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Further Investigation of Slurry Additives for Selective Polishing of SiO_2 Films over Si_3N_4 Using Ceria Dispersions

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Following our earlier analysis of amino acids, we investigated the effectiveness of acetic acid, pyridine, and sorbitol that were chosen to represent carboxylic acid, amine and alcohol functional group families, respectively, as additives in ceria dispersions for polishing SiO_2 and Si_3N_4 films. By comparing the speciation of the additives available and the material removal rates with respect to pH, we identified that the removal rates of nitride, but not oxide, are suppressed to <1 nm/min in the pH range where the additive species containing a protonated amino group or a neutral carboxylic group or a neutral hydroxyl group are dominant. All of these species are strong *hydrogen bond donors* and can form strong hydrogen bonds with Si_3N_4 surface while their corresponding bonding on SiO_2 surface sites is weaker. The stronger hydrogen bonding hinders Si_3N_4 hydrolysis and suppresses Si_3N_4 removal. In contrast, the weakly bound additive species are easily removed from the SiO_2 surface by the polishing pad and the ceria abrasives, leading to high SiO_2 to Si_3N_4 removal rate selectivity. Similar results were also obtained with valeric acid, imidazole, glucose, sucrose, and mannitol, confirming the importance of a strong hydrogen bond formation in a broader class of additives.

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Shallow trench isolation (STI), which helps isolate the transistors and prevents shorting and cross-talk, is a widely used process in semiconductor device fabrication. The STI process includes the deposition of silicon nitride on a thermally grown pad oxide followed by the etching of a shallow trench into the silicon substrate. A layer of silicon oxide such as tetraethyl ortho silicate (TEOS) oxide, high density plasma (HDP) oxide, or high aspect ratio process (HARP) oxide is deposited on the entire substrate surface, not only filling the trenches but also creating an uneven topography. After the trenches are filled, the excess deposited oxide needs to be removed and the topography planarized before the fabrication of any IC elements. So far, chemical mechanical polishing/planarization (CMP) has been the only viable technique to remove the overburden oxide and planarize the topographies. This STI CMP step requires a slurry which polishes the overburden oxide with high oxide removal rate (RR) and stops on the underlying nitride surface with minimal nitride loss and oxide dishing.

Ceria-based dispersions[1] containing various additives have a huge market position for planarizing these STI structures efficiently because of their superior ability to polish oxide films at high rates using only a low solids loading of ∼1 wt% or less and to stop on the underlying nitride film with minimal loss as well as dishing.[2,3] In the absence of any additive, these same ceria slurries would also produce significant nitride RRs and lead to considerable nitride loss. Hence, many types of additives (amino acids, amines, surfactants, polymers and acids) were investigated to achieve high oxide-to-nitride rate selectivity.[4–12] For example, America and Babu[6] reported that amino acid additives can suppress nitride RR if the amino group is bonded to the α-carbon adjacent to the carboxylic groups and the amine has at least one hydrogen atom attached to the nitrogen. Later, Carter et al.[7] reported that the additive should have pKa values between 3 and 7. However, the nitride suppression mechanism is not clear.

In our recent publication,[12] we investigated several alpha, non-alpha, cyclic, and aliphatic amino acid additives in ceria slurries for polishing SiO_2 and Si_3N_4 films in the pH range 2–12 and discovered that the amino acid species containing a protonated amino group are responsible for the suppression of nitride RRs. However, the role of the carboxylic functional group of the amino acid additives in the suppression of nitride RRs was not identified and we do that here by examining the effect of acetic acid and pyridine as additives on the oxide and nitride RRs. Unlike amino acids, acetic acid contains only a carboxylic acid group while pyridine contains only an amine group. We also investigated sorbitol, which contains only hydroxyl groups, as additive.

The nitride RRs in the presence of these additives in the pH range 2–12 are suppressed when the amine group of pyridine is protonated as before or when the carboxylic or hydroxyl groups have their associated proton. The nitride RRs were not suppressed once these species lose the proton. These results were also confirmed when valeric acid, imidazole, mannitol and other sugars were used as additives. Thermogravimetric measurements that quantify the adsorption of pyridine and sorbitol on the oxide, nitride and ceria surfaces were used to relate the observed variation in removal rates of oxide and nitride films.

