AN INVESTIGATION OF ELECTRONIC PASSIVATION OF SILICON <100> SURFACES IN SOLUTIONS OF P-BENZOQUINONE

by

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ABSTRACT

Silicon <100> surfaces under passivation by p-benzoquinone/methanol solutions have shown significant increases in minority carrier lifetime relative to hydrogen terminated surfaces. This appears to be a good candidate system for future improvements to existing Si solar technologies but little is known about the physical mechanism of passivation. The following work focuses on three areas; the importance of solvent choice in the observed passivation effect, passivation of surfaces with thin native oxides, and analysis of surface coverage and composition using X-ray Photoelectron Spectroscopy (XPS). Previous studies have largely ignored solvent choice, primarily using methanol. It is shown that on Si < 100 > surfaces using methanol as a solvent provides higher minority carrier lifetimes while also reaching plateau values more quickly than solutions with diethyl ether as the solvent. Next oxidized wafers are investigated. A wafer with native oxide of roughly 2 nm shows a significant increase in minority carrier lifetime when immersed in solutions of p-benzoquinone/methanol. When the native oxide layer is 22 nm thick however there is no observed passivation effect. Lastly a surface analysis of Si < 100 > wafers out of the box (native oxide on the surface), after etching with piranha and HF (hydrogen terminated surface), after 1 hour in methanol, after 1 hour in p-benzoquinone/methanol, and after 1 hour in hydroquinone/methanol was done by XPS. The p-benzoquinone and methanol treated surfaces show signs of Si-O bonding however the peak heights after the 1 hour period are too small to be conclusive. We conclude that there is insufficient surface coverage to provide sufficient signal strength.

Chapter 1 INTRODUCTION

With increasing interest in alternative energy there has been a push to drive down cost of the associated technologies. One such area focuses on decreasing cost of silicon based solar cells while maintaining current efficiencies. In this approach the main cost cutting method is to simply use less silicon per cell by making thin films. This, however, brings up a new set of issues stemming from the increase in the ratio of surface area to bulk volume. Because there is now more surface area, effects at the surface that cause loss of efficiency become increasingly important. The study of surface passivation is thus important to increasing our overall understanding of how we can produce high efficiency thin film solar cells.

It has been observed that silicon $\langle 100 \rangle$ wafers show high minority carrier lifetimes when immersed in a solution of quinhydrone and methanol.[1] Quinhydrone itself is a mixture of p-benzoquinone and hydroquinone. Further it has been seen that after removal from solution these wafers tend to show increased lifetimes for several days.This system is suitable for study of the mechanisms through which surface passivation occurs. The following work is concerned with the study of what specifically about the interaction of p-benzoquinone with a silicon $\langle 100 \rangle$ surface results in the observation of increased minority carrier lifetimes. Note that in the below presentation the term passivation refers specifically to treatments which may reduce the surface recombination velocity (or identically increase the minority carrier lifetime) of a given sample.

The contribution of both p-benzoquinone and hydroquinone to the observed passivation has been investigated. It is conclusively shown p-benzoquinone is the active component thus it is relevant to primarily investigate the effects of solutions of benzoquinone.[2] It is however important to make comparisons between the effect of p-benzoquinone and hydroquinone solutions on carrier lifetime as hydroquinone solutions have also been shown to increase the carrier lifetimes.

The physical origins of the passivation have been discussed somewhat recently.[3] It is suggested that one way of reducing the surface recombination velocity is to decrease the number of charge carriers present at the surface. It is possible that quinhydrone treatments create Si-O-Ph bonds which generally creates a negative charge near the interface. This effectively creates an electric field, forcing more of the charge carriers into the bulk thus reducing surface recombination velocity.

