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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_2O 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_2O 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_2O 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 monlayer 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_2O or H_2O_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_2O 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.

$$ZrCl_4(g) + 2\ H_2O(g) \rightarrow ZrO_2(s) + 4\ HCl(g) \quad (1)$$

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.

$$S\text{-}Zr\text{-}OH(ad) + ZrCl_4(g) \rightarrow S\text{-}Zr\text{-}O\text{-}ZrCl_3(ad) + HCl(g) \quad (2)$$

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

In the second step, H_2O reacts with $ZnCl_x$ species on the surface to substitute Cl with OH on the surface.

$$S\text{-}Zr\text{-}Cl(ad) + H_2O(g) \rightarrow S\text{-}Zr\text{-}OH(ad) + HCl(g) \quad (3)$$

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_2O is strait forward. 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 film 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 2×10^{-10} torr. X-ray photoelectron spectra were recorded using a non-monochromatic 300 W Mg Kα 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 × 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 1.0×10^{-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_2O at 140 K. A physisorbed H_2O layer is formed at this temperature. (c) The SiO_2/Si(111) surface covered with physisorbed H_2O was heated to 500 K. H_2O is decomposed at this temperature and OH groups are produced.

$ZrCl_4$ was purchased from Sigma-Aldrich. $ZrCl_4$ and H_2O were introduced into the chamber using precision leak valves.

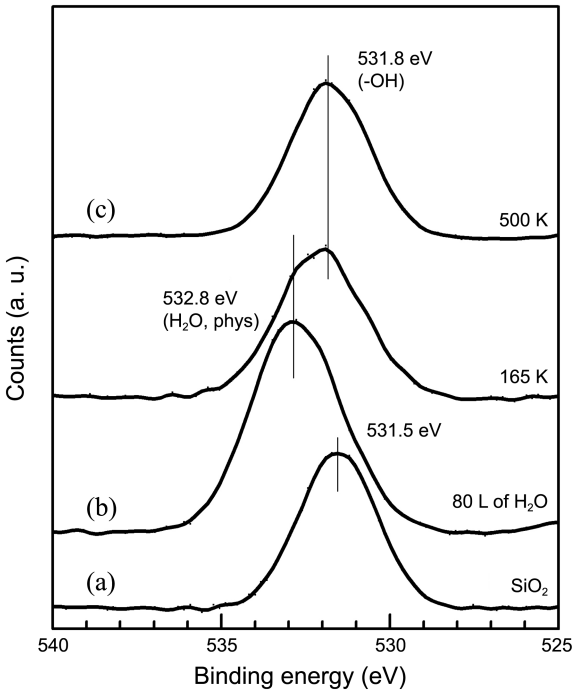


Figure 1. Oxygen 1s XPS features after treating the Si (111) surface with O_2 and H_2O. (a) The Si(111) surface was heated at 1090 K for 30 min in 1.0×10^{-4} torr of O_2. (b) The surface (a) was exposed to 80 L of H_2O at 140 K. (c) The surface (b) was heated to 500 K.