Materials

An aqueous dispersion of ceria abrasives (d_{mean} ∼ 140 nm, 50 wt%) supplied by Ferro Corp. was used in our experiments. Fumed SiO_2 (Aerosol 130, surface area of 130 m^2/g) and Si_3N_4 (110 m^2/g) powders were supplied by Degussa and Sigma Aldrich, respectively. The same SiO_2 and Si_3N_4 particles were used in our earlier work for adsorption studies.[12] All the additives used here and the pH adjusting agents (KOH and HNO_3) were obtained from Sigma-Aldrich and used without further purification. The polishing pad (IC1000, K-grove) and 4″ diamond-grit conditioner used were supplied by Dow Electronic Materials and 3M, respectively. Thermal SiO_2 (2000 nm thick, grown at ∼900°C) and Si_3N_4 (500 nm thick, ∼800 MPa tensile stress, grown by low pressure chemical vapor deposition at ∼790°C) films, both grown on 8″ diameter silicon substrates, were obtained from WRS Materials. The nitride blanket wafers have an intervening 100 nm thick SiO_2 layer between the nitride film and the silicon substrate.

Experimental

Polishing.— The oxide and nitride blanket wafers were polished for one minute on a G&P polisher at 4/5.5 psi wafer/retainer ring pressures, 75/75 rpm carrier/platen speeds, and a slurry flow rate of

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200 mL/min. In situ conditioning was performed using a 4″ diamond grit conditioner.

RR determination.— A Filmetrics F-20 interferometer was used to measure the thickness of both the SiO_2 and Si_3N_4 films before and after polishing. The RR was determined from the difference between pre- and post-polished film thickness values. The reported RR for each experiment is the arithmetic average of the RRs measured for two different wafers, each at 20 points located across a diameter of the wafer. The standard deviation in the RRs was based on the data for these 40 points.

Thermogravimetric Analysis (TGA).— A Perkin-Elmer thermogravimetric analyzer, Pyris 1, was used to quantify the adsorption of pyridine and sorbitol on SiO_2, Si_3N_4, and CeO_2 surfaces. Since acetic acid has a lower boiling point than water, these measurements were not done for this additive. The adsorption studies were carried out using SiO_2 and Si_3N_4 particles (representing SiO_2 and Si_3N_4 films, respectively) and CeO_2 abrasives. Initially, 1 wt% of $SiO_2/Si_3N_4/CeO_2$ dispersions containing sorbitol and pyridine at different concentrations and pH values were prepared and centrifuged at 6000 rpm for 30 minutes. The supernatant was decanted, and the sediment collected and dried in an oven at 75°C for about 24 hrs. The dried sample was pulverized and then used for TGA in which the weight of the sample was measured as a function of time while the temperature was increased. The temperature of the sample was initially raised from room temperature to 100°C and maintained there for 20 min to remove any residual moisture and then increased to 600°C at a rate of 15°C/min, all in an Ar atmosphere. The reported weight loss data were adjusted by deducting the weight loss of the appropriate blank powders.

Results and Discussion

Polish data and correlation with pH-dependent species distribution.— Figures 1a and 1b show the RRs of silicon dioxide and silicon nitride films, respectively, as a function of pH obtained using 0.1 wt% ceria ($d_{mean} \sim 140$ nm) slurry in the absence and presence of 0.01 M of each of these additives. In the absence of any additive, the RRs of both oxide and nitride films are low below pH = 3 above which they increase to about 250 nm/min and 35 nm/min, respectively. On adding 0.01 M amount of either acetic acid or sorbitol, the oxide RRs remain essentially the same in the entire pH range 2–10 while pyridine decreased the oxide RRs significantly at pH 4 but not much at the other pH values. A similar result was reported earlier with pyridine by Dandu et al.[9]

In the case of nitride films, both acetic acid and pyridine suppressed the RRs to <1 nm/min till pH 5 and do not affect above this pH value. In contrast, sorbitol also suppressed the RRs to <1 nm/min, but over the entire pH range 2–12. Based on these results, it appears that sorbitol provides a broader pH window for oxide-to-nitride removal selectivity while acetic acid and pyridine provide useful rate selectivity only for pH 4 to 5.

