Characterization of Surfaces and Thin Films
Using a High Performance Grazing Incidence X-ray Diffractometer

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Abstract
A newly developed grazing-incidence X-ray diffractometer system was used for the characterization of surfaces and thin films. The system uses a high-intensity rotating anode X-ray generator, a parabolic graded multilayer mirror, and an asymmetric-cut Ge(220) channel monochrometer to generate an intense, parallel and monochromatic incident Cu Kα X-ray beam for grazing-incidence X-ray analysis. A reflectivity analysis of ultra thin SiO2 films on Si substrates and a grazing-incidence diffraction analysis of a polycrystalline Ti film deposited on Si and epitaxial Si films grown on sapphire substrates have been successfully obtained.

Introduction
Grazing-incidence X-ray techniques have been used extensively for the characterization of surfaces and thin films (1), (2). Grazing-incidence X-ray reflectivity technique is used for determining the values of layer thickness, density and roughness of thin films, while grazing incidence X-ray diffraction techniques are used for analysis of in-plane and out-of-plane thin-film structures. Ultra thin-film experiments can best be done using a high-intensity synchrotron radiation source (3), (4). It is, however, inconvenient and difficult to use synchrotron radiation in most development and manufacturing environments.

In this paper, we report the use of a newly developed grazing-incidence X-ray diffractometer system with a high-intensity laboratory X-ray source for the analysis of surfaces and thin films. Results on the characterization of Ultra thin SiO2 films on Si substrates, a polycrystalline Ti film deposited on Si and epitaxial Si films grown on sapphire substrates are also given.

Grazing-Incidence X-Ray Diffraction System
A high-performance grazing-incidence X-ray diffractometer system has recently been developed for characterization of thin films. As shown in Fig. 1, the system consists of an
18-kW rotating anode X-ray generator, a graded parabolic multilayer mirror a Ge(220) asymmetric channel-cut monochrometer, a specially designed four-axis goniometer, etc.\(^{(5)}\).

**Fig. 1 Schematic illustration of the grazing-incidence X-ray diffractometer system**

Divergent incidence Cu K X-rays from the rotating anode X-ray generator are first collimated and monochromatized by the graded multilayer mirror to a broad Cu K \(\alpha\) X-ray beam with 0.045\(^{\circ}\) divergence (see Fig. 2a). The Cu K \(\alpha\) X-ray beam is further collimated to a narrow and parallel X-ray beam of 0.015\(^{\circ}\) divergence by the asymmetric-cut Ge(220) channel-cut monochromater (Fig. 2b).

**Fig. 2 X-ray rocking curves of Si(004) obtained with:** (a) a parabolic graded multilayers, and (b) a parabolic multilayers and asymmetric-cut Ge(220) channel monochrometer

The four-axis goniometer has two conventional \(\omega / 2 \theta\) axes and two in-plane \(\phi / 2 \theta_{x}\) axes. As shown in Fig. 3, the \(\phi / 2 \theta_{x}\) axes are mounted horizontally on the vertical \(\omega\) axis. The \(\omega / 2 \theta\) axes are used for measurements of out-of-plane diffraction, and the \(\phi / 2 \theta_{x}\) axes for in-plane diffraction. A switch between in-plane and out-of-plane measurements can
be done rapidly.

The specimen stage has two rotation axes, Rx and Ry, for tilting the specimen surface so that the surface normal is properly aligned parallel to the φ axis and centered at the intersection of the φ and the ω axes.

![Fig. 3 Schematic illustration of four-axis goniometer](image)

**Results and Discussion**

**GIXR Analysis of Ultra Thin SiO₂ Films on Si Wafers**

Two SiO₂ films grown by the thermal oxidation process on Si wafers were used in this study. Specimen 1 was grown under pure O₂, and Specimen 2 under N₂/O₂ (see Fig. 4).

![Fig. 4 Preparation procedure for an ultra thin SiO₂ film thermally grown on a Si substrate](image)

![Fig. 5 (a) X-ray specular reflectivity curves for Specimen 1 and 2, and (b) Fourier transform of the reflectivity curves for Specimen 1](image)
The GIXR technique was used to determine the layer thickness, surface and interface roughness of the films. The experimental reflectivity curves for Specimen 1 and 2 are plotted in Fig. 5a. The interface fringes were weak because of a small difference between the electron densities for SiO$_2$ and Si. Reflectivity intensities, varied over eight orders of magnitude, were collected so that a reliable analysis of the reflectivity data could be obtained. A Fourier transform analysis of both reflectivity curves shows that each strong peak at thickness of 6.5nm (see Fig. 5b for Specimen 1).

The experimental reflectivity curves were also analyzed by fitting with calculated reflectivity curves derived from Parratt's recursive formula modified with the distorted wave Born approximation (DWBA)\(^{(6), (7)}\). The Marquardt method was used in this study to match the calculated with the experimental reflectivity data. The fitting results for Specimen 1 are shown in Fig. 6, and the analysis results on layer thickness and roughness for both specimens are given in Table 1.

