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Generalized grazing-incidence-angle X-ray diffraction (G-GIXD) using image plates

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A new and more 'generalized' grazing-incidence-angle X-ray diffraction (G-GIXD) method which enables simultaneous measurements both of in- and out-of-plane diffraction images from surface and interface structures has been developed. While the method uses grazing-incidence-angle X-rays like synchrotron radiation as an incident beam in the same manner as in 'traditional' GIXD, two-dimensional (area) detectors like image plates and a spherical-type goniometer are used as the data-collection system. In this way, diffraction images both in the Seemann–Bohlin (out-of-plane) and GIXD geometry (in-plane) can be measured simultaneously without scanning the detectors. The method can be applied not only to the analysis of the in-plane crystal structure of epitaxically grown thin films, but also to more general research topics like the structural analysis of polycrystalline mixed phases of thin surface and interface layers.

Keywords: G-GIXD; image plates; MgO; epitaxic growth.

1. Introduction

Since Marra *et al.* (1979) first used grazing-incidence X-rays to analyse in-plane crystal structure, the grazing-incidence-angle X-ray diffraction (GIXD) method has been commonly used to analyse 'in-plane' crystal structures of thin surface layers. However, as the terminology GIXD indicates, the method in principle only defines the use of the grazing-'incidence' X-ray beam, and does not define measuring the grazing Bragg diffraction. As Kosaka *et al.* (1996) demonstrated by using a traditional one-dimensional scan with a scintillation counter, measurements of 'out-of-plane' structures under a grazing-incidence angle are also important together with traditional 'in-plane' structures for investigating crystal orientations in polycrystalline surface layers. If we use two-dimensional detectors like image plates (IPs), simultaneous measurements of both in-plane and out-of-plane crystal structures become possible. Minor and diffuse diffraction arcs can also be recognized more easily by large-area two-dimensional detectors.

The purpose of this report is to introduce a new and more 'generalized' grazing-incidence-angle X-ray diffraction (G-GIXD) method using IPs, by which simultaneous measurements of both the in-plane and out-of-plane crystal structures from thin layers on surface and interface become possible.

2. General concept of the G-GIXD method

In traditional GIXD methodology, not only the incidence X-ray beam but also the diffraction beam are at grazing angles with respect to a sample surface plane, and therefore only the 'in-plane' crystal structures of the surface can be analysed by such procedures. However, the terminology 'grazing-incidence X-ray diffraction' defines that only the incidence X-ray beam should be at a grazing angle; there should be no restriction on the angle of the diffraction beam. Therefore, more information can be obtained if we measure more generalized diffraction angles.

Such measurements will be realized easily if two-dimensional detectors such as IPs and a spherical-type goniometer (Takagi *et al.*, 1995) are used, together with a grazing-incidence-angle synchrotron radiation beam, as shown schematically in Fig. 1.

In this configuration both the Seemann–Bohlin geometry (out-of-plane: $2\theta_{out}$) [or similarly, grazing-incidence-angle asymmetric Bragg (GIAB) geometry (Huang *et al.*, 1987)] and GIXD geometry (in-plane: $2\theta_{in}$) can be used simultaneously without scanning detectors.

3. General experimental setting at PF-BL3A for G-GIXD measurements

A high-flux beam, vertically and horizontally focused by two total-reflection mirrors and a double-crystal Matsushita-type monochromator, was used as an incident beam (Takagi *et al.*, 1993, 1994) A rectangular-shaped IP of size 200 × 400 mm was pasted onto an inner surface of an IP cylindrical holder (curvature: r = 310 mm). The IP holder was set either horizontally or vertically on the spherical-type goniometer. The incident beam was further cut horizontally by a divergent slit to avoid an excess spread of the beam onto the sample surface, which becomes an origin of unfavourable background-level increase and worsens the resolution. A large lead-covered screen was installed in front of the goniometer to avoid any air-scattered incident beam on the IP. The average incident angles, θ_{in}, were 0.3–0.5°, depending on the critical angles of the surface layers of the samples. Since the incident angles that can achieve a total reflection condition are usually very low, in most cases conventional divergent slits cannot effectively restrict the vertical width of the incident beam, and the beam unavoidably spills over the samples. Therefore, the sample width towards the beam direction must be carefully chosen as a compromise between spatial resolution and diffraction intensity depending on the purpose of the analysis. An NaI scintillation counter was mounted on the 2θ axis of the four-circle goniometer (Takagi *et al.*, 1995) and scanned to confirm a total-reflection beam. The average exposure time of the IPs was about

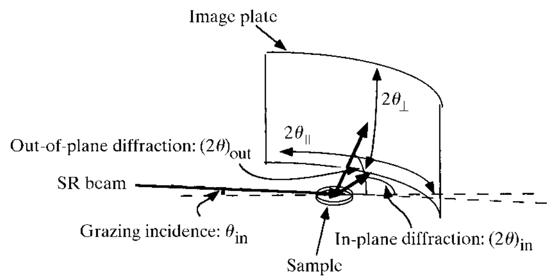

Figure 1
G-GIXD geometry under which both in-plane, $(2\theta)_{in}$, and out-of-plane, $(2\theta)_{out}$, reflections can be measured simultaneously. SR = synchrotron radiation.

