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Citation: *Appl. Phys. Lett.* **93**, 141905 (2008); doi: 10.1063/1.2992632

View online: <http://dx.doi.org/10.1063/1.2992632>

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## Influence of reaction with XeF<sub>2</sub> on surface adhesion of Al and Al<sub>2</sub>O<sub>3</sub> surfaces

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(Received 28 July 2008; accepted 11 September 2008; published online 10 October 2008)

The change in surface adhesion after fluorination of Al and Al<sub>2</sub>O<sub>3</sub> surfaces using XeF<sub>2</sub> was investigated with atomic force microscopy. The chemical interaction between XeF<sub>2</sub> and Al and Al<sub>2</sub>O<sub>3</sub> surfaces was studied by *in situ* x-ray photoelectron spectroscopy. Fresh Al and Al<sub>2</sub>O<sub>3</sub> surfaces were obtained by etching top silicon layers of Si/Al and Si/Al<sub>2</sub>O<sub>3</sub> with XeF<sub>2</sub>. The surface adhesion and chemical composition were measured after the exposure to air or annealing (at 200 °C under vacuum). The correlation between the adhesion force increase and presence of AlF<sub>3</sub> on the surface was revealed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2992632]

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.<sup>1</sup> The studies of the F-chemistry etched surfaces are of great impact to both microelectronics processing and device performance. XeF<sub>2</sub> has been a widely used isotropic etchant of silicon, because of its high etch rate and selectivity against many metals, dielectrics, and polymers used in traditional integrated circuit fabrications.<sup>1,2</sup> XeF<sub>2</sub> is also used as a fluorination reagent in organic chemistry due to its mild reactivity and high selectivity.<sup>3,4</sup>

While materials, such as Al and Al<sub>2</sub>O<sub>3</sub>, are commonly used as conducting or dielectric materials in the integrated circuit industry, there are limited studies on the fluorination of these materials.<sup>5–7</sup> In present work we investigate the interaction between XeF<sub>2</sub> and these structural materials. It is crucial to understand the influence of etching on chemical and mechanical properties of these structural materials.<sup>8</sup>

In the present study we investigate the reaction of Al and Al<sub>2</sub>O<sub>3</sub> with XeF<sub>2</sub>. We use x-ray photoelectron spectroscopy (XPS) to study the surface species after reaction, and use atomic force microscopy<sup>9–12</sup> (AFM) to measure the surface adhesion between fluorinated Al or Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> film was prepared by Ar reactive ion sputtering of Al in O<sub>2</sub>. The Al and Al<sub>2</sub>O<sub>3</sub> films were both about 300 Å in thickness. After Al and Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> films were free of contamination in air. The surface roughnesses are about 0.2 and 2 nm for the Al<sub>2</sub>O<sub>3</sub> and Al surfaces, based on AFM studies, respectively. The Si-covered Al/Al<sub>2</sub>O<sub>3</sub> film was then introduced in a XeF<sub>2</sub> etch cell to remove the Si layer and to become fluorinated. XeF<sub>2</sub> etch was conducted in an etch chamber (~2 l in vol-

ume) with a base pressure of  $2 \times 10^{-8}$  Torr. XeF<sub>2</sub> 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<sub>2</sub> (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<sub>2</sub>O<sub>3</sub> samples were exposed to XeF<sub>2</sub> for about 10 min 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  $5 \times 10^{-7}$  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 ultrahigh vacuum (UHV) chamber equipped with a Perkin-Elmer PHI 5300 XPS spectrometer with a position-sensitive detector and a hemispherical energy analyzer. The Al K $\alpha$  (beam energy=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 1 s to 285 eV. Alternatively, the O 1 s 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.<sup>13</sup> 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 six times at different positions on the surface. After measurements were done on all of the three surfaces, we repeated the measurements on them and obtained similar values, as before, to make sure the tip did not change during measurements. Depending on the nature of tip-sample contact, the adhesion force can be greatly affected.<sup>14</sup> After the force-distance measurement, we imaged the surface and did

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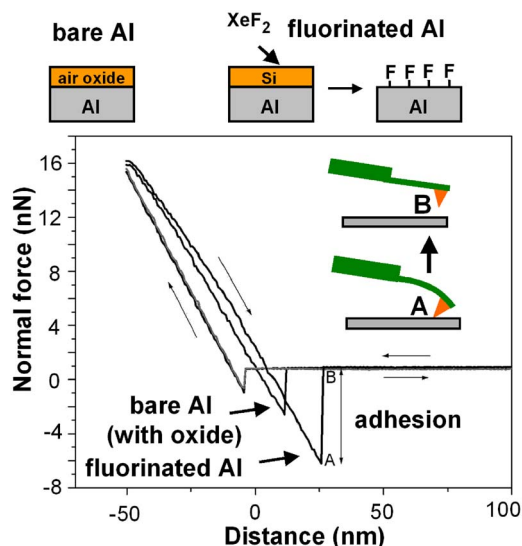


FIG. 1. (Color online) Approach and retraction curves of adhesion force measurement on an Al surface and a fluorinated Al surface.