Depending on the pH, acetic acid can exist in two forms, labeled as S1 and S2 and shown in Fig 2a. S1 species contains the neutral COOH group and is nonionic while in the S2 species, the COOH group is deprotonated and negatively charged. The nonionic species is the predominant species below the pKa value of 4.76 and disappears at pH ~6. Above this pH, only the S2 species is available. Coincidentally, the RRs of nitride films are not affected for pH ≥6, suggesting that S1, but not S2, suppresses the nitride RRs. Specifically, the results suggest that the neutral -COOH is responsible for the suppression of nitride RRs. However, no such correlation was observed between the oxide RRs and either of these two species.

Similarly, pyridine can also exist as two species, again labeled as S1 and S2 (shown in Figure 2b). S1 contains the protonated amino group while S2 is nonionic with the amino group unprotonated. S1 is the predominant species below the pKa value with a very low

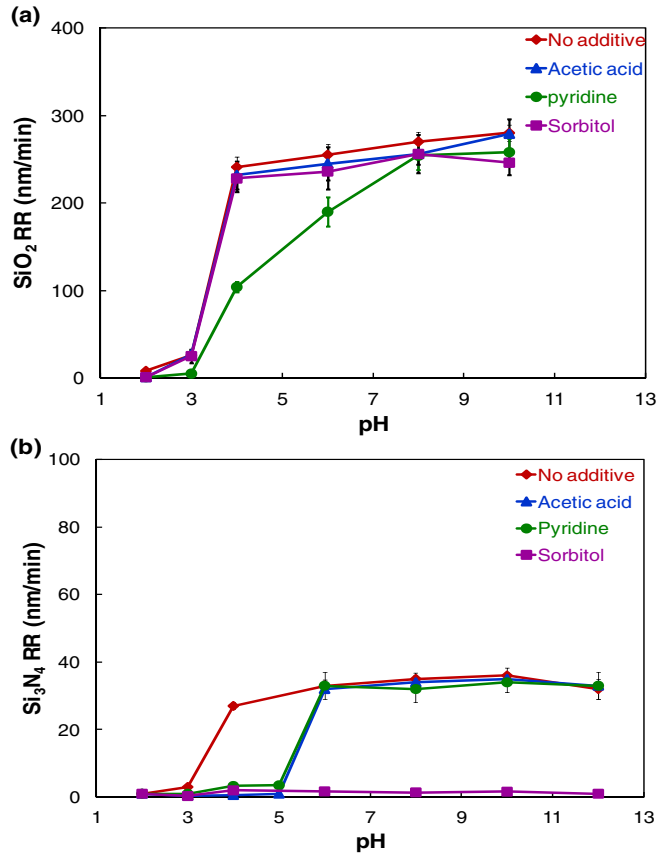

Figure 1. RRs of SiO_2 (a) and Si_3N_4 (b) films as a function of pH obtained using 0.1 wt% ceria (d_{mean}~140 nm) without and with 0.01 M of three additives.

concentration at ≈pH 6 above which it completely disappears. Again, beyond this pH, only the S2 species are available where nitride RRs were not suppressed, suggesting that S1 with the protonated amino group is responsible for the suppression of the nitride RR, consistent with our earlier observation with amino acids.[12]

In contrast, as shown in Figure 2c, sorbitol consists of several neutral hydroxyl groups none of which is deprotonated in the pH range 2–12. Interestingly, the nitride RRs were suppressed in the entire pH range, strongly suggestive of significant role for the neutral OH groups in the observed suppression.

We also investigated several other compounds such as valeric acid, imidazole, glucose, sucrose, mannitol etc., chosen from the family of carboxylic acids or amines or alcohols as additives. All these additives suppressed nitride RRs but only in the pH range where their functional groups retain the associated proton and not when they were deprotonated. The results are summarized in Table I.

All these results suggest that only when the species containing an associated proton are present, the nitride RRs are suppressed and deprotonation does not lead to suppression. Indeed, this proton is essential to form a strong hydrogen bond with the species on the nitride surface that is crucial to rate suppression, as discussed later.

