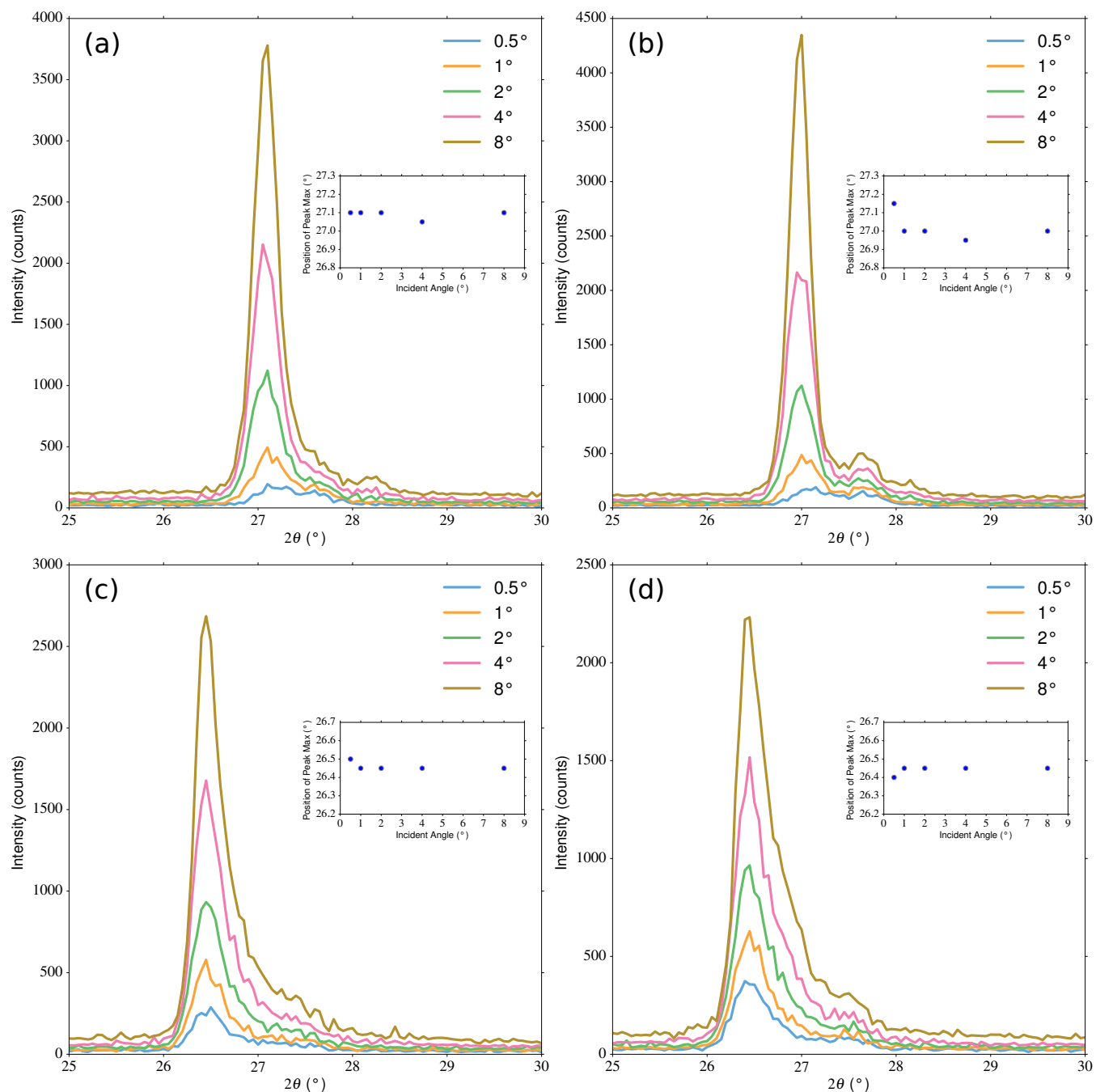


Figure 5.12: GI-XRD patterns with varying angles of incidence of chalcopyrite films produced from precursors with (a) 4 μm Se cap and no Ag, (b) 8 μm Se cap and no Ag, (c) 4 μm Se cap and Ag, and (d) 8 μm Se cap and Ag. Insets show the position of the peak maxima as a function of incident angle (Note that the figures have different y-axis scales; all samples were produced with 10% H_2S).

the process variables, especially gas phase concentration of sulfur and thickness of selenium have a significant effect on the film, primarily in composition, which, in turn affects the material band gap and the device voltage. All else equal, a higher band gap absorber layer will result in a device with higher voltage, but lower current. However, we cannot predict *a priori* what the best values of process variables are, and must analyze devices separately. Devices produced using this process are described in Section 5.5; from results herein, it can be predicted that increasing H_2S concentration will increase the band gap of the film, which, with all else equal, will increase the open circuit voltage and decrease the short circuit current. Likewise, increasing selenium thickness may decrease the voltage, but because selenium thickness affects mostly the film bulk and not the front surface, where the p-n junction is formed, the effect may be small. Increasing selenium thickness may increase the current of the device, as absorption occurs through the bulk of the film, and the lower band gap allows for more light absorption. However, it should be noted that solar cell device operation is inherently complex, and other factors that are hard (or sometimes impossible) to identify from material analysis alone, may drive the device performance; these include conductivity and doping, electronic defects, electric fields from band gap gradients, local fluctuations of electric fields at grain boundaries, and impurities with low concentrations (especially sodium that diffuses from the glass substrate).

5.4 Reaction Modeling

The selenium-capped reaction process can also be examined using the stochastic model discussed in Chapter 3. Figure 5.13 shows the resulting depth profiles from modeling the selenium-capped reaction with high and low sulfur adsorption propensity and with 4 μm and 8 μm (40 and 80 lattice sites) thick selenium capping layers. Selenium adsorption propensity is reduced by an order of magnitude, but not set to zero, because in this process, evaporated selenium remains in the reactor near the sample and may still react with the sample. Some similar trends are observed, such as increasing sulfur content with increasing sulfur adsorption propensity and decreasing

Table 5.5: New substitution reactions to be included in the stochastic reaction model to account for post-reaction modification of the surface from H_2S .

Event Class	Event
Substitution Reactions	$2\text{S} + \text{CuInSe}_2 \longrightarrow 2\text{Se} + \text{CuInS}_2$
	$2\text{S} + \text{CuGaSe}_2 \longrightarrow 2\text{Se} + \text{CuGaS}_2$
	$2\text{Se} + \text{CuInS}_2 \longrightarrow 2\text{S} + \text{CuInSe}_2$
	$2\text{Se} + \text{CuGaS}_2 \longrightarrow 2\text{S} + \text{CuGaSe}_2$

selenium thickness. The model also correctly predicts the maximum in gallium that was observed by comparing front-side and back-side EDX measurements. However, the model, in its current form, does not predict the correct through-film distribution of sulfur, with high sulfur content near the front of the films. This is most likely the result of additional “substitution” reactions, proposed in Table 5.5, where the high concentration of sulfur in the atmosphere causes it to replace selenium in an already-reacted sample.

5.5 Device Fabrication and Analysis

The most common method of solar cell analysis is to measure the current density-voltage relationship (JV curve) with and without illumination [116]. While more sophisticated methods, including quantum efficiency measurements, various types of capacitance spectroscopy [117] and luminescence measurements [118, 119] are applied for more complete understanding of the device physics, they are beyond the scope of the present work and recommended for future investigation.

