GRAZING-INCIDENCE X-RAY DIFFRACTOMETER FOR DETERMINING IN-PLANE STRUCTURE OF THIN FILMS

Kazuhiko Omote and Jimpei Harada

X-ray Research Laboratory, Rigaku Corporation, Akishima, Tokyo 196-8666, Japan

ABSTRACT

A high-intensity grazing-incidence X-ray diffractometer system, which uses a parabolic graded multilayer mirror and an 18-kW rotating-anode generator, has recently been developed for the structural characterization of surfaces and thin films. Its goniometer has two in-plane $\varphi2\theta_x$ axes and two conventional $\alpha2\theta_\alpha$ axes for measurements of in-plane and out-of-plane diffraction, respectively. The diffractometer can be used for grazing-incidence asymmetric Bragg diffraction, in-plane diffraction and/or X-ray reflectivity measurements. An in-plane diffraction analysis of polycrystalline Co-alloy thin-film recording media reveals lateral structural anisotropy in high-density recording media. In-plane diffraction and reflectivity measurements of an organosilane monolayer prepared by Langmuir method on a silicon substrate were also successfully made.

INTRODUCTION

When an X-ray beam impinges onto a specimen surface at a grazing angle ($\alpha$) equal to its critical angle for total reflection ($\alpha_c$), X-rays are totally reflected. Under this condition, X-rays can penetrate only a few nanometers in depth. An X-ray wave is formed that propagates parallel to the surface. This surface-propagated X-ray beam can be diffracted by a set of crystal planes that are perpendicular to the specimen surface if the Bragg condition is satisfied. The diffracted X-ray beam exits the surface at an angle $\alpha_{\text{out}}$ as showed in Fig. 1. This is called in-plane diffraction, and it can be used to study the lateral structure of a surface layer. The diffracted beam

![Fig. 1. Schematic of X-ray optics for in-plane diffraction.](image-url)
has good peak-to-background ratios, which are relatively free from interference from underlayer(s) and the substrate.

For in-plane diffraction, a parallel incident X-ray beam collimated in both horizontal and vertical directions is required. A synchrotron radiation source would be best suited for this purpose.\(^1\) It is, however, inconvenient and difficult to use synchrotron radiation in most development and manufacturing environments. Therefore, there has been a need for the development of a system using a laboratory X-ray source for measuring in-plane diffraction.

In this paper, characteristics of grazing-incidence and in-plane diffraction will be first given. These are followed by a description of the grazing-incidence diffractometer and its optical system. Results on the analyses of polycrystalline Co magnetic recording disks and an organosilane monolayer grown on a Si substrate by the in-plane diffraction system are also given.

**GRAZING INCIDENCE AND IN-PLANE DIFFRACTION**

One of the applications for grazing-incidence X-rays is the asymmetric-Bragg diffraction technique (GIABD).\(^2\) This technique has been widely used for many years to characterize non-textured thin films. The scattering vector for GIABD is inclined to the film surface, and the inclination of the scattering vector changes continuously with the scanning \(2\theta\). It is, therefore, difficult and sometimes impossible to use GIABD to analyze highly textured or epitaxial thin films.

On the other hand, the scattering vector of in-plane diffraction is always parallel to the film surface, and the direction of the scattering vector moves horizontally with the scanning \(\phi/2\theta\). This makes possible a direct measurement of lateral crystal-structure parameters including lattice constants, crystallite sizes, film orientation, long-range ordering, etc. In-plane diffraction has been used for the characterization of magnetic Co-Pt thin films epitaxially grown on GaAs single-crystal substrates. Successful detection of multiple epitaxial domains, determination of film and substrate orientation relationships and calculation of long-range order parameters have been reported.\(^3\)

As stated earlier, the incident angle for in-plane diffraction is equal to the critical angle for total reflection \(\alpha_c\). The 1/e penetration depth \(D(\alpha)\) increases rapidly when the incident angle \(\alpha\) increases above \(\alpha_c\). Typical values of \(D(\alpha)\) for Si, Cu, Co and Au are plotted in Fig. 2. Values of \(D(\alpha)\) depend not only on the value of \(\alpha\), but also on the electron density of the material. The dependency of \(D(\alpha)\) on \(\alpha\) makes it possible for one to control and limit X-rays within a desired depth below the surface. Calculated X-ray reflectivity curves \(R(\alpha)\) for Si, Cu, Co and Au calculated as a function of \(\alpha\) are also plotted in Fig. 2. Reflectivity data can be used to determine thickness, density and roughness of individual layer(s) of a thin film.

GIABD, in-plane diffraction and X-ray reflectivity are three important grazing-incidence X-ray techniques for the characterization of surfaces and thin films.
IN-PLANE DIFFRACTOMETER SYSTEM

A new diffractometer system (namely, Rigaku ATX-G) has recently been developed for thin-film characterization using GIABD, in-plane diffraction and/or X-ray reflectivity techniques. Details of the system will be given elsewhere.\(^4\) The incident X-ray optics, the goniometer and the specimen stage are briefly described below.

