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# Sputter damage in Si (0 0 1) surface by combination of $C_{60}^+$ and $Ar^+$ ion beams

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## ABSTRACT

The damage to the solid by low-energy single atomic projectiles and high-energy cluster ion beams is analyzed by evaluating the Si (0 0 1) surface after ion sputtering, with angle-resolved x-ray photoelectron spectroscopy (ARXPS), high-resolution transmission electron microscopy (HRTEM), and atomic force microscopy (AFM). The depth distribution of Ar and C was determined using ARXPS. It was found that the primary ion implant region thickness in the Si is estimated to be 2.34, 1.68, and 1.63 nm for Ar<sup>+</sup>, C<sub>60</sub><sup>+</sup>, and mixed Ar<sup>+</sup>-C<sub>60</sub><sup>+</sup> sputtering, respectively. Similarly, 5–8, 4–6, and 3–5 nm thick rearranged layers were observed directly with HRTEM. The results indicate that cluster ion beams cause shallower damage to the solid. On the other hand, AFM revealed 0.44, 2.58, and 2.63 nm surface roughness indicating that cluster ion beams induce significantly rougher interfaces. This interfacial roughening will ultimately determine the depth resolution of the depth profile.

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#### 1. Introduction

Sputter depth profiling using ion beams has been widely used in secondary ion mass spectrometry (SIMS), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS). The high surface sensitivity and depth resolution for these techniques are used in studying the outermost layers of metals, semiconductors, ceramics, and polymers. Low energy single atomic projectiles and high-energy cluster ions are recently being applied in order to minimize the surface damage that ultimately limits the depth resolution of the depth profile.

Monoatomic argon sputtering is the most accepted technique in removing surface contaminants and obtaining information on the depth distribution of an element within a sample. However, this erosion technique is known to cause severe damage to organic samples [1] owing to preferential sputtering and/or sputter reduction (e.g. the oxygen atom in sulfonate is removed, causing the reduction of sulfur). Hence, information on the chemical composition and the chemical state of elements is lost and argon sputtering cannot be used for depth profiling of polymer materials. Such damage is still observable at low (0.20 kV) beam energy [2] and with other monoatomic ion species [3]. Recently, buckminsterfullerene ( $C_{60}$ ) ion guns were constructed by lonoptika Ltd. [4,5], and were used to sputter materials for studying surface compositions. Molecular dynamics (MD) calculations suggested that  $C_{60}^+$  ions are more efficient in removing material [6] and leaving behind a relatively thin damage layer [7]. Using  $C_{60}^+$  sputtering as the ion source for SIMS [8–10] and to remove the surface layer for XPS depth profiling [4,11,12], a few reports have confirmed that the sputtering yield is increased and the damage to the chemical structure is reduced compared with the use of monoatomic argon sputtering. In addition, we recently reported that such a sputtering technique could be used to analyze multi-layer organic and organic–inorganic composite thin films [12].

Although the  $C_{60}^+$  erosion is a promising method for depth profiling organic materials, the sputter rate observed during prolonged sputtering was unsteady due to the deposition of amorphous carbon on the surface [12] and ion-induced crosslinking [13]. When equilibrium between sputtering and deposition is reached, the  $C_{60}^+$  ion beam can no longer erode the surface and information beneath the surface cannot be revealed.

To overcome this limitation, a low energy single atom projectile that can disrupt the atom deposition from the cluster ion beams was applied concurrently with the high-energy cluster projectile. The mixed sputtering technique greatly extends the application of the cluster ion sputtering for profiling thick and multi-layered organic devices [2]. Although the results of this depth profiling technique are promising, the damage distribution in the solid was



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Fig. 1. Elemental distribution of incident elements in Si (0 0 1) surface after 60 min sputtering: (a) sputtered with 0.2 kV Ar<sup>+</sup> ions, (b) sputtered with 10 kV  $C_{60}^+$  ions, and (c) sputtered with mixed 0.2 kV Ar<sup>+</sup> and 10 kV  $C_{60}^+$  ions.

not yet measured. However, the damage effect is crucial in the resolution of depth profiling and needs to be examined quantitatively.

With ion bombardment, trace amounts of the ion species are deposited in the surface layer that, indicate the damage layer. With medium energy ion scattering (MEIS), Shin et al. [14] measured the implantation of Ar in the Si surface to determine sputter damage thickness. The results revealed that the damage thickness decreased significantly with high incident angle and low beam energy.