To understand the current voltage relationship, a solar cell can be most simply described as a diode in parallel with a current source, resulting in the expression:

$$J = J_0 \left[\exp \left(\frac{qV}{kT} \right) - 1 \right] - J_{sc} \quad (5.2)$$

where J is current density, V is voltage, J_0 is the saturation current density, q is the elementary charge, k is Boltzmann’s constant, T is temperature, and J_{sc} is the short circuit current density (*i.e.* current density at $V = 0$). While this model is usually

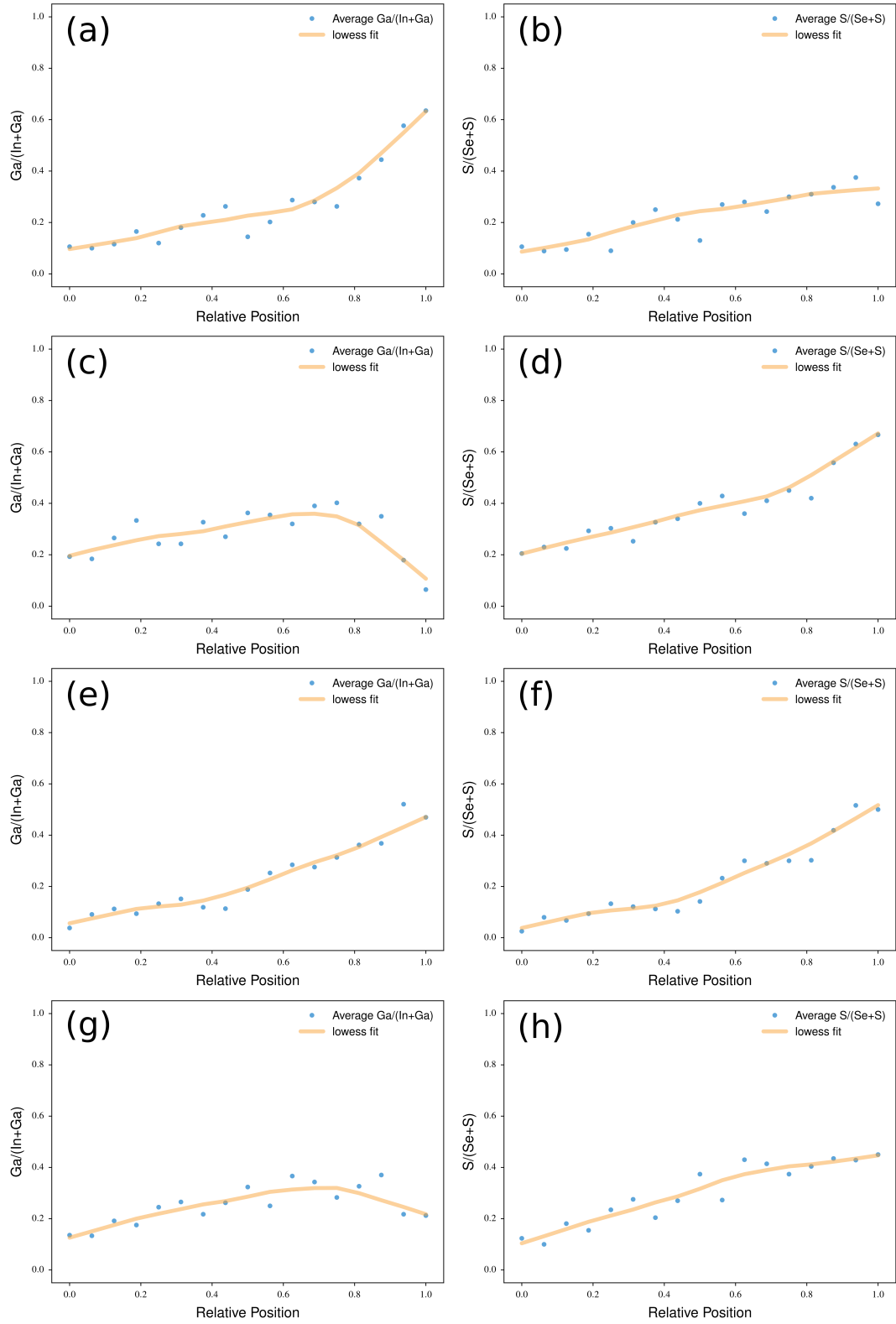


Figure 5.13: Model predictions for composition profiles using (a-b) low S adsorption and Se layer, (c-d) high S adsorption and low Se layer, (e-f) low S adsorption and high Se layer, and (g-h) high S adsorption and Se layer.

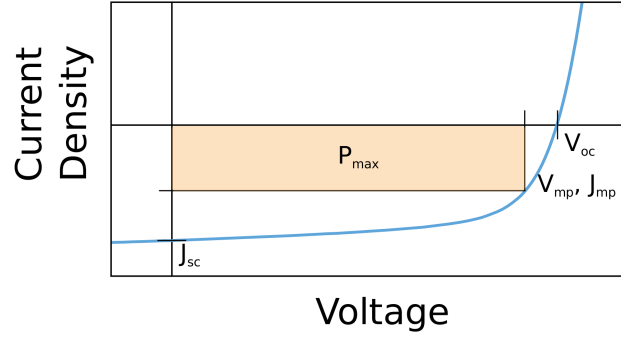


Figure 5.14: A typical JV curve showing the maximum power point (V_{mp} , J_{mp}), short circuit current (0 , J_{sc}), and open circuit voltage (V_{oc} , 0). The fill factor, FF , is the ratio of the area of the rectangle formed by the maximum power point (and shown in the figure) and the area of the rectangle formed by V_{oc} and J_{sc} .

insufficient—even high quality devices deviate from this simplification—it is still useful to help understand the parameters from a JV curve.

Equation 5.2 shows that the JV curve for most devices is approximately an exponential function shifted downward in current (using the sign convention that negative power is extracted from the system). An example of a simple JV curve is shown in Figure 5.14, with the important parameters labeled; the maximum output power density is therefore the product of open circuit voltage, V_{oc} , short circuit current, J_{sc} and fill factor, FF . The device efficiency can therefore obtained from these parameters as:

$$\eta = \frac{V_{oc} J_{sc} FF}{P_{in}} \quad (5.3)$$

where P_{in} is the incident power density.

The JV curve, and therefore the device efficiency, is a strong function of external variables, most importantly temperature, solar intensity, and incident spectrum. Therefore, all measurements were performed under Standard Test Conditions: 25 °C, 1000 W/m² intensity, and the AM 1.5 spectrum defined in ASTM G173-03 [120].

5.5.1 Fabrication Process and Cell Testing

Complete devices were fabricated from the Cu(InGa)(SeS)_2 thin film absorber layers deposited using the RTP system. The complete device structure is glass/Mo/ Cu(InGa)(SeS)_2 /CdS/ZnO/ITO. First, the CdS layer (50 nm) was deposited by chemical bath deposition using an alkaline solution with $\text{pH} \approx 9$ containing cadmium sulfate (CdSO_4), ammonia (NH_4), and thiourea ($\text{SC(NH}_2)_2$). Next, a zinc oxide (ZnO, 50 nm) window layer and indium tin oxide (ITO, 150 nm) were deposited by RF sputtering. A nickel aluminum grid was deposited by thermal evaporation, and the samples were mechanically scribed to form 4 individual cells.

JV curves were obtained at standard test conditions (25 °C, 1000 W/m², AM 1.5 radiation).

5.5.2 Device Analysis

Among the films produced from selenium capped precursors, only those at high temperature will be considered. Devices made from films fabricated with low temperature (500 °C) reactions were tested, but their JV curves were nearly straight lines—*i.e.* resistors following Ohm’s law—with no photodiode-like behavior and near 0% efficiency. The high-temperature process, however, yielded better-performing devices. Three devices, with absorber layers produced using reactions at 600 °C, 4 μm Se cap layers, and with 1%, 5.5%, and 10% H_2S , were fabricated and tested. Their JV curves (highest efficiency among the 4 on each sample) are shown in Figure 5.15.

Several trends are apparent from these JV curves. First, V_{oc} tends to increase with increasing H_2S concentration; J_{sc} decreases between Figure 5.15a and c, though b has the lowest current among all of them. Aside from the unusually low current observed on the sample produced with 5.5% H_2S , these observations would be expected based on the predicted band gap of the devices: more S in the film increases the band gap, which increases voltage but decreases current.

