Formation of Artificially Controlled Zirconium–Hafnium Multilayers on a Solid Surface by Use of Metal–Ligand Bonds

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Films of alternately layered zirconium and hafnium phosphonates have been prepared on a silicon substrate by immersing a silicon wafer, modified with an anchoring agent [$OHSiMe_2$–$(CH_2)_3PO_3H_2$ 1], into aqueous solutions in the following order: $ZrOCl_2$, $H_2O_3P(CH_2)_{10}PO_3H_2$ (DBPA), $HfOCl_2$, DBPA, $ZrOCl_2$.

We report the formation of a film of alternate layers of zirconium and hafnium phosphonates on a solid surface. The formation of the layers is confirmed by the angle dependence of the observed X-ray photoelecton spectra (XPS). This is an application of the method recently reported by Lee et al. for bimetallic systems.[1,2]

We used a single-crystal silicon wafer as a substrate. 3-(Hydroxydimethylsilyl)propylphosphonic acid 1 was used as an anchoring agent and 1,10-decanediylbis(phosphonic acid) (DBPA) as a bridging agent between two different kinds of metal ions (Fig. 1). A silicon wafer was washed with trichloroethylene for 5 min, with propan-2-ol for 10 min and finally with distilled water for 20 min before use. Compound 1 and DBPA were synthesized according to the literature.[2] These agents were diluted to about 5 mmol dm^{-3} aqueous solutions. Metal ions were provided as 5 mmol dm^{-3} aqueous solutions of zirconyl chloride octahydrate or hafnyl chloride octahydrate (reagent grade). Anchoring was performed by immersing a silicon wafer for 4 months in a solution of 1 at pH 7. Subsequently the wafer was immersed for 30–60 min for binding metal ions or a bridging agent. The binding energies shown in photoelectron spectra were corrected so that the peak position of the single-crystal silicon 2p line was set at 99.15 eV as standard. We used Mg–Kα (1253.6 eV) radiation as the X-ray source.

Fig. 2 shows the photoelectron spectra when the silicon substrates, anchored as described above, were immersed firstly in a solution of Zr ions and then in a solution of DBPA and lastly in a solution of Hf ions. The film is denoted by Si–$(Zr-Hf)_n$ (n = 1). In Fig. 2, the spectra are shown as obtained at various take-off angles, α, between the surface
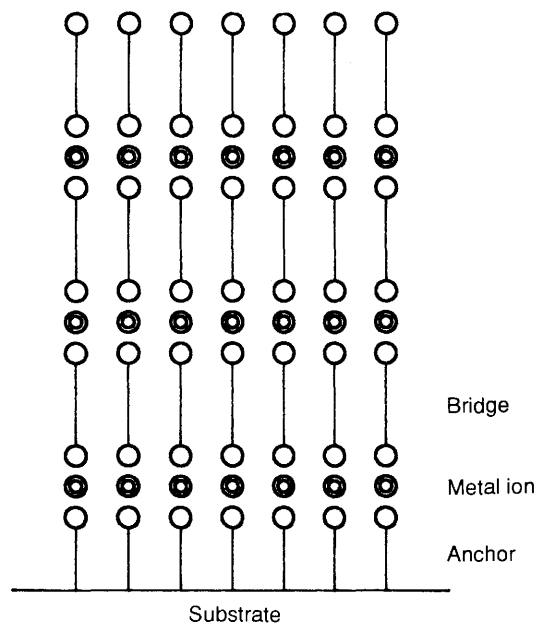
normal and the detector. As the take-off angle increases, the contribution to the observed XPS peaks of the electrons emitted from the deeper part decreases. As shown in Fig. 2, the Si 2s (153 eV) decreases as α increases until it disappears at α = 70.0°. This shows that the silicon wafer is covered completely with the layer, leaving no uncoated areas on the surface. The P 2s peak (191 eV) intensity is independent of the change of the take-off angle. This implies that the phosphorus atoms contributing to the peak intensity come from the ligand

