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ATOMIC-SCALE MECHANISTIC STUDY OF IODINE/ALCOHOL PASSIVATED SI(100)

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Solutions of iodine in alcohol have been shown to passivate H_x-Si(100), decreasing the number of surface states. The degree of passivation depends upon the structure of the alcohol; methanol provides the most stable surface, with an order of magnitude fewer unpassivated sites than H_x-Si(100). Our experiments have allowed us to develop a mechanistic understanding of the reaction of the iodine/alcohol solution with the hydrogen-terminated surface. The passivation mechanism appears to be light activated iodination of the surface followed by nucleophilic substitution by the alcohol.

Our data suggests that this methoxy-terminated surface is exceptionally stable in the cleanroom ambient because the Si-O bond and the unreactive methoxy moiety hinder further reactions with contaminants. Upon annealing, we find that the passivation is readily removed, and the surface reconstructs to clean Si(100) 2x1 without the formation of silicon carbide.

INTRODUCTION

The immediate goal of this work is a chemically well-defined surface that is more stable in the cleanroom ambient than the hydrogen-terminated surface, yet cleanly and reproducibly replaced by the next solid phase. A surface passivated in this manner would eliminate the need for recleaning in between steps and provide for longer queuing times. The practice of duplicate cleaning steps, both after a process and before the next step, provides a unique opportunity for minimizing the chemical usage and water waste in a front-end-of-the-line cleaning scheme, as wafer cleaning is the most frequently repeated cycle in semiconductor processing, consuming 30% of all processing steps and 25% of all processing time.[1]

Using Radio Frequency Photoconductance Decay (RFPCD) as an *in situ* monitor of surface quality, we have demonstrated that a dilute solution of iodine in methanol provides highly effective electronic passivation[1]. The solution provides a passivation that has an order of magnitude fewer unpassivated sites than hydrogen-terminated Si(100), as demonstrated by surface recombination lifetime measurements. Our iodine in methanol treatment is superior to the hydrogen-terminated surface in that the air stability is dramatically increased, allowing for longer queuing times and greater reliability from batch to batch. RFPCD is an extremely sensitive probe of the electronic condition of the surface but gives no chemical information about the surface species. Developing a structural description of the surface is key to elucidating a mechanism for the reaction. It is essential to understand the nature of the surface on an atomic level, if we are to minimize environmental impact, while maintaining effective surface passivation.

Our studies indicate that the passivation mechanism involves light induced iodination of the surface, followed by nucleophilic substitution by the methanol, as shown in Figure 1. Light dissociates I_2, and the resulting atomic iodine removes a hydrogen atom from the surface. The radical chain reaction is perpetuated by attack of the silicon radical on another molecule of I_2 to form the Si-I bond and another atom of I. The Si-I bond is susceptible to nucleophilic attack by the methanol, as iodide anion is an excellent leaving group. The resulting surface is methoxy-terminated.

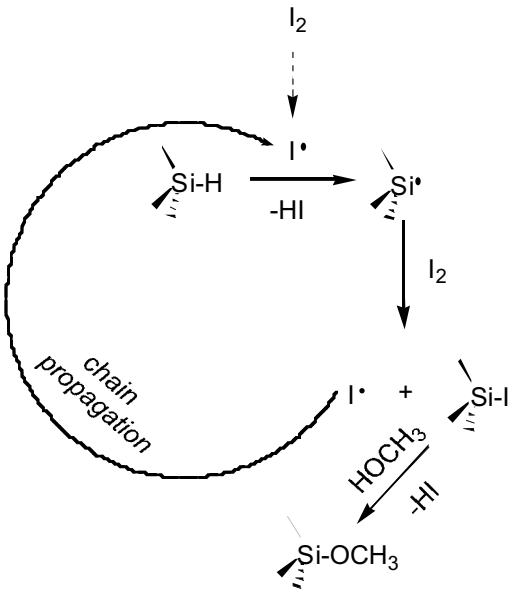

Figure 1. The passivation mechanism for H-Si treated with 5 X 10^{-4} M I_2 in methanol.