The films all have similar fill factors, which characterize resistive losses in the film. However, the best devices from literature often have much higher fill factors,

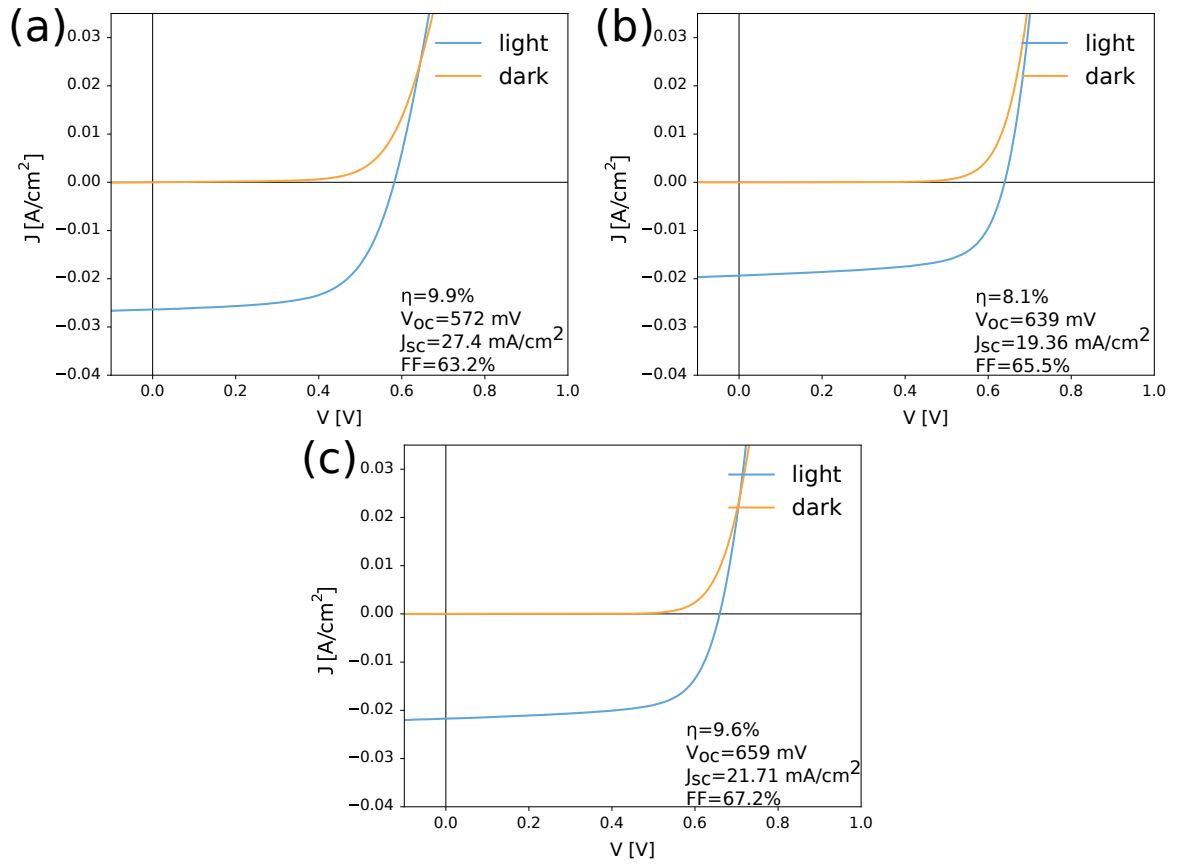


Figure 5.15: JV curves of devices produced from films reacted with 4 μm Se caps, at 600 $^{\circ}\text{C}$ for 10 minutes and with (a) 1.%, (b) 5.5%, and (c) 10.% H_2S concentrations. Efficiency, V_{oc} , J_{sc} , and FF are shown for each device.

greater than 80%. The relatively low fill factors could be results of lateral non-uniformity or because the other device layers (contacts, windows) have not been optimized for this process.

5.5.3 Empirical Device Optimization

In this section, empirical response surface optimization methods are applied to obtain the highest efficiency device that uses only a Cu-In-Ga (no Ag) precursor and a single stage, short (10 minute) reaction process. Temperature, H₂S concentration, and selenium layer thickness were identified above as significant factors affecting film properties; therefore, these were selected as variables over which to optimize.

A Box-Behnken response surface design was used to determine the ideal operating conditions as it avoids extreme conditions that could result in nonfunctional devices. For temperature, 550 °C was used as a minimum to assure complete reaction, and 625 °C as a maximum, as higher temperature may warp the glass. H₂S was varied from 1% to 10% and Se thickness from 4 µm to 8 µm, as before. Unfortunately, by necessity, the design must be blocked by precursor run, as batch-to-batch variation may affect the device performance.

The response surface design and resulting efficiencies are shown in Table 5.6. At the 10% significance level, only the precursor batch (the blocking variable, p=.057) and H₂S concentration (p=0.098) were found to affect efficiency, which suggests that there is too much noise in the process and too strong of an effect of batch-to-batch precursor variation; in principle, increasing replicates would be required, but would be too tedious and is beyond the scope of this project. Were this process, or a similar process, to be implemented commercially, very careful control of each step would be necessary to reduce the variation, at which point a more effective optimization routine could be applied.

Table 5.6: Box-Behnken response surface design used to optimize process variables for device efficiency. The block variable represents precursor batch.

Temperature (°C)	H ₂ S (%)	Se Thickness (μm)	Block	Efficiency (%)
550	1	6	1	1.6
625	1	6	1	5.4
550	10	6	1	0.8
625	10	6	1	5.0
550	5.5	4	2	2.6
625	5.5	4	2	8.8
550	5.5	8	2	5.9
625	5.5	8	2	0.0
587.5	1	4	2	12.7
587.5	10	4	2	2.8
587.5	1	8	2	10.6
587.5	10	8	2	0.0
587.5	5.5	6	1	0.1
587.5	5.5	6	1	4.6
587.5	5.5	6	1	5.6

Nevertheless, the model was fit using ordinary least squares including all parameters up to order 2 and averaged over the blocking variable:

$$\begin{aligned}
\eta = & -443 + 1.28x_1 - 1.37x_2 + 23.2x_3 \\
& + 8.7 \times 10^{-4}x_1^2 - 4.86 \times 10^{-2}x_2^2 \\
& + 6.0 \times 10^{-4}x_1x_2 - 4.03 \times 10^{-2}x_1x_3 - 1.9 \times 10^{-2}x_2x_3
\end{aligned} \tag{5.4}$$

where x_1 is temperature in °C, x_2 is H₂S concentration in percent, and x_3 is Se layer thickness in μm (note that the coefficient for x_3^2 is aliased with that of the blocking variable, precursor batch, and cannot be estimated). Bounded optimization results in a predicted optimum at one of the boundaries: 625 °C, 1% H₂S, and 4 μm Se. However, the predicted mean efficiency is 12.05 ± 11.13 , where the 95% confidence interval is too wide for the estimate to be meaningful.

This optimization procedure did, however, result in the best efficiency device obtained in this work, with $\eta = 12.7\%$, produced using 1% H₂S, 4 μm Se, and reacted at 587.5 °C. The JV curve for this device is shown in Figure 5.16.

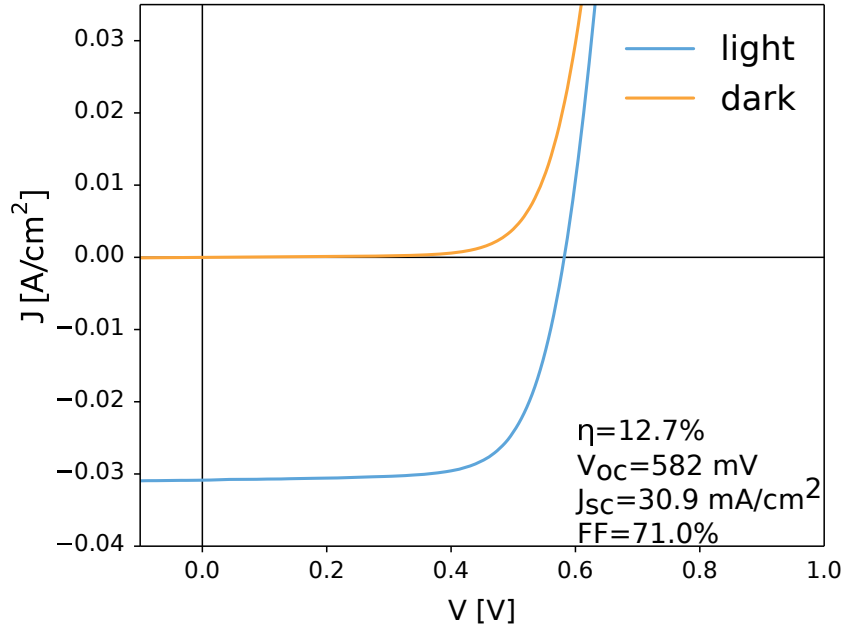


Figure 5.16: JV curve of the highest efficiency device obtained in this work that was produced using 1% H₂S, 4 μ m Se and reacted at 587.5 °C.