This is commonly referred to as field effect passivation. In the case of the p-benzoquinone/methanol system it is suggested that the p-benzoquinone molecule bonds to the surface dihydride sites and molecular hydrogen leaves. This reaction is supported by ATR FTIR spectroscopy, showing the Si-O and Ph-O regions. This requires further investigation perhaps looking into the viability of transition states and experimentally looking for the in solution reaction products. The former may be done by DFT calculations and the later by looking at the chemical makeup of solutions, by NMR, after interaction with a large surface area silicon sample

Other studies have targeted the effect of different types of cleans on surface roughness and effective minority carrier lifetime.^[4] This study focused on RCA and Piranha cleans. While the RCA clean was found to produce a more ordered surface the carrier lifetimes of Piranha cleaned surfaces showed longer carrier lifetimes. Despite differences in morphology and electronic properties the surfaces both exhibit similar chemical reactivities with respect to surface modification.

More studies have been conducted regarding the electronic properties of hydrogen terminated surfaces by various etching techniques, particularly looking at the effect of light exposure on observed passivation. Minority carrier lifetime measurements were taken for Si wafers in HF solutions with exposure to a diffuse light source before measurement (but not during) and without exposure. The effect of varying the concentration of HF was also investigated.[5] It was found that illuminating samples before measurement provided increased measured minority carrier lifetimes. Further it was shown that the surface recombination velocity shows different behaviors with respect to concentration. A qualitative band theory approach is also considered. In this description the the bands bend upward at the surface for n-type silicon and downward for p-type accumulating electrons or holes respectively. Thus there should be a charge distributed across the surface which depends on the doping of the sample for wafers in HF solutions.

The following work investigates the general phenomenon of Si <100> surface passivation by treatments with p-benzoquinone and hydroquinone solutions separately with the goal of determining the nature of the interaction and to suggest possible reaction mechancs.

Chapter 2 SOLVENT CHOICE AND PASSIVATION

Increased minority carrier lifetimes have been previously observed in solutions of p-benzoquinone and methanol. Moreover studies on passivation in iodine and quinhydrone have been carried out primarily using ethanol and methanol as solvents. [1, 2, 6, 7] These experiments have shown order of magnitude increases in the carrier lifetime of treated samples. The key drawback of these methods is that the treatments are relatively unstable with respect to oxidation when removed from solution. To further understand this effect it is important to investigate the effect of different solutions, in this case diethyl ether, on the observed passivation.

Previously it has been extensively shown that methanol on a hydrogen terminated silicon <111> surface will readily react to form a methoxy terminated surface.[8] The reaction proceeds on the mono-hydride sites. Hydrogen is replaced with a methoxy group and the hydrogen from the hydroxy group on methanol leaves thus the reaction produces a methoxy terminated site and a hydrogen molecule, which leaves. In the case of diethyl ether this reaction should not occur.

The following details a set of solution experiments designed to investigate the possibility of solvent effects on the measured passivation. Anhydrous diethyl ether (or more commonly ether) was used and its minority carrier lifetime measurements compared against that of methanol solutions. Ether was chosen because it is a common aprotic solvent. In theory this should provide a different atmosphere for any surface / p-benzoquinone interaction. The purpose of this choice is to investigate the importance of available hydrogen molecules from the solvent on any reaction that may be occurring.

2.1 Experimental Setup

Experiments were done using the Sinton lifetime tool to characterize any possible reactions occurring at the Si <100> surface. The Sinton Instruments WCT-120 lifetime tool is essentially a camera flash mounted on a stage containing an inductive coil. A sample is placed on the stage and flashed with a high intensity pulse of light. This in turn excites some electrons into conduction, inducing a current in the sample. This current is coupled to the current in the inductive coil and thus by measuring the current in the coil as a function of time one can obtain a measure of the carrier lifetime in the sample.[9]

A set of experiments was performed first on p-type wafers then a set of n-type wafers. The p-type, boron doped wafers are 2 inch square samples cut from a 100 mm diameter wafer. They have 10,000 ohm-cm resistivity, 525 μ m thickness and are double side polished. The n-type wafers are phosphorous doped 2 inch diameter samples. They have 20-30 ohm-cm resistivity, 500 μ m thickness and are double side polished. Three samples were used for each type of wafer; a control wafer immersed in pure solvent (either methanol or diethyl ether), a wafer immersed in a 0.01 M hydroquinone solution and a wafer immersed in a 0.01 M p-benzoquinone solution.