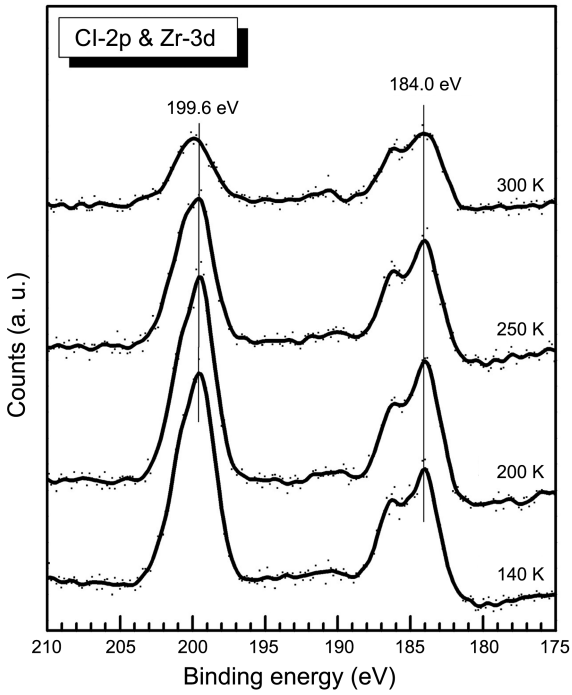


Figure 2. The Cl 2p and Zr 3d XPS features of $ZrCl_4$ adsorbed on the $OH/SiO_2/Si(111)$ surface. The surface was prepared by dosing 100 L of $ZrCl_4$ at 140 K and heated to the indicated temperatures.

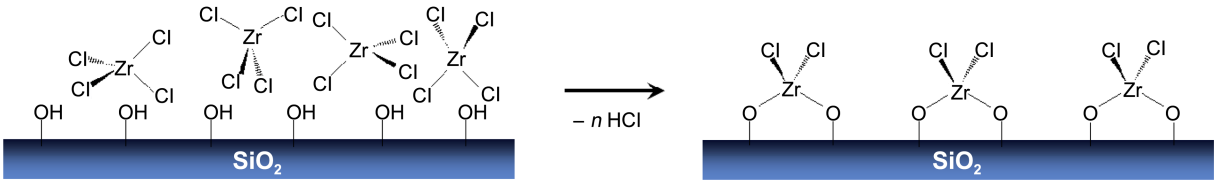
Results and Discussion

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.[16] 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 at 140 K is $ZrCl_4$, and 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_2O to remove Cl. Some Cl was removed when the surface was exposed to H_2O at 300 K. Chlorine was completely removed



Scheme 1

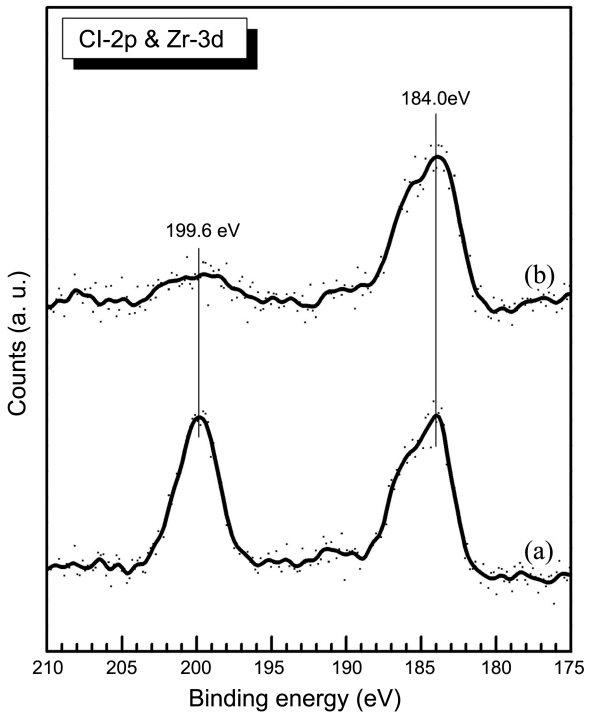


Figure 3. Change of Cl 2p and Zr 3d XPS features of $ZrCl_2$ species produced on the $OH/SiO_2/Si(111)$ surface. The surfaces were prepared as follows: (a) The surface covered with $ZrCl_4$ was heated to 300 K to produce $ZrCl_2$ species. (b) The surface (a) was exposed to H_2O at 300 K followed by heating to 600 K.