5.6 Summary and Conclusions

In this chapter, a method for fabricating chalcopyrite thin films using selenium-capped precursors was presented. The effects of process variables, including thickness of selenium layer, concentration of H₂S in the gas phase, reaction temperature, silver incorporation, and temperature ramp rate were examined. It was found that all main effects, except for the temperature ramp rate, affected the composition of the final film, in particular, the through-film profiles of gallium and sulfur. More homogeneous gallium profiles were obtained from reactions at higher temperature. Increasing H₂S significantly increases the sulfur incorporation, especially in the near surface region. Selenium layer thickness affected the sulfur incorporation as well, primarily in the bulk rather than near surface region of the film. Most of these effects are captured by the stochastic model that was presented in Chapter 3; the exception was the effect of sulfur on the surface. Assuming that the parabolic reaction model (wherein the front surface is converted to chalcopyrite first, and chalcogen species diffuse through the

reacted layers toward unreacted precursor species) is reasonable, this likely results from additional “substitution” reactions due to the large chemical potential of sulfur when concentration H_2S is high—future work should consider the effect of these additional reactions on the through-film sulfur profile.

The effectiveness of the process was validated by fabrication of solar cell devices that could achieve approximately 10% power conversion efficiencies over a range of compositions by adjusting the processing conditions. The multistep process has several uncontrolled sources of variability, especially batch-to-batch variability in the precursors, that prevented successful optimization of efficiency. However, during the optimization procedure, a high efficiency device, 12.7%, was obtained and characterized.

While the efficiencies of these devices are lower than the state-of-the-art, they have similar efficiency to those produced commercially. Further, outside of absorber preparation, these devices have not been optimized for lower resistive losses (by engineering the front contact properties), for reduced parasitic absorption (by engineering the CdS buffer layer), or for reduced reflective losses (by depositing an anti-reflective coating). Each of these procedures is recommended for future work, and I believe that they will enable this process to produce much higher efficiencies.

Chapter 6

SUMMARY, CONCLUSIONS, AND FUTURE WORK

This dissertation presented my approach to the design and analysis of a rapid thermal processing system for the production of Cu(InGa)(SeS)_2 thin films for application as the absorber layer in thin film solar cells. The rapid thermal processing method is a promising approach for high-throughput production of these absorber layers, and the process described herein may potentially be applied on an industrial scale; in fact, some companies are currently commercializing similar approaches.

Three key achievements of this work are:

1. Design and implementation of a novel temperature control system for a rapid thermal processing reactor.
2. Development of a stochastic model of solid state thin film deposition, as well as the application of this model to chalcopyrite film growth.
3. Demonstration of a selenium-capped precursor reaction process capable of producing chalcopyrite solar cells with efficiencies exceeding 12%.

6.1 Reactor Design and Effective Temperature Control

In Chapter 2, the reactor design approach was described; thermal models solved using finite element analysis and simple energy balances were applied to size equipment, in particular to select a heat lamp that is effective for heating the samples rapidly. However, reactor design was only one challenge in implementing the reactor; achieving effective temperature control is vital.

Temperature control in the RTP system is complicated by two intrinsic process characteristics: (i) the temperature of interest, that of the reacting chalcopyrite films, cannot be measured directly, and (ii) the process is significantly nonlinear due to the

effect of radiative heat transfer at temperatures greater than 500 °C. These challenges were overcome by carefully modeling the heat transfer in the system, using a lumped parameter and a distributed parameter model, and applying these models to the design of two control system components: an observer that provides the requisite state estimates for adequate control and a PII² controller that can effectively track the linear ramp rates even with the intrinsic nonlinearity of the heat transfer process.

The control system design approach that was described here is mathematically general and was applied to a previously unsolved problem: control of a distributed parameter system with boundary sensing and actuation and nonlinear boundary conditions. The method therefore has the potential to be applied as an important component of the overall control strategy for several industries, especially where thin film semiconductors or other advanced coatings are deposited.

6.2 Stochastic Model of Thin Film Deposition

Chapter 3 describes a stochastic model of thin film deposition and its application to the system of interest, selenization and sulfization of a Cu-In-Ga precursor. I described a simplified reaction mechanism that contains enough of the physics to be meaningful, without containing all of the experimentally observed species, which appear to be highly process dependent. The model can be used to simulate the reaction and produce through-film profiles of composition, especially the profiles of gallium and sulfur. Several example processes were examined, including the single stage reaction with H₂Se, simultaneous reaction with H₂S and H₂Se, and reaction of a selenium-capped precursor; subsequent chapters compared these results to our experimental results, showing several similar trends, however, the reaction model does not capture the near surface sulfur ratio observed in selenium-capped precursor reactions.

The effect of composition and film thickness on lateral heterogeneity was also examined by fitting the agglomeration data to the negative binomial distribution using maximum likelihood estimation, finding that both variables affect the average agglomeration size and that these effects are easily captured by parameters of the negative

binomial distribution.

6.2.1 Future Work

The physics of the model are easily generalized to three dimensions or to materials with complex internal geometry, resulting in N effective dimensions. However, the solution algorithm is not as easily generalized; future work should investigate an optimum solution algorithm for N dimensional simulations. A similar approach would likely be appropriate: the “lattice” should be transformed to a 1D array of interface kinds, but the transformation will be more complicated and the length of the list will increase exponentially with dimensionality. The increase in array length may not be important, however, as it is unlikely that realistic material systems will have geometries that cannot be represented with fairly low dimensionality.

Another addition to the model that may be valuable is the introduction of non-isotropic effects. It is conceptually simple to adjust the event propensities as a function of direction, and may result in a better description of non-isotropic materials.

6.3 Reaction of Precursors in Hydride Gases

The efficacy of the RTP system and process was examined by studying the reaction of Cu-In-Ga precursors in H_2S and H_2Se gases. Several different reaction methods were examined, including single stage, multistage, and thermal spike reactions. Composition measurements and diffraction patterns showed that in each of these methods, gallium was segregated near the back of the film, which usually leads to low voltage, low efficiency devices.

6.3.1 Future Work

The films produced using these methods could not be used to fabricate devices because the adhesion of the chalcopyrite layer to the Mo layer was very weak, and the films would flake off during processing. A more comprehensive study of film adhesion is recommended to understand the cause of the poor adhesion and how to improve it. It would appear that the poor adhesion is not a result of only rapid expansion of

volume, as the same process would occur in the selenium-capped reaction process; yet, no issue with adhesion was encountered when reacting selenium-capped precursors.

6.4 Reaction of Selenium-Capped Precursors

The selenium-capped precursor reaction process was used to produce chalcopyrite solar cells. First, the effects of several process variables was examined, including temperature ramp rate, dwell temperature, selenium thickness, H_2S concentration, and incorporation of silver in the precursor. It was found that each of these variables, except for temperature ramp rate, significantly affects the composition of the film. Higher H_2S concentrations and temperatures increase the gallium near the front of the film, whereas silver incorporation reduces the gallium near the front. Diffraction patterns were also obtained from each of the films, showing that increased temperature and no silver incorporation corresponded with sharper peaks that indicate a larger-grained, more crystalline film.

Next, devices were fabricated from chalcopyrite films produced using this process. It was found that the efficiency was not strongly affected by the incorporation of sulfur, but other electrical properties were affected. Increasing the H_2S concentration increased the device voltage, but decreased the current, as would be expected from increasing the band gap.

Finally, a response surface method was used to attempt to optimize device efficiency within the process space. Although the variance intrinsic to the process and the batch-to-batch variability made the optimization procedure impractical, the individual experiments resulted in the highest efficiency device obtained in this work, with a 12.7% efficiency device.

