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Micro X-ray diffraction analysis of thin films using grazing-exit conditions

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An X-ray diffraction technique using a hard X-ray microbeam for thin-film analysis has been developed. To optimize the spatial resolution and the surface sensitivity, the X-ray microbeam strikes the sample surface at a large glancing angle while the diffracted X-ray signal is detected with a small (grazing) exit angle. Kirkpatrick–Baez optics developed at the Photon Factory were used, in combination with a multilayer monochromator, for focusing X-rays. The focused beam size was about 10 × 10 μm. X-ray diffraction patterns of Pd, Pt and their layered structure were measured. Using a small exit angle, the signal-to-background ratio was improved due to a shallow escape depth. Under the grazing-exit condition, the refraction effect of diffracted X-rays was observed, indicating the possibility of surface sensitivity.

Keywords: X-ray microbeams; grazing exits; thin films.

1. Introduction

Thin-film materials are widely used in various devices, and an understanding of their crystallographic and structure information is important for the development of their applications. Grazing-incidence X-ray diffraction has been commonly used in surface-structure analysis in recent years (Feidenhans'l, 1989). For polycrystalline thin films the technique using grazing-incidence X-rays and asymmetric Bragg diffraction is also useful for structural analysis (Huang, 1990). Using the grazing-incidence condition, surface sensitivity is enhanced, but it is difficult to make a small area analysis because the incident X-rays irradiate a large area of sample surface.

On the other hand, the grazing-exit condition combined with an X-ray microbeam enables surface-sensitive analysis over a small area. In the case of X-ray fluorescence analysis, the grazing-exit condition was confirmed to be useful for small-area surface analysis (Noma & Iida, 1994). In this paper, the grazing-exit micro X-ray diffraction technique is applied to thin-film characterization with a high spatial resolution.

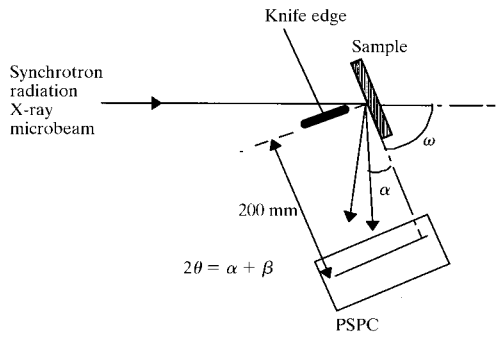

Figure 1
Experimental arrangement for grazing-exit micro X-ray diffraction.

2. Experimental

Fig. 1 shows the experimental arrangement. The experiments were performed at the Photon Factory (PF) on the beamline 4A, to which synchrotron radiation from a bending magnet was delivered. We used a synthetic multilayer to produce monochromatic X-ray beams with high photon flux. For focusing optics, the Kirkpatrick–Baez system was used. A detailed description and the characteristics of the focusing optics has been given by Iida & Noma (1993). The beam size was about 10 μm × 10 μm at the sample position (focusing point) in the present experiment. The X-ray energy used was 8 keV (0.154 nm). The angular divergence of the incident beam to the sample was about 0.5 mrad in both the vertical and horizontal directions. The angular resolution of the present system was determined by the 10^{-2} energy bandwidth, $\Delta E/E$, of the multilayer and is 3.8 mrad at an angle θ of 20°.

The sample was mounted on XZ translation stages, which were mounted on an ω-rotation stage with a vertical rotation axis. The XZ translation stages were used for sample positioning. An optical microscope was used for the alignment of the ω-rotation stage and the sample to the focal point. A position-sensitive proportional counter (PSPC) was placed 200 mm from the sample to detect X-rays scattered from the sample. In this geometry, the diffraction angle (2θ) of X-rays measured by the PSPC is $\omega + \alpha$, where ω is the incidence angle of the primary X-ray beam to the sample surface and α is the exit angle of the diffracted X-rays, as illustrated in Fig. 1.