EXPERIMENTAL

Hydrogen-terminated silicon (H-Si) samples were prepared by two different methods. For the Si(111) samples, n-type Si (0.1-0.9 ohm-cm resistivity) wafers were cleaned in a 1:4, 30% H_2O_2: H_2SO_4 solution at 100°C for 10 minutes, rinsed with ultra pure water (UPW), and etched in 40% NH_4F for 15 minutes. For Si(100) samples, p-type Si (1-4 ohm-cm resistivity) wafers were etched in 1:100, 49% HF:H_2O solution for 2 minutes, rinsed with UPW, cleaned in a 1:4, 30% H_2O_2: H_2SO_4 solution at 100°C for 4 minutes, rinsed with UPW, and etched in 1:50, 49% HF:H_2O solution for 2 minutes. For

the Si(100) samples, the final etching process was performed in a glovebox under a nitrogen atmosphere to eliminate the effects of molecular oxygen and water on the hydrogen-terminated surface.

The H_x-Si(100) surfaces were passivated by immersion in solutions of 5 X 10^{-4} M I_2 in alcohol for 20 minutes. The methanol solution was made with dry methanol and sparged with argon to remove dissolved oxygen. All passivations were performed in a nitrogen atmosphere.

Iodination of the Si(111) surface was achieved on a diffusion-pumped glass vacuum line with a base pressure of 10^{-5} torr. UV exposure was performed using a broad band 365 nm light (Spectroline MB100). The iodinated surface was transferred under Ar to the analysis chamber.

Conventional X-ray photoelectron spectroscopy was performed with a Surface Science Model 150 XPS spectrometer. Peak fitting and scaling with atomic sensitivity factors were accomplished using the instrument software package.

For the synchrotron radiation photoemission measurements, the samples were introduced through a glovebox to a nitrogen purged load-lock for transfer into the analysis chamber. The analysis chamber is equipped with a cylindrical mirror analyzer (PHI) and has a base pressure of 10^{-10} torr. Analyses were performed at BL 8-1 and BL 10-1 of the Stanford Synchrotron Radiation Laboratory. The fitting procedure for the spectra is described in a previous study[2]. The monolayer coverages of surface species were determined from the photoelectron signal, accounting for exponential attenuation of the electrons from the bulk, as described by Himpsel, *et. al.*[3]

Infrared spectra were obtained with a Mattson RS-10000 Fourier-transform infrared spectrometer in the ATR geometry, and the 5 cm x 2 cm x 1 mm ATR crystals (Harrick) had 45^o bevels to enable the light to enter and exit the crystal. The light exiting the crystal was collected using a liquid-nitrogen cooled narrow-band MCT detector (EG&G Judson). Spectra were obtained at 4 cm^{-1} resolution and ratioed against spectra of silicon with a chemical oxide present.

RFPCD measurements were performed with an instrument described elsewhere[4]. The lifetimes measured are inversely proportional to the number of surface states, thus the lifetimes reflect the relative degree of surface passivation.[1]

RESULTS AND DISCUSSION

Conventional XPS measurements reveal that after the iodine/methanol passivation, carbon, oxygen, and iodine are present in a 10:10:1 ratio, comprising nearly a monolayer of surface coverage. The high coverage of carbon and oxygen suggest that the passivation process is more complex than the simple iodine bonding to the silicon dangling bonds on the surface that had been previously postulated[5] because that model would show a minority species of silicon bound to iodine, as the hydrogen-terminated surface should provide few sites that require passivation.

Synchrotron photoemission studies of the Si 2p core level confirm that the passivation process is dramatically changing the bonding at the Si surface. If iodine were only to react with the few dangling bonds on the surface, the Si 2p spectra would be largely unchanged , with mostly Si-H bonds and a few Si-I bonds as previously suggested

in reference 5. Yet the Si 2p spectrum in Figure 2(c) shows large amounts of silicon in the +1, +2, and +3 oxidation states, and these oxidized silicon atoms correspond to 0.8 monolayers of the surface atoms. This suggests that the passivation has surface silicon atoms with multiple bonds to methoxy groups. If iodine is not present in solution (Fig. 2(b)), the core levels remain unchanged from the hydrogen-terminated sample (Fig. 2(a)).