6.4.1 Future Work

There were indications that the through-film profile for gallium in at least some cases contained an interior maximum. Composition measurements from the front and back side both showed gallium incorporation lower than the known bulk average. The

model also predicts this behavior for some process variables. Therefore, the through-film composition of these films should be measured experimentally to confirm or refute these data. Through-film measurements can be obtained by Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), or glow discharge optical emission spectroscopy (GDOES)¹.

All of the devices had large voltage deficits, suggesting electrical defects in the films. Examining the physics of the devices in more detail to determine the loss mechanisms and how to improve performance is recommended.

Finally, reducing the batch-to-batch variability is essential for this work. This may be impractical in an academic environment, but would be vital should this method, or a similar method, be used on a commercial scale. Batch-to-batch variability can come from several sources: material suppliers, glass cleaning, waiting time between process steps, and others. Each of these must be examined systematically to determine the source of variability and allow for more consistent process performance, which could then be optimized for consistent product quality.

¹ The method for through-film estimation of the profile using EDX measurements, presented in Appendix C does not apply here because an appropriate functional form for the profile is not known *a priori*.

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Appendix A

PARAMETER ESTIMATION AND VALIDATION FOR AGGLOMERATION DISTRIBUTION

In this appendix, we use a slightly altered version of the negative binomial probability model (first shown in Equation 3.19), given by

$$f(x|r, p) = \frac{\Gamma(x+r)}{(x)!\Gamma(r)} p^x (1-p)^r, \text{ for } x = 0, 1, 2, \dots \quad (\text{A.1})$$

to characterize the agglomeration size distribution. In this form, the domain of x has been shifted leftward by 1 unit; thus the data should be shifted down by 1 unit (*i.e.*, size-1 agglomerations will be considered size-0 agglomerations), but the parameter values remain unchanged. The two parameters, r and p were estimated using Maximum Likelihood Estimation (MLE). The likelihood function for a sample of agglomeration data, $\mathbf{X}$ is then obtained as:

$$L(r, p|\mathbf{X}) = \prod_{x \in \mathbf{X}} \frac{\Gamma(x+r)}{(x)!\Gamma(r)} p^x (1-p)^r \quad (\text{A.2})$$

and for a total of N agglomeration samples, the log-likelihood function is:

$$l(r, p|\mathbf{X}) = Nr \ln(1-p) - N \ln(\Gamma(r)) + \sum_{x \in \mathbf{X}} (\ln(\Gamma(x-1+r)) - \ln((x-1)!) + x \ln(p)) \quad (\text{A.3})$$

To maximize the log-likelihood function (equivalent to maximizing the likelihood function) the partial derivatives of the log-likelihood function with respect to the parameters are set to zero:

$$\begin{aligned} \frac{\partial l(r, p)}{\partial r} = 0 &= N \ln(1-p) - N \Psi(r) + \sum_{x \in \mathbf{X}} \Psi(x-1+r) \\ \frac{\partial l(r, p)}{\partial p} = 0 &= Nr p - \frac{\sum_{x \in \mathbf{X}} x}{p} \end{aligned} \quad (\text{A.4})$$

Table A.1: Results from MLE estimates and χ^2 tests of the negative binomial parameters from the agglomeration distribution data. There is no evidence to reject the null hypothesis that the model is adequate in any case. The thickness and composition values were selected to complete a face-centered cubic response surface design. For the “N/A” cases, the sample size was too small for the chi-square test to be valid, but the fit appeared good visually.

Thickness	Ga/(In+Ga)	N	p	r	$Pr(C^2 > \chi^2(m - 3))$
4	.05	481	0.2182	0.2290	N/A
10	.05	1173	0.1935	0.5371	0.098
4	.45	1228	0.8690	0.3993	0.526
10	.45	2662	0.9058	0.3192	0.592
4	.25	1442	0.6433	0.4028	0.508
10	.25	3454	0.6568	0.4352	0.557
7	.05	808	0.1685	0.4826	N/A
7	.45	1858	0.9035	0.3333	0.567
7	.25	2428	0.6456	0.4280	0.407

where $\Psi(x)$ is the digamma function, or $\Gamma'(x)/\Gamma(x)$. While the second of these equations can be solved explicitly for p , in general, there is no closed form solution to Equations A.4 for r and p . The system of equations is solved numerically to obtain the parameter estimates.

In order to validate this approach, simulations were run with varying film thicknesses and gallium fractions, p and r were estimated, and a χ^2 test was applied to compare model predictions to data. The response surface method (see Appendix B) was used to select the specific values of film thickness and gallium fraction. The χ^2 test statistic is:

$$C^2 = \sum_i^m \frac{(f_i - \phi_i)^2}{\phi_i} \quad (\text{A.5})$$

f_i is the observed count of agglomerations of size i , ϕ_i is the predicted count using the negative binomial distribution with MLE parameter estimates, and m is the largest agglomeration size with at least 5 instances. If the model is appropriate, C^2 should approximate a $\chi^2(\nu)$ random variable with $\nu = m - 3$ degrees of freedom. Thus, we calculate the probability that $C^2 > \chi^2(m - 3)$ and if this value is less than 0.05 (a

commonly-used significance level), then we reject the null hypothesis that that model is appropriate. The results of the χ^2 tests are shown in Table [A.1](#) and there is no evidence to reject the null hypothesis in any of the cases.

Appendix B

RESPONSE SURFACE METHODS FOR AGGLOMERATION DISTRIBUTION

Response surface methodology is an experimental design approach usually used for optimizing a process with a response variable that is approximated as a 2nd order function of several input (or factor) variables. In this work, we use the methodology to understand empirically the effects of film thickness and composition on the negative binomial random variable parameters, (p, r) . We postulate that the following model is appropriate:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 \quad (\text{B.1})$$

where y is the response variable (p or r), x_1 is film thickness and x_2 is Ga/(In+Ga). We employ a face-centered cubic response surface design and the results from each run are shown in Table II (traditionally, two or more replicates of the center point are included—we include only one replicate because of the low variance resulting from simulated, rather than experimental, data). The parameters (β_i) were estimated using ordinary least squares and insignificant effects ($p > 0.05$, assuming normally distributed error) were removed from the models. The resulting response surfaces (plotted in Figs. 3.5e-f) are:

$$\begin{aligned} p &= 0.05 + 3.07x_2 - 2.64x_2^2 & (R^2 = 0.997) \\ r &= 0.06x_1 + 1.12x_2 - .18x_1x_2 & (R^2 = 0.991) \end{aligned} \quad (\text{B.2})$$

Appendix C

DEPTH PROFILE MEASUREMENT USING ENERGY DISPERSIVE X-RAY SPECTROSCOPY

C.1 Introduction and Project Goal

One of the challenges of this work was the inability to measure the through-film composition profile of a chalcopyrite material using in-house equipment. Here, I will investigate a method for determining the composition profile using EDX measurements, which can be obtained using an SEM. The method was not applied in this work because it requires *a priori* knowledge about the shape of the composition profile. However, it is valuable as it was applied successfully to measure the composition profile of chalcopyrite films deposited by co-evaporation, for which the shape of the depth profile is simpler and, for the process used here, known in advance.

C.2 Approach

Typically, the raw data from EDX measurements are used to obtain the weight concentration (*e.g.*, g/cm³) of each element in the film using a method referred to as “spectral quantification.” Spectral quantification uses measurements from a known standard to obtain the composition of an unknown sample by solving the following optimization problem:

$$\min_{\mathbf{W}_{\text{samp}}} \|\mathbf{S}_{\text{samp}} - \mathbf{W}_{\text{std}}^T \mathbf{S}_{\text{std}} \mathbf{W}_{\text{samp}}\|_{L_2} \quad (\text{C.1})$$

The problem is linear has the following solution (notice that it is an ordinary least squares problem):

$$\hat{\mathbf{W}}_{\text{samp}} = \left((\mathbf{W}_{\text{std}}^T \mathbf{S}_{\text{std}})^T \mathbf{W}_{\text{std}}^T \mathbf{S}_{\text{std}} \right)^{-1} (\mathbf{W}_{\text{std}}^T \mathbf{S}_{\text{std}})^T \mathbf{S}_{\text{samp}} \quad (\text{C.2})$$

Where $\mathbf{W}_i$ and $\mathbf{S}_i$ for ($i = \text{std}, \text{samp}$) are column vectors of the weight concentrations of each species and the measured x-ray spectra (appropriately discretized) in the sample and the standard, respectively. The mass fraction for each species is obtained by multiplying by the known density of the standard (note that the problem is not constrained, therefore random variation results in the mass fractions *not* summing up to exactly 1). From here, it is trivial to obtain the mole fractions from the molecular weights.