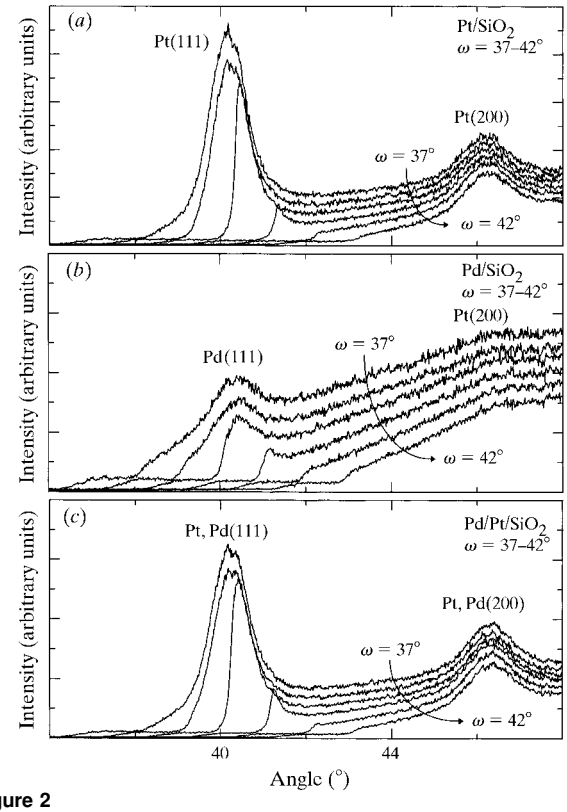

Figure 2
X-ray diffraction patterns at various incidence angles (ω). (*a*) Pt/SiO_2, (*b*) Pd/SiO_2, (*c*) $Pd/Pt/SiO_2$.

Platinum and palladium thin films were prepared as samples. Platinum thin films were deposited on a quartz substrate by electron beam evaporation and patterned by the technique of photolithography. Palladium thin films were formed by spin coating of a palladium complex solution followed by successive processes, including baking and reduction with hydrogen.

3. Results and discussion

A series of X-ray diffraction patterns measured at various incidence angles (ω = 37–42°) is shown in Fig. 2. Each curve corresponds to the X-ray intensity distribution at a fixed ω. Since the abscissa is the diffraction angle of X-rays ($\omega + \alpha$), the exit angle (α) is changed from point to point in each curve. The angle, at which the diffracted X-ray intensity increased abruptly in each curve, corresponds to the critical angle. It was also confirmed experimentally by scanning the patterned samples that the lateral spatial resolution was 12 μm (H) × 10 μm (V). Thus the present microbeam system has sufficient resolution to analyse thin films.

Fig. 2(*a*) shows the data from a Pt film (50 nm thick) on SiO_2. X-ray diffraction peaks of Pt(111) and Pt(200) are clearly observed. Fig. 2(*b*) shows the data from a Pd film (8 nm thick) on SiO_2. Pd(111) is observed while Pd(200) is very weak. Fig. 2(*c*) shows the data from a Pt film (~30 nm) on SiO_2 coated with Pd film (8 nm thick). Since the thickness of the Pd film is thin compared with that of the Pt film and the diffraction peaks of Pd are very close to those of Pt, the diffraction patterns are similar to those in Fig. 2(*a*). As may be seen from each figure, the background intensity increases rapidly with increasing α because the escape depth of the scattered radiation increases with increasing α. It was very hard to distinguish the diffraction peaks from the large background, especially the Pd peaks, with the symmetrical diffraction condition (equal glancing- and exit-angle conditions). It can be seen that the signal-to-background ratio is improved under the grazing-exit condition.

The X-ray diffraction patterns in Fig. 2 should contain crystallographic information on thin films. The measured diffraction profile, however, is deformed by absorption and refraction effects due to the grazing-exit condition. The diffraction curves are a combination of the 2θ-dependent diffraction curve and the α-dependent X-ray transmission curve. It is convenient to convert the measured data to the form in which the diffraction profile at a constant α is a function of 2θ. The 2θ-dependent diffraction curve at the exit angle α_m was obtained by extracting intensity data at $2\theta_n = \omega_n + \alpha_m$ from the diffraction curves for ω_n.

Fig. 3 shows the converted diffraction profiles. Each curve corresponds to constant α; the curve of small α contains surface information alone. It is also seen that the diffraction peak slightly changes its position as a function of α. From the full-width-at-half-maximum analysis, the grain sizes were determined to be 8.6 nm and 7.1 nm for the Pt and Pd films, respectively. In order to analyse the diffraction profile, the diffraction peaks were fitted with Gaussian functions. The Pt(111) peak was fitted with two Gaussian components, while the Pd(111) peak was fitted with a single Gaussian. The component analysis of the diffraction from the Pd/Pt/SiO_2 shows that the Pd peak intensity is about one-third of the Pd peak intensity from the Pd/SiO_2. These peak intensities are modified by the effect of the preferred orientation. The results suggest that the texture of the Pd film on Pt is different from that of the Pd film on SiO_2.