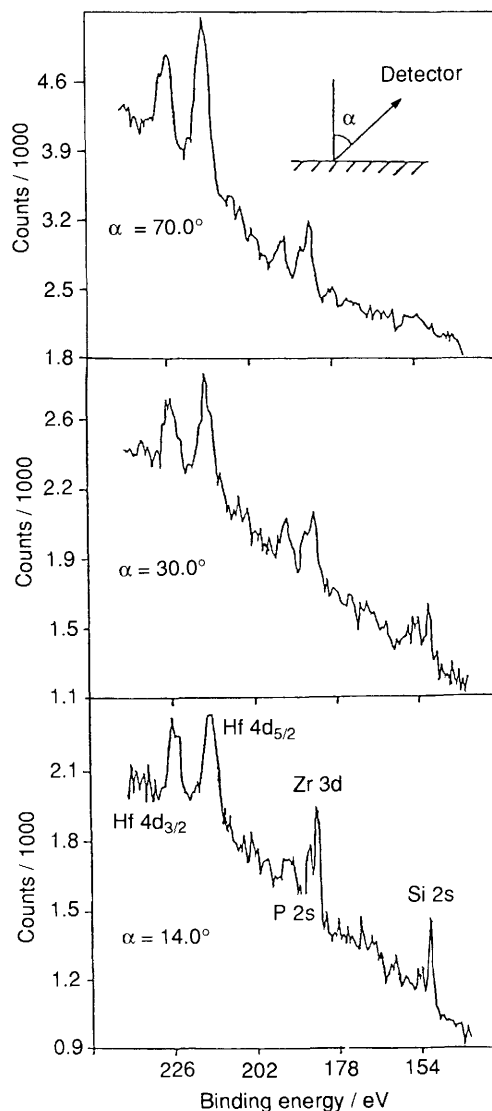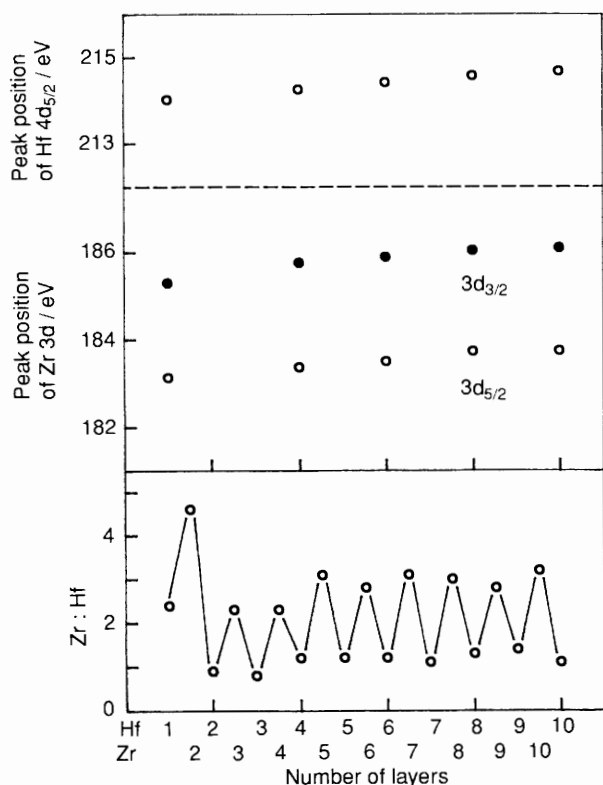Fig. 1 Scheme for the metal ion multilayers on a solid substrate

Fig. 2 The XPS spectra of the Zr–Hf multilayers formed on a silicon substrate at various take-off angles. The horizontal axis is the binding energy (eV) corrected to the Si 2p electrons (99.15 eV). The take-off angle, α, is 70.0° (upper), 30.0° (middle) and 14.0° (lower), respectively.

Fig. 3 The dependences of the peak positions of Hf(4$d_{5/2}$) (upper), Zr(3d) (middle) and the relative intensity of Zr(3d) to Hf(4$d_{5/2}$) on the number of layers. Here the number of layers denotes the number of the unit sequence of Zr, Hf and a bridging agent included in the film.

part of DBPA coordinating Hf ions. The Zr 3d electrons show two peaks: the lower one at 183 eV is assigned to 3$d_{5/2}$ and the higher one at 185 eV is to 3$d_{3/2}$. The relative intensity of the peaks due to Hf 4$d_{5/2}$ (214 eV) against the peak due to Zr 3$d_{5/2}$

and 3$d_{3/2}$ increases as α increases. These results strongly support the view that the phosphonate film present has a bilayer structure with the Hf layer over the Zr layer on the surface.

The multilayers, Si–(Zr–Hf)$_n$ ($n = 2$–10), were prepared by the repeated deposition of DBPA, Zr, DBPA and Hf in this order over the thin film prepared as above. The lower part of Fig. 3 shows the change of the ratio of the intensity of the peak due to Zr 3$d_{5/2, 3/2}$ to that due to Hf 4$d_{5/2}$ as a function of the number of layers, n. From the Zr third layer to the Hf tenth layer, the relative intensity exhibits a periodic change, supporting the view that the multilayers are built up exactly in a layer-by-layer way with no occurrence of collapse. The relative intensity takes a higher value from the Hf first layer to the Zr second layer. This is ascribed to the contribution of the electrons from the first Zr layer that are reflected elastically at the interface of the film and the substrate. Such an effect is negligible for other layers, since the electrons have to travel too far to reach the substrate surface.

The upper part of Fig. 3 shows the shift of the peak positions with the increase of the film thickness. All of the peaks are displaced to a higher binding energy with the increase in the number of deposited layers. One of the possible reasons for the shift is that the charging of the layers takes place during the XPS measurements. This is consistent with the fact that the slopes of the shifts against the number of layers, n, are almost equal for the three peaks.

The present results have confirmed that the alternative multilayers of Zr and Hf ions are formed by utilizing the metal–ligand bonding. This methodology may be applied to other kinds of metal ions and bridging ligands.

References

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