Samples are cleaned using a piranha clean. Wafers are first immersed in 4:1 hydrogen peroxide and sulfuric acid solution for 5 minutes. They are then rinsed in DI water for 5 minutes. After the rinse they are immersed in 10% aqueous HF for 2 minutes. Wafers are then rinsed briefly in DI water and blown dry with nitrogen. Following the clean their lifetimes are measured (before being place in solution). Wafers are then placed in each solution inside an acid proof bag. The samples are then measured at 5 minute intervals in the case of the methanol solutions and 10 minute intervals in the case of ether solutions over a period of 2 hours. Minority carrier lifetime versus passivation time is plotted for each sample.

2.2 Lifetimes for Each Solvent

The obtained carrier lifetimes are plotted against passivation time for each of the wafer types. Two plots are obtained for each solvent, one for n-type samples and one for p-type. Observed lifetimes for hydroquinone and the control samples are shown in the inset plots.

P-type samples tested showed the previously observed trends in methanol. That is, the minority carrier lifetime of the p-benzoquinone/methanol sample rapidly increases to a plateau where it is maintained (figure 2.1). The corresponding sample in the ether solution however shows a slower increase in minority carrier lifetime with passivation time (figure 2.2). Over the 2 hour measurement time the pbenzoquinone/ether sample does not appear to definitively reach a plateau value. The hydroquinone/methanol sample shows a slow but consistent increase in lifetime over the measurement period compared to the control. In the hydroquinone/ether sample this is not observed, perhaps due to a decrease in the rate of passivation.



Figure 2.1: Plot of p-type samples in solutions p-benzoquinone and hydroquinone in methanol along with a methanol control sample. The inset emphasizes the slight increase in lifetime of the hydroquinone/methanol solution versus the control.



Figure 2.2: Plot of p-type samples in solutions p-benzoquinone and hydroquinone in diethyl ether along with a diethyl ether control sample. The inset emphasizes the slight increase in lifetime of the hydroquinone/ether solution versus the control.

Trends in the n-type samples mimic that of the p-type. The p-benzoquinone sample lifetime in methanol increases rapidly to a plateau value and levels off (figure 2.3). The lifetime of the sample in ether increases more slowly and never appears to reach a plateau (figure 2.4). In hydroquinone solutions the methanol sample the lifetime increases more slowly than in the p-benzoquinone but it still shows a significant increase relative to the control. Similar to the p-type sample, the same trend is not shown in the hydroquinone/ether sample. These lifetimes appear no different from those of the control.



Figure 2.3: Plot of n-type samples in solutions p-benzoquinone and hydroquinone in methanol along with a methanol control sample. The inset emphasizes the slight increase in lifetime of the hydroquinone/methanol solution versus the control.



Figure 2.4: Plot of n-type samples in solutions p-benzoquinone and hydroquinone in diethyl ether along with a diethyl ether control sample. The inset emphasizes the slight increase in lifetime of the hydroquinone/ether solution versus the control.

2.3 Discussion

Methanol provides increases in wafer lifetimes in p-benzoquinone solutions more rapidly than ether. Increase in carrier lifetime is also observed in hydroquinone/methanol solutions but not in hydroquinone/ether solutions over a 2 hour period. As mentioned above this may be due to a combination of hydroquinone passivation occurring more slowly than p-benzoquinone passivation and ether being a slower solvent for this passivation than methanol. It is possible that over a longer measurement period the hydroquinone/ether samples may show some passivation.

It is worth noting that the data collected for p-type wafers is significantly more scattered than that of the n-type wafers. It is possible that this is due to the high resistivity of the p-type samples. Some samples of high resistivity have shown negative sheet resistance, which is clearly not physical. Repeating measurement on these samples can produce positive sheet resistance. It is likely an issue with the model for calculating the resistance that is the cause. The lifetime data is repeatable for samples reading both positive and negative resistances and is thus not suspect.

