Surface-Normal Structure of Te and Cd UPD Layer Formed on an Au(111) Substrate Analyzed by Specular X-ray Reflectivity

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The formation of cadmium chalcogenide layers such as CdTe on Au single-crystal substrates has been investigated from the viewpoint of their application to solar cells. A single atomic layer can be formed using underpotential deposition (UPD), which is a surface-limited reaction to a sub-monolayer or monolayer (ML) coverage. Therefore, the UPDs of Te and Cd are alternated on an Au(111) substrate, and epitaxial CdTe films can be obtained. The method is referred to as the electrochemical atomic layer epitaxy (ECALE),[1] and, in the formation of CdTe films by ECALE, it is important to understand the true character of the UPD of Te and Cd on an Au(111) substrate, by analyzing the surface structure in situ. However, structural analysis using STM and AFM is limited to the two-dimensional surface structure and cannot be used to directly investigate the three-dimensional surface structure, such as the surface-normal structure of the adsorbate layer consisting of more than one layer, and the buried interface structure between the adsorbate layer and the substrate. In the present study, the structure normal to the substrate surface of the Te and Cd UPD layer formed on an Au(111) substrate have been investigated by *in situ* specular X-ray reflectivity measurements.[2, 3]

The *in situ* specular X-ray reflectivity measurements were carried out using a κ-type multi-axis diffractometer installed on beamline 14B1 at SPring-8, Japan. The wavelength utilized was λ = 0.110 nm. The Te and Cd UPD layer were formed on a pre-treated Au(111) disk electrode in the electrolytic solution of 0.1 mM TeO_2 + 10 mM H_2SO_4, and 1 mM $CdSO_4$ + 10 mM H_2SO_4, respectively. The potential for the Te and Cd UPD were applied to the Au(111) electrode during the reflectivity measurements, respectively. The theoretical specular reflectivity for the electrode surface is given by the kinematical approximation. In the quantitative determination of the structure of the near-surface layers that include the surface adsorbate layers and the underlying Au layers, the parameters representing the electron density profiles of each layer are optimized so as to adequately describe the observed reflectivity.

Te UPD Layer. — The measurements were carried out for a series of samples which were kept at UPD potential for 4 to 59 hours. The specular reflectivity for the Te UPD layer formed on an Au(111) substrate is shown as the black square in Fig.1. The data collection started from 39 hours after the UPD potential was applied and lasted for 20 hours for the measurement. The solid line is calculated profile based on a model which assumes that the first layer consists of 0.33ML Te and 0.08 ML Au, while the second layer consists of 0.92 ML Au. The X-ray reflectivity measurement indicates that a portion of Au atoms migrate from the top layer of the Au(111) substrate to the top-most Te layer. In consequence, the Te UPD layer formed on an Au(111) substrate is not stable for a long period of time.

Cd UPD Layer. — Figure 2 shows the specular reflectivity for the first (black circle) and the second Cd UPD layer (gray triangle), respectively. The black line is the calculated reflectivity profile for the first UPD layer based on the model where a 0.50 ML Cd atomic layer is on the reconstructed Au(111) surface and a 0.25 ML sulfuric acid anion layer is above the Cd atomic layer. The gray line is the calculated reflectivity profile for the second UPD layer which is based on the almost similar model to the first UPD layer. The specular reflectivity measurement shows that the Cd UPD layer consists of both sulfuric acid anions and Cd atoms. However, the coverage of the Cd UPD layer changes little although the applied potential is different, which is contrary to the STM studies.[4] Probably, the adsorption phase of the sulfuric acid anion in the Cd UPD layer changes when the applied UPD potential is changed, so that the different STM images might be obtained at the different UPD potential.

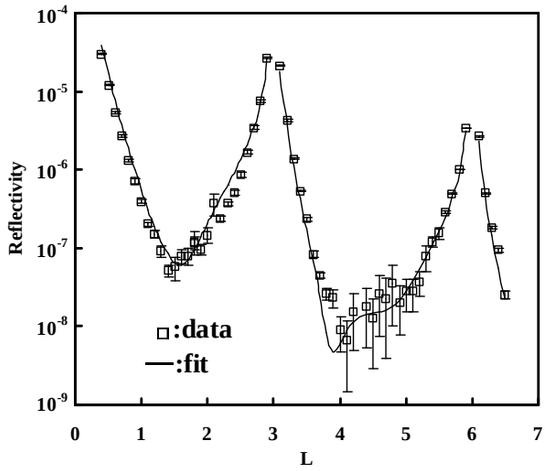
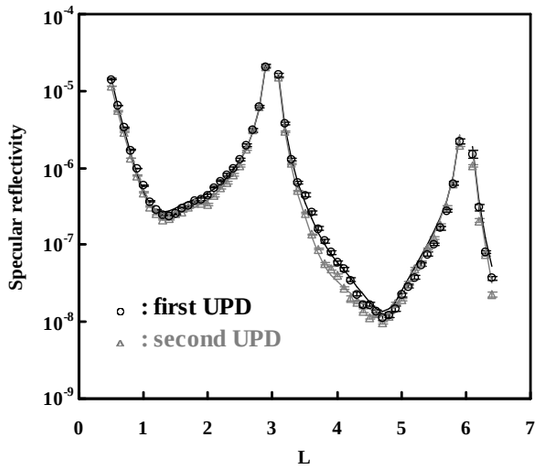


Figure 1. Specular X-ray reflectivity from the Te UPD layer on the Au(111) substratre. The data collection was started from 39 to 59 h after holding the potential.

Figure 2. Specular X-ray reflectivities from the first and second Cd UPD layer on the Au(111) substrate.



References

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4. J. C. Bondos, et al., *J. Phys. Chem.*, **100**, 8617 (1996).