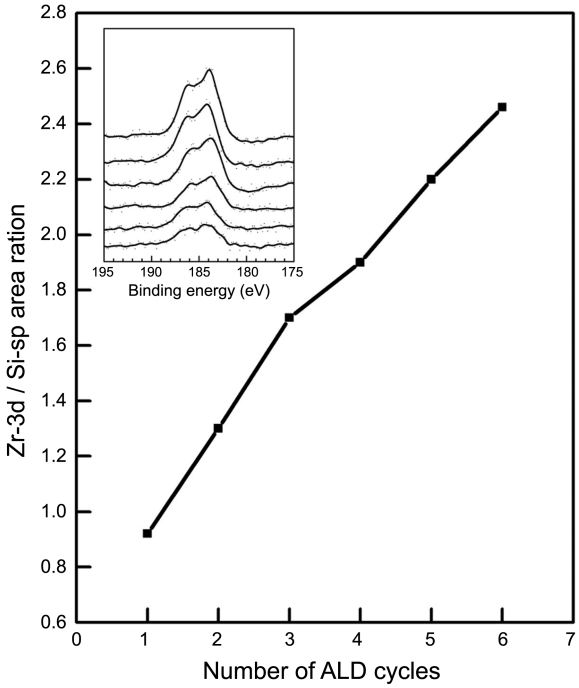


Figure 4. The XPS peak area ratio of Zr 3d to Si 2p. One ALD cycle is completed by $ZrCl_4$ dosing at 140 K, heating to 550 K, H_2O dosing at 300 K, and heating to 600 K. The insert figure shows XPS features of ZrO_2 after each cycle.

by repeated cycles of H_2O dosing (100-200 L) at 300 K followed by heating to 600 K. The total amount of H_2O exposure was 1800 L. Figure 3(a) is the XP spectrum of the $SiO_2/Si(111)$ surface covered with $ZrCl_2$ before H_2O treatment. Figure 3(b) was obtained after H_2O treatment. The Cl 2p peak disappears almost completely but the intensity of the Zr 3d peak does not change after H_2O treatment. This observation indicates that Cl is removed from the surface by the following reaction.

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

where, S-ZrX_2 is the surface species bonded to O atoms on the surface. Scheme 2 shows the reaction of H_2O on the surface covered with $ZrCl_2$ species.

The $ZrCl_4$ dosing and H_2O treatment cycle was repeated and the change of the surface composition was investigated with XPS. First, 70 L of $ZrCl_4$ was dosed at 140 K followed by heating to 550 K. After $ZrCl_4$ dosing, the surface was treated with H_2O 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 $ZrCl_4$ dosing and H_2O treatment cycle. The insert figure in Figure 4 is the XP spectrum after each ALD cycle. The uniform increase of the Zr 3d to Si 2p XPS peak ratio shows layer-by-layer deposition of ZrO_2.

Conclusions

The ZrO_2 thin film was synthesized by dosing $ZrCl_4$ and H_2O alternatively on Si(111) under UHV conditions as a model study of the ZrO_2 ALD process. The results and main conclusions are as follows:

1. $ZrCl_4$ was adsorbed on the $SiO_2/Si(111)$ surface covered by OH groups at 140 K. At 300 K, $ZrCl_4$ lost two Cl atoms to produce $ZrCl_2$ species on the surface.
2. The surface covered by $ZrCl_2$ species was treated with H_2O. When the surface was exposed to H_2O at 300 K and then heated to 600 K, chlorine was completely removed.
3. The ZrO_2 thin layer was successfully synthesized by repeating the $ZrCl_4$ dosing and H_2O treating cycle in UHV.

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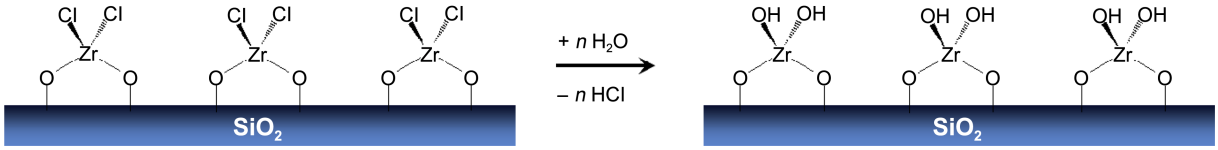

Scheme 2

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