Title

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Author

Zhang, Tianfu

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Influence of Reaction with XeF_2 on Surface Adhesion of Al and Al_2O_3 Surfaces

Tianfu Zhang, Jeong Y. Park, Wenyu Huang, and Gabor A. Somorjai[*]

Department of Chemistry, University of California, Berkeley, CA, 94720

Materials Science Division and Chemical Sciences Division, Lawrence Berkeley National Lab, Berkeley, CA 94720

The change of surface adhesion after fluorination of Al and Al_2O_3 surfaces using XeF_2 was investigated with atomic force microscopy. The chemical interaction between XeF_2 and Al and Al_2O_3 surfaces was studied by in situ x-ray photoelectron spectroscopy. Fresh Al and Al_2O_3 surfaces were obtained by etching top silicon layers of Si/Al and Si/Al_2O_3 with XeF_2. The surface adhesion and chemical composition were measured as a function of time after the exposure to air or annealing (at 200 °C under vauum). The correlation between the adhesion force increase and presence of AlF_3 on the surface was revealed.

[*] To whom correspondence should be addressed. E-mail:somorjai@berkeley.edu

Fluorine (F)-based chemistry is widely used to etch Si and other materials in microelectronics fabrications. The surfaces after going through the F-based etching chemistry are typically covered by a layer of fluorine-containing species, e.g. it is well-known that a fluorocarbon layer presents on the sidewalls of the structural materials from the Bosch process [1]. The studies of the F-chemistry etched surfaces are of great impact to both microelectronics processing and device performance. XeF_2 is an isotropic gas phase etchant of Si. Because of its high etch rate and high selectivity against many metals, dielectrics, and polymers used in traditional integrated circuit fabrications, XeF_2 has been a widely used to etch Silicon isotropically etchant in microelectromechanical systems (MEMS)[1] processing since 1995 [2]. XeF_2 is also used as a fluorination reagent in organic chemistry, due to its mild reactivity and high selectivity [3, 4]

While XeF_2 is a good etchant of silicon[5], Al and Al_2O_3 are among the materials which are not etched by XeF_2 and therefore are commonly used as structural materials. There are limited studies on the interaction between XeF_2 and the structural materials such as Al and Al_2O_3 after etching in spite of wide application of XeF_2 etching on structural materials [6, 7]. It is crucial to understand the influence of XeF_2 etching on chemical and mechanical properties of these structural materials. [8].

In the present study we investigate the reaction of Al and Al_2O_3 with XeF_2. We use X-ray photoelectron spectroscopy (XPS) to study the surface species after reaction, and use atomic force microscopy (AFM) [9-12] to measure the surface adhesion between fluorinated Al or Al_2O_3 surfaces and the AFM tips. The correlation between the surface adhesion forces and surface compositions is presented.

Al film was prepared by Ar sputtering of an Al source on a Si substrate. Al_2O_3 film was prepared by Ar reactive ion sputtering of Al in O_2. The Al and Al_2O_3 films were both about 300 Å in thickness. After Al and Al_2O_3 film deposition, a thin Si film (~ 500 Å) was sputter deposited in the same deposition chamber without breaking vacuum so that the Al and Al_2O_3 films were free of contamination in air. The surface roughness is about 0.2 nm and 2 nm for the Al_2O_3 and Al surfaces, based on AFM studies, respectively. The Si-covered Al/Al_2O_3 film was then introduced in a XeF_2 etch cell to remove the Si layer and to become fluorinated. XeF_2 etch was conducted in an etch chamber (~ 2 liter in volume) with a base pressure of $2x10^{-8}$ Torr. XeF_2 vapor was introduced into the chamber through a canister that works as a buffer volume, to speed up gas dose. Based on the vapor pressure of XeF_2 (4 Torr) and the volumes of the canister and the etch chamber, the initial pressure in the etch chamber was about 1-2 Torr. The Si/Al and Si/Al_2O_3 samples were exposed to XeF_2 for about 10 minutes and the top Si layer was completely removed, as confirmed by XPS analysis. After etch the chamber was pumped firstly by a diaphragm pump through a bypass and then by a turbo pump to reach a pressure below 5×10^{-7} Torr, the sample was then transferred *in vacuo* into a directly attached XPS chamber in which XPS analysis was performed. A 600 W lamp was used to heat the sample with irradiation of light through windows.