Thermogravimetric measurements.— As stated earlier, since acetic acid has a lower boiling point than water, these measurements were not made with it. So only the data for pyridine and sorbitol were obtained and discussed in the following. Figure 3a shows the concentration dependence of the total amount of pyridine adsorbed at pH 4 and 8 while Figure 3b shows the same for sorbitol. These two pH values allow us to distinguish the effects of the protonated amino species from that of the unprotonated amino species on the adsorption behavior for pyridine, while in the case of sorbitol, the OH groups re-

Table I. Summary of the observed suppression of nitride RRs. The RRs in the last column are for the pH range shown in the fourth column where the additive retains the proton.

Additive Class	Additive	pKa	pH range of protonation	Nitride RR (nm/min)
Carboxylic acid	Acetic acid/valeric acid	∼4.8	< ∼ 6	∼1
Amine	pyridine	∼5.2	< ∼ 6	∼2
	Imidazole	∼6.9	< ∼ 9	∼1
Alcohol	Sorbitol, mannitol and glucose	∼12.2	2–12	∼1

tain thier protons at all pH values. The amounts of pyridine adsorbed on both SiO_2 and Si_3N_4 at pH 4 increases gradually to about 50 to 60 mg/g of solid as the concentration of pyridine in the dispersion is increased from 0 to 1 wt%. Dandu et al.[9] reported similar adsorption of pyridine on oxide surface as a function of pyridine concentration at pH 4 and 5. In contrast, the amounts of pyridine adsorbed on both SiO_2 and Si_3N_4 at pH 8 is very low at <1 mg/g of solid, suggesting pyridine does not adsorb much, if at all, at pH 8. This must undoubtedly be a reflection of the difference in the species present at these pH values (protonated vs unprotonated).

In the case of sorbitol, the amounts adsorbed on both SiO_2 and Si_3N_4 at both pH 4 and 8 increase more or less to about 150–200 mg/g of solid as the concentration of sorbitol in the dispersion is increased from 0 to 2 wt%. This is perhaps due to the presence of same species at both pH 4 and 8. In comparison, the adsorption of pyridine and sorbitol on ceria surfaces is very low at both 4 and 8.

Effect of adsorption of pyridine and sorbitol on SiO_2 surfaces on oxide RRs.— Earlier Dandu et al.[9] showed that the oxide RRs are

