Platinum is one of the metals that exhibit excellent physicochemical properties such as a high melting point, resistance to corrosion, and catalytic activity, as well as thermal and electrical conductivities. However, its limited application due to its high price has prompted research regarding its recycling and the use of alternative materials. Considerations of catalysis at the surface or an electrode system suggest the possibility of using a thin film instead of a bulk material in order to reduce the amount of platinum required for an application. A study of the surface chemistry, with the aim of elucidating catalytic or electrode reactions, indicates the necessity of a reproducible preparation to create a well-defined (electrode) surface. In spite of relatively large lattice mismatch (ca. –23%), platinum has been grown epitaxially on yttria-stabilized zirconia (YSZ), and thin films of platinum have been deposited by pulse laser deposition (PLD) or sputtering. It should be noted that Pt/YSZ is an important model system for solid fuel cells. The research group of Beck has conducted an extensive study of platinum film growth on YSZ by PLD deposition. They reported that platinum films on (111) and (100) YSZ are of an epitaxial single-crystalline and polycrystalline forms, respectively. They also reported that "the single crystalline epitaxial films have not been reproduced by other authors up to now". The constraints of applied physics suggest that a relatively inexpensive and highly reliable experimental apparatus is needed, and that sputtering would be more advantageous than PLD. Indeed, sputtering is widely used as a deposition apparatus for the mass production of the magnetic disk, which is a key component of a storage device such as a hard disk. Here, we attempted to grow a single-crystalline epitaxial platinum film on a YSZ substrate using sputtering as the deposition method. Inductively coupled plasma (ICP)-assisted sputtering and postdeposition annealing were applied to optimize the quality of the films in order to obtain an atomically flat well-defined surface that is even suitable for surface chemistry research regarding surface sensitivity. As a result, we have successfully obtained atomically flat Pt(111) film with a root mean square (rms) surface roughness better than 0.2 nm. Bulk mirror-polished and single-crystal YSZ measuring 10 mm square with a thickness of 0.5 mm and orientation of (111) ±0.3° was purchased from Techno Chemics. The YSZ substrates were annealed at 1250 °C for 12 h to obtain a clear step and terrace structure. Platinum films were deposited by rf sputtering in an argon atmosphere. The thickness of the film was 200 nm, except for the "failed sample". Many voids formed when the film thickness was less than 200 nm. We used two types of rf sputtering apparatus: Sanyu Electron SC-701HMC for no substrate temperature control, and ULVAC MB02-5002 for ICP-assisted sputtering with substrate temperature control up to about 700 °C. The ICP power was held constant at 20 W. In the former case for post-deposition annealing, the platinum films were transferred to a vacuum chamber equipped with a custom-made electron beam heating system for annealing at a temperature of 750–850 °C from 30 min to 4 h. All atomic force microscopy (AFM) images were obtained using Pico-Plus AFM (Molecular Imaging) and MFP-3D (Asylum Research) in the AC mode (known as the tapping mode). The software programs used to perform image processing ("Flatten" and "Equalize") were Takeuchi’s Image Filing Software (TIFS: http://www2.big.or.jp/~osamu/TIFS/) and WSxM (http://www.nanotech.es/). The surface roughness (rms) in topographic images was analyzed using WSxM. The X-ray diffraction (XRD) data were measured under atmospheric conditions at room temperature with Rigaku UltimaIV using both Kα1 and Kα2 radiation with 40 kV and 40 mA.

Figure 1 shows a set of AFM images of YSZ(111) after annealing at 1250 °C for 12 h, prior to the platinum deposition. The large- and small-area images clearly show the step and terrace structure. The step height in these images is 0.3 nm, which corresponds to the single step spacing of the YSZ(111) plane. The numerous black (depressed) regions probably originated from flaws that occurred during the polishing process. It should be noted that the step density is a function of the off-angle (misorientation angle), which
depends on the precision of the polishing process performed by the manufacturer.