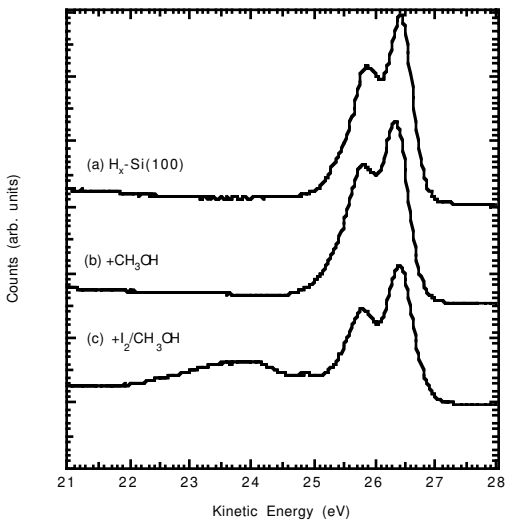

Figure 2. Si 2p photoemission spectra for Si(100) at a photon energy of 130 eV for (a) H_x-Si(100), (b) after treatment with methanol, and (c) after treatment with iodine in methanol.

It is possible to directly observe the disappearance of the hydrogen termination after the methoxy passivation by examining the IR spectra. The Si-H stretching region shown in Figure 3 indicates that if the H_x-Si(100) is immersed in methanol alone (b), the hydrogen-termination is preserved, but if the methanol solution contains iodine (c), the hydrogen-termination disappears. The initial H_x-Si(100) surface is microscopically rough, as evidenced by the mono-, di-, and tri-hydride stretches[6] in 3(a), so it is not surprising that multiple oxidation states are seen in the Si 2p spectrum (Fig. 2(c)) after reaction with I_2/methanol.

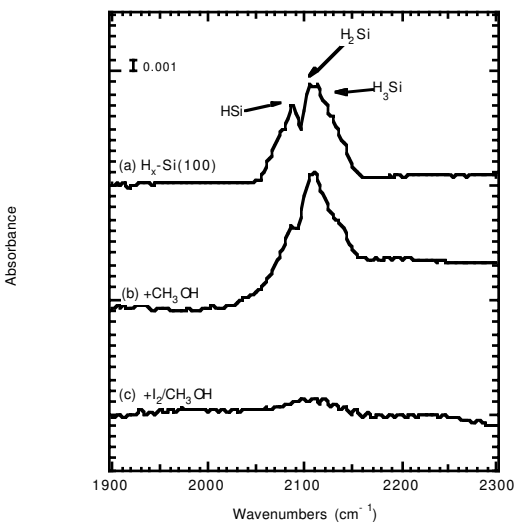

Figure 3. The Si-H stretching region of the IR spectra of Si(100) for (a) H_x-Si(100), (b) after treatment with methanol, and (c) after treatment with iodine in methanol.

If the alkoxy passivation of the surface involves the nucleophilic substitution reaction shown in Figure 1, there may be a decreased degree of reaction for more sterically

hindered alcohols because bulky alcohols should be less able to displace the iodine. The IR spectra for H_x-Si(100) incubated in various iodine/alcohol solutions (Fig. 4) confirms that less sterically hindered alcohols more thoroughly remove the hydrogen termination. H_x-Si(100) treated with iodine in ethanol has more H-termination remaining than when treated with I_2/methanol, but less than with I_2/isopropanol. We have observed that bulkier alcohols result in less effective passivation of the surface.

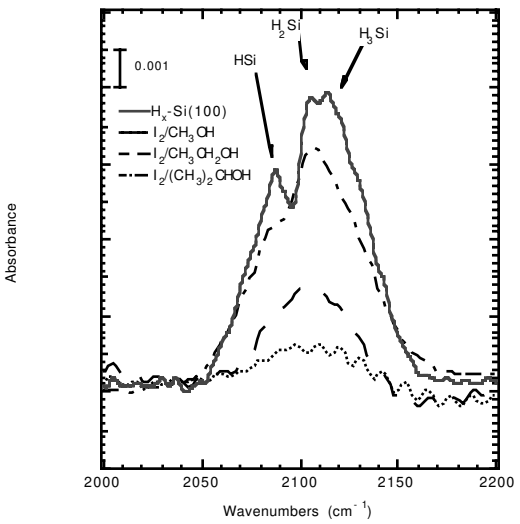

Figure 4. The IR spectra of H_x-Si(100) treated with solutions of iodine in alcohol.