Now, the development above is exactly valid only if the composition profile through the film is uniform. Essentially, we assume that each species contributes equally to the measured spectrum, but that will not be the case if there is depth variation. When there is depth variation, the quantity of emitted x-rays as a function of depth must be estimated. Such an estimate can be obtained by Monte Carlo methods, that are applied here using the software package DTSA-II from the National Institute of Standards and Technology [121] (this software package was chosen because it was open source, which allowed the source code to be altered to simulate films with composition gradients).

Using these Monte Carlo methods, plots of x-ray emission intensity versus depth in film can be produced. For a uniform film, an appropriate approximate analytical form is a “double Gaussian” [122]:

$$\Phi(z) = \begin{cases} \Phi_m \exp\left(\frac{-(z-z_m)^2}{\beta^2}\right) & \text{for } z \leq z_m \\ \Phi_m \exp\left(\frac{-(z-z_m)^2}{\alpha^2}\right) & \text{for } z > z_m \end{cases} \quad (\text{C.3})$$

where Φ is the emitted x-ray intensity, z is the depth in the film, Φ_m is the maximum emitted x-ray intensity, z_m is the position in the film at which $\Phi(z) = \Phi_m$, and α and β are constants:

$$\begin{aligned} \alpha &= \frac{z_x - z_m}{\sqrt{-\ln(0.01/\Phi_m)}} \\ \beta &= \frac{z_m \ln(\Phi_m)}{\sqrt{\Phi_0}} \end{aligned} \quad (\text{C.4})$$

where Φ_0 is the emitted x-ray intensity from the surface, and z_x the position at which emitted x-ray intensity is 1% of its maximum (and beyond which is, $\Phi(z)$ is considered negligible).

It is straightforward to show that another estimate of weight concentration can be obtained from:

$$\hat{W}_{i,\text{alt}} = \frac{\int_0^{z_x} \Phi_{i,\text{samp}}(z) dz}{\int_0^{z_x} \Phi_{i,\text{std}}(z) dz} W_{i,\text{std}} \quad (\text{C.5})$$

where i is an element of interest (for W) or the x-ray line used to quantify that element of interest (for Φ); the subscript “alt” emphasizes that this method provides an alternative second estimate of W , in addition to Equation C.2. In this work, we augment these equations to include the weight concentration of an element and the acceleration voltage of the electron beam explicitly. Therefore, define the parameters ($\theta = [\Phi_m, \Phi_0, z_m, z_x]$) as functions of weight concentration and acceleration voltage and postulate that each of the parameters can be approximated as a multivariable polynomial function with coefficients that can be found by linear least squares optimization.

The following method to determine the complete depth profile of a particular element in a thin film is proposed:

1. Determine, via Monte Carlo simulation, $\Phi(z)$ for a particular x-ray line of interest for varying concentration and acceleration potential.
2. For each curve, fit θ to Equation C.3 using nonlinear optimization (*e.g.*, the Levenburg-Marquart algorithm [123]). Initial guesses are easy to obtain from reading points off of the plot (*e.g.*, the optimized Φ_0 will be very close to the observed value of $\Phi(0)$ from the Monte Carlo simulation).
3. For each x-ray line of interest, determine, via ordinary least squares, the parameters as polynomial functions of concentration and acceleration potential.
4. Select an appropriate functional form, with parameters θ_{profile} for the composition depth profile, $W_i = f(z)$ and an appropriate initial guess.
5. Use a nonlinear optimization routine (*e.g.*, the Nelder-Mead simplex method [124] or similar approaches are recommended because the complex functional form could make gradient methods unstable) to solve the optimization problem:

$$\min_{\theta_{\text{profile}}} \|\hat{W}_{i,\text{samp}} - \hat{W}_{i,\text{alt}}\|_{L_2} \quad (\text{C.6})$$

Which is solved to find $\hat{\boldsymbol{\theta}}_{\text{profile}}$.

Notice that neither $\hat{W}_{i,\text{samp}}$ nor $\hat{W}_{i,\text{alt}}$ are truly estimates of the bulk weight concentration, but weighted averages of weight concentration where the weights are the emission intensities. The desired information, that is the estimated depth profile of weight concentration, will be given by $f(z|\hat{\boldsymbol{\theta}}_{\text{profile}})$.

C.3 Results and Discussion

The method described in the previous section was applied to a Cu(InGa)Se₂ thin film deposited by 3-stage co-evaporation, a process which is known to yield a “double linear” composition profile in gallium, resulting in the function:

$$f(z) = \begin{cases} m_1(z - z_{\min}) + W_{\min} & \text{for } z \leq z_{\min} \\ m_2(z - z_{\min}) + W_{\min} & \text{for } z \geq z_{\min} \end{cases} \quad (\text{C.7})$$

where $z_{\min}$ and $W_{\min}$ are the position and value of the minimum gallium concentration and m_i ($i = 1, 2$) are the slopes of the two lines.

Figure C.1 shows plots of $\Phi(z)$ obtained from DTSA-II from Monte Carlo simulation of uniform films and the curves fitted to Equation C.3 for the gallium K-L2 emission line with varying incorporation of gallium in the film. Similar figures could be obtained from varying acceleration potential instead of gallium concentration.

Following through the procedure for a sample that was deposited by co-evaporation, and the through-film profile of gallium is known from transmission electron microscopy (TEM) cross section measurements, results in the depth profile seen in Figure C.2. The TEM data was *not* used to obtain the EDX depth profile—only EDX measurements at several acceleration potentials and the procedure given above were used.

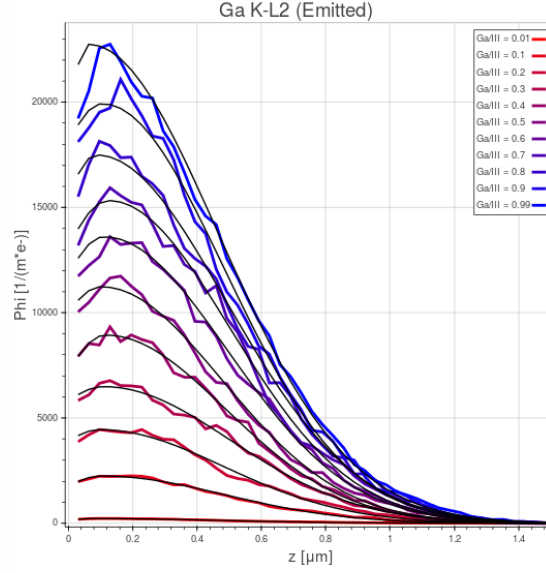


Figure C.1: Intensity of gallium K-L2 x-ray emission as a function of depth in film from Monte Carlo simulations (color curves) and fitted to Equation C.3 (black curves).

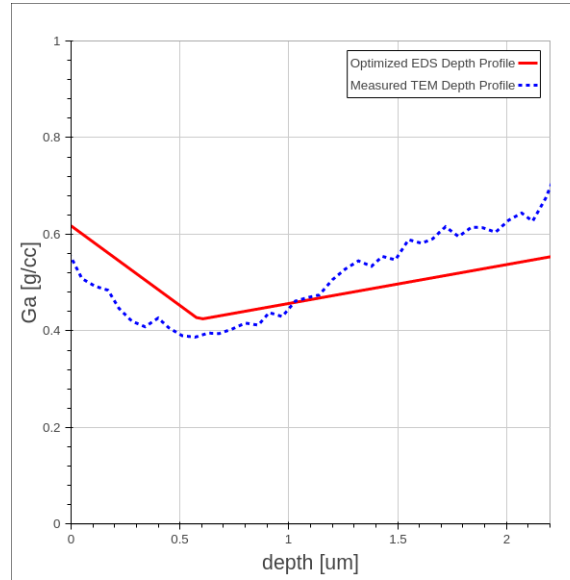


Figure C.2: EDX-estimated depth profile with actual depth profile measured by a transmission electron microscopy (TEM) cross section. The parameter values fit to Equation C.7 are $z_{min} = 0.59 \mu\text{m}$, $C_{min} = 0.42 \text{ g/cm}^3$, $m_1 = -0.33 \text{ g}/(\text{cm}^3 \mu\text{m})$, and $m_2 = 0.08 \text{ g}/(\text{cm}^3 \mu\text{m})$.