As mentioned in the introduction, Beck et al. conducted thermal treatment at 750 °C to produce platinum films deposited by pulsed laser deposition on (111)-orientated single-crystalline YSZ with a negligible concentration of grain boundaries. Since there seem to be almost no subsequent studies of single-crystalline epitaxial films of platinum on YSZ(111) made by the metal deposition method of rf sputtering, we first tried annealing platinum film that was rf sputtered on YSZ(111). Figures 2(a) and 2(b) show AFM images of a YSZ(111) substrate with platinum deposited by rf sputtering (without ICP) and postdeposition annealed at 750–800 °C in vacuum for 4 h. The rms roughness values were determined to be (a) 0.55 and (b) 0.42 nm. Although these values are not large and the small-area image [Fig. 2(b)] shows the existence of single atomic steps, the surface structure of the large-area image [Fig. 2(a)] appears inadequate.

For comparison, we deposited platinum with ICP-assisted sputtering on YSZ(111) heated at ca. 700 °C and investigated the surface morphology by AFM, as shown in Figs. 2(c) and 2(d). The roughness values were determined to be 0.59 nm [Fig. 2(c)] and 0.58 nm [Fig. 2(d)]. Although these values are close to those in Figs. 2(a) and 2(b), the overall surface morphology appears to be more like a fish scale than a typical fcc (111) surface, resembling the surface of atomically flat gold mica with a hexagonal symmetry. Each fragment of the observed fish-scale-like structure probably corresponds to a single atomic layer, and the typical diameter appears to be 100 nm or less. A consideration of surface science using scanning probe microscopy suggests that this platinum film may not be well defined and is therefore not suitable for research without a postdeposition treatment process.

To investigate the crystallinity of the platinum films produced in this study, X-ray diffraction (XRD) data were measured under atmospheric conditions at room temperature, as shown in Fig. 3. We performed a θ/2θ scan around the 111 peak of platinum [Fig. 3(a)], θ/2θ scans of the {220} peaks [Fig. 3(b)], and ϕ scans of the [111] peaks at Χ = 70.5° [Fig. 3(c)]. Platinum films deposited at RT, and postdeposition annealed at 750–800 °C (dashed line) and those produced by ICP-assisted sputtering at ~700 °C (bold line) were found to be (111)-oriented films. The main difference can be seen in the ϕ scans of the {220} peaks [Fig. 3(b)]. The platinum film deposited by ICP-assisted rf sputtering showed six sharp {220} peaks separated by 60°. Moreover, this film...
also showed six sharp (220) peaks separated by 60° in Fig. 3(c). These results suggest the film to be a twinned single crystal. On the other hand, the platinum film without ICP showed twelve relatively broad (220) peaks separated by 30° with spurious peaks at 15 and 250°, indicating a polycrystalline film. We regard this poor crystallinity as the main reason for the poor surface morphology of the platinum film deposited without ICP [Figs. 2(a) and 2(b)]. It should be noted that the result obtained for the platinum film without ICP showing a polycrystalline form is not inconsistent with Beck et al.’s report, as mentioned previously.11 We briefly discuss the reason for the poor (fish-scale-type) surface morphology and good crystallinity of the ICP-assisted platinum film. In film growth processes, one of the most important parameters is the substrate temperature, since the substrate temperature determines the diffusion coefficient. When the substrate temperature is raised, for some reason it cannot be sufficiently raised 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.16 Thus ICP enables deposition at a lower substrate temperature owing to the ion-induced crystallization effect. Because of the limited substrate annealing temperature of ICP sputtering used in this study, this effect probably contributed to the better crystallinity, as was clearly revealed by the XRD measurements. However, it is also well known that ICP can etch the surface.16 This will probably contribute to a poor surface morphology, such as the fragmented terraces visualized in the AFM images [Figs. 2(c) and 2(d)].

