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XAFS spectra from reflectivity measurements

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The reflectivity of $TiSi_2$ films was measured as a function of photon energy E at the Ti K-edge region at a glancing angle θ close to the critical angle θ_C of total reflection. $TiSi_2$ silicide films (about 30 nm thickness) were prepared by silicidation of Ti thin films deposited on Si(001) substrates. Since the Fresnel reflectivity $R(\theta,E)$ is a function of the dispersion $\delta(E)$ and of the absorption $\beta(E)$, the absorption $\beta(E)$ which carries the XAFS signal can be solved as $\beta(\theta,\delta,R)$ for observed reflectivity R and for estimated δ. The dispersion $\delta(E)$ is related to the absorption $\beta(E)$ by the Kramers–Kronig (K–K) relations since the refractive index is $n(E) = 1 - \delta(E) - i\beta(E)$. $\beta(E)$ was calculated from the observed reflectivity $R(\theta,E)$ using theoretical values for initial $\delta(E)$. Titanium K-edge XAFS for $TiSi_2$ was extracted from the reflectivity by 'ReflXAFS'.

Keywords: total reflection; Fresnel reflectivity; ReflXAFS; $TiSi_2$.

1. Introduction

Reflectivity measurement at grazing incidence has provided a powerful tool for characterizing thin films or multilayers grown on substrates. It has been used for measuring film thickness, density and microscopic surface or interface roughness (Parratt, 1954). The high intensity beam, reflected totally by only a few atomic layers, enables us to carry out surface-sensitive experiments with a conventional X-ray source. Reflectivity measurement does not require such a high intensity X-ray source as other surface XAFS techniques, which excite secondary particles.

Reflectivity as a function of photon energy with the glancing angle close to the critical angle reveals XAFS-like spectra called 'ReflXAFS' spectra (Martens & Rabe, 1980). ReflXAFS is an extremely effective technique for the examination of thin layers on a substrate. Several procedures have been proposed for extracting XAFS from ReflXAFS. In order to estimate $\delta(E)$ from $\beta(E)$, the K–K relations have been calculated (Poumellec, 1986; Picard-Lagnel *et al.*, 1989). Without integrating the K–K relations explicitly, owing to the lack of sufficient data sets, the dispersion δ and the absorption β were determined so that the Fresnel reflectivity fits the measured values (Tani *et al.*, 1993). We analysed ReflXAFS spectra varying with every change of glancing angle.

The silicide $TiSi_2$ is employed in the MOS fabrication process and is used for gate, source and drain contacts because of its low resistivity and high stability against thermal processes. Two different phases of $TiSi_2$, C49 (the metastable phase with high resistivity) and C54 (the stable phase with low resistivity), have been examined quantitatively by grazing incidence diffraction (GID) (Tomita *et al.*, 1995). It is known that C49 transforms to C54 at high temperature (973–1123 K).

2. Experimental

Titanium thin films (30 nm) were deposited on Si(001) substrates by sputtering. They underwent a rapid thermal annealing (RTA), first at ~973 K and then at ~1073 K. Two $TiSi_2$ samples, #1 (after the first RTA) and #2 (after the second RTA), were prepared.

Reflectivity at the glancing angle θ close to the critical angle θ_C was measured as a function of photon energy around the Ti K-edge. Measurements were carried out at BL-4 at AURORA (a compact synchrotron at the Ritsumeikan Synchrotron Radiation Center) using an Si(220) double-crystal monochromator and a goniometer in a vacuum. Owing to equipment limitations, measurements were carried out with π-polarization and a horizontal beam divergence of 0.3 mrad (1σ). This beam divergence reduces the angular resolution of the observed reflectivity. The reflectivity $I(E)/I_o(E)$ was normalized by a scale factor, where $I(E)$

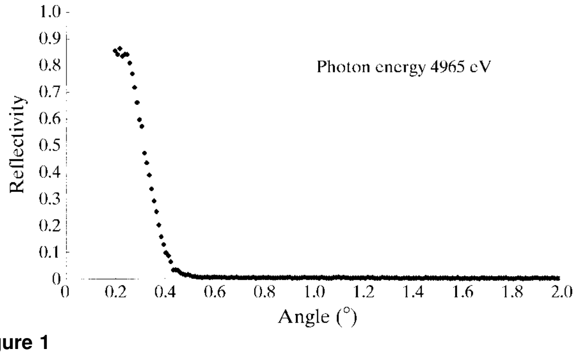

Figure 1
The reflectivity of $TiSi_2$ sample #1 *versus* the glancing angle.

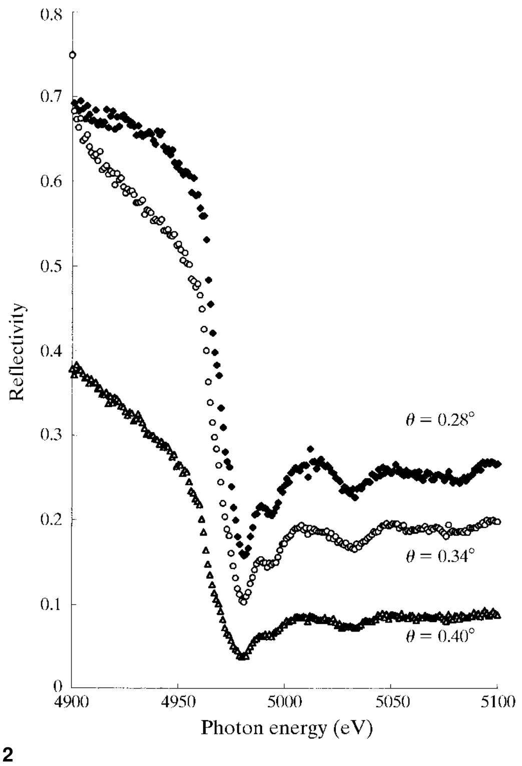

Figure 2
The reflectivity of $TiSi_2$ sample #1 at glancing angles of 0.28, 0.34 and 0.40°.