From the data it appears that the p-benzoquinone/methanol samples in both p and n-type wafers reach a plateau after roughly 20 minutes. The corresponding ether samples do not appear to reach a plateau after the 2 hour measurement period. Thus more investigation is necessary over longer time periods to solidify the presented results. This will reveal two things; first the long term behavior of p-benzoquinone/ether samples, and second the trend in the hydroquinone/methanol samples over long periods.

Chapter 3

PASSIVATION OF OXIDIZED SILICON SURFACES

Hydrogen terminated silicon surfaces have been extensively studied as they are an important starting point for for further surface modification. Electronic properties of oxidized surfaces under p-benzoquinone passivation, however have not been investigated. Silicon surfaces left in air readily form a thin coating of oxide. Oxidized surfaces are very chemically different than hydrogen terminated surfaces, thus one would expect passivations schemes to behave differently. However we have observed that surfaces with native oxide under passivation with p-benzoquinone / methanol solutions still show significant increases in minority carrier lifetime.

This appears to conflict with the notion that chemical bonding is an important factor in p-benzoquinone surface passivation and is thus worth investigating. It may be possible that field effect passivation is driven by charge localization at the surface through a physical interaction instead of a strictly chemical bond.

3.1 Oxide Growth and Thickness Measurement

Oxides were initially targeted to be roughly 500 nm thick. The growth was carried out in a wet oxide furnace for 120 minutes at a temperature of 1050 C under N_2 and O_2 . Although we targeted 500 nm oxides the actual thickness turned out to be close to 430 nm of native oxide.

To obtain wafers with desired oxide thickness after growth a buffered oxide etch (BOE) is used. This is a 6:1 solution of 40% ammonium fluoride (NH_4F) and 49% HF. A buffer is created when a buffer compound, usually a conjugate base to the acid, is used to maintain a stable pH in solution. In BOE the purpose of the buffer is to create a solution which will maintain a constant etch rate.

The etch rate of the solution can be determined by generating a calibration curve of the oxide thickness versus time in the BOE solution. Data was collected for 3 test wafers, 5 measurements per wafer including the initial thickness. Several periods were plotted to determine the lines which decrease monotonically with time in solution. The decrease in thickness with time in BOE solution should be linear. Once the correct thicknesses for each sample were determined they were fit to a line using least squares. The etch rate is the slope of this line.



Figure 3.1: Thickness versus etch time data for the 22 nm oxide wafer. The red line indicates the best fit line used to determine the etch rate of the sample in BOE. This sample was etched from 435 nm to 22 nm.

Ellipsometry is used to measure the oxide thickness on the wafers. In this experiment a beam of linearly polarized light is shined on the sample. It is reflected off the sample, through a polarizer, and into a detector such that the angle of incidence and angle of reflectance are equal. The amplitudes of the component of the reflected wave polarized parallel, rp, and perpendicular, rs, to the incident wave are measured and the complex reflectance ratio, , is calculated. We model this ratio as

$$\rho = \frac{r_p}{r_s} = \tan(\Psi) \exp(i\Delta)$$

Where $\tan(\Psi)$ is the reflected amplitude ratio and Δ is the phase shift after reflection. Both Ψ and Δ can be calculated by the Fresnel equations, given proper optical constants and thickness. Data analysis is done by exploiting this and fitting the and to the data and backing out the optical constants and the sample thickness.

One drawback of these measurements is that the model typically used for measuring the thickness of a film on a substrate relies on use of periodic functions to represent the reflected amplitudes. Because of this the thickness obtained is periodic with some known period. Thus some prior information about the sample is required to accurately describe the thickness of a film. In the case of the following experiment oxide thickness can be roughly estimated based on the growth process, so this should not be an issue.

3.2 Experimental Methods

In these experiments the effect of oxide thickness on minority carrier lifetime is investigated. This is done by measuring the minority carrier lifetime vs passivation time of wafers with varying thickness of SiO₂ on the surface. The wafers used are p-type, FZ, boron doped samples cut to 2 inch squares from a 100 mm diameter wafer. They have 10000 ohm-cm resistivity, 525 μ m thickness and are double side polished. Measurements were taken both on samples which had simply been left out in air and on samples with oxide grown in a furnace. The out of the box samples with native oxide have about 2 nm oxide on the surface while the furnace grown samples will be target to have roughly 10 nm of oxide.[10]

The oxide is initially grown to roughly 430 nm. This is then etched down using BOE to close to our desired thickness. The etch rate for our solution was determined to be about 2.6 nm / s.