Since ~700 °C is the maximum heating temperature of the ICP-assisted rf sputtering system used in this study, a higher postdeposition annealing temperature was used ex-situ in vacuum at 800–850 °C. Figures 4(a) and 4(b) show AFM images of a platinum-deposited YSZ(111) substrate subjected to ICP-assisted rf sputtering with substrate heating at ~700 °C and postdeposition annealing at ~800 °C in vacuum for 1 h. The rms roughness values were determined to be 0.18 [Fig. 4(a)] and 0.15 nm [Fig. 4(b)]. The small roughness allowed narrow terraces and a single atomic step (0.23 nm) to be clearly seen in the AFM images. It is evident that the postdeposition annealing process is effective for surface flattening, and these roughness values are close to that of an atomically flat gold mica substrate. However, the observed surface morphology is completely different from that of gold mica. The main feature of the observed AFM images is a one-way terraced structure and an occasional depression with a depth of a few nanometers, as can be seen in the center of Fig. 4(a). Prior to platinum deposition, the surface morphology of YSZ(111) was imaged with AFM (Fig. 1). The bare surface of YSZ(111) also showed a one-way terraced structure and had a depression that may have originated from a polishing flaw. Since the platinum film was epitaxially grown on YSZ(111), we speculate that the off-angle from the (111) plane of the YSZ(111) substrate may be taken over the surface of the Pt(111) epitaxial film.

We further postdeposition annealed this Pt/YSZ sample at ~850 °C for 1 h, as shown in Figs. 4(c) and 4(d). The roughness values were determined to be 0.77 nm [Fig. 4(c)] and 0.39 nm [Fig. 4(d)]. These values are 2 to 4 times larger than those obtained previously (the Pt/YSZ sample postdeposition annealed at 800 °C). Moreover, the surface morphology changed dramatically. Results showed a few to a dozen steps bunched together to form macrosteps, separating wide and extremely flat (111) terraces. Hahn et al. reported the morphology of a vicinal Pt(997) surface, which is misoriented from (111) by 6.5° towards [112].17 They observed that a few steps were bunched together, generating extended flat (111) terraces of nearly double and triple width at 920 K and fully faceted regions on the surface at 1160 K. Since we are working on platinum film deposited on a YSZ(111) substrate with less than ±0.3° disorientation from (111), the data cannot be directly compared. At least the postdeposition annealing temperature in our study is within their range. We therefore consider that postdeposition annealing at 850 °C induced the observed step bunching.

We also applied postdeposition annealing to a failed sample. We deposited platinum at a thickness of about 100 nm (approximately half the thickness in Figs. 2–4) and which was full of voids, as shown in Figs. 5(a) and 5(b). The rms roughness values were determined to be 4.0 [Fig. 5(a)] and 4.8 nm [Fig. 5(b)]. Mainly because of the deep voids, these values are almost one order of magnitude larger than those for an atomically flat surface. We postdeposition annealed this sample in vacuum at 750 °C and observed the subsequent change in morphology a AFM imaging, as shown in Figs. 5(c) and 5(d). The rms roughness values decreased dramatically to 1.4 [Fig. 5(c)] and 0.79 nm [Fig. 5(d)]. The number of voids was considerably reduced. The remaining voids had a shallow bottom with a depth of only a few nanometers, as shown in Fig. 5(c). The overall morphology indicated step bunching and terraces with a width on the order of a few hundred nanometers. It should be noted that the surface appeared to be covered with some contaminant, as seen in Fig. 5(d). This may have been caused by exposure to air during sample transfer and AFM imaging. Since it is well known that such contaminants can be removed by ion
We do not discuss this matter further. We conclude that postdeposition annealing is effective for the production of platinum films as thin as 100 nm, and this process is useful for reducing the amount of platinum utilized in an application.