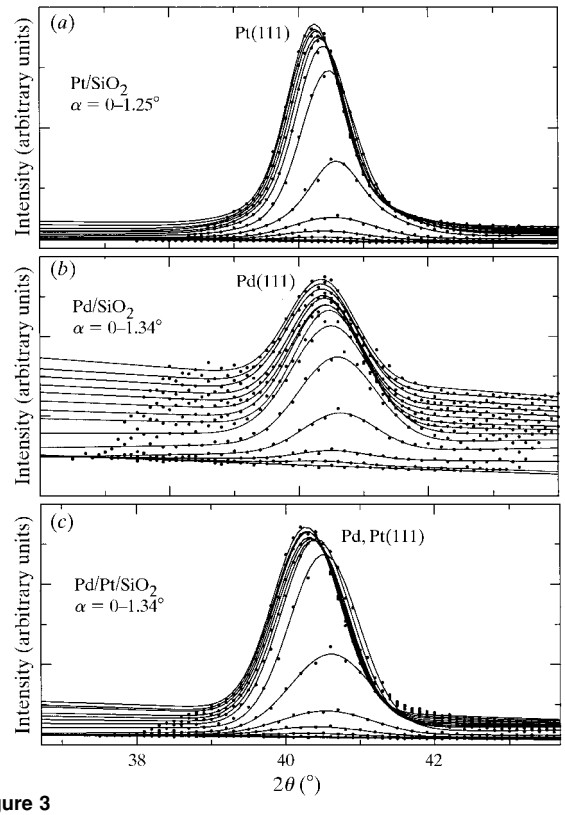

Figure 3
Converted X-ray diffraction curves at various exit angles (α). Each diffraction curve is the diffraction curve at a constant α as a function of 2θ. (*a*) Pt/SiO_2, (*b*) Pd/SiO_2, (*c*) Pd/Pt/SiO_2.

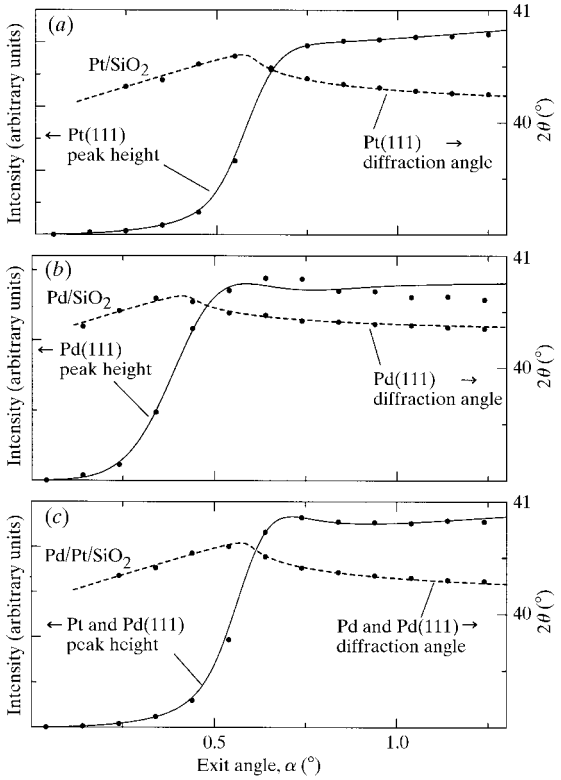

Figure 4
Diffraction peak height and diffraction angle as a function of exit angle. (*a*) Pt/SiO_2, (*b*) Pd/SiO_2, (*c*) Pd/Pt/SiO_2. Full circles: measured data. Solid lines: calculated curves for diffraction peak height. Dashed lines: calculated curves for diffraction angle.

Table 1
Thin-film parameters determined from experiment.

	Thickness (nm)	Roughness (r.m.s.) (nm)	Density (g cm^{-3})
(*a*) Pt/SiO_2	50	1	21.5
(*b*) Pd/SiO_2	8	3	9.6
(*c*) $Pd/Pt/SiO_2$	28	1.5	21.5

The diffraction peak height and the diffraction angle are shown as a function of exit angle in Fig. 4. Using the exit-angle dependences of diffraction peak height, the thin-film structure, such as film thickness, surface roughness and near-surface density, can be determined. The solid lines in Fig. 4 are the curves calculated using a layered thin-film model (Parratt, 1954). The calculation procedure is similar to that of the exit-angle dependence of fluorescence X-ray intensity (Noma & Iida, 1994). The parameters, thus determined, are given in Table 1. For the Pd/SiO_2 film, the density is rather smaller than the bulk value (12.02 g cm^{-3}) indicating the loose-packed fine grain of the Pd thin film. For the $Pd/Pt/SiO_2$ film, the calculation was made for a single-layer model, because the number of data points and the statistics are not sufficient to determine the parameters for the thin Pd film.

The change in diffraction-peak position is due to the effect of refraction. The dashed lines in Fig. 4 show the calculated peak position using the parameters given in Table 1. These curves agree with the experimental data very well. The diffraction angle has a maximum at a critical angle for total reflection. These results suggest that the diffraction data obtained under the grazing-exit condition, near the critical angle, could provide surface structural information.

4. Conclusions

Crystallographic and surface-structure information over a small area of thin films was obtained with a synchrotron X-ray microbeam. From signal-to-background considerations, films as thin as 1 nm can be analysed using this technique. The analysis of the X-ray diffraction peak intensity and angle as a function of exit angle shows the refraction effect and enables the determination of the thin-film structure, such as film thickness, surface roughness and near-surface density. This technique enables thin-film characterization with a high spatial resolution.

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