XPS experiments were performed in an ultra high vacuum (UHV) chamber with base pressure of 2×10^{-9} Torr, equipped with a Perkin-Elmer PHI 5300 XPS spectrometer. The Al-Kα (*BE*= 1486.6 eV) X-ray source of the XPS spectrometer was operated at 350 W with 15 kV acceleration voltage. Since all sample substrate studied are semiconductors, electron charge accumulates on the surface and causes the binding energy to shift.

Therefore, we normally calibrate the binding energy by setting the measured binding energy of C 1s to 285 eV. Alternatively, the O 1s main peak (531 eV) was also used for the reference peak of a sample where carbon is absent.

Commercial AFM (Molecular Imaging) was employed to measure the adhesion force of the surface and obtain a topographical image of the surface in air [13]. A silicon nitride tip with nominal spring constants of 0.27 N/m was used in our measurements. The AFM image was obtained in contact mode and at low loads (< 5 nN). From the AFM image, the typical roughness of the surface can be obtained. The radii of the tips were 30-40 nm, as measured by scanning electron microscopy. Measurements on every surface were performed at least 6 times at different positions on the surface. Depending on the nature of tip-sample contact, the adhesion force can be greatly affected [14]. After the force-distance measurement, we imaged the surface and did not observe any plastic deformation on the surface, confirming that the tip-sample contact is in the elastic regime. The adhesion force on a surface was averaged using all of the measurements. After the Si/Al sample was etched in the preparation chamber, XPS measurement was carried out and then taken out of UHV chamber for the adhesion measurements. The adhesion measurements were carried out within 2 hours after the XeF_2 etching of samples. Adhesion force was measured on an Al surface (with native oxide on top).

Figure 1 shows a typical adhesion force measurement on an Al surface (with native oxide on top) and a fluorinated Al surface. As the tip retracted from the surface, the attractive force between the surface and the tip (adhesion) could no longer maintain the contact at point A and the tip snapped out of contact with the surface [10, 15]. The force between point A and B is therefore attributed to the adhesion force between the tip and the surface [14]. Adhesion force between the silicon nitride tip and the fluorinated Al surface was about 7 nN, higher than that of oxidized Al surface by a factor of two. Likewise, adhesion force between the Si_3N_4 tip and the fluorinated Al_2O_3 surface was about 6.5 nN, higher than that of Al_2O_3 surface that was exposed to air (3.5 nN).

XPS survey of the as-etched Al surface revealed a spectrum free of carbon, as shown in Figure 2. Al and F peaks were revealed on the surface as shown in Figure 2. C1s and O1s peaks (when carbon is absent on the surface) were used to calibrate the binding energy. Using the XPS sensitivity factors of Al2p, F1s and C1s peaks and the integrated peak area, the relative surface composition was estimated to be $AlF_{3.6}C_0$. The Al2p spectra are shown in figure 2(a). The peak at 72 eV (full width at half maximum (FWHM) 1.1 eV) can be assigned to metallic Al, and the peak at 77 eV (FWHM 2 eV) corresponds to fluorinated Al. [16] Figure 2(b) shows the F1s peak of the as-etched Al surface at 686 eV[16]. O1s were used to calibrate the binding energy because carbon peak is absent on the surface. Figure 2 also shows a comparison of Al2p, C1s, and F1s spectra before and after air exposure. The F peaks undergo some changes on the shape, possibly due to the adsorbate in air. There was no C at all right after Al was etched, but C accumulated on the surface after it is exposed to air. The main peak at 285 eV is the adventitious C from the ambient air. A new carbon peak ~ 290 eV appears, which we assign to C-F species, most likely due to C bonding to two F atoms by comparing the previous report about CF_x species [17]. Because it is not observed right after etch and fluorocarbons do not commonly exist in ambient air, CF_x peak could be formed in air between the C adsorbate with some reactive F species on the sample surface.

As-etched AlOx surface (as shown in Figure 3) has been characterized with XPS. After the Si/Al_2O_3 sample was etched by XeF_2, the surface exhibited a stoichiometry of $Al_2O_3F_{4.4}$ C_0. Figure 3a shows the XPS spectra of Al 2p peak of Al_2O_3 surface after fluorinated by XeF_2. It is obvious that there is shoulder on the Al 2p peak which is due to F. Peak fitting reveals a peak at 77 eV which is the position of Al 2p in AlF_3. The main peak at 75 eV is attributed to Al 2p in Al_2O_3. The O 1s peak in Figure 3d shows a small high-binding energy peak at 537 eV after XeF_2 etch (red spectrum), which almost decays to zero after one day air exposure (blue spectrum). The high-binding energy O 1s peak could be due to the interaction of O with F.