These etches are done by first immersing the wafer into the BOE solution. The wafer is removed after the desired time and rinsed thoroughly with DI water. It is then blown dry with nitrogen. Because this is all done by hand it is difficult to control the time the wafer spends in contact with the BOE solution precisely. Thus we are only able to etch to roughly tens of nanometers. Two tests were done: one with a wafer with only native oxide on the surface (2 nm), and one with about 22 nm of oxide.

Samples are then immersed in p-benzoquinone/methanol solutions and their minority carrier lifetimes measured. This is done identically to the previous solution experiments, that is the WCT-120 lifetime tool is used and measurements are taking in 0.01 M solution inside acid proof bags. A measurement is taken every 5 minutes and the recorded minority carrier lifetimes are plotted against passivation time.

3.3 Lifetimes of Oxidized Surfaces

A sample calibration curve, figure 3.1, is shown to illustrate two things. First this curve was used to determine the etch rate for the BOE solution. Second this shows the etch data and thicknesses of the 22 nm oxide wafer. The thickness starts at 435 nm and is etched down to 22 nm. It is important with the presented thickness values to bear in mind that there is significant difference in the measured thickness values of oxides by different methods.[9] For the purpose of this discussion rough values are given but these values are only for the specific sample used based strictly on measurement by ellipsometry.

As before minority carrier lifetime is plotted versus passivation time for each sample at a fixed minority carrier density in figure 3.2. The curve for the out of the box sample shows a steady increase to a plateau value in the range of 350 us. This sample increases in lifetime more slowly than a hydrogen terminated sample and also reaches a much lower plateau value. The wafer with 22 nm oxide shows no sign of passivation; in fact, the data resembles that of the control samples used in the solvent experiments. The minority carrier lifetime initially decreases and then levels off at a value slightly lower than its initial lifetime.



Figure 3.2: Minority carrier lifetime vs Passivation time for a Si <100> surface with roughly 2 nm of native oxide (red) and with 22 nm of native oxide (black). Each sample is measured in a 0.01 M solution of p-benzoquinone in methanol.

3.4 Discussion

It is difficult to draw any firm conclusions from only 2 sets of data but the trend seen is real and warrants further investigation. It is clear from the results that a wafer with a small amount of oxide, single nanometers in thickness, on the surface will respond to p-benzoquinone/methanol solutions. The magnitude of the passivation appears to be less than that of a clean hydrogen terminated sample. With thicker oxide, in the tens of nanometers, no passivation is observed. There are two possible examples for why this is taking place.

First, it is possible that the chemical reaction with the surface is being blocked by the presence of SiO_2 on the surface. If all possible bonding sites are covered then no passivation should be observed. For the thick oxide this is likely the case. For the thinner oxide it is possible that the surface is not completely covered, leading to the p-benzoquinone reacting only partially with the surface resulting in some passivation but not the full magnitude that would be seen with a hydrogen terminated surface. The second possibility is that there is physical charge aggregation at the surface, on top of the oxide. In this case for the thin oxide the SiO₂/Si interface is likely to be affected by the electric field generated due to this charge aggregation. As the charge is pushed further away the electric field strength at the SiO₂/Si interface decreases, if the interaction is simply coulombic, like $1/r^2$. Thus for an oxide that is sufficiently thick there should be no observed passivation effect. This is another example of the previously suggested field effect passivation.

As illustrated above, having a strong understanding of whether this interaction is physical or chemical is critical to the further development of this and related passivation methods. Further work looking at passivation on oxide surfaces can provide insight into the exact nature of this phenomenon. In the future it would be beneficial to conduct experiments using wafers with very uniform surfaces and oxide coverage and of varying thicknesses between about 1 - 20 nm.