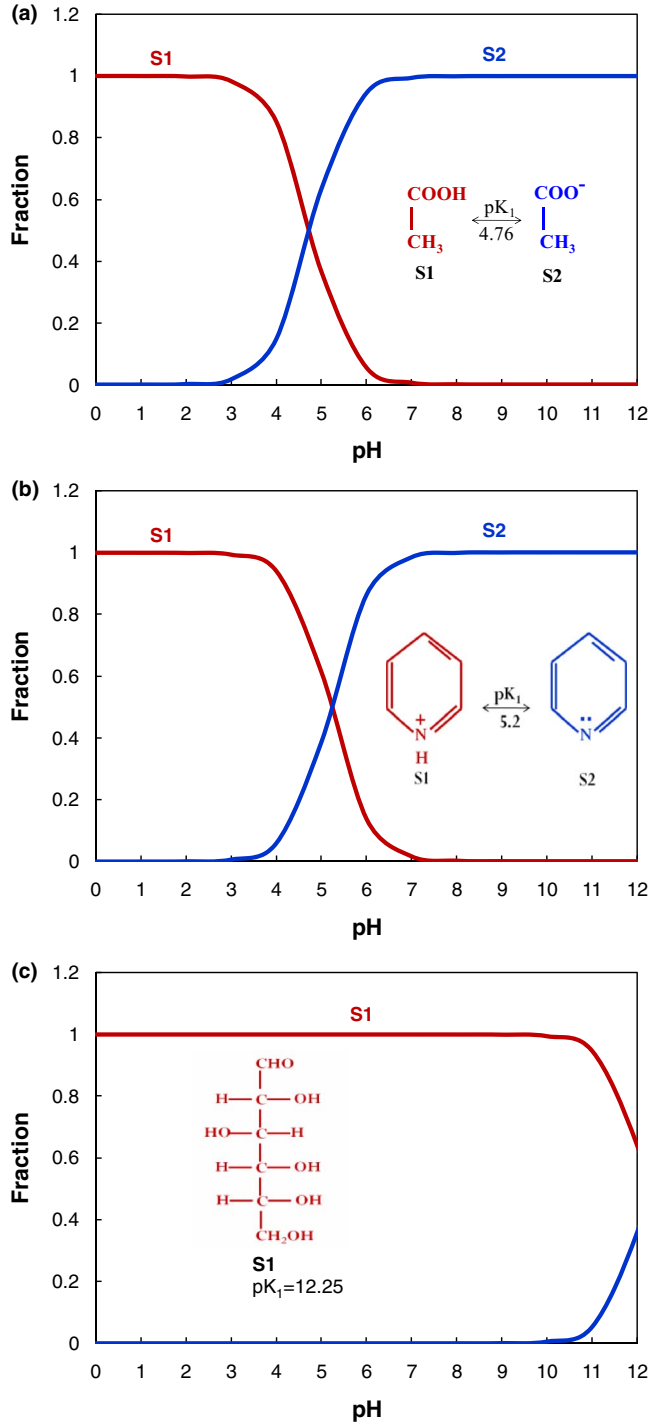

Figure 2. Speciation diagram of (a) acetic acid and (b) pyridine (c) sorbitol.

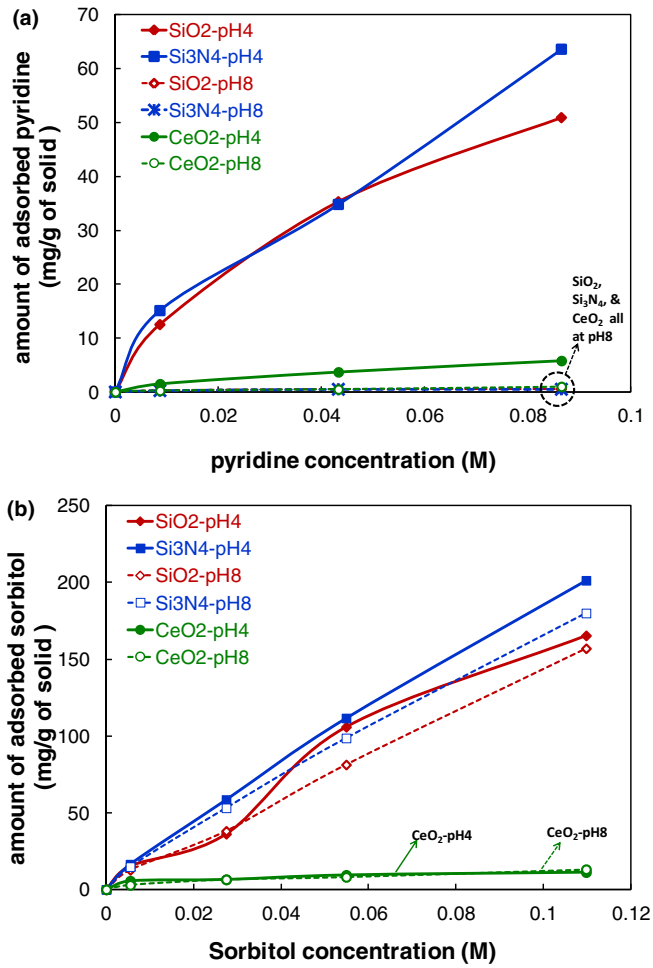

Figure 3. Adsorption isotherms of pyridine (a) and sorbitol (b) on SiO_2, Si_3N_4, CeO_2 at pH 4 and pH 8. The isotherms in (a) for pyridine at pH = 8 are not distinguishable for the three surfaces due to similar and very small adsorption amounts, same as with ceria at pH 4 and 8 for sorbitol.

suppressed somewhat as the pyridine concentration is increased in the slurry at pH 4, similar to our data in Fig. 1. They suggested that the nitrogen group of the pyridine interacts with the silanol groups of the oxide surface through hydrogen bonding which may be lowering the oxide rates.

