Single crystalline epitaxial platinum film on Al₂O₃(0001) prepared by oxygen-doped sputtering deposition

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Abstract

We have deposited platinum by inductively coupled plasma-assisted radio frequency sputtering on an Al₂O₃(0001) substrate annealed at approximately 700 °C with and without oxygen blend. The surface morphology and crystallinity of the obtained Pt films with a thickness of approximately 200 nm were subjected to atomic force microscope (AFM) and X-ray diffraction (XRD) investigations. Without oxygen being introduced during the sputtering process, a (111)-oriented polycrystalline film was obtained. The introduction of oxygen led to the generation of twin single crystalline epitaxial Pt(111) films with a typical fcc(111) surface morphology of hexagonal symmetry.

Platinum (Pt) is well known for its superior physicochemical properties such as low resistivity, high thermal stability, and high stability in oxygen environments at high temperatures. A wide variety of applications utilize Pt in one form or another, from the manufacture of ornaments to its use as a catalyst. The major drawback in utilizing Pt is related to its high cost due to its rarity. Consequently, applications that can utilize Pt as a thin film are more cost-effective. One of the most utilized substrates for Pt films is Al₂O₃(0001) since the lattice mismatching between (111) Pt and (0001) Al₂O₃ is very small (0.9%). Misfit dislocations are rarely observed in Pt(111) films fabricated on Al₂O₃(0001) substrates. In fact, the growth of Pt on Al₂O₃(0001) has been fabricated extensively using various deposition methods such as evaporation, metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), and sputtering. Epitaxial Pt(111) films have also been employed as a buffer (seed) layer material between a perovskite oxide and a single crystal thin film with a thickness of 3 to 15 nm were grown on atomically smooth Al₂O₃(0001) surfaces aimed at the fabrication of optically transparent metal substrates. Al₂O₃ has been utilized for the crystal growth of GaN thin films. In terms of cost, the use of Al₂O₃ is more advantageous than the use of other materials such as yttria-stabilized zirconia (YSZ), MgO, and SrTiO₃. It has recently been reported that atomically flat Pt(111) films with a thickness of 3 to 15 nm were grown on atomically smooth Al₂O₃(0001) single crystal surfaces aimed at the fabrication of optically transparent metal substrates. However, to the best of our knowledge, no report has detailed the growth of a single crystalline epitaxial platinum film with a thickness of a few hundred nanometers on an Al₂O₃(0001) substrate. As shown in our previous paper, we used an inductively coupled plasma-assisted radio frequency (ICP-RF) magnetron sputtering process to synthesize atomically flat Pt(111) single crystal thin films on YSZ(111). When the substrate temperature, for some reason, cannot be sufficiently increased to the pure thermal crystallization temperature, the ions that have been accelerated by ICP play an important role as an alternative to the thermal energy.

By combining ICP-RF sputtering and post annealing, we obtained single crystalline epitaxial films with a root mean square (RMS) roughness smaller than 0.2 nm. This previous result encouraged us to consider the possibility of success-
The surface RMS roughness \( R\) (nm) of each image was calculated and is shown in the upper part of the image. The roughnesses are 0.32 nm [Fig. 1(a)] and 0.24 nm [Fig. 1(b)]. Both values are close to those obtained for an atomically flat substrate such as gold mica (ca. 0.3 nm).\(^{18}\) Single atomic steps can be recognized, especially in the small-area image. However, many peaks and valleys are visible in the large area image, and there appears to be almost no indication of the fcc(111)-like morphology of the facets of hexagonal symmetry in either image. Although the roughness may be comparable to that of commercially available gold mica, which is well known for its atomically flat deposited epitaxial metal film,\(^{18}\) the surface morphology differs from that of the typical fcc(111) of facets with hexagonal symmetry.

In an effort to investigate the crystallinity of this Pt film, XRD data were measured under atmospheric conditions at room temperature as shown in Fig. 2. We performed \( \theta/2\theta \) scans around the 111 peak of platinum [Fig. 2(a)], \( \phi \) scans of the (220) peaks [Fig. 2(b)], and \( \phi \) scans of the (111) peaks at \( \chi = 70.5^\circ \) [Fig. 2(c)]. Pt films on Al\(_2\)O\(_3\)(0001) produced by ICP-RF sputtering without oxygen being introduced and annealed at \( \sim 700^\circ \)C were found to comprise (111)-oriented structures, as shown in Fig. 2(a) by a broken line. Note that the 111 peak consisting of two peaks results from the use of the XRD apparatus employing both K\(\alpha_1\) and K\(\alpha_2\) radiations. At the lower part of Fig. 2(b), twelve [220] peaks separated by 30° are observed, indicating that the in-plane orientation is not single. Moreover, at the lower part of Fig. 2(c), the twelve [220] peaks separated by 30° are also observed, although some peaks are barely discernible. From the above XRD data, the Pt films on Al\(_2\)O\(_3\)(0001) produced by ICP-assisted sputtering without oxygen at \( \sim 700^\circ \)C (broken line) were found to comprise (111)-oriented polycrystalline structures. In 1987, Adachi et al. fabricated...
epitaxial Pt(111) films on Al₂O₃(0001) substrates as a buffer (seed) layer for PZT growth by RF sputtering. They determined the optimum content of gas comprising Ar (80%)+O₂ (20%) for [111]-oriented PZT film growth on Pt(111) films on Al₂O₃(0001). Note that the mixing of O₂ with Ar gas for Pt film growth is not clearly described in the literature.

