1. Introduction

Surfaces/interfaces play important roles in various kinds of materials such as semiconductors. The situation is the same in metals and alloys; surface reactions such as oxidation and corrosion, are important issues to use metals and alloys in various environments. Even macroscopic phenomena are often dominated by microscopic reactions at surfaces/interfaces; e.g. mechanical properties can be controlled by morphology of interfaces of grains (or grain boundaries).

When X-ray diffraction is applied to investigate structures of surfaces/interfaces, it has unique points compared with other approaches: non-destructive, in situ observation at high temperatures in gas, high accuracy of determination of atomic structures with an order less than 10^{-3} nm and so on.

But a hard X-ray beam penetrates deep into materials; for example, the penetration depth is almost 150 µm, when Al_2O_3 powder is investigated by a conventional X-ray diffractometry with CuKα. Many kinds of approaches have been attempted to overcome this point and to apply X-ray diffraction to surfaces/interfaces. Evanescent diffraction is one of them, and its principle is reviewed in the next chapter. Then experimental methods (Chap. 3) and results of their application (Chap. 4) are shown. Future of this field is discussed with special attention to usage of area detectors (Chap. 5).

2. Evanescent Diffraction

Index of refraction can be given as follows:

\[ n(r) = 1 - \delta + i\beta, \]  \hspace{1cm} (1)

\[ \delta = \frac{\lambda^2 r_e}{2\pi v_c} \sum_j \left( z_j + f'_j \right), \]  \hspace{1cm} (2)

where \( \lambda \) = the wavelength of X-ray, \( r_e \) = classical electron radius, \( Z \) = atomic number, \( f_j + i f'_j \) = anomalous dispersion of atomic scattering factors, and \( v_c \) = unit cell volume. The values of \( \delta \) and \( \beta \) are determined by the electron density and the absorption of X-ray of the scattering material. As the values of \( \delta \) and \( \beta \) are usually in the order of 10^{-5}-10^{-6}, the index of refraction is a little smaller than unity. In other words, an X-ray beam passing through gas can be totally reflected at the surface of solid or liquid, when the incident angle is smaller than the critical angle \( \alpha_c \), which is given as follows:

\[ \alpha_c = \sqrt{2\delta} \]  \hspace{1cm} (4)

This situation can be compared to the case where a visible light passes through an optical fiber; the index of refraction of the fiber is larger than unity, and the light is totally reflected at the interface of the fiber/the air.

Here we think about the situation where an ideal surface is irradiated by an X-ray beam at the critical angle: \( \alpha_c \) (Fig. 1). The X-ray beam is reflected at the surface, but it also penetrates into the near-surface region as shown in Fig. 1. The intensities of X-ray along the depth direction become maximum at the surface, and decays rapidly along the depth. This wave, “evanescent wave”, is localized near the surface, and phenomena caused by this wave give us information on the near-surface region. For example, evanescent wave, causes the following phenomena: diffraction, fluorescence and XAFS (X-ray Absorption Fine Structures), and they can be used for...
investigation of atomic structures of surfaces and interfaces in a depth of a few atomic layers [1-5].

The information obtained by evanescent diffraction is not merely surface-sensitive, but is unique compared with a conventional diffraction method (Fig. 2). In evanescent diffraction, the scattering vector $\mathbf{k}$ is almost parallel to the surface (“in-plane diffraction”), and diffracted intensities are measured by scanning a detector in a plane parallel to the surface. Thus evanescent diffraction gives us information on the two-dimensional periodic structure in the near-surface region and its change along the depth direction, which is essential for understanding surfaces/interfaces.

Compare to this, in a conventional diffraction method for surface application, only the information on the three-dimensional periodic structure of bulk near the surface can be obtained, where the angle between $\mathbf{k}$ and the surface is large (“out-of-plane diffraction”) and diffracted intensities are measured by scanning a detector in a plane perpendicular to the surface with the incident angle near a few degree.
3. Experimental Viewpoints

In order to measure intensities of evanescent diffraction, we need an X-ray beam with high-quality and special optical setups. In a case when a specimen is a single crystal, an in-house X-ray generator can be used for measurements [2, 3]. X-ray obtained by synchrotron radiation is required for more complicated application [1].

In this chapter, an example of system for evanescent diffraction using an in-house X-ray generator is shown, which is designed based on the previous work [2-4].

3.1. Outline

The system, composed of an X-ray generator and a surface diffractometer, is designed to measure the following properties:

(a) reflectivity: density, roughness, and thickness of surface layers
(b) intensities of evanescent diffraction: the two-dimensional periodic structure in surfaces/interfaces
(c) fluorescence by standing wave: atomic structures of top few layers along the depth

3.2. X-ray Generator

An X-ray beam is generated by a rotating-anode system ("ultrax 18", Rigaku Co., Japan), and is monochromatic by a channel-cut crystal of Si (111) or a flat crystal of Ge (111). The details are as follows:

- Maximum X-ray power: 60 kV, 300 mA (normal focus)
- Size of the beam: 0.5 x 1.0 mm²
- Monochromater: Channel-cut crystal of Si(111) or flat crystal of Ge(111) with slits before and after the crystal

In this system, FWHM of the direct beam is less than 0.06 deg at the detector.