However, our TGA results showed that only the protonated pyridine (pyridinium) species, but not the unprotonated pyridine, adsorbs on a silica surface and it is this adsorption that has to affect the oxide RRs, especially at pH = 4. At this pH, the fraction of pyrdinium ion is 0.94 and decreases rapidly with increasing pH and disappears at pH ~6, suggesting that the higher the pyridinium ion concentration, the higher the suppression of oxide RR. The adsorption of pyridnium ion is driven by either electrostatic interaction of the positively charged pyridinium ion with the fewer negatively charged silanolates or by hydrogen bonding between the protonated amino group ($\equiv N^{+}$-$H^{\delta+}$) of the pyridinium ion, a hydrogen bond donor, and the predominant silanol groups,[13] hydrogen bond acceptors, on the silica surface. Several authors[12–19] suggested that the lone pair of electrons from the electronegative oxygen atom of the silanol ($\equiv SiO^{\delta-}H^{\delta+}$) group has only a weak attraction toward hydrogen bond donors, for example the protonated amine groups in our case. Hence, the resulting hydrogen bonding is weak and the electrostatic adsorption of the charged pyridinium ion is more likely the cause of the observed reduction in oxide RR.

In the case of sorbitol, TGA results showed that it can also adsorb on silica surfaces but it does not affect the oxide RRs. The adsorption of sorbitol occurs only through the weaker hydrogen bonding between the hydroxyl groups of sorbitol and the predominant silanols on the oxide surface. Presumably, during polishing, these weakly bound organic sorbitol molecules are easily removed by the pad and the ceria abrasives and hence do not suppress the oxide RRs.

Effect of the adsorption of pyridine and sorbitol on Si_3N_4 surfaces on nitride RRs.— TGA results showed that both the protonated pyridine and the hydroxyl-rich sorbitol adsorb on Si_3N_4 surfaces for pH values where the RRs are suppressed. In our earlier work,[12] we suggested that the protonated amino group ($\equiv N^{+}$-$H^{\delta+}$) of an amino acid additive easily attracts the lone pair of the electronegative nitrogen atom of Si_xNH_y, the predominant surface group present on the nitride surface, and forms a strong hydrogen bond. The higher strength of this hydrogen bonding contrasts with the weaker hydrogen bonding on the oxide surfaces.[12] Lorenzelli et al.[20] and Bergstrom[21] proposed a similar strong adsorption of additives that act as hydrogen bond donors on Si_3N_4 surfaces. In a similar manner, in the case of either pyridine or acetic acid or sorbitol or similar additives, the protonated amino group ($\equiv N^{+}$-$H^{\delta+}$) or the neutral carboxylic group (-COOH) or the hydroxyl group (-OH) acts as a hydrogen bond donor and forms a strong hydrogen bond with the nitride surface.

This strong hydrogen bonding on the nitride surface hinders the hydrolysis reaction, a rate limiting step in nitride removal mechanism,[7,22,23] by either impeding the reaction of water with the surface amines[22] or by blocking the surface amine protonation and subsequent water attack[23] and, hence, suppresses the nitride RRs.

Therefore, both pyridine and acetic acid species with associated proton below pH 6 are able to bind to nitride surface amines through hydrogen bonding and hinder the hydrolysis reaction, there by suppressing the nitride RR. In contrast, sorbitol has a wider pH window to retain the associated proton and, therefore, able to hinder hydrolysis reaction and suppress rates in the entire pH range 2–12.

These results extend the validity of our earlier observations[12] regarding the crucial role of strong hydrogen bond formation (and the associated pH range) in suppressing nitride removal rates to a much broader class of additive compounds. We anticipate that this role of hydrogen bond formation and pH on suppressing nitride removal rates will persist even when patterned nitride films are polished since their chemical structure will remain the same, even though the removal rates may not match precisely with those obtained with blanket films.

Conclusions

A strong correlation was found between the suppression of silicon nitride RRs and the pH dependent species of acetic acid, pyridine, and sorbitol as well as several other compounds and extends our earlier observations[12] to a broader class of additives. Only the additive species containing associated proton suppressed the nitride RR while their deprotonation did not affect the RRs. No such correlation was observed with the oxide rates and the rates were not suppressed by these species, except in the case of pyridine at pH ~4 to 5. Furthermore, it is suggested that similar to the aminoacids investigated earlier,[12] in the pH range where these additives retain either protonated amine, or -COOH, or –OH functional groups, as the case may be, they adsorb comparatively strongly on nitride surfaces but weakly on silica surfaces resulting in selective suppression of the nitride RRs.

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