Oxidation of Pd–Al(111) Epitaxial Films in Ultra-High Vacuum

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Epitaxial Pd–Al alloy films were grown on α-Al2O3(0001) substrates by sputter-deposition. The composition of the films was approximately Pd0.5Al0.5. The films were completely oriented with (111) plane parallel to the surface without any trace of other intermetallic compounds. The oxidation behavior of the films in ultra-high vacuum at elevated temperature was studied. It was revealed that only aluminum was oxidized and the growth of alumina film stopped quickly at 0.5 nm in thickness. There were some indications that the alumina film was crystalline.

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1. Introduction

Growth of ultra-thin alumina films has attracted attention in the fields of catalysis, electronics, and more recently, spintronics. In the case of epitaxial growth, lattice matching is one of the most important factors. The NiAl(110) is a well-known substrate for the well-ordered two dimensional flat alumina.1) For this reason some researches have investigated similar intermetallic compounds such as CoAl2) and FeAl3) for substrate use. Those compounds have a body-centered cubic structure and do not have a plane with hexagonal symmetry, whereas alumina films on those substrates exhibited quasi-hexagonal symmetry derived from the arrangement of oxygen atoms. These observations led to the idea of growing alumina films on surfaces with hexagonal symmetry; i.e. (111) plane of fcc (face centered cubic) metals or (0001) plane of hcp (hexagonally closed pack) metals such as Ru4) and Re.5) In such experiments, metallic aluminum was deposited onto these metals and was oxidized later.

It is known that in the case of alumina growth on MAI(110) (M = Ni, Co and Fe), oxygen-induced aluminum segregation is involved in the growth process. However, up to the present there were no reports on the similar mechanism alumina growth on the fcc or hcp metals. We have studied the growth of alumina on the Cu–Al(111) alloy single crystal for the first time and have been successful in forming well-ordered high quality thin films.6–8) We have chosen Cu–Al alloy for the reason of its high electric conductivity. It should be noted that the lattice parameters of the Cu–Al alloy and alumina do not match well. Therefore, we had to search for a possible Al-containing alloy with fcc or hcp structure whose lattice parameter matches better with alumina. Interatomic distances of various fcc or hcp metals are compared with that of Al2O3 in Table 1. For Al2O3, oxygen-oxygen distance is listed in the table because hexagonal oxygen sublattice dominates the crystal structures in ultra-thin alumina films. Although α-Al2O3 is the most stable phase as a bulk, γ-type Al2O3 is mostly grown in ultra-thin film forms. From the table, either Pd or Pt will match γ-Al2O3 lattice. In the present study, we report the oxidation of Pd–Al alloy.

Oxidation of Pd–Al alloy is also interesting because small clusters of Pd on alumina were extensively studied in the field of catalysis, where the oxidation and reduction of Pd play a major role. In the effort to reduce CO dissociation temperature, bimetallic clusters including Pd have been studied. Interaction of Pd and Al has also been studied from the viewpoint of valence band design for catalytic reactions.13)

2. Experiments

The specimens were prepared by cosputtering of Pd and Al onto α-Al2O3(0001) substrates. The multifaceted sputtering target used for deposition of the alloy films was composed of Pd with small Al sheets attached to its surface. Figure 1 shows the photograph of the target. The fraction of the area that belongs to the Al sheets was determined from the desired chemical composition of the alloy and the sputtering ratio of Pd to Al. The sputtering yields of Pd and Al are 1.6 and 0.9 for 500 eV Ar ion sputtering. Approximate area ratio in the erosion region is 3 (Pd) to 1 (Al). Films were deposited by r.f. magnetron sputtering method with 100 W for 20 min. at ambient temperature under 0.53 Pa Ar. The film thickness determined by a stylus profiler was 2–2.5 μm. X-ray diffraction and EDX were used to characterize the films.