Just like Al surface, the main peak of C adsorbate species (at 285 eV) and another small peak at ~ 290 eV (C-F species) are revealed after the air exposure for one day. F 1s shows a symmetric peak at 686.4 eV with a FWHM of 2.6 eV. This is very close to the F 1s peak of fluorinated Al surface (figure 3c). The adhesion forces on Al surfaces were measured after air exposure as a function of the exposure time. All of the above measurements are shown in Figure 4. As shown in Figure 4a, the adhesion force of the as-etched (2 hour) Al surface was 8 nN, and dropped to 5 nN after one day. After two days the adhesion force of the etched Al surface was the same as that of the Al surface. The F concentration of the surface measured with XPS is also shown is the figure, from which we can see the decay of fluorine concentration. Figure 4b shows that annealing at 200 ^{o}C under vacuum significantly reduced the adhesion force. The fluorine concentration also drops considerably. XPS analysis shows that there is a significant amount of oxide formation after annealing in air.

We can also use AFM to obtain the topographical image of the surface. There is no obvious change on the surface after fluorination. This indicates that although XeF_2 reacts with the Al surface, the fluorination product (AlF_3) stays on the surface and does not change the surface roughness (~ 0.2 nm).

The same adhesion force measurements are performed on the fluorinated Al_2O_3 surfaces, as shown in figure 4c and 4d. The adhesion force of the as-etched Al_2O_3 surface is about 6.5 nN and decayed over time while the fluorine concentration did not decay over two days, suggesting no direct correlation between surface adhesion and fluorine concentration for fluorinated Al_2O_3 surface. This can be associated with the evolution of the reactive fluorine into chemically stable fluorine species, such as CF_x that appeared after one day of etching. Annealing in air, however, caused a significant reduction of surface adhesion, together with a loss of F and accumulation of C and O, as shown in figure 4d. Therefore, the high surface adhesion after XeF_2 etching can be directly attributed to the AlF_3 layer formed on both of Al and Al_2O_3 surfaces.

In conclusion, the surface chemical compositions and adhesion forces of the Al and Al_2O_3 surface fluorinated by XeF_2 are studied by XPS and AFM, respectively. The high surface adhesion is positively correlated to the presence of the reactive F on the surfaces. We found that the surface adhesion decreases upon exposure to air or heating as fluorocarbons replace the reactive F. Combining XPS and AFM allows us to understand the correlation between the surface chemical compositions and adhesion forces that is of important impact to design and processing of nanoscale building blocking.

Acknowledgement

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Figure Captions

Figure 1. (Color online) Approach and retraction curves of adhesion force measurement on an Al surface and a fluorinated Al surface.

Figure 2. (Color online) XPS spectra of Al surface after XeF_2 etch (red) and one day air exposure (blue). (a) Al 2p, (b) C 1s, and (c) F 1s.

Figure 3. (Color online) XPS spectra of AlO_x surface after XeF_2 etch (red) and one day air exposure (blue). (a) Al 2p, (b) C 1s, (c) F 1s, and (d) O1s.

Figure 4. (Color online) The plot of adhesion force (measured by AFM) and the ratio of F to Al (measured by XPS) as a function of time (a) on etched Al surfaces (b) on the etched and annealed Al surface. The plot of adhesion force and the ratio of F to Al (measured by XPS) (c) on etched Al_2O_3 surfaces and (d) on the etched and annealed Al surface as a function of time.

[Delete Fig 4a and 4c]