To improve the crystallinity and surface morphology of Pt films, we added O₂ gas without changing other conditions such as the partial pressure of the Ar gas, substrate temperature, RF power, or deposition time. The surface morphologies of Pt films deposited by ICP-RF sputtering with gas contents of Ar (80%)+O₂ (20%) and Ar (67%)+O₂ (33%) were imaged by AFM, as shown in Figs. 1(c) and 1(d) and 1(e) and 1(f), respectively. The surface roughness of both large-area AFM images [Figs. 1(c) and 1(e)] does not differ markedly from that in Fig. 1(a) (sputtered without oxygen gas), although the surface morphology is clearly different. A few steps are bunched together to generate multisteps and extended flat (111) terraces. In fact, the extended flat areas [Figs. 1(d) and 1(f)] have a surface roughness of less than 0.2 nm, and the total roughness of the large area has not been markedly reduced owing to the multisteps. In these images, the height of the multisteps is in the range of 1–2 nm (refer to the color pallet), and the typical width of the extended terraces is ca. 200 nm (refer to the scale bar). Note that the extended terraces possess facets of hexagonal symmetry, showing a typical fcc(111)-like morphology. Gold mica substrates are well known as atomically flat metal substrates commercially available for use in self-assembled monolayer growth and are expected to possess terraces wider than 100 nm. Although individual research scopes vary, we believe that our Pt films have a quality that is almost comparable to that of commercially available gold mica substrates, and their use could be helpful in various research fields.

To investigate the crystallinity of Pt films, XRD data were measured in the same manner as the previous films and are shown in Fig. 2. Both films fabricated by ICP-assisted sputtering with oxygen gas were found to be (111)-oriented films, as shown by dotted (20%) and solid (33%) lines in Fig. 1(a). The upper XRD patterns in Figs. 1(b) and 1(c) only show results of 33%, since the difference between these films is negligible. The in-plane XRD pattern shows six sharp and strong [220] peaks separated by 60°, indicating that the in-plane orientation is single. The q scans of the [111] peaks at $\phi = 70.5^\circ$ [Fig. 2(c) upper] also show six sharp and strong [220] peaks separated by 60°. These XRD results suggest that the films comprise high-quality twin single crystal forms and are in good agreement with the observed AFM images of typical fcc(111)-like surface morphologies [Figs. 1(d) and 1(f)]. Since the film growth conditions were identical except for the oxygen blend during sputtering deposition, we consider that the oxygen blend is responsible for these marked improvements in both crystallinity and surface morphology. Although we do not currently have sufficient evidence to delineate the oxygen effect, we shall briefly refer to one possible explanation that accounts for this effect. Xu et al. reported that epitaxial Pt film growth on SrTiO₃ observed under oxygen plasma is believed to result from the oxygen ashing of S-containing impurities in the Pt target, since sulfur atoms might be absorbed and form nucleation seeds for Pt thin films. It is well known that sputtering targets often contain impurities such as sulfur and carbon at ppm levels, and that plasma ashing (with oxygen) removes organic matter. Moreover, ICP increases the density of plasma. We expect that the introduction of oxygen will result in a chemical reaction between the impurities and oxygen to form volatile vapors during the sputtering process. Thus, we consider that one possible explanation for the observed improvement may involve the oxygen ashing of impurities such as sulfur and carbon.

In conclusion, 200-nm-thick platinum films were deposited by ICP-RF sputtering on Al₂O₃(0001) substrates heated at ca. 700 °C. The surface morphology and crystallinity of the obtained platinum films were measured by AFM and XRD under ambient conditions. Without oxygen being introduced, although Pt films were (111)-oriented, terrace widths were relatively small (ca. 100 nm), and the films were polycrystalline and had a low crystalline quality. The platinum film deposited by ICP-RF sputtering with oxygen gas showed an atomically flat surface morphology, with an rms roughness of ca. 0.4 nm for an area of 8 µm² and smaller than 0.2 nm for an area of 1 µm², and exhibited the fcc(111)-like morphology of the facets with hexagonal symmetry. The XRD measurements revealed that the Pt film comprises a twin single crystal. It is anticipated that future investigations including substrate pretreatment should elucidate the initial film growth mechanism, and may very well eliminate twin formation.

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