The specimens were introduced to an ultra-high vacuum (UHV) chamber equipped with the X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction

| Table 1 The list of crystallographic information. |
|---|---|---|---|
| metal | M–M distance in a plane with hexagonal symmetry | solution limit (at Al%) | crystal structure |
| Al | 0.2864 | — | fcc |
| Ni | 0.2492 | 21 | fcc |
| Cu | 0.2556 | 19 | fcc |
| Zn | 0.2665 | 3 | hcp |
| Ru | 0.2650 | 3 | hcp |
| Rh | 0.2690 | no | fcc |
| Pd | 0.2751 | 20 | fcc |
| Ag | 0.2889 | 20 | fcc |
| Re | 0.2741 | 3 | hcp |
| Os | 0.2675 | not available | hcp |
| Ir | 0.2715 | 18 | fcc |
| Pt | 0.2775 | 15 | fcc |
| Au | 0.2884 | 16 | fcc |
| α-Al2O3 | 0.275(1) | — | corundum |
| γ-Al2O3 | 0.280(2) | — | spinel |
(LEED) instruments. Monochromatized Al Kα radiation was used for XPS measurement. The take-off angle of photoelectrons was 45 degrees. The sensitivity factors, 5.637 for Pd 3d and 0.256 for Al 2p, were used to calculate surface composition.

3. Results and Discussions

The EDX measurements showed that the atomic concentration of Al in the specimen was about 20%. This is almost the solid solution limit in the bulk phase diagram. The results of X-ray diffraction are shown in Fig. 2. The comparison of diffraction from the Pd–Al alloy specimen with that from polycrystalline Pd revealed that the Pd–Al alloy film was epitaxially grown with (111) plane parallel to the surface and there was no detectable amount of other intermetallic compounds. The inter-plane distance calculated from this result is 2.24 nm while the inter-plane distance of bulk Pd and bulk Al are 2.25 and 2.34 nm, respectively. Since the inter-plane distance in bulk Al is larger than that in bulk Pd, one could expect that the inter-plane distance in the Pd–Al alloy should be between the two. However, the inter-plane distance in the Pd–Al alloy film was slightly shorter than that in the bulk Pd. It is known that in the films prepared by sputter-deposition the inter-plane distance parallel to the surface becomes smaller. In such cases, lattice parameters perpendicular to the surface are often expanded.

The epitaxial Pd–Al(111) film was introduced to the UHV chamber and sputter cleaned. Then the specimen was heated up to approximately 1000 K and oxygen was introduced with the partial pressure of $6.7 \times 10^{-6}$ Pa while the specimen was kept at this temperature. We chose 1000 K because it is the optimum temperature for the analogous process during the high temperature oxidation of NiAl(110). Figure 3 shows the evolution of the wide range XPS spectra of the specimen during oxidation. The surface concentration of Al calculated from the peak intensity ratios from Pd 3d and Al 2p for clean surface was about 20 at%. It suggests that the surface composition was almost same as in the bulk. Although O 1s peak overlaps with Pd 3p peak, the oxygen uptake can be observed by the increase of the O KLL Auger peak intensity. After the oxidation, the intensity of the Pd signal had decreased and that of Al 2p had increased.

Figure 4 shows XPS spectra of Pd 3d and Al 2p after the oxidation measured at the take off angle of 45 degrees. The Pd 3d spectra from a clean polycrystalline Pd, and partially oxidized Pd, as well as the Al 2p spectrum of polycrystalline Al with native oxide are also shown in the figure as references. It can be seen that Pd is not oxidized and there is a small binding energy shift by alloying with Al. The peak of Al (3+) from alumina is observed, its binding energy is lower than that of the native oxide on polycrystalline Al. From the figure it is clear that only Al was oxidized. Due to the partial overlap of the Al (0) peak with the Al (3+) signal,
it is difficult to detect a small chemical shift which could be introduced by alloying. Since the peak ratio of Al (3+) to Al (0) is higher for 15 degrees take off angle measurement (not shown in the figure), alumina existed on the surface.