Chapter 4

X-RAY PHOTOELECTRON SPECTROSCOPY OF PASSIVATED SURFACES

To better understand this chemistry it is important that we probe the surface to see how p-benzoquinone/methanol solutions interact with the available silicon sites. It has previously been suggested that the benzoquinone molecule bonds to the Si surface through a Si-O-C bond. This idea was supported by FTIR spectra showing the presence of characteristic peaks for the various types of bonding at the surface and in the ring structure. In this work we will investigate the surface using X-ray photoelectron spectroscopy (XPS). XPS provides us both the elemental composition of the surface as well as evidence of specific types of bonds at the surface.

In XPS an x-ray source is shined on a sample. The sample then emits electrons of various kinetic energies. The number of electrons is measured as a function of the kinetic energy Since we know the energy of the incident x-rays, the energy of the electrons, and the work function (a property of the tool) we can calculate the binding energy of the measured electrons. The end result is a plot of number of counts versus binding energy. At certain binding energies characteristic peaks appear which correspond to certain orbital energies, for example the carbon 1s (C1s) peak is discussed below.

So by reading the characteristic peaks one can determine the elemental composition of a sample. More information can be obtained by looking at the relative positions of the peaks as well. The energy of an orbital (and by extension the binding energy) will change when the bonding or local chemical environment changes thus we would expect, for example, that the energy of the C1s peak would be different for a C-O or C-Si bond. In this example the peak should shift to a lower energy for a C-Si bond relative to the C-O bond. These two pieces of information combined can provide a good picture of the ways in which benzoquinone interacts with Si surfaces.

4.1 Experimental Setup

Samples are prepared from p-type, FZ, double side polished, Si <100> wafers with 10,000 ohm-cm resistivity, and 525 um thickness. Spectra will be taken from 5 samples: an as-is sample cut from one of the above wafers with native oxide, a hydrogen terminated wafer, a hydrogen terminated wafer which has been immersed in p-benzoquinone for 1 hour, a hydrogen terminated wafer which has been immersed in hydroquinone for 1 hour, and a hydrogen terminated wafer which has been immersed in methanol for 1 hour. Each hydrogen terminated surface is prepared using a piranha clean followed by an HF dip, as previously described. Samples are promptly placed in solution after being cleaned, where they are kept until being transferred into the XPS system. Contact with air after cleaning and treatment is minimal.

Samples are then transferred to the XPS. Our system is a Physical Electronics 5600. Samples are run using a Mg x-ray source. All XPS measurements were taken at pressure lower than 3.0×10^{-8} torr. For each sample a full spectrum was collected at a pass energy of 93.90 eV and a region spectrum collected for the Si2p, O1s, and C1s regions at a pass energy of 11.75 eV.

4.2 Spectra

All results are shown as plots of number of counts vs binding energy. Full spectra were obtained for each sample. Several of the characteristic peaks are measured in a higher resolution region spectrum to better show any potential shifts that occur in the peak positions. Each of the data sets is normalized and plotted together with the corresponding data for all the other samples. The ordinate axis is number of counts however, all plots are shifted relative to each other and data is normalized so the plots are designed to show relative positions of the peaks.



Figure 4.1: Full spectra of Si <100> samples after several different treatments. Each data set is normalized and all are shifted vertically relative to each other for clarity.



Figure 4.2: Si2p region of Si <100> samples after several different treatments. Each data set is normalized and all are shifted vertically relative to each other for clarity.



Figure 4.3: C1s region of Si <100> samples after several different treatments. Each data set is normalized and all are shifted vertically relative to each other for clarity.



Figure 4.4: O1s region of Si <100> samples after several different treatments. Each data set is normalized and all are shifted vertically relative to each other for clarity.

4.3 Discussion

The purpose of selecting the variety of samples used is to probe the composition of the surface through the entire treatment process. Thus we look first at the SiO_2 surface to describe our sample before any treatment. The surfaces are intended to be considered sequentially to help understand the changes throughout treatment.