3.3. Surface Diffractometer

The diffractometer system is composed of two "2θ-θ" diffractometers", the rotating axes of which are perpendicular to each other. The diffractometer: DIFF, whose rotating axes (2θv-θv) are vertical, controls the incident angle of X-ray to the surface: αi. The diffractometer DIFFh, whose rotating axes (2θh-θh)
are horizontal, is placed on the θv axis of DIFFv. The specimen holder tilts and shifts the specimen, and is placed on the θh axis of DIFFh.

Intensities of evanescent diffraction are measured by a detector, such as a scintillation counter, placed on the 2θh arm of DIFFh. Intensities of fluorescence are measured by a detector, such as a solid-state detector, placed on the arm rotated by the 2θv arm of DIFFv.

Various information of surface/interfaces mentioned above can be measured by combination of the diffractometers and the detectors:

(a) reflectivity and intensities of “out-of-plane diffraction” are measured by the detector placed on the 2θv axis of DIFFv.
(b) intensities of “in-plane diffraction” (or evanescent diffraction) are measured by the detector placed on the 2θh arm of DIFFh. The out-going angle: αf of the diffracted beam can be controlled by tilting the detector against the 2θh-θh plan e.
(c) intensities of fluorescence are measured by the detector placed on the 2θv arm of DIFFv. The information can be used as monitoring of I0 of evanescent wave as well as structure analysis by the standing wave method [5].

When an area detector, such as an image plate (IP), is used, information on both of “in-plane diffraction” and “out-of-plane diffraction” can be measured at the same time, where a change of the two-dimensional structure along the depth can be obtained (Chap. 5).

### 3.4. Reflectivity Measurements

The performance of this system was checked by measuring reflectivity of a thin film of Ti deposited on a Si substrate, and one of the results is shown in Fig. 4. Reflectivity measurements were performed in three regions of the incident angle (αi) with different counting-times and thickness of absorber. A scintillation counter (NaI) was used to measure intensities and counting-correction was performed.

A wide range of intensities should be covered in order to analyze surface structures based on reflectivity measurements; existence of a thin layer, for example, results in an oscillation of reflectivity curve with a large periodicity [13]. Fig. 4 shows that reflectivity was measured down to 10^-4, and that it is in good agreement with the calculated one, showing that this system can be applied to investigate surfaces/interfaces by evanescent diffraction. Now this system is used for measuring reflectivity, Bragg in-plane diffraction, and fluorescence of surfaces/interfaces of a single-crystal of metals such as Fe and steel.

However, a stronger X-ray beam has to be combined with this kind of diffractometer system for further investigation of surfaces/interfaces, such as measurements of diffuse in-plane intensities. An application of this system with synchrotron radiation to a surface of intermetallic is shown in the following chapter.

### 4. Application of Evanescent Diffraction - Order-disorder Structural Phase Transition at Intermetallic Surfaces [7-9] -

#### 4.1. Order-disorder Phase Transformation of Cu3Au System

The intermetallic Cu3Au, which undergoes a structural phase transformation from the A1 to the L10 structure at the (bulk) critical temperature Tc=663 K, is considered a classic example of an order-disorder phase transformation. In the L10 structure, Au atoms have 12 Cu atoms at nearest-neighbor (NN) sites and Cu atoms have 4 Au and 8 Cu atoms at NN sites. This alloy is one of the best for studying a change in long-range order (LRO) and short-range order (SRO) near Tc by X-rays because of the high degree of contrast to X-rays between Cu and Au, the relatively small change in lattice constant during the transformation, its resistance against corrosion and oxidation, and the low Tc.

Atomic order of Cu3Au above Tc has been investigated intensively for the bulk and it is well understood [9-11]. The latest result shows the existence of small ordered-domains of 1-10 unit cells surrounded by a disordered matrix at T=703 K; some of the larger domains consist of smaller ones separated by anti-phase boundary (APB) on {100} planes.

Surfaces or interfaces are expected to show different behavior from bulk in an order-disorder transformation, because atoms at surfaces are co-
ordinated by less atoms and are less tightly bound than those of bulk so that the strain energy might be less important. And the Cu$_3$Au (001) surface has been paid attention recently and investigated by new techniques to a general understanding of surfaces/interfaces. The results of investigation of Cu$_3$Au (001) surface by evanescent diffraction are shown.

4.2. Experiments & Results

Evanescent diffraction measurements were performed by a geometry similar to the one described in Chap. 3. The difference is a special surface chamber was used to prepare a clean surface under UHV [7, 8].