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. 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.<sup>10,15</sup> The force between points A and B is therefore attributed to the adhesion force between the tip and the surface.<sup>14</sup> 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 2. Likewise, adhesion force between the Si<sub>3</sub>N<sub>4</sub> tip and the fluorinated Al<sub>2</sub>O<sub>3</sub> surface was about 6.5 nN, higher than that of Al<sub>2</sub>O<sub>3</sub> 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 Fig. 2. Al and F peaks were revealed on the surface, as shown in Fig. 2. C 1s and O 1s peaks (when carbon is absent on the surface) were used to calibrate the binding energy. Using the XPS sensitivity factors of Al 2p, F 1s, and C 1s peaks and the integrated peak area, the relative surface composition was estimated to be

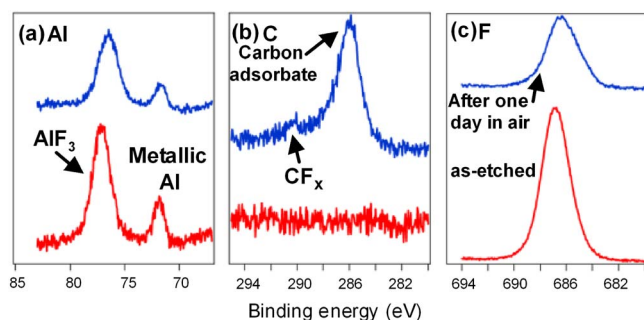


FIG. 2. (Color online) XPS spectra of Al surface after XeF<sub>2</sub> etch (lower red line) and 1 day air exposure (upper blue line). (a) Al 2p, (b) C 1s, and (c) F 1s.

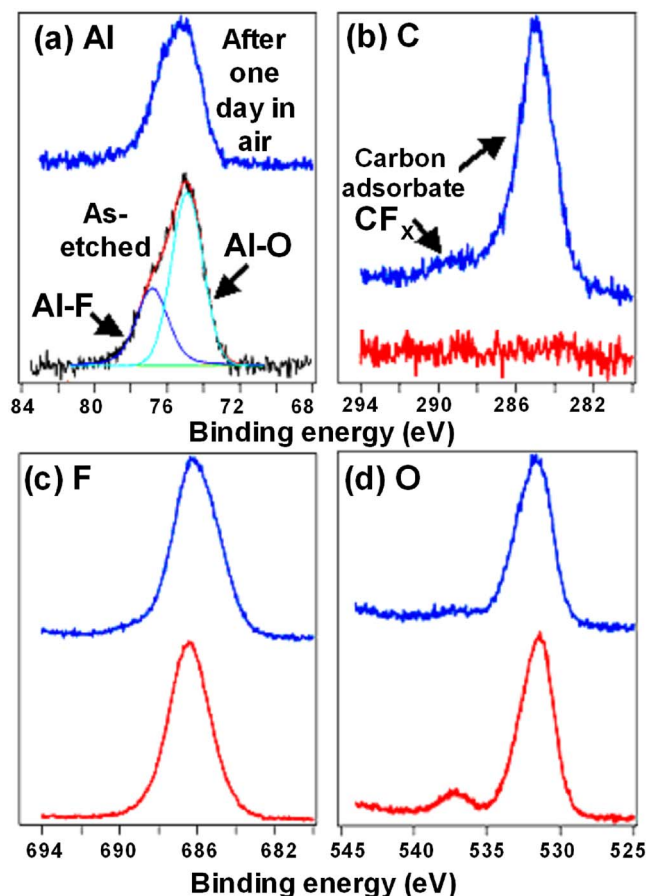


FIG. 3. (Color online) XPS spectra of AlO<sub>x</sub> surface after XeF<sub>2</sub> etch (lower red line) and 1 day air exposure (upper blue line). (a) Al 2p, (b) C 1s, (c) F 1s, and (d) O 1s.