Valence band photoemission at a photon energy of 55 eV reveals structure in the carbon 2s based molecular orbitals that is consistent with an alkoxy-terminated surface. The spectra shown in Figure 5 for iodine solutions of (a)methanol, (b)ethanol, and (c)isopropanol indicate that the appropriate alkyl group is present. The C 2s region of the valence band from kinetic energies of 30-38 eV contains one molecular orbital per carbon atom in the alkoxy group. The alkoxy groups appear to remain intact after bonding to the surface. This result is directly analogous to our study of alkyl adsorbates on the simpler Si(111) surface.[2]

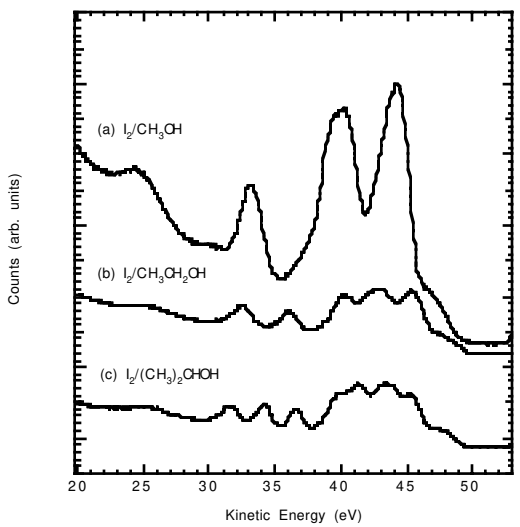

Figure 5. The valence band photoemission spectra at 55 eV photon energy for H_x-Si(100) after treatment with (a) I_2/methanol, (b) I_2/ethanol, and (c) I_2/isopropanol.

The kinetic energy of the oxygen 1s photoelectrons from a H_x-Si(100) sample after 20 minutes in I_2/methanol exhibit a chemical shift that is 0.4 eV higher than SiO_2. The oxygen in the methoxy group is chemically bonded to the electron donating Si atom and is distinct from the chemical shift of physisorbed methanol, confirming that the alkyl signal in the valence band (Fig. 5) is due to an alkoxy moiety bound to Si.[7]

Iodine is necessary to passivate the surface but is not the major species present after reaction, so it must form an activated intermediate. To begin to understand how iodine activates the Si surface, we examined gas phase reactions on the simpler H-Si(111) surface. Chlorine photodissociates and terminates this surface,[2] so iodine should behave in a similar manner. The Si 2p photoemission spectra at 130 eV photon energy of H-Si(111) after exposure to I_2(g) for 15 minutes, both (top panel) with UV light and (bottom panel) in the dark, are shown in Figure 6. When UV light is present, the resulting surface has a 0.6 ML coverage of Si^{+1} iodine termination. Yet when the dosing is performed in the absence of light, the surface has only 0.1 ML of Si^{+1} iodine termination.[3] The gas phase reaction of iodine with H-Si(111) is clearly photoinduced. We have attempted to reproduce these experiments in methanol, but the result was ambiguous. The dark surface had the same termination as the surface prepared in room light, however this result could be due to the difficulties involved in liquid transfer in the dark.

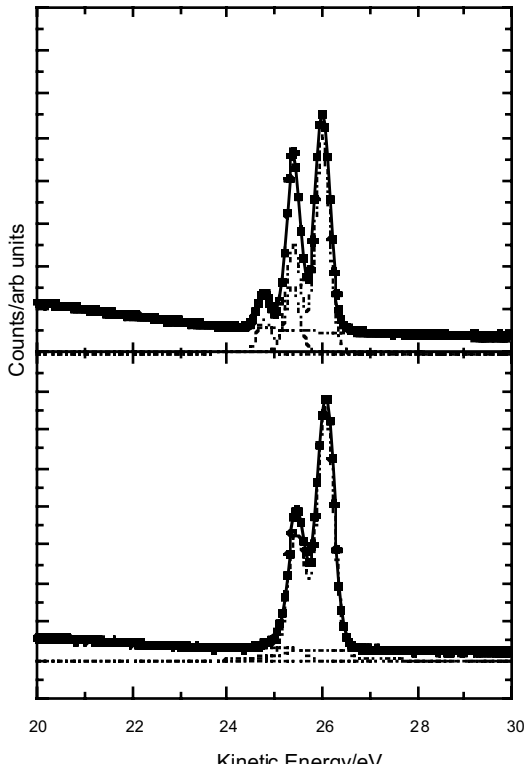

Figure 6. The Si 2p photoemission spectra at 130 eV for H-Si(111) dosed with I_2(g) for 15 minutes under UV light (top panel) and in the dark (bottom panel).

