Grazing-incidence X-ray specular reflectivity study on a rutile (110) surface

Mari MIZUSAWA and Kenji SAKURAI*
National Institute for Materials Science, Sengen, Tsukuba, Ibaraki 305-0047, Japan

Introduction

Fine rutile (TiO_2) powder is one of the most promising materials for future solar cell applications. Since the powder's electronic properties depend highly on the degree of preferred <110> orientation, studying a single crystal (110) surface in a realistic environment is significant [1]. In this study, grazing incidence X-ray scattering has been employed to observe the annealing effect.

Experimental

The samples measured are mirror-polished rutile (110) single crystal substrates that are commercially available (Nakazumi). The surface has been cleaned in a dilute HNO_3 bath (10vol%, 100°C, 15min). Sample A is as cleaned, and sample B is annealed at 300°C for 1 h in a vacuum (10^{-3}Pa) after HNO_3 cleaning. The colour of sample B did not change after annealing. The experiment was carried out with 16keV monochromatic X-rays.

Results and Discussion

Figure 1 shows the specular reflectivity with 8.5 decades for the rutile (110) surfaces, A and B. The critical angle is 2.45 mrad, indicating that the density is around 4.26g/cm^3, which agrees well with that for solid bulk rutile. The slow oscillation observed at 10~28mrad indicates some density gradient at the near surface. Calculations have been made based on Parratt's model assuming thin surface layers with different density and thickness. The calculated reflectivity curves show good agreement with the experimental results.

Proposed models for the sample A and B are shown in Figure 2. They have an interesting density profile, i.e,, (i) an extremely low density layer (0~10 Å , density ~1), which could correspond to some adsorption, (ii) a moderately low density layer (15~30 Å , density 2.77~4.26), which is probably due to some near-surface damage caused by polishing and (iii) a transition region (10~15 Å). In the early stage of analysis, we obtained a good fit for the 2 thin layers model, shown as a dashed line in Figure 1. The model was not adopted because it was concluded that the density for the 2nd layer is 3~6 % higher than the bulk, which can not be explained reasonably. However, it definitely suggested a remarkable density contrast in the near-surface region, and the profile proposed in Figure 2 interprets this well. One should note that sample B has a lower density than A because of annealing. The averages for the whole surface layers are 2.55 and 2.37, for A and B, respectively; the averages for the moderately low density layers are 3.43 and 3.34, for A and B, respectively.

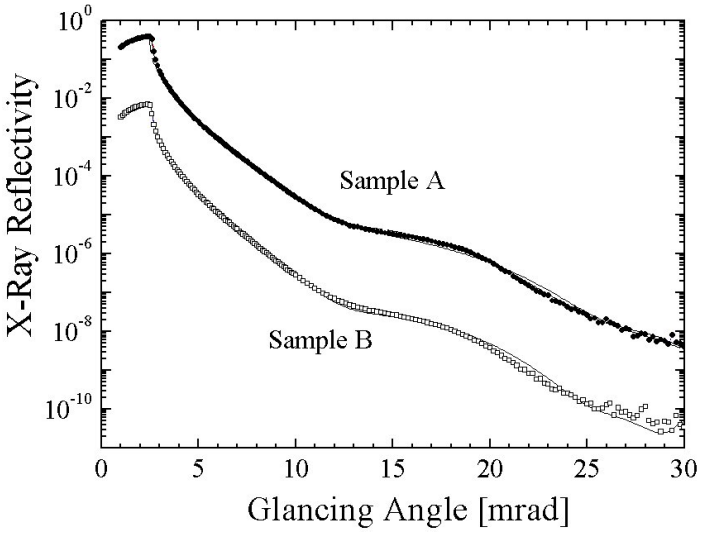
Another comparison between A and B can be discussed in terms of their surface morphologies. The diffuse scattering measurements performed for these samples did not show that great a difference, but the rather weak intensity of sample B could indicate that annealing can contribute to some flattening of the surface.

The authors would like to thank Prof. S. Kishimoto and Dr. S. Kuwajima for their kind assistance during the experiment.

References

[1] P.A.M. Hostenpiller et al, J. Phys. Chem. B, **102**, 3216 (1998)

*sakurai@yuhgiri.nims.go.jp



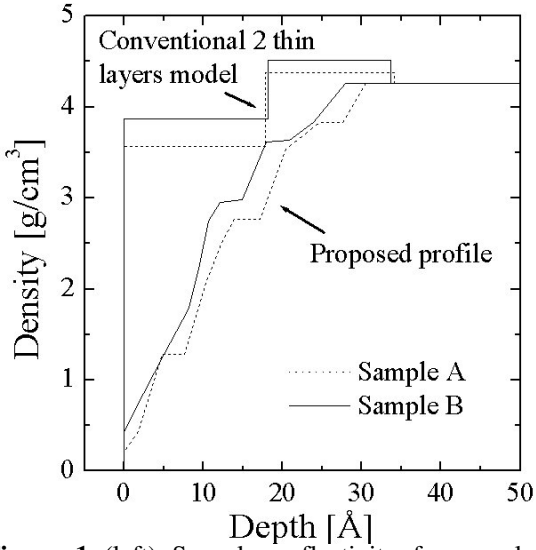


Figure 1 (left) Specular reflectivity for sample A (squares), and B (circles). The curve-fitting results are shown with solid lines (density gradient density model) and dashed lines (2 thin layers model).
Figure 2 (up) Proposed surface density profile.