AlF<sub>3.6</sub>C<sub>0</sub>. The Al 2p spectra are shown in Fig. 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.<sup>16</sup> Figure 2(b) shows the F 1s peak of the as-etched Al surface. Since the sample is a semiconductor, there is a charge effect on the spectrum and all of the peaks tend to upshift on the binding energy. O 1s were used to calibrate the binding energy because carbon peak is absent on the surface. The F 1s peak at 686 eV (Ref. 16) exhibits a symmetric peak with a FWHM of 2.6 eV. Figure 2 also shows a comparison of Al 2p, C 1s, and F 1s spectra before and after air exposure. The F peaks undergo some changes in 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<sub>x</sub> species.<sup>17</sup> Because it is not observed right after etch and fluorocarbons do not commonly exist in ambient air, CF<sub>x</sub> peak could be formed in air between the C adsorbate with some reactive F species on the sample surface.

As-etched AlO<sub>x</sub> surface (as shown in Fig. 3) has been characterized with XPS. After the Si/Al<sub>2</sub>O<sub>3</sub> sample was etched with XeF<sub>2</sub>, the surface exhibited a stoichiometry of Al<sub>2</sub>O<sub>3</sub>F<sub>4.4</sub>C<sub>0</sub>. The Al/O ratio is same as the stoichiometry of Al<sub>2</sub>O<sub>3</sub>, probably suggesting that F is incorporated into the surface. Figure 3(a) shows the XPS spectra of Al 2p peak of



$\text{Al}_2\text{O}_3$  surface after fluorinated by  $\text{XeF}_2$ . It is obvious that there is a 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  $\text{AlF}_3$ . The main peak at 75 eV is attributed to Al  $2p$  in  $\text{Al}_2\text{O}_3$ . The O  $1s$  peak in Fig. 3(d) shows a small high-binding energy peak at 537 eV after  $\text{XeF}_2$  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  $\sim 290$  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 [Fig. 3(c)]. The adhesion forces on Al and  $\text{Al}_2\text{O}_3$  surfaces were measured after air exposure as a function of the exposure time after annealing. Figure 4(a) shows that annealing at 200 °C under vacuum significantly reduced the adhesion force. The F concentration of the surface measured with XPS is also shown in the figure, from which we can see the decay of fluorine concentration. 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 in the surface after fluorination. This indicates that although  $\text{XeF}_2$  reacts with the Al surface, the fluorination product ( $\text{AlF}_3$ ) stays on the surface and does not change the surface roughness ( $\sim 0.2$  nm).

The same adhesion force measurements are performed on the fluorinated  $\text{Al}_2\text{O}_3$  surfaces, as shown in Figs. 4(b). Annealing in air caused a significant reduction in surface adhesion, together with a loss of F and accumulation of C and O, as shown in Fig. 4(b). Therefore, the high surface adhesion after  $\text{XeF}_2$  etching can be directly attributed to the  $\text{AlF}_3$  layer formed on both of Al and  $\text{Al}_2\text{O}_3$  surfaces.

In conclusion, we characterize of the Al and  $\text{Al}_2\text{O}_3$  surface fluorinated by  $\text{XeF}_2$ . The surface chemical compositions and adhesion forces are studied by XPS and AFM, respectively. AFM reveals the high surface adhesion on the as-fluorinated Al and  $\text{Al}_2\text{O}_3$  surfaces by  $\text{XeF}_2$ . The high surface adhesion is positively correlated to the presence of the reactive F on the surfaces. Combining XPS and AFM allows us to understand the correlation between the surface chemical compositions and adhesion forces that has important impact

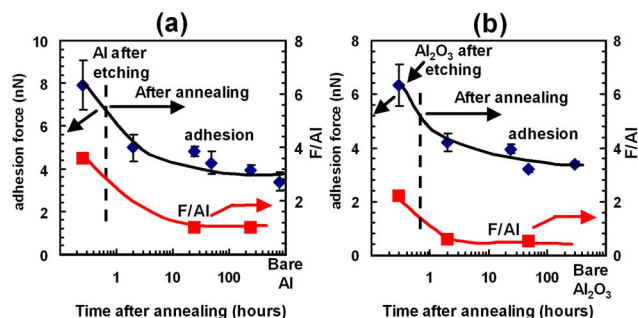


FIG. 4. (Color online) The plot of adhesion force (measured by AFM) and the ratio of F to Al (measured by XPS) as a function of time (a) on the etched and annealed Al surface, and (b)  $\text{Al}_2\text{O}_3$  surface.

on the design and processing of nanoscale building blocks.

This work was funded through UC discovery Grant No. ELE05-10221 and was partially supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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