Appendix D

MODELING OF DOPANT CONCENTRATION IN CADMIUM TELLURIDE VAPOR TRANSPORT DEPOSITION PROCESS

D.1 Introduction and Project Goals

This work focused on the production of Cu(InGa)(SeS)_2 thin film production. However, another inorganic thin film is commonly used as the absorber layer in thin film solar cells: CdTe. CdTe absorber layers for solar cells are currently produced commercially over large areas using a vapor transport (VT) deposition process [125]. CdTe-based devices have many similar properties to chalcopyrites, and have achieved nearly as high efficiencies, with the manufacturer First Solar recently demonstrating a cell with 22.1% efficiency [126].

The primary loss mechanism in high-efficiency CdTe solar cells is a low V_{oc} . Therefore, methods for improving the voltage of CdTe solar cells have the potential to increase efficiency more effectively than optimization of current or fill factor. Currently, most CdTe devices are intrinsically doped, meaning their p-type conductivity is a result of intrinsic defects (specifically, Cd vacancies) in a pure CdTe crystalline film. However, the alternative approach of extrinsic doping, whereby the material's conductivity is a function of extrinsic defects, has the potential to increase the p-type conductivity of CdTe [127], which could improve the voltage of the device.

In this work, the VT deposition process will be examined as a method for depositing CdTe films that contain extrinsic dopants, specifically phosphorous and antimony. The VT process contains an enrichment zone, where the low pressure (working pressure is approximately 20 torr) carrier gas is enriched with cadmium (Cd), tellurium (Te_2), and dopant gases, and a deposition zone, where the lower temperature results in a supercritical gas that is deposited on a moving substrate. This appendix will describe

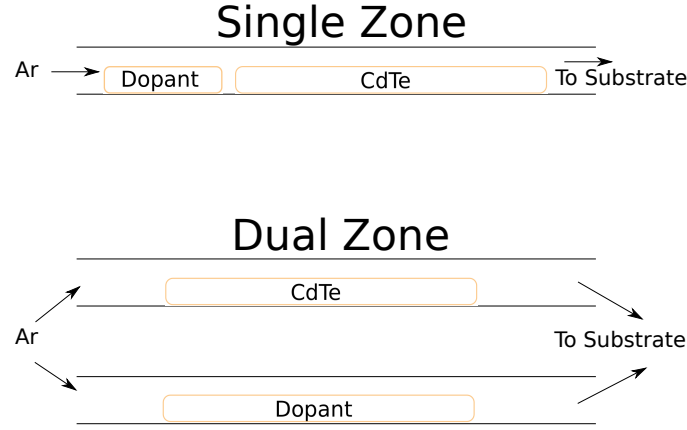


Figure D.1: Schematic showing single and dual enrichment zones for a CdTe VT deposition system with extrinsic dopants. Dopant is either Cd_3P_2 or Cd_3Sb_2 . Ampoule diameter is 1. cm.

a model of the enrichment zone and show how to tune the dopant concentration in the gas phase using a single or dual zone method.

D.2 Model Development

A schematic of the enrichment zone (single or dual) is shown in Figure D.1. For the single enrichment zone, the enrichment zone is a single glass ampoule with dopant crystals placed near the entrance and CdTe crystals throughout most of the rest of the ampoule. The gas will saturate with cadmium and tellurium vapor, but the dopant concentration will be limited by the length of the dopant zone. In the dual zone, there are two glass ampoules; temperature and flow rate can be independently controlled in each zone, allowing for robust control of dopant concentration over a large range.

The concentration of gaseous species at the exit to the ampoule(s) is controlled by equilibrium and mass transfer limitations. The equilibrium concentrations can be found from thermodynamics. First, applying the general equilibrium criterion:

$$f_i^g = f_i^{s/l} \quad (\text{D.1})$$

where f_i is the fugacity of species i ; the superscript g represents gas phase, s/l represents the solid or liquid phase (as the temperature of the ampoule will be above

the solidus of Cd_3Sb_2). In all cases, the gas phase is treated as ideal, justified by low pressure, therefore,

$$f_i^g = P_i \quad (\text{D.2})$$

where P_i is the partial pressure of species i .

For the solid species, CdTe and Cd_3P_2 :

$$f_i^s = P_i^{vap} \quad (\text{D.3})$$

where P_i^{vap} is the total vapor pressure. Vapor pressure of individual components must be determined equilibrium from constants for the gas phase species and the constraint:

$$P_i^{vap} = \sum_{j=\text{gas species}} P_j \quad (\text{D.4})$$

For CdTe , vapor pressure is given by Madelung et al. [128]; no equilibrium calculations are necessary as Cd and Te_2 are the only gas-phase species. However, for Cd_3P_2 , both P_2 and P_4 are present and gas phase equilibrium calculations are necessary; Lazarev et al. [129] provides the vapor pressures and the equilibrium constants.

When the dopant species is liquid (as in Cd_2Sb_3), the calculations are more complex as congruent evaporation can no longer be expected. Vapor pressures are calculated independently for each element using an activity coefficient model:

$$f_i^l = x_i \gamma_i P_i^{vap} \quad (\text{D.5})$$

where x_i and γ_i are the mole fraction and activity coefficients, respectively, for species i in the liquid phase. The gas-phase concentrations must again be corrected for equilibrium, as Sb , Sb_2 , Sb_3 , and Sb_4 may be present. The activity coefficients for the liquid phase are provided by Predel [130] and the gas-phase equilibrium constants from Gibbs formation energies (recall that the equilibrium constant can be found from: $K = \exp(-\Delta G_{\text{rxn}}/(RT))$) are available from [131].

With an understanding of the equilibrium limits, the mass transfer constraints are now examined. Here, we make a simplifying assumption that the gas flow is linear

and plug flow. Velocity gradients along the enrichment zone would increase mass transfer, therefore, the results set a lower limit on the gas phase concentrations. Under these assumptions, the time constant for diffusion in the gas is given by:

$$\tau_D = \frac{l_d^2}{D} \quad (\text{D.6})$$

where l_d is the characteristic diffusion length, in this case the diameter of the ampoule, and D is the diffusion coefficient, which can be estimated by Chapman-Enskog theory [71]:

$$D = 0.0018583 \frac{\sqrt{T^3 \left[\left(\frac{1}{M_i} \right) + \left(\frac{1}{M_{Ar}} \right) \right]}}{P \sigma_{i,Ar}^2 \Omega_{D,i,Ar}} \quad (\text{D.7})$$

The resulting ordinary differential equations for each species, i , are used to find species pressure as a function of position:

$$\frac{dP_i}{dx} = \frac{P_i^{vap} - P}{v_{x,avg} \tau_{D,i}} + \frac{P_i^{eq} - P_i}{v_{x,avg} * \tau_{rxn}} \quad (\text{D.8})$$

where the first term on the right hand side accounts for mass transfer limitations from evaporation and the second accounts for gas phase reactions to reach equilibrium (should the temperature be non-constant across the enrichment zone). $v_{x,avg}$ is the average gas velocity, P_i^{eq} is the equilibrium pressure of species i , and τ_{rxn} is the time constant for the equilibrium reaction. We assume $\tau_{rxn} \ll \tau_D$, that is, a rapid gas-phase equilibrium, which will make the equations stiff; however, stiffness is not a challenge for many modern ODE solvers.

D.3 Model Results and Discussion

Example simulations of the single zone configuration for phosphorous and antimony dopants are shown in Figure D.2. Control of dopant concentration, especially at the low concentrations (less than 1%) that would be desired for doping, is challenging because the temperature and velocity of the dopant enrichment zone and CdTe enrichment zone are coupled. Figure D.3 shows examples of simulations from dual zone enrichment reactor configurations. The ability to control each flow rate independently makes it easier to achieve the required low concentrations for doping CdTe films.