In order to gain more insight in the cluster ion sputtering, the sputter damage generated by these ion beams need to be studied. Using both XPS and time-of-flight SIMS, the damage to polymers caused by C<sub>60</sub> ion sputtering are studied indirectly and it is concluded that higher incident angles are better for depthprofiling polymers [15]. In this work, we attempted to directly observe the sputter damage in the solid using angle resolved XPS (ARXPS), high resolution transmission electron microscope (HRTEM), and atomic force microscope (AFM). In order to observe the damage layer directly with HRTEM, the solid needs to be highly crystalline so that the changes in atomic arrangement directly reflect the damage layer. In addition, to observe the ion beaminduced topography with AFM, the starting solid must be of high flatness. Most organic materials cannot fulfill these criteria so highly polished single crystalline silicon wafer is chosen for this work.

## 2. Experimental

XPS spectra were recorded on a PHI 5000 VersaProbe (ULVAC-PHI, Chigasaki, Japan) system using a microfocused (100  $\mu$ m, 25 W) monochromatic Al X-ray K $\alpha$  beam. The photoelectron take-off angles (TOA) at sin (TOA) between 0.2 and 0.95 with an interval of 0.05 were used. The analyzer pass energy was set at 93.9 eV and the peak-to-noise ratio is greater than 50. The angle resolved spectra were then analyzed with MultiPak (V8.2B, ULVAC-PHI). A dual beam charge neutralizer (7 V Ar<sup>+</sup> and 30 V flooding electron beam) was used to compensate the charge-up effect. The Ar<sup>+</sup> ion source (FIG-5CE) was operated at 0.2 kV using a floating voltage of 500 V with ~200  $\mu$ m spot size. The 300 nA current is measured by the sample current on an Au foil and was controlled by the strength of condenser lens. The beam was rastered over an area of 2 mm  $\times$  2 mm at an incident angle of 45°. A Wien-filtered C<sub>60</sub><sup>+</sup> ion source (IOG C<sub>60</sub>-10, Ionoptika, Chandler's Ford, UK) was

operated at 10 nA and 10 kV (spot size ~600  $\mu m$ ), with rastering over an area of 2 mm  $\times$  2 mm at an incident angle of 70° (70° from the normal to the surface for analysis). The base pressure of the main chamber (<1  $\times$  10<sup>-7</sup> Pa) was achieved by evacuation using turbomolecular and ion-getter pumps.

The HRTEM images were taken with a JEM-2100F (JEOL, Japan) operated at 200 kV. The magnification was calibrated using the spacing of Si single crystal. The cross-sectional specimens were prepared using a standard mechanical polish and ion-milling procedure. AFM images were taken with an Innova scanning probe microscope (Veeco, Woodbury, NY) using tapping mode with a closed-loop scanner.

## 3. Results and discussion

ARXPS was acquired immediately after sputtering with given ion beam(s) for 30 and 60 min. The identical results at different sputtering time indicate that the specimens reached the steady state within 30 min of sputtering. Using the ultra thin-film analysis software built in MultiPak to analyze the result of ARXPS, Fig. 1a shows the elemental distribution of the Si (0 0 1) surface after it was sputtered with 0.2 kV Ar<sup>+</sup> beam for 60 min. At a fixed primary ion incidence angle of 45°, about 4% Ar was found within the topmost 2.34 nm indicating the primary ion implant region thickness of 0.2 kV Ar<sup>+</sup> beam is about 2.34 nm. This result is comparable with the results reported by Shin et al., where 3.5 and 5.3 nm thick primary ion implant layers were observed with 0.5 and 1 kV Ar bombardment at 45°, respectively. As the beam energy is lower (0.2 kV) in this research, a thinner primary ion implant layer (2.34 nm) is observed.

Fig. 1b and c shows the elemental distributions of implanted C in the Si (0 0 1) surface. Regardless of the use of the low-energy Ar<sup>+</sup> beam, the implantation thickness and the chemical composition were almost identical. This result further supports the argument [2] that the function of the low-energy Ar<sup>+</sup> beam is merely disrupting the carbon deposition instead of actually removing the carbon layer. Although the Ar<sup>+</sup> beam was used in Fig. 1c, Ar was not clearly observable in the specimen. This result is consistent with the high sputtering rate of 10 kV C<sub>60</sub><sup>+</sup> beam removing the surface layer faster than the implantation of Ar. Therefore the Ar was not accumulated in the surface and was not observed.