![Fig. 6 Experimental reflectivity data (open circles) and fitted curves (solid line) for Specimen 1](image)

### Table 1. Sample Preparation Conditions and Their Analyzed Results

<table>
<thead>
<tr>
<th></th>
<th>Specimen 1</th>
<th>Specimen 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>N2/O$_2$-flow</td>
<td>O$_2$-flow</td>
</tr>
<tr>
<td>Temperature(°C)</td>
<td>1000</td>
<td>900</td>
</tr>
<tr>
<td>Time(min)</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>SiO$_2$ thickness(nm)</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Surface roughness(nm)</td>
<td>0.36</td>
<td>0.32</td>
</tr>
<tr>
<td>Interface roughness(nm)</td>
<td>0.1</td>
<td>0.25</td>
</tr>
</tbody>
</table>

As shown in Table 1, both Specimens 1 and 2 have the same SiO$_2$ layer thickness of 6.5nm, in good agreement with the results obtained by the Fourier transform method.
Values of the SiO2 surface roughness for the both specimens were approximately the same and within 0.04nm. The interface roughness between the SiO2 layers and the Si substrate for the two specimens are, however, significantly different from each other with 0.1nm for specimen 1 and 0.25nm for specimen 2. The results indicate that the buried interface between the SiO2 layer and its Si substrate were significantly smoother for the layer thermally grown under N2/O2 than under O2.

In-Plane XRD Measurements of TiSi2 Films on Si Wafer

The film used in this study was prepared by the procedure shown in Fig. 7. A thin film was first deposited from a Ti target onto a Si substrate. The film was subsequently annealed at 650°C for 1 minute under nitrogen atmosphere.

![Reaction of Si and Ti](Thickness: about 75nm)

A conventional X-ray diffraction pattern for the film obtained by a ω/2θ (or θ/2θ) scan is shown in Fig. 8a. A strong and sharp TiSi2(150) diffraction peak together with two relatively weaker and broad TiN(111) and TiN(200) peaks were observed. No Ti diffraction peaks were detected. This indicates that the Ti film was reacted with the Si substrate during high-temperature annealing process and transformed into TiSi2, and that the Ti film reacted also with the nitrogen gas to form a thin TiN layer.

The in-plane diffraction technique was used to positively identify the surface and the interface layers. In-plane diffraction patterns obtained with incident angles (ω) fixed at 0.20, 0.25 and 0.30 are plotted in Fig. 8b. For the pattern obtained at ω=0.20°, only two TiN peaks, TiN(111) and TiN(200), were detected. At ω=0.20°, the 1/e penetration depth for a Cu Kα X-ray beam was calculated to be 4nm. At larger incident angles, the X-ray beam penetrates deeper into the film. TiSi2 C49(060) and C49(131) peaks began to appear when ω increased to 0.25 and 0.30° (see Fig. 8b).

It can be concluded from the X-ray diffraction results that the Ti film transformed into two layers: a TiN layer with an estimated surface thickness of about 10nm at the surface, and a TiSi2 layer at the interface between the film and the Si substrate (see Fig. 9).
In-Plane X-ray Rocking Curve Measurements of Si Films on Sapphire Substrates

The procedure for growing epitaxial Si films on Sapphire substrate (SOS) is shown in Fig. 10. Two SOS films were used in this study: Film A was prepared with and Film B without substrate cooling during Si ion implantation (see Fig. 10).

In-plane X-ray rocking curve (XRC) measurements were done by rotating the specimen about the \( \phi \) axis, while keeping the detector at a fixed angle \( 2 \theta \) to record the Si(040) peak. The in-plane XRC obtained with an incident angle \( \omega =0.25^\circ \) is plotted in Fig. 11. It shows that the full width at half maximum (FWHM) for Film A is narrower than that for Film B. This indicates that the epitaxial Si film obtained with substrate cooling had a smaller in-plane Si(040) axis dispersion and better crystallinity than the film without substrate cooling. Similar results with smaller FWHMs for Film A and larger FWHMs for Film B were also observed.
obtained at $\omega = 0.15, 0.20, 0.25, 0.30$ and $0.35^\circ$. (see Fig. 12). Values of FWHM are found to be more uniform for Film A than for Film B.

Fig. 11 In-plane XRC of Si(040) at $\omega = 0.25$deg

Fig. 12 FWHM of Si(040) profiles

The penetration depth of the X-ray beam changes from a few nm to a few hundred nm as one changes $\omega$. We therefore made clear the difference between the SOS samples. The crystallinity of one Si thin film (Not cooled) changes from surface to substrate, and crystallinity of the other Si thin film (Cooled substrate) is uniform from surface to substrate. In this way, In-plane XRC using a changing incident angle can clarify the depth profiles of crystallinity on a nm scale.

Conclusions

A high-intensity grazing-incidence X-ray diffractometer system was developed for the characterization of surfaces and thin films. Reflectivity measurements were done on two ultra thin films thermally grown on Si substrates with one under pure O$_2$ and the other under N$_2$/O$_2$. Results showed that both films had essentially the same thickness and surface roughness, but different SiO$_2$/Si interface roughness. Diffraction patterns obtained with a conventional $\omega / 2\theta$ scan and in-plane $\phi / 2\theta$ $\chi$ scans for a polycrystalline Ti films deposited on a Si substrate revealed the Ti film transformed into a TiN surface layer and a TiSi$_2$ interface layer after annealing at 650°C for 1 minute under nitrogen atmosphere. The grazing-incidence in-plane rocking curve measurements were used to analyze two epitaxial Si films grown on sapphire substrates. Results showed that the film prepared with substrate cooling during the Si ion-implantation process had smaller in-plane Si(040)-axis dispersions, better crystallinity and was more uniform throughout the depth of the film than the film without substrate cooling.

Acknowledgments

The authors are grateful to Mr. S. Ibe, Dr. K. Neki, Mr. T. Konishi, Mr. T. Yamada, Mr. A. Yasujima, and all members of Analytical and Computational Science Laboratories for
their fruitful discussions and continuous encouragement. One of the authors (S. -Y. M.) would like to thank Dr. T. C. Huang for reading the manuscript.

References