Evidence for the Diffusion of Au Atoms into the Te UPD Layer Formed on an Au(111) Substrate

A single atomic layer can be formed by electrochemical processes using underpotential deposition (UPD), which is a surface-limited reaction to a sub-monolayer or monolayer (ML) coverage. In UPD, the electrochemical deposition of foreign metal atoms onto substrate is performed at a positive potential relative to the reversible Nernst potential for bulk deposition (Fig. 1(a)). By alternating the UPD of two different elements we can obtain a binary compound with a layer-by-layer grown structure, that is the electrochemical atomic layer epitaxy (ECALE) (Fig. 1(b)) [1]. Epitaxial growth CdTe layers on an Au single crystal substrate are very important and interesting from the viewpoint of their applications to solar cells.

Since it is considered that the deposition of Cd on an Au substrate easily produces intermetallic compounds, the first step to the formation of CdTe films by ECALE is the UPD of the Te. The structure of Te UPD layer has been studied using a scanning tunneling microscopy (STM) [2,3] and an atomic force microscopy (AFM) [4]. However, structural analysis using STM and AFM is still limited to two-dimensional surface structure. In the present study, the structure which is normal to the surface of the Te UPD layer was revealed by *in situ* specular X-ray reflectivity measurements [5].

The *in situ* specular X-ray reflectivity measurements were carried out using a κ-type multi-axis diffractometer installed at beamline **BL14B1**. The wavelength utilized was λ = 0.110 nm. The Te UPD layer is formed on a pre-treated Au(111) disk electrode in an electrolytic solution contained 0.1 mM TeO_2 and 10 mM H_2SO_4 as the supporting electrolyte. The potential for the Te UPD is applied to the Au(111) electrode during reflectivity measurements. The theoretical specular reflectivity for the electrode surface is given by the kinematical approximation. In the quantitative determination of the near-surface structure of Te- and Au-layers, the parameters representing the electron density profiles of each layer are optimized so as to adequately describe the observed reflectivity.

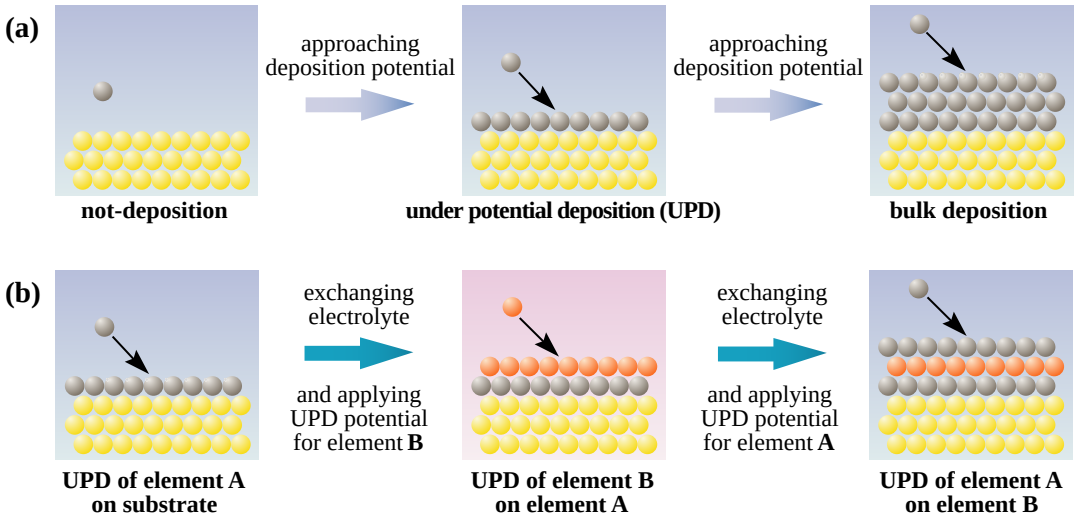

Fig. 1. Schematic illustrations of ***(a)*** *underpotential deposition (UPD) and* ***(b)*** *electrochemical atomic layer epitaxy (ECALE).*

The measurements were carried out for the samples which were kept at the UPD potential for 4 to 59 hours. The specular reflectivity for the Te UPD layer formed on an Au(111) substrate is shown as solid circles in Fig. 2. The data collection was performed between 39 to 59 hours after the UPD potential was applied. The dashed red line is calculated profile based on a model that the Te UPD layer is formed just on the Au(111) substrate; we assume the electron density profile in Fig. 3(a), and the Te-coverage of 0.33 ML which is determined from the electrochemical measurement. However, the calculated profile does not fit the observed reflectivity. Therefore, we assume another electron density profile shown in Fig. 3(b); here, the first layer consists of 0.33 ML Te and 0.08 ML Au, while the second layer consists of 0.92 ML Au. The calculated reflectivity (solid blue line in Fig. 2) reproduces the experimental results very well. From the X-ray reflectivity measurements we can conclude that a portion of Au atoms migrates from the top layer of the Au(111) substrate into the top-most Te layer. In consequence, an ideal pure atomic layer formed by the UPD process is not always stable for a long period of time, but atomic interdiffusion may occur within the near-surface layers.