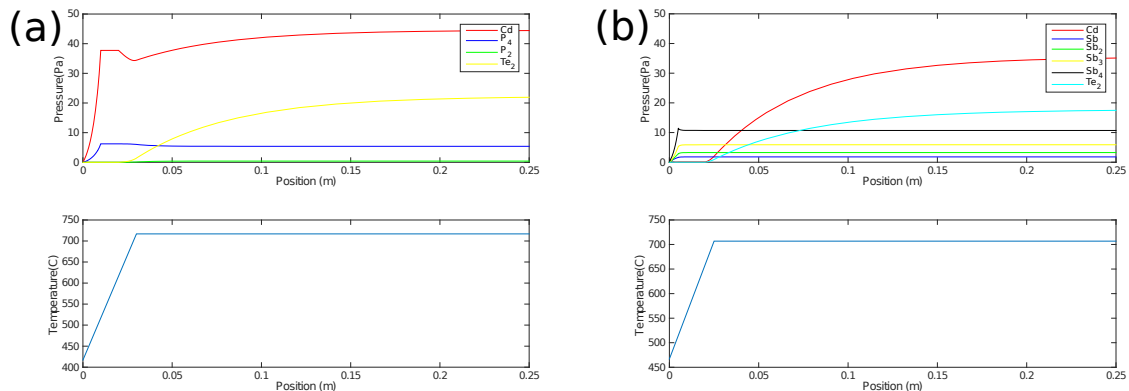


Figure D.2: Gas partial pressures (balance is argon) for Cd, Te₂ and dopant species in a single zone configuration with the temperature profile across the enrichment zone shown. Dopant source is either (a) Cd₃P₂ or (b) Cd₃Sb₂. The gas velocity is 0.1 m/s.

Using the dual zone configuration allows for simple tuning of the outlet mole fraction of doping. Figure D.4 shows the outlet mole fraction in “solvent-free” terms (*i.e.*, Ar is not included). From these results, it is clear that equilibrium considerations, in tandem with process design (adjusting temperatures and flow rates) allows for robust specification of dopant concentration over a large range by using the dual zone configuration.

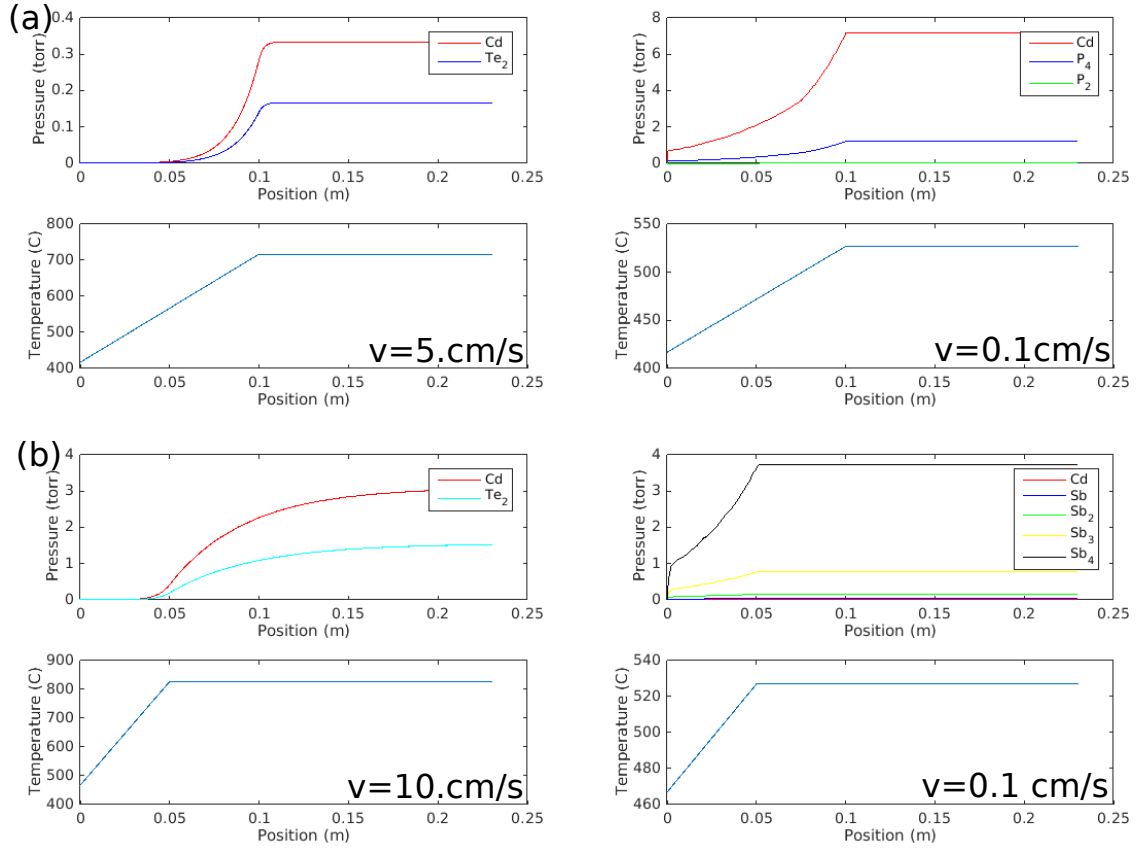


Figure D.3: Gas partial pressures (balance is argon) for Cd, Te_2 and dopant species in a double zone configuration with the temperature profile across the enrichment zones shown. Dopant source is either (a) Cd_3P_2 or (b) Cd_3Sb_2 . The gas velocities are shown.

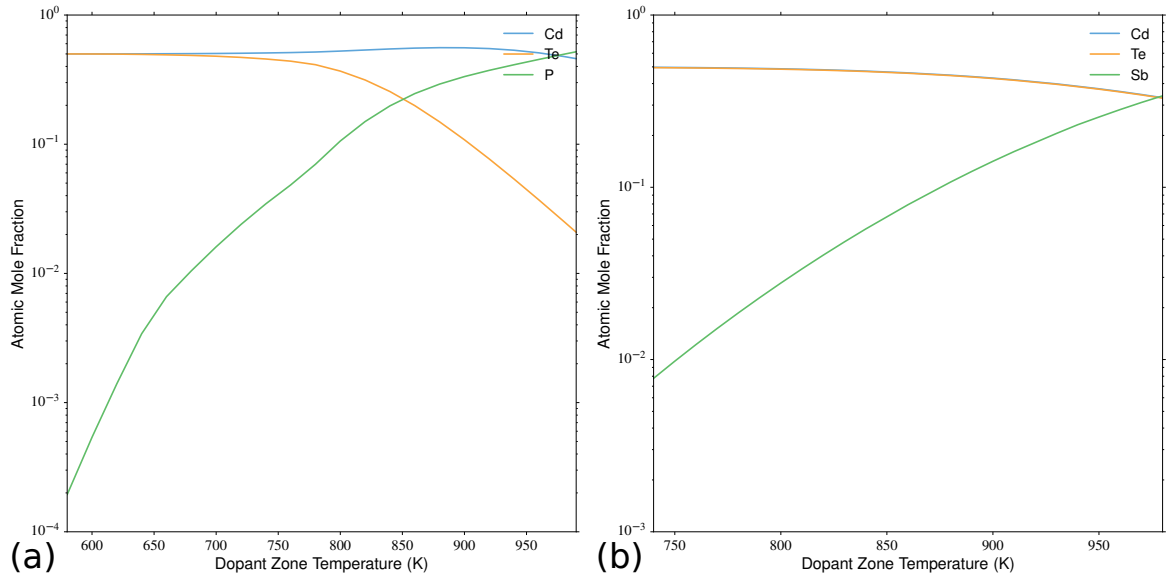


Figure D.4: Mole fraction of Cd, Te, and dopant atoms as a function of dopant zone temperature for (a) P doping and (b) Sb doping. For (a), CdTe zone temperature is 990 K with gas velocity of 0.05 m/s; dopant zone gas velocity is 0.001 m/s. For (b), CdTe zone temperature is 1100 K with gas velocity of 0.1 m/s; dopant zone gas velocity is 0.001 m/s.

Appendix E

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