This starts with the out of the box SiO_2 surface. The full spectrum shows the characteristic O1s peak with an intensity significantly greater than that of the C1s and Si2p peaks which are also present. Looking more closely at the Si2p peak it can be seen that a large peak occurs around 100 eV corresponding to Si-Si bonding. Shifted to a slightly higher energy at roughly 104 eV is another peak showing the presence of Si-O bonds. There is also some carbon contamination present, however the C1s peak is lower in intensity than the O1s and Si2p peaks. This is all what would be expected in a spectrum of a SiO₂ sample.

Next we consider the H-terminated surface keeping in mind that this surface has been cleaned with piranha followed by an HF dip and exposed to air for less than 5 minutes after cleaning. The Si2p peak dominates in this sample indicating that the surface is almost completely hydrogen terminated. There are O1s and C1s peaks present as well but these are substantially smaller than the Si2p peak and thus likely represent small amounts of contamination which likely occurred during the process of introducing the sample into the XPS. One notable feature however is that the C1s peak is shifted to lower energy relative to the SiO₂ peak.

After cleaning the sample is put through one of several treatments. Methanol has been shown to modify Si surfaces over long time periods but has been previously used as a control on our experiments. We look at a sample which has been immersed in methanol in this case not as a control but to see any effect this solvent may have on the surface by independently. Looking at the O1s peak, it appears that there is more oxygen on the surface than in the hydrogen terminated sample alone. It has been shown that methanol can form a methoxy terminated surface, but despite the apparent increase in oxygen bound to the surface there is very little carbon seen in the C1s multiplex. There is also no Si-O bonding peak (like in the SiO_2 sample) in the Si2p region. It is difficult to say that the carbon and oxygen present on the surface is any different contamination.

For the hydroquinone sample we would expect to see an increase in the C1s and O1s peaks relative to the hydrogen terminated sample. If the hydroquinone is bonding to the surface there should also be indications of Si-O bonding in the Si2p region but there is no such peak. In the measurements the O1s peak is slightly larger than that of the peak for the hydrogen terminated surface but not significantly so. In the C1s region the peak is similar to that of the hydrogen terminated surface however it appears to be two peaks, one at 285 eV and one shifted to a higher energy by roughly 1.5 eV. If this is true than it is possible that these peaks correspond to C-O and C-C bonding respectively. It is hard to say that this is the case with any certainty as the peak is not strongly distinguishable from standard contamination.

Finally, looking at the benzoquinone treated surface its full spectrum looks very similar to that of the methanol treated surface. The two main differences being the larger O1s and C1s peaks. As with the hydroquinone sample if there is bonding on the surface it is expected that there should be peaks corresponding to C-O, C-C and Si-O bonding. In the Si2p region there is no Si-O peak. The O1s region is very similar to that of the other samples, excluding the SiO₂ sample, but the C1s region is different. The peak looks more broad and slightly shifted relative to the hydrogen terminated surface. It is possible that this is due to measuring the C-O and C-C bonds as described above. Overall as with the previous two samples it is difficult to argue that these features are real and anything more than surface contamination due to the low signal intensity.

It is possible that the low intensities relative to the noise level of the C1s peaks in the methanol, hydroquinone and benzoquinone samples is due to poor surface coverage. Samples were only immersed for an hour before being introduced to the XPS and although (at least in the case of benzoquinone) this is sufficient time to measure an extreme passivation effect it is perhaps insufficient to allow for significant surface coverage. It may be informative to conduct experiments where samples are kept in solution for very long times, on the order of days, to potentially allow for greater surface coverage.

Chapter 5

CONCLUSION

Passivation of Si <100> surfaces by quinhydrone solutions has been investigated above with the goal of providing an extensive characterization of a possible surface chemistry. Three main experiments were done. First a study was done investigating the solvent dependence of the passivation effect using both methanol and diethyl ether as solvents. The purpose of this study was to determine the importance of available hydrogen from the solvent to passivation time and observed minority carrier lifetime. Second, a study was conducted to further describe the observation that p-benzoquinone will passivate an oxidized surface in much the same way as a hydrogen terminated surface. Wafers of additional thickness were grown and their minority carrier lifetimes tested in solution. Lastly the surface composition across all stages of the experiments were analyzed by XPS.