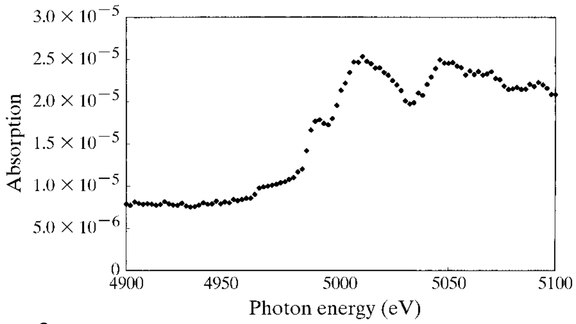

Figure 3
XANES spectra of $TiSi_2$ sample #1 extracted from the reflectivity.

and $I_o(E)$ represent the reflected beam intensity and the incident beam intensity, respectively, measured with an ionization chamber. Without an incident beam monitor, $I(E)$and $I_o(E)$ were not recorded at the same time.

An initial experiment was carried out to record the reflectivity *versus* the glancing angle at constant energies (4955, 4965 and 4975 eV) to check the quality of the sample surface and to calculate the initial critical angles θ_C. Fig. 1 shows the reflectivity of sample #1 measured at a photon energy of 4965 eV. Then, $R(E)$ spectra were recorded from 4900 to 5500 eV for various glancing angles (0.28, 0.34 and 0.40°) close to the critical angle (0.40°).

3. Results and Discussions

Fig. 2 shows reflectivity spectra for sample #1. The reflectivity $R(\theta/\theta_C,E)$, depending on the photon energy E through $\delta(E)$ and $\beta(E)$, can be described by the Fresnel equation. Since the dispersion $\delta(E)$ and the absorption $\beta(E)$ are the components of the complex refractive index $n(E) = 1 - \delta(E) - i\beta(E)$, they are related to each other by the K–K relations. We calculated $\beta(E)$ from the measured reflectivity $R(\theta/\theta_C,E)$ using theoretical values (Henke *et al.*, 1993) for initial $\delta(E)$.

Fig. 3 shows XANES spectra extracted from the reflectivity of sample #1. The energy dependence of the reflectivity was measured with several photon glancing angles (θ = 0.28, 0.34 and 0.40°) around the critical angle θ_C of total reflection.

The reflectivity of a smooth flat surface is given by

$$R(E,x) = \frac{h - x[2(h-1)]^{1/2}}{h + x[2(h-1)]^{1/2}},$$

where

$$h = x^2 + [(x^2-1)^2 + (\beta/\delta)^2]^{1/2}$$

and $x = \theta/\theta_C$. The normalized glancing angle x has energy dependence because $\theta_c = (2\delta)^{1/2}$.

$$(\beta/\delta)^2 = 2x^2(1 - B^{-1})[1 - B^{-1}x^2 + B^{-1}x^2(1 - 2Bx^{-2})^{1/2}] - 1,$$

where $B = (1-R)^2/(1+R)^2$. Using these equations, we can extract $\beta(E)$ from R using initial values of $\delta(E)$.

The reflectivity spectra recorded with the glancing angles 0.28 and 0.34° have essentially the same XANES. Fine signals decrease in XANES spectra calculated from the reflectivity with the critical angle 0.40°.

The reflectivity feature of $TiSi_2$ sample #2 is broader than that of sample #1. This shows an increase of the interface roughness because of the growth of $TiSi_2$ grains.

4. Conclusions

The shapes of ReflXAFS spectra vary with photon glancing angle θ. The ReflXAFS defined by $\beta_R(E) - \beta_0(E)$ is a superposition of β-XAFS and δ-XAFS with the relative contribution dβ/dδ according to

$$\beta_R(E) - \beta_0(E) = [\beta(E) - \beta_0(E)] - (\mathrm{d}\beta/\mathrm{d}\delta)[\delta(E) - \delta_0(E)].$$

For glancing angles below the critical angle θ_C, dβ/dδ is small and the ReflXAFS is essentially equal to β-XAFS, and for larger glancing angles, dβ/dδ increases rapidly and δ-XAFS becomes dominant. If the glancing angle $\theta \ll \theta_C$, the absorption decreases and the ReflXAFS signal is weakened. On the other hand, at a glancing angle close to θ_C the reflectivity decreases rapidly. ReflXAFS defined in the limit $\theta \to 0$ can be considered as (000) diffraction anomalous fine structure (DAFS). We have obtained XANES spectra from $TiSi_2$ thin films on Si(001) substrates from their ReflXAFS measured with the normalized glancing angle θ/θ_C in the range 0.7–0.85 by calculating the Fresnel reflectivity.

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