Fig. 2 shows the cross-sectional lattice image of the Si  $(0 \ 0 \ 1)$  surface after sputtering. Although the outermost surface is still primarily crystalline, the darker contrast indicates the disruption



**Fig. 2.** Cross-sectional HRTEM image of Si (0 0 l) surface after 60 min sputtering: (a) sputtered with 0.2 kV Ar<sup>+</sup> ions, (b) sputtered with 10 kV C<sub>60</sub><sup>+</sup> ions, and (c) sputtered with mixed 0.2 kV Ar<sup>+</sup> and 10 kV C<sub>60</sub><sup>+</sup> ions.



**Fig. 3.** AFM topography of Si (0 0 1) surface after 60 min sputtering: (a) sputtered with 0.2 kV Ar<sup>+</sup> ions, (b) sputtered with 10 kV  $C_{60}^+$  ions, and (c) sputtered with mixed 0.2 kV Ar<sup>+</sup> and 10 kV  $C_{60}^+$  ions. The primary ion is coming from the *x*-direction of the image.

of the atomic arrangement. In other words, the dark contrast near the surface indicates the damage layer that was induced by the ion sputtering. Without  $Ar^+$  (Fig. 2b,  $C_{60}^+$  only), the dark region is not as prominent as those with  $Ar^+$  (Fig. 2a and c,  $Ar^+$  only and  $Ar^+-C_{60}^+$ , respectively) indicating that the disruption in atomic arrangement is limited with  $C_{60}^+$  sputtering. This result is consistent with the MD calculation that  $C_{60}^+$  ion beams cause less damage in the remaining surface [16].

The thickness of the damage layer observed in the HRTEM is about 5–8, 4–6, and 3–5 nm for sputtering with  $Ar^+$ ,  $C_{60}^+$ , and mixed ions, respectively. The reason the damage thickness observed in HRTEM is higher compared to the ARXPS result is elaborated below. When the ion reaches a certain depth and collides with the Si atom, the energy of the ion will be transferred to the Si atom. Through the lattice vibration, the energy is transferred deeper into the solid than the penetration depth of the ion. Hence, the true damage thickness is thicker than the depth where ions are deposited. Therefore, the damage thickness is underestimated in the ARXPS.

Combining the ion distribution and the damage thickness results in the silicon wafer, it is clear that single atom projectiles, even with low energy, penetrated deeper in the solid and create a thicker damage layer than cluster ion beams. For loosely packed soft materials, the ion can penetrate much deeper and the difference between ion beams will be more dramatic. Considering that the usual sampling depth of XPS and AES is less than 10 nm, the structure is significantly damaged by the single atom projectile and true information of the specimen cannot be acquired. As cluster ion beams cause shallower damage to the solid, information closer to the true chemical structure could be retrieved after the ion beam sputtering. Fig. 3 compares the surface topography of the Si (001) surface after sputtering. The surface roughness introduced by the ion beam is 0.4420, 2.5776, and 2.6267 nm RMS for sputtering with  $Ar^+$ ,  $C_{60}^+$ , and mixed ions, respectively. The lamellar features are induced because the ion beam is coming from a fixed direction relative to the surface. In Fig. 3c, an additional fine lamellar structure can be observed with a 33° rotation with respect to the main structure. As this angle is consistent with the geometry arrangement of two ion guns, this additional secondary structure is due to the Ar<sup>+</sup> beam. It is clear that the  $C_{60}^+$  ion beams induced larger grains (~42 nm) compared to the Ar<sup>+</sup> (~16 nm) and the surface roughness was dramatically increased. This ion beam-induced surface roughness will ultimately determine the depth resolution of the  $C_{60}^+$  ion beams profiling.

### 4. Conclusion

In situ cluster ion beam sputtering is a promising technique for depth profiling solid specimens in XPS, AES, and SIMS. By studying the ion beam-induced damage in Si (0 0 1) surface after 0.2 kV Ar<sup>+</sup>, 10 kV C<sub>60</sub><sup>+</sup>, and mixed Ar<sup>+</sup>-C<sub>60</sub><sup>+</sup> sputtering, it is found that the thickness of the damage layer is thinner with cluster ion beams. However, the RMS topography of the sample after C<sub>60</sub><sup>+</sup> sputtering is about  $6 \times$  greater than after Ar<sup>+</sup> sputtering. Ultimately, this topography will limit the depth resolution of the depth profile by causing interface mixing and interface broadening.

Because the damage inside the surface caused by monoatomic ion beams will be more noticeable in soft materials, the results partly explain the successful depth profiling of organic thin films that generally have thicker escape depth for low energy photoelectrons using cluster ion beams. Nevertheless, for densely packed inorganic materials, the significant surface roughness generated by the cluster ion beams becomes the limiting factor of the successful profiling.

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