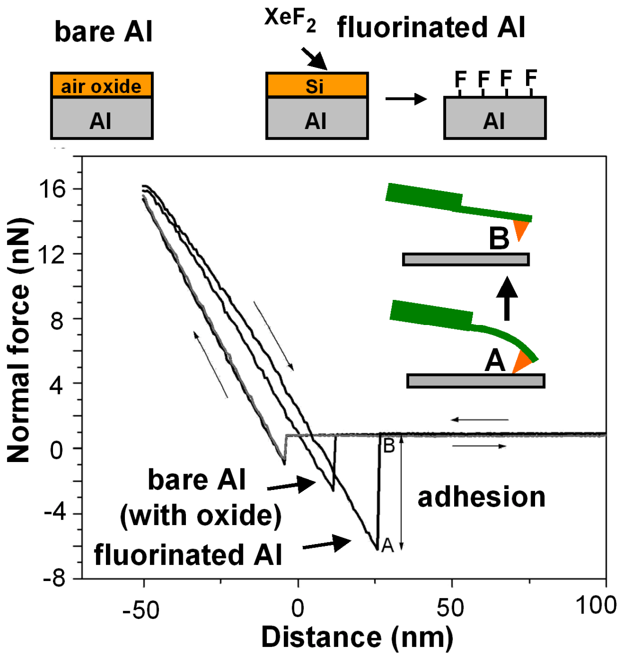

Figure 1

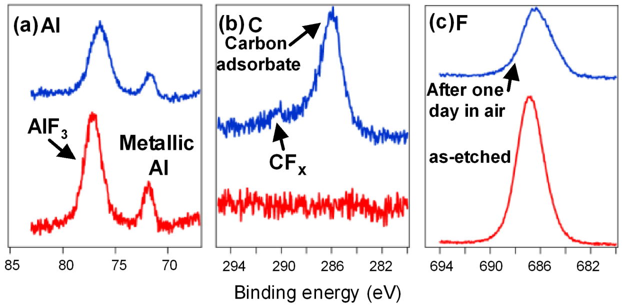

Figure 2

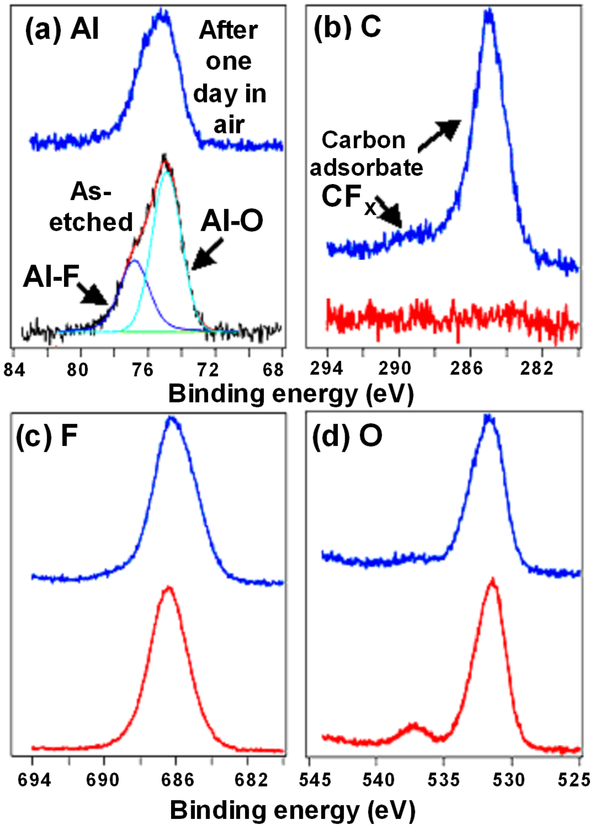

Figure 3

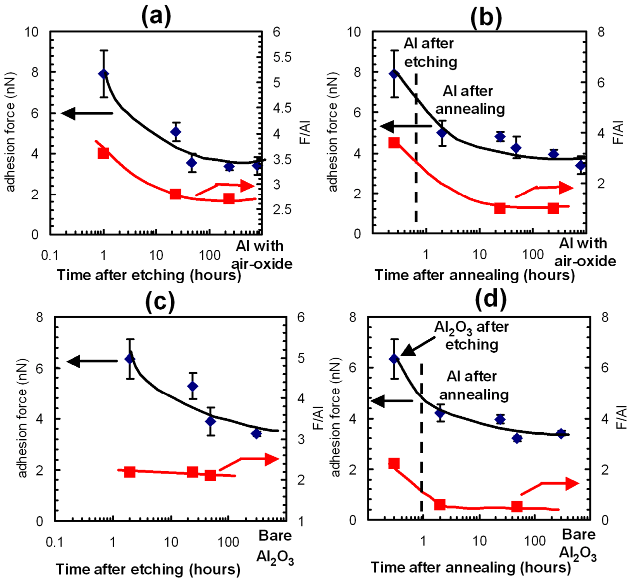

Figure 4