Atomic Layer Deposition (ALD) of ZrO$_2$ in Ultrahigh Vacuum (UHV)

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The atomic layer deposition (ALD) of ZrO$_2$ was conducted in ultrahigh vacuum (UHV) conditions. The surface was exposed to ZrCl$_4$ and H$_2$O in sequence and the surface species produced after each step were identified in situ with X-ray photoelectron spectroscopy (XPS). ZrCl$_4$ is molecularly adsorbed at 140 K on the SiO$_2$/Si(111) surface covered with OH groups. When the surface is heated to 300 K, ZrCl$_4$ loses two Cl atoms to produce ZrCl$_2$ species. Remaining Cl atoms of ZrCl$_2$ species can be completely removed by exposing the surface to H$_2$O at 300 K followed by heating to 600 K. The layer-by-layer deposition of ZrO$_2$ was successfully accomplished by repeated cycles of ZrCl$_4$ dosing and H$_2$O treatment.

**Key Words:** ZrO$_2$, ALD, UHV, XPS

**Introduction**

Atomic layer deposition (ALD) is a thin-film deposition method. In the ALD process, gaseous precursors are successively introduced to the substrate surface in a repeated cycle.$^{1-6}$ In an ideal ALD process, the surface becomes saturated with reactant molecules when the surface is exposed to one precursor, so that only one monolayer is formed per each cycle. Because the film grows by self-limiting reactions of precursors in each cycle, the surface chemistry of precursor molecules on the substrate surface is important to elucidate the growth mechanism and optimize the growth condition.

Zirconium oxide (ZrO$_2$) has attracted a lot of interest in the microelectronics industry as an alternative high-permittivity (high-k) material to replace SiO$_2$ for a gate dielectric.$^{7,12}$ The ZrO$_2$ thin films have been successfully grown by ALD methods using ZrCl$_4$ for the metal precursor and H$_2$O or H$_2$O$_2$ for the oxygen source.$^{13,14}$

In the atomic layer deposition of ZrO$_2$, the film is generally prepared by repeated cycles of ZrCl$_4$ dosing-N$_2$ purge-H$_2$O dosing-N$_2$ purge sequence. The typical deposition temperature is 500-700 K and the pressure of precursor gases is 1-5 torr. The overall reaction is as follows.

$$\text{ZrCl}_4(g) + 2 \text{H}_2\text{O}(g) \rightarrow \text{ZrO}_2(s) + 4 \text{HCl}(g) \quad (1)$$

The reaction is completed by two steps. In the first step, ZrCl$_4$ reacts with the OH groups on the surface. A ZrCl$_3$ species is formed on the surface by liberating HCl.

$$\text{S-Zr-OH(ad)} + \text{ZrCl}_4(g) \rightarrow \text{S-Zr-O-ZrCl}_4(ad) + \text{HCl}(g) \quad (2)$$

where, S-Zr-X is the surface-bound species.

In the second step, H$_2$O reacts with ZnCl$_3$ species on the surface to substitute Cl with OH on the surface.

$$\text{S-Zr-Cl(ad)} + \text{H}_2\text{O}(g) \rightarrow \text{S-Zr-OH(ad)} + \text{HCl}(g) \quad (3)$$

The ZrO$_2$ thin layer is formed by repeating reactions (2) and (3).

The atomic layer deposition (ALD) of ZrO$_2$ using ZrCl$_4$ and H$_2$O is straightforward. However, most studies have been focused on the ALD conditions such as gas pressures and substrate temperatures, characterization of thin films, and some theoretical modeling. We have grown ZrO$_2$ thin films on Si(111) in ultrahigh vacuum (UHV) conditions to identify chemical species on the surface after the exposure of each reaction gases. The surface was investigated in situ using X-ray photoelectron spectroscopy (XPS) and the surface species, which were produced at each step, were successfully characterized.

**Experimental Methods**

All of experiments reported here were carried out in an ultrahigh vacuum chamber (UHV) whose base pressure was lower than $2 \times 10^{-10}$ torr. X-ray photoelectron spectra were recorded using a non-monochromatic 300 W Mg K$_\alpha$ X-ray source and a 100 mm radius hemispherical analyzer (model VG Cram2).

The Si(111) sample was mounted using Ta foils and clips. The Ta foil was sandwiched with two pieces of Si samples and fixed with Ta clips. The Si sample was indirectly heated by heating the Ta foil resistively. The Si(111) sample was cleaned by heating up to 1200 K followed by gradual cooling in UHV. This cycle was repeated until the clear ($7 \times 7$) LEED pattern was obtained.

The SiO$_2$ surface covered with OH groups was prepared as follows (Figure 1).$^{15}$ (a) The Si(111) surface was heated at 1090 K for 30 minutes in $1.0 \times 10^{-4}$ torr of oxygen to produce the SiO$_2$ layer on Si(111). (b) The SiO$_2$/Si(111) surface was exposed to 80 L of H$_2$O at 140 K. A physisorbed H$_2$O layer is formed at this temperature. (c) The SiO$_2$/Si(111) surface covered with physisorbed H$_2$O was heated to 500 K. H$_2$O is decomposed at this temperature and OH groups are produced.