In conclusion, platinum films with thicknesses of 200 nm were deposited by ICP-assisted sputtering on a YSZ(111) substrate heated at ca. 700 °C. Although XRD measurements revealed that the platinum films have a (111)-oriented twinned single-crystal form, the surface morphology was more like a fish scale than facets showing hexagonal symmetry. Post-annealing in vacuum at 750–850 °C resulted in a drastic change of surface morphology. AFM imaging and data analysis of the platinum film postdeposition annealed at 800 °C revealed an atomically flat surface morphology with an rms roughness better than 0.2 nm. Further postdeposition annealing at 850 °C resulted in larger step bunching. To the best of our knowledge, this work is the first report detailing the fabrication of high-quality platinum films by ICP-assisted sputtering as the deposition method. We hope future investigations will elucidate the film growth mechanism and the postdeposition annealing effect.

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Fig. 5. (Color online) AFM images of platinum film with a thickness of 100 nm deposited by ICP-assisted rf sputtering on YSZ(111) without (a, b) and with postdeposition annealing at 750 °C (c, d). The area size, pixel number, and rms surface roughness \( R \) are, respectively, (a) 8 \( \times \) 8 \( \mu m^2 \), 1024 \( \times \) 1024 pixels, and 4.0 nm, (b) 4 \( \times \) 4 \( \mu m^2 \), 1024 \( \times \) 1024 pixels, and 4.8 nm, (c) 8 \( \times \) 8 \( \mu m^2 \), 1024 \( \times \) 1024 pixels, and 1.4 nm, and (d) 4 \( \times \) 4 \( \mu m^2 \), 1024 \( \times \) 1024 pixels, and 0.79 nm.

1) G. Beck, C. Bachmann, R. Bretzler, and R. Kmeth, Mater. Chem. Phys. 158, 107 (2015).
2) G. Beck, H. Fischer, E. Mutoro, V. Srot, K. Petrikowski, E. Tchernychova, M. Wuttig, M. Ruhle, B. Luersen, and J. Janek, Solid State Ionics 178, 327 (2007).
3) R. G. Musket, W. McLean, C. A. Colmenares, D. M. Makowiecki, and W. J. Siekhaus, Appl. Surf. Sci. 10, 143 (1982).
4) G. Beck and J. Janek, Solid State Ionics 227, 57 (2012).
5) G. Beck and C. Bachmann, Solid State Ionics 262, 508 (2014).
6) E. Mutoro, B. Luersen, S. Gunther, and J. Janek, Solid State Ionics 179, 1214 (2008).
7) A. K. Opitz and J. Fleig, Solid State Ionics 181, 684 (2010).
8) G. Beck, H. Pöpke, B. Luersen, and J. Janek, J. Cryst. Growth 322, 95 (2011).
9) S. Geiss, M. Fischer, M. Schreck, and B. Stritzker, J. Cryst. Growth 311, 3731 (2009).
10) M. Trassin, N. Viart, C. Ulhaq-Bouillet, G. Versini, S. Barre, C. Leuvrey, and G. Pourroy, J. Appl. Phys. 105, 106101 (2009).
11) H. Galinski, T. Ryll, P. Reibisch, L. Schlagenhauf, I. Schenker, and L. J. Gauckler, Acta Mater. 61, 3297 (2013).
12) D. Hesse, S. K. Lee, and U. Giseler, Phys. Status Solidi A 202, 2287 (2005).
13) T. Honke, H. Fujikawa, J. Ohta, and M. Oshima, J. Vac. Sci. Technol. A 22, 2487 (2004).
14) H. Tanaka and M. Taniguchi, Jpn. J. Appl. Phys. 55, 078003 (2016).
15) J. A. DeRose, T. Thundat, L. A. Nagahara, and S. M. Lindsay, Surf. Sci. 256, 102 (1991).
16) N. Kikuchi and E. Kusano, J. Vac. Sci. Technol., Jpn. J. 50, 15 (2007) [in Japanese].
17) E. Hahn, H. Schief, V. Marsico, A. Prticke, and K. Kern, Phys. Rev. Lett. 72, 3378 (1994).