30–120 s. Exposed IPs were read by an IP reader, either a BAS 2000 of Fuji Film Co. Ltd or a SIN-MAC ONE (Takagi *et al.*, 1998) of MAC Science Co. Ltd.

4. Example 1: a polycrystalline case – MgO layers on Al–Mg alloys

It is well known that layers of magnesium oxide of thickness of the order of a few tens of nanometres are formed during the fabrication process of industrially prepared Mg-containing Al alloy sheets (Fig. 2) (Mizuno & Takagi, 1996). However, little was known about its crystal structure since the oxide layers are too thin and the surface roughness is too large (sometimes reaching a peak-to-peak value of a few mm) to employ traditional structural analysis methods.

4.1. *Sample preparation and experimental procedure*

The sample used in the study was a 4.5 wt% Mg-containing Al alloy sheet. After soaking in 10 wt% H_2SO_4 solution at 323 K for 13 s, the sample was annealed at 723 K for 2 h in the atmosphere to form an oxide layer on the surface of the alloy.

A grazing synchrotron radiation beam (λ = 1.45 Å) was used at $\theta_{\rm in}$ = 0.4°. The total reflection beam from the sample was confirmed by a $2\theta_\perp$ scan with a scintillation counter at the grazing condition. Several samples having different widths were used in order to find the optimum width both for spatial resolution and diffraction intensity. As shown in the following section, the diffraction arcs from MgO were very diffuse and homogeneous; a relatively wider sample (~8 mm) was chosen to give higher priority to diffraction intensity rather than to spatial resolution. The image plate was set horizontally on the cylindrical holder mounted on the spherical-type goniometer described in Fig. 1.

4.2. *Results and discussion*

A two-dimensional diffraction IP image from the sample is shown in Fig. 3. A diffuse but clear image of the diffraction arc of the cubic MgO 200 reflection was observed together with Al (a solid solution phase with Mg) 111 and Al 200. The widths of the diffraction arcs correspond roughly to the sample width (~8 mm). The image indicates that the surface layer consists of non-oriented cubic MgO having very small crystallites. The reflections from bulk structure, Al 111 and Al 200, are also relatively strong, which indicates that not only the surface layer but also some bulk regions contributed to the diffraction due to the surface roughness. Granular-like contrasts in the arcs of Al 111 and Al 200 will be topographical projections of the crystal grain shapes of the matrix crystal grains, the sizes of which are much larger than those of MgO.

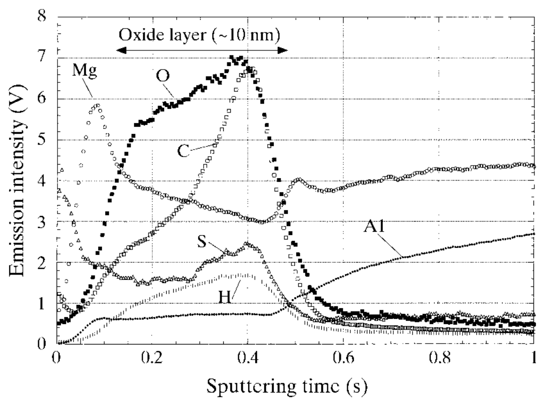

Figure 2
A composition depth profile of a 4.5 wt% Mg-containing Al alloy sheet (0.5 mm thick) by glow discharge optical emission spectroscopy (GDOES).

5. Example 2: a single crystalline case – epitaxically grown Cu on MgO

In the GIXD geometry, the penetration of an X-ray beam into the surface is sensitive to the incident angle, $\theta_{\rm in}$, and diffraction angle, $\theta_{\rm out}$, which determine q_z, the component of the scattering vector that is perpendicular to the surface plane. By measuring the in-plane diffraction for different q_z, information on in-plane structures at different depths can be detected. An attempt to use an IP as a two-dimensional area detector to measure in- and out-of-plane diffraction simultaneously was made for the first time for the above-mentioned depth analysis.

5.1. *Sample preparations and experimental procedures*

A thin film of Cu (001) (300 nm) was grown on MgO (001) substrate with a buffer layer of $Ni_{0.8}Fe_{0.2}$ (~0.8 nm). The buffer layer is supposed to relax the mismatch between the Cu film and the substrate (Takebayashi & Mukai, 1995). Epitaxic growth of the Cu (001) film was confirmed by measurements of X-ray diffraction with a focusing geometry in advance of the synchrotron radiation experiment.

In the single-crystal experiment, unlike the former polycrystalline example, the resolution is apparently more important than the intensity. However, since it was difficult this time to prepare samples having different sizes, we used the edge part of the sample in order to control the irradiated width by moving the sample towards the beam direction with a linear stage after setting the beam on the centre. This method was convenient when samples having various widths were not available, but it is difficult to know the exact irradiated width and the spatial resolution; also, the chance of obtaining a higher background by scattering beams from the edge increases.