ZrCl$_4$ was purchased from Sigma-Aldrich. ZrCl$_4$ and H$_2$O were introduced into the chamber using precision leak valves.
Results and Discussion

The OH-covered SiO$_2$/Si(111) surface was exposed to ZrCl$_4$ and the surface reaction was investigated with X-ray photoelectron spectroscopy (XPS). Figure 2 shows the XPS features of the OH/SiO$_2$/Si(111) surface covered with ZrCl$_4$. The surface was prepared by exposing the OH/SiO$_2$/Si(111) surface to 100 L of ZrCl$_4$ at 140 K. Two peaks at 184.0 eV and 185.5 eV correspond to Zr 3d$_{5/2}$ and 3d$_{3/2}$ features, respectively. The peak at 199.6 eV is the Cl 2p$_{3/2}$ feature. The Cl 2p$_{1/2}$ feature is not well-resolved but shown as a shoulder feature.

The area of the XPS peak is proportional to the amount of the element on the surface, regardless of the chemical state of the element. The peak-area ratio of Zr 3d to Cl 2p is 1:2. The XPS sensitivity factor for Zr 3d is 1.11 and that for Cl 2p is 2.22. The peak ratio of Zr 3d to Cl 2p becomes 1:4 after calibration using sensitivity factors. This observation indicates that the stoichiometry of zirconium chloride adsorbed on the OH/SiO$_2$/Si(111) surface is ZrCl$_4$. Zirconium chloride is molecularly adsorbed at this temperature.

The surface covered with ZrCl$_4$ was heated and the change of the XPS feature was investigated. As the surface temperature increases, the peak intensities of both Zr 3d and Cl 2p decrease. This is due to the desorption of multilayer ZrCl$_4$ as the surface temperature increases up to 250 K. While the peak ratio of Zr 3d to Cl 2p remains unchanged up to 250 K, the relative ratio of Cl 2p decreases as the surface temperature becomes higher than 250 K. When the surface temperature reaches 300 K, the intensity attenuation of the Cl 2p peak is much greater than that of the Zr 3d peak. At 300 K, the peak-area ratio of Zr 3d to Cl 2p becomes 1:2 (calibrated ratio). This result clearly shows that ZrCl$_4$ is decomposed on the OH/SiO$_2$/Si(111) surface and two Cl atoms per one ZrCl$_4$ molecule are desorbed from the surface.

While the XPS peak area of Zr decreases, the binding energy of Zr 3d does not change. The constant binding energy of Zr indicates that the oxidation state of Zr does not change when it loses two Cl atoms. The only possible reaction is the substitution of Cl by O on the surface as Scheme 1 shows.

The surface terminated with ZrCl$_2$ was treated with H$_2$O to remove Cl. Some Cl was removed when the surface was exposed to H$_2$O at 300 K. Chlorine was completely removed.
by repeated cycles of H₂O dosing (100-200 L) at 300 K followed by heating to 600 K. The total amount of H₂O exposure was 1800 L. Figure 3(a) is the XP spectrum of the SiO₂/Si(111) surface covered with ZrCl₂ before H₂O treatment. Figure 3(b) was obtained after H₂O treatment. The Cl 2p peak disappears almost completely but the intensity of the Zr 3d peak does not change after H₂O treatment. This observation indicates that Cl is removed from the surface by the following reaction.

$$\text{S-ZrCl}_2(\text{ad}) + 2 \text{H}_2\text{O}(\text{ad}) \rightarrow \text{S-Zr(OH)}_2 + 2 \text{HCl(g)}$$

where, S-ZrX₂ is the surface species bonded to O atoms on the surface. Scheme 2 shows the reaction of H₂O on the surface covered with ZrCl₂ species.

The ZrCl₄ dosing and H₂O treatment cycle was repeated and the change of the surface composition was investigated with XPS. First, 70 L of ZrCl₄ was dosed at 140 K followed by heating to 550 K. After ZrCl₄ dosing, the surface was treated with H₂O as previously mentioned until Cl was not detected by XPS. Figure 4 shows the change of the ratio of the Zr 3d to the Si 2p peak area after each ZrCl₄ dosing and H₂O treatment cycle. The uniform increase of the Zr 3d to Si 2p XPS peak ratio shows layer-by-layer deposition of ZrO₂.

Conclusions

The ZrO₂ thin film was synthesized by dosing ZrCl₄ and H₂O alternatively on Si(111) under UHV conditions as a model study of the ZrO₂ ALD process. The results and main conclusions are as follows:

1. ZrCl₄ was adsorbed on the SiO₂/Si(111) surface covered by OH groups at 140 K. At 300 K, ZrCl₄ lost two Cl atoms to produce ZrCl₂ species on the surface.

2. The surface covered by ZrCl₂ species was treated with H₂O. When the surface was exposed to H₂O at 300 K and then heated to 600 K, chlorine was completely removed.

3. The ZrO₂ thin layer was successfully synthesized by repeating the ZrCl₄ dosing and H₂O treating cycle in UHV.

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References