The thickness of alumina \( d \) was calculated from the peak ratio of Al (3+) to Al (0) under take-off angle of 45 degrees using the following equation.

\[
d = \frac{I_{\text{Al}}^{2p}}{C_1 \sin \theta / C_2} \times \ln \left( \frac{I_{\text{Pd-Al}}^{2p}}{C_2} \times \frac{I_{\text{Al}}^{2p}}{C_1} + 1 \right),
\]

where \( I_{\text{Al}}^{2p} \) and \( I_{\text{Pd-Al}}^{2p} \) are the Al 2p intensity from alumina (Al (3+)) and Pd–Al alloy (Al (0)). The effective attenuation length of Al 2p photoelectron (kinetic energy of ca. 1400 eV) in \( \text{Al}_2\text{O}_3 \), \( \lambda_{\text{Al}_2\text{O}_3}^{2p} \) is 2.83 nm, that in Pd–Al alloy, \( \lambda_{\text{Pd-Al}}^{2p} \) is 1.45 nm.\(^{15}\) \( N_{\text{Al}}^{\text{Al}_2\text{O}_3} \) and \( N_{\text{Al}}^{\text{Pd-Al}} \) are atomic densities of Al in Pd–Al alloy and in \( \text{Al}_2\text{O}_3 \). They are equal to \( 1.40 \times 10^{22} \text{ cm}^{-3} \) and \( 4.69 \times 10^{22} \text{ cm}^{-3} \) respectively. \( \theta \) is a take-off angle of photoelectrons. The estimated thickness of the alumina film after 5100 L oxygen exposure is approximately 0.5 nm.

Oxidation process had stopped very quickly and there was no increase of the alumina thickness. This behavior is quite different from that observed from the Pd clusters deposited onto 0.5 nm-thick alumina film on NiAl(110).\(^{16}\) When Pd clusters on 0.5 nm alumina/NiAl(110) were heated under \( 1.3 \times 10^{-6} \text{ Pa} \) of oxygen, Pd dissociated an oxygen molecule, and oxygen atom penetrated into the substrate causing increase of the alumina thickness as well as destruction of the crystal structure of the initial alumina. It is suggested that oxygen atoms migrate through defects in 0.5 nm alumina, reach alumina/NiAl(110) interface and oxidize Al in NiAl. In our experiments on the oxidation of Pd–Al alloys, no further oxidation occurred. This suggests that oxidation was dominated by the oxygen-induced Al segregation and the surface was completely covered with alumina, leaving no chance for Pd atoms to remain on the surface as clusters.

Figure 5 shows LEED patterns of the oxidized Pd–Al alloy film at the primary electron energy of 136, 119 and 59 eV. In all patterns, some streaky lines were observed. The line-to-line distance indicated in the figure increases with decreasing primary electron energy, suggesting that those lines belong to alumina, and are not due to any artifacts. Although patterns are not clear, we can see that alumina has some long-range order and is not amorphous. In most cases of high temperature oxidation under relatively low oxygen partial pressures,
crystalline alumina films have been obtained even though lattice parameters do not match. As it was shown in our previous studies, the precise control of oxidation temperature and oxygen partial pressure is very important for the growth of well-ordered alumina thin film. Therefore, there is a possibility that a well-ordered alumina film could be obtained by optimizing oxidation condition.

4. Conclusion

An epitaxial Pd–Al alloy film was sputter-deposited on a $\alpha$-Al$_2$O$_3$ (0001) substrate using a multifaceted Pd–Al target. The desirable composition of the alloy was achieved by controlling the relative erosion areas of Al and Pd with the sputtering yields of Al and Pd being taken into consideration. By oxidizing this alloy film in ultra-high vacuum at 1000 K under oxygen partial pressure of $6 \times 10^{-6}$ Pa, crystalline alumina film was formed without any subsequent annealing. Oxygen uptake occurred at the very beginning of the oxidation and then quickly saturated. The thickness of alumina calculated from XSP peak intensity after 5100 L oxygen exposure was 0.5 nm. The oxidation behavior was quite different from Pd clusters on well-ordered 0.5 nm-thick alumina films, where Pd works as an oxidation catalyst and the thickening of alumina film occurs. It is concluded that the oxygen-induced Al segregation dominated oxidation of the alloy, and alumina film had completely covered the surface of the specimen blocking Pd from oxygen.

REFERENCES