The solution experiments were carried out using both p-type and n-type Si although there appeared to be no significant difference between the two types. Samples immersed in solutions of benzoquinone in methanol showed increases in minority carrier lifetime faster than solutions with ether as the solvent. This indicates that the choice of solvent is important to the passivation time. There are several possible reasons for this. The available hydrogen on the alcohol group could contribute. It is also possible that the reaction of methanol with the Si surface could be a factor, however the XPS data indicates that within our experimental conditions surface coverage is low for methanol treatments.

The hydroquinone/methanol solutions initially do not show a significant increase in minority carrier lifetime over the two hour measurement period but began to increase toward the end. If given more time it is likely that the lifetime would continue to increase. In future work it would be informative to test hydroquinone/methanol samples for longer time periods, perhaps several days, to see if a clear trend presents itself. It may also be relevant to test methanol control samples over long periods of time as greater methoxy surface coverage may be achieved over long time periods. If over long times the data forms a clean continuous curve it would be possible to fit to models for the kinetics of the system.

It is also worth looking into the importance of the size of the solvent on the kinetics. Size is not considered in our experiment but by using an alcohol and ether with a different size than methanol and diethyl ether the dependence could be determined. This is a relatively simple test and could be done inexpensively. Two possible candidates for solvents are ethanol and tetrahydrofuran (THF).

The effect of oxide thickness on minority carrier lifetime in wafers with native SiO_2 in solutions of benzoquinone was also measured. Samples with an oxide of a roughly 2 nm demonstrated the same increase in lifetime as their hydrogen terminated counterparts but samples with an oxide of about 20 nm showed no such increase. As discussed previously samples were prepared by first growing a 430 nm oxide and subsequently etched down to the desired thickness using BOE. This is all done by hand and due to human error oxides were only able to be consistently etched to tens of nanometers. We were unable to produce a sample with a surface oxide thickness in the range between 2 and 20 nm. In the future it would be relevant to measure samples within this range. This would provide data on the effect of separation of any charging or layer formation which occurs on the oxide surface from the Si/SiO₂ interface.

It is also worth noting that the measured minority carrier lifetime of an oxidized wafer reaches a plateau at a value lower than that of a hydrogen terminated sample. Thus it is likely that the separation distance of the SiO_2 surface from the Si/SiO_2 interface is an important factor in passivation of oxidized wafers with benzoquinone solutions. This follows a now common hypothesis that a surface charge is responsible for the passivation. More data points in the range where passivation effects are observed could provide a more complete idea of the dependence of oxide thickness on minority carrier lifetime especially if a surface charge can be measured. Outside of what has been done in this work it would be useful to conduct Kelvin probe force microscopy measurements to determine the surface charge of the various samples.

Lastly the surfaces were analyzed by XPS. The starting SiO_2 and the subsequent hydrogen terminated surface gave spectra showing peaks where they were expected and with little contamination. The treated surfaces showed some peaks larger than that of the hydrogen terminated sample for both O1s and C1s regions but they were not significantly larger to the point where they could be distinguished from normal contamination. This indicates that although strong passivation can be observed in benzoquinone samples after only an hour of immersion in solution there is poor surface coverage, at least in this stage.

As with the solution experiments, it is relevant to look at samples which have been in solution for longer time periods. Samples can be left in solution for several day before measurement in XPS. At this point it would be more likely that there would be significant coverage and the bonding at the Si surface could be better described.

Overall there is an indication that a surface charge, not any sort of monolayer formation, is driving the increase in minority carrier lifetimes in Si <100> wafers exposed to benzoquinone/methanol solutions. This can be better understood by further investigating how separation of this charge from the Si/SiO₂ interface effects peak lifetimes. The kinetics of this interaction may be clarified by collecting long passivation time measurements of wafers in hydroquinone/methanol solutions as well as in methanol alone.

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