At first, LRO of the stoichiometric Cu$_3$Au (001) surface was investigated above the bulk critical temperature ($T_c$) by evanescent diffraction. (“inplane diffraction”). “Out-of-plane diffraction”, which shows atomic order of the bulk, was also measured at the same time at elevated temperatures.

Figure 5 shows the temperature dependence of intensities of the 001 and 100 peaks, which are “in-plane diffraction (surface)” and “out-of-plane diffraction (bulk)” respectively. It has shown a significant difference in the range $T > T_c$; the 001 peak becomes diffuse above the bulk $T_c$, but the 100 peak remains sharp at and above $T_c$ (Fig. 5). This means that the surface shows a 2nd order-like transition and remains some order though the bulk becomes disordered above $T_c$, which cannot be explained by conventional theories such as “wetting theory” [12].

The diffuse intensities were measured throughout a two-dimensional region of reciprocal space in order to obtain information on SRO in the surface. The diffuse intensity was analyzed quantitatively in the two-dimensional reciprocal lattice, and Cowley-Warren short-range-order parameters, $\alpha_{lm}$ were determined. Monte-Carlo simulation based on these values have revealed a unique atomic configurations in the surface: ordered domains with $\{10\}$ APB in a disordered matrix.

A result at $T=T_c+56$K is shown in Fig. 6, where the atomic structure of Cu$_3$Au (001) surface is shown schematically. Ordered domains are surrounded with $\{10\}$ APB more often than other boundaries and the size is 3-5 unit cells as shown in Fig. 6. The top layers with high-degree of order can be expected to be affected by APB energy, which is in the same way as the bulk, resulting in that the SRO near the surface is also affected by the same type of APB. These facts suggest that in this system the correlation among atoms are so strong that the APB goes through just near the surface. This is quite different situation from ‘the wetting layer’ model.

This kind of information can be obtained only by evanescent diffraction, where in situ observation and quantitative information of atomic structure with high accuracy are available. It has been shown that evanescent diffraction has a potential of application of to investigation of surfaces/interfaces of metals.
5. Future of Evanescent Diffraction -Usage of Area Detectors-

As mentioned above, the penetration of X-ray beam into the surface is sensitive to the angles of incidence $\alpha_i$ and outgoing $\alpha_f$. Thus when a series of measurements are performed for different $\alpha_i$ and $\alpha_f$, depth-sensitive analysis can be possible.\(^1\) PSPC (Position Sensitive Proportional Counter, a linear detector) was utilized to measure intensities for various $\alpha_f$ without scanning the detector [1].

When an area detector is used, it can detect diffracted intensities not only for various $\alpha_f$ but also for various diffracted angles of 2$\theta$ without scanning the detector, which corresponds to measuring in- and out-of-plane diffraction simultaneously. This attempt was tried by a combination of an image plate (IP) and a surface diffractometer [6]. The geometry of the surface diffractometer is the similar to the one shown in Chap. 3. IP with a size of 200 X 400 mm was used as a detector and is attached on a curved IP holder (the curvature $r=310$mm). Experiments were performed using synchrotron radiation at BL3A of Photon Factory in Tsukuba, Japan.

A thin film of Cu (001) (300nm) has been 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 Cu film and the substrate. Epitaxial growth of Cu (001) film has been confirmed by measurements of X-ray diffraction with focusing geometry.

The lattice constant in the surface direction was estimated from in-plane 002 diffraction from the (001) surface with evanescent diffraction. Measurements were carried out for $\alpha_i=0$ and 1.2$\alpha_c$ with a wave length of 0.145 nm. Scintillation counter (SC) was also used to measure in-plane 002 diffraction, in order to check the geometry.

Figure 7 shows 200 spot from the Cu (001) film, under the condition of $\alpha_i=1.0\alpha_c$. The exposure time is 120 sec. Strong intensities were measured in a range of $q_z=0.015-0.025$ in the depth direction. The intensity profile in the $q_z$ direction is in good agreement with the theoretical one [1].

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\(^1\)When intensities of evanescent diffraction are measured by a point detector such as a scintillation detector with a slit covering a narrow range of $\alpha_f$, the obtained information is averaged over the depth of penetration and not depth-sensitive as far as $\alpha_f$ is fixed.
improve a resolution in $q_{\text{in-plane}}$ direction. In this experiments, it is the same as the width and the divergence of the incident beam, and further experimental consideration will be required for more accurate measurements.

Evanescent diffraction will be one of the powerful methods to perform in situ measurements of surfaces/interfaces in various environments such as at high temperatures in a reaction gas. A various methods, used in the bulk, can be applied to evanescent diffraction; a usage of an area detector is just one example and a various attempts have been tried, such as anomalous scattering, a combination of diffraction and XAFS.

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