If this passivation is to be incorporated into a semiconductor fabrication scheme, it will be necessary to remove the alkoxy termination. An I_2/methanol passivated sample was annealed step-wise in vacuum in an attempt to remove the methoxy termination. The Si 2p photoemission spectra at a photon energy of 130 eV are shown in Figure 7. Annealing to 725°C results in the characteristic high kinetic energy surface peak of the clean Si(100) 2x1 reconstruction.[8] The 2x1 structure has also been confirmed by LEED.

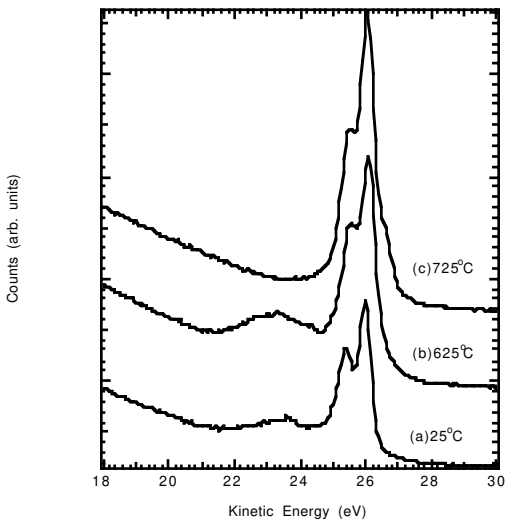

Figure 7. Si 2p photoemission spectra at a photon energy of 130 eV (a) prior to annealing, after reaching (b) 625°C, and after reaching (c) 725°C.

After reaching 675°C, the valence band annealing data for the same sample (Fig. 8) has no features in the 30-38 eV kinetic energy C 2s region of the spectra. The absence of carbon features confirms that silicon carbide is not formed during the anneal.

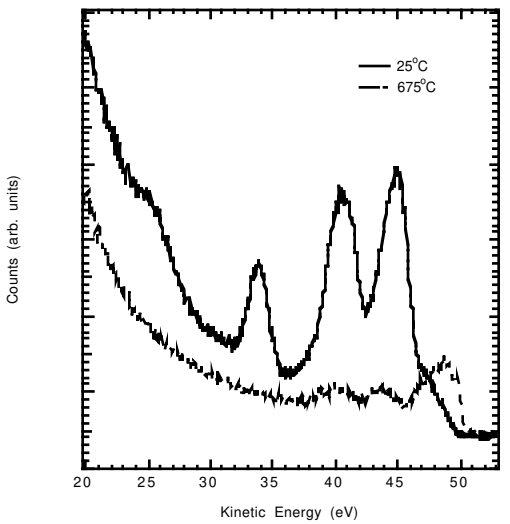

Figure 8. Valence band photoemission spectra at a photon energy of 55 eV prior to annealing and after reaching 675°C.

This annealing study was conducted under UHV conditions. Annealing the surface in the presence of an oxidizing agent, such as in a furnace, should afford even less potential for silicon carbide formation.

CONCLUSION

Dilute solutions of iodine in methanol provide an effective surface passivation. Spectroscopic evidence supports iodine-activated nucleophilic substitution as the mechanism for passivation. The resulting surface is predominantly methoxy-terminated.

Our results confirm that the passivation may be removed without silicon carbide formation by annealing in vacuum. Thus, the passivation shows potential for incorporation into a fabrication scheme to eliminate the need for redundant cleaning steps, lengthen queuing times, and increase batch reliability. Additional experiments are necessary to determine the resistance of this surface to metal contamination and to investigate the properties of devices built on this surface.

ACKNOWLEDGMENTS

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