The ATX-G uses a parabolic graded multilayer mirror\(^5\) to monochromatize the incident beam from a laboratory Cu-target X-ray source to Cu K\(_\alpha\) radiation with a \(I_{\text{Cu K}\alpha}/I_{\text{Cu K}\beta}\) ratio of 500/1 and to collimate the divergent incident X-rays to a parallel beam with 0.045° divergence perpendicular to the specimen surface. Two sets of Soller slits, one before and another after the specimen, are used to limit the horizontal divergence of the incident and the diffracted beam to 0.5°.

The goniometer has two in-plane \(\phi'2\theta_x\) axes and two conventional \(\omega'2\theta\) axes for the measurements of both in-plane and out-of-plane diffraction, respectively. Similar to a four-circle diffractometer, this diffractometer can be used to measure all reciprocal points within an Ewald sphere.

---

**Fig. 2.** Calculated X-ray \(1/e\) penetration depths and reflectivity curves for Si, Cu, Co and Au.
The specimen stage has two rotation axes, $R_x$ and $R_y$, to control the orientation of the specimen surface, and a translation $z$-axis to center the specimen at a proper height. The in-plane $2\theta_x$ axis and a detector are mounted on the $2\theta$ axis of the diffractometer so that the detector can have both in-plane and out-of-plane movements. The detector behind a receiving slit can be moved perpendicular to the specimen surface to measure the diffracted beam exited at the $\alpha_{out}$ angle from the specimen surface (see Fig. 1).

**CHARACTERIZATION OF CO THIN-FILM RECORDING MEDIA**

In the research and development of a new high-density magnetic recording medium, it is important to determine the crystalline structure of the medium and to correlate the structure with its magnetic properties.

Cobalt-alloy thin films are widely used as high-density magnetic recording media. A recording disk usually consists of four layers: a very thin carbon capping layer, a Co magnetic layer, a Cr under-layer, and a NiP amorphous layer deposited on an Al disk as shown in Fig. 3. The Co layer is known to be magnetized horizontally with its easy axis for magnetization (i.e., hexagonal c-axis) lying parallel to the surface of the disk.

![Fig. 3. The orientation of Co and Cr crystallites in magnetic recording media.](image)
A typical X-ray diffraction pattern for a Co thin-film disk obtained by a conventional \(\theta/2\theta\) scan is shown in Fig. 3(a). The diffraction pattern is dominated by three strong Al(200), Al(220), Al(311) peaks and a huge and broad NiP amorphous peak centered at 46° in 2\(\theta\). This makes it very difficult, if not impossible, to study the major Co and Cr peaks (namely Co(100), Co(002), Co(101) and Cr(110)), buried under the amorphous peak between 41° and 47°. As shown in Fig. 4(a), only two weak Co(110) and Cr(002) peaks at 64° and 74° are detectable from the Co magnetic layer and the Cr under-layer, respectively.

Interference from the intense Al and NiP peaks can be greatly reduced using grazing incidence diffraction. For example, GIABD patterns obtained with incident angles \(\alpha = 0.4°, 0.5°\) and \(0.6°\) are plotted in Fig. 4(b). The Al (200) peak is no longer detectable because of the limited X-ray penetration. X-ray penetration increases with increasing \(\alpha\) from 0.4° to 0.6°, which causes scattering from the NiP amorphous layer to gradually appear. Co and Cr peaks from Co(100), Co(002) and Cr(110) crystal planes, which are inclined to the layer surface, are now observable (see Fig. 3). The Co(002) peak is very weak in intensity suggesting that the Co c-axis is probably oriented parallel to the layer surface.

![Fig. 4. XRD patterns for a Co recording disk: (a) conventional \(\theta/2\theta\) scan, (b) GIABD scan.](image)

In-plane diffraction was used to study the Co c-axis and crystalline structure oriented parallel to the surface of a disk. The disk surface was first oriented to fix the X-ray incident angle \(\alpha\) at the critical angle for total reflection for Co. The X-rays penetration was, therefore, limited to the carbon and the Co layers at and near the surface of the disk. Both \(\varphi/2\theta\_\alpha\) scans and \(\varphi\) scans were used for in-plane diffraction measurements.

Two \(\varphi/2\theta\_\alpha\) -scan patterns for disk #1 are shown in Fig. 5(a). The patterns were recorded with the scattering vector fixed along two perpendicular directions, i.e. the circumferential and the radial directions of the disk. Both patterns show three Co peaks and are free of interference from
Al, NiP and Cr. Among the three Co peaks, Co(002) has the highest intensities. This indicates that the Co c-axis was preferentially oriented horizontally parallel to the disk surface. The Co(002) peak is much stronger in the pattern measured along the circumferential direction than that in the radial direction. This indicates Co in-plane structural anisotropy.