The lattice constant in the in-plane direction was estimated from an in-plane 002 diffraction from the (001) surface using G-GIXD. Measurements were carried out for $\theta_{\rm in}$ = 1.0 and $1.2\alpha_c$

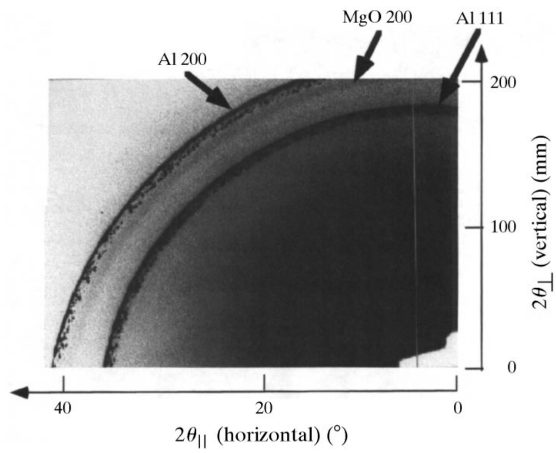

Figure 3
An IP diffraction image under G-GIXD geometry ($\theta_{\rm in}$ = 0.4°) from an MgO surface thin layer (~20 nm) formed on an Al 4.5 wt% Mg heat-treated alloy.

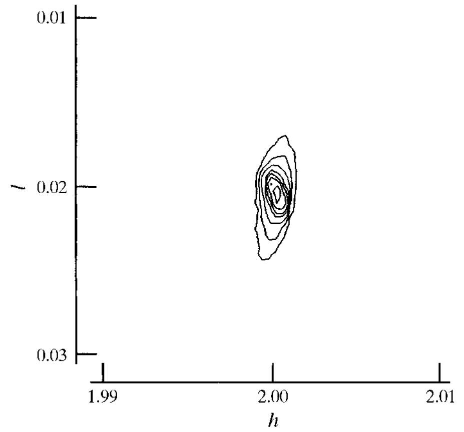

Figure 4
The 200 spot from the Cu (001) film under the condition of $\theta_{\rm in}$ = 1.0α_c. k = 0.0. Contour lines are for 500, 1000, 2500, 5000, 10000, 20000 and 40000 counts.

with a wavelength of 1.45 Å, where α_c is the critical angle. A scintillation counter was also used to measure in-plane 002 diffraction to confirm the geometry. The setting geometry of the spherical-type goniometer is the same as described in Fig. 1.

5.2. *Results and discussion*

Fig. 4 shows the 200 spot from the Cu (001) film for $\theta_{\rm in}$ = 1.0α_c. The exposure time is 120 s. Diffraction spots having strong intensities were measured in the range $\theta_{\rm in}$ = 0.8–1.3α_c in the q_z direction. The intensity profile in the q_z direction is in good agreement with the theoretical one (Dosch, 1992).

The lattice constant of Cu was calculated from the data and is plotted in Fig. 5. The lines *AB* and *CD* correspond to the results for $\theta_{\rm in}$ = 1.0 and 1.2α_c, respectively. The result obtained using the scintillation counter (SC) and the value of the bulk data are shown by open and closed circles, respectively.

These results show that the in-plane lattice constant of Cu is almost constant and is identical to its bulk value. In other words, the buffer layer of $Ni_{0.8}Fe_{0.2}$ works well. Experiments for a thinner film without the buffer layer may show interesting results, such as changes of lattice constants throughout the depth.

6. Conclusions

It has become clear that more general information on crystal structures, like crystal orientation and its change along the depth direction, by quantitative analysis of diffraction images may be obtained by G-GIXD.

A remaining problem is how to improve the resolution in the $\theta_{\rm in}$-plane direction without reducing the signal-to-noise ratios. In the present study, the spatial resolution was simply limited by the irradiated sample width. Further improvements of experimental settings, like using a lower-emittance incident beam or installing some elaborate divergence and receiving slits, will be required to improve the resolution.

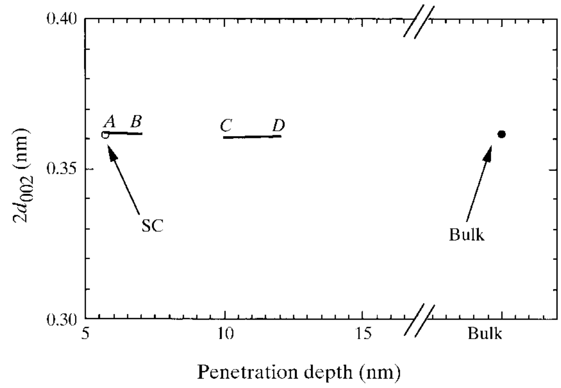

Figure 5
The lattice constant of Cu calculated from the data $\theta_{\rm in}$ = 1.0 and 1.2α_c.

The method will also be powerful for revealing dynamic phenomena, such as formation processes of surface oxidation layers.

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