The $\varphi$-scan method was used to measure the in-plane distribution of the Co c-axis. The $\varphi$-scan profile for the Co(002) reflection was obtained by rotating the disk around its surface normal through a 360° rotation (i.e., from -180° to 180°) while keeping the detector fixed at $2\theta_x = 44°$. As shown in Fig. 5(b), the Co(002) profile shows two broad peaks that are strongest when the Co c-axis is oriented along the circumference and weakest when oriented along the radial directions. The width of the peaks is 60°, which suggests that the Co c-axis is mainly oriented along the circumference direction with about ±30° dispersion.

In-plane diffraction was also done on two other Co disks (#2 and #3). The diffraction patterns for disks #2 and #3 are shown in Figs. 6 and 7, respectively. The in-plane diffraction patterns obtained by $\varphi/2\theta_x$ and $\varphi$ scans for disk #2 are similar to those of disk #1, showing Co c-axis in-plane anisotropy.

Fig. 5. In-plane diffraction patterns for disk #1: (a) $\varphi/2\theta_x$ scan, (b) $\varphi$ scan. There are also shown the two-arrangements of the scattering vector fixed along the circumferential and the radial directions of the disk.
There are, however, two differences between the patterns of disks #2 and #1: the maximum Co(002) intensity is lower for disk #2 (i.e., 650 cps for disk #2 comparing to 700 cps for disk #1) and the c-axis dispersion along the circumference is larger (+35° dispersion for disk #2 and ±30° for disk #1).

The patterns for disk #3 are significantly different from those for disks #1 and #2. The \( \phi/2\theta_x \)-scan patterns along the circumference and the radial directions for disk #3 are practically the same with very weak Co intensities. The intensities of the \( \phi \)-scan pattern are essentially constant with no peaks detectable over a 360° rotation. This indicates no Co in-plane structural anisotropy for disk #3.
A correlation between the in-plane structures and the magnetic properties for the disks can be made. Both disks #1 and #2 with Co in-plane structural anisotropy had high recording density (i.e., 3.5 GB), while disk #3 with no Co in-plane structural anisotropy had low recording density (2.0 GB). Disk #1 with higher Co(002) peak intensity and smaller c-axis dispersion had higher coercivity than disk #2.

**CHARACTERIZATION OF AN ORGANOSILANE MONOLAYER**

In this study, alkyltrichlorosilane was first polymerized at the surface of water by the Langmuir method. The organosilane monolayer was then grown on a Si(111) substrate by the upward drawing method. The monolayer has high stability due to its immobilization and strong chemical bonding forces with the Si surface.

In-plane diffraction and reflectivity measurements of the monolayer were made. The in-plane diffraction pattern for CH$_3$(CH$_2$)$_{11}$SiCl$_3$ monolayer obtained by a $\phi2\theta_\chi$ scan are plotted in Fig. 8(a). An incident angle $\alpha = 0.2^\circ$, which is larger than the critical angle for total reflection for CH$_3$(CH$_2$)$_{11}$SiCl$_3$ but smaller than that of Si, was used. As shown in Fig. 8(a), there is a diffraction peak at 21° in the $\phi2\theta_\chi$-scan pattern, which indicates that the in-plane spacing (or...)

---

**Fig. 8.** X-ray patterns for an organosilane monolayer grown on a Si(111) substrate: (a) in-plane diffraction, (b) specular reflectivity.
horizontal separation) for the CH₃(CH₂)₁₁SiCl₃ molecule is 0.42 nm.

The experimental reflectivity and the calculated curves obtained by refinement are plotted in Fig. 8(b). The refinement results give the layer thickness of the CH₃(CH₂)₁₁SiCl₃ monolayer perpendicular to the Si-substrate surface as about 1.7 nm, which is consistent to the length of the CH₃(CH₂)₁₁SiCl₃ molecule.

It can be concluded from the in-plane diffraction and reflectivity analyses that two-dimensional CH₃(CH₂)₁₁SiCl₃ crystals with a vertical length of 1.7 nm and horizontal molecular separation of 0.42 nm were formed on the Si substrate.

SUMMARY

The Rigaku ATX-G diffraction system with a conventional X-ray source has been developed for the characterization of surfaces and thin films using GIABD, in-plane diffraction and/or reflectivity techniques. An in-plane diffraction analysis of polycrystalline Co thin-film disks revealed lateral structural anisotropy for 3.5 GB disks and structural isotropy for a 2.0 GB disk. An in-plane diffraction and reflectivity analysis of an organosilane monolayer grown on a Si substrate was also successful.

ACKNOWLEDGMENT

The authors want to thank Professors T. Kajiyama, A. Takahara and Mr. K. Kojio of Kyushu University for providing the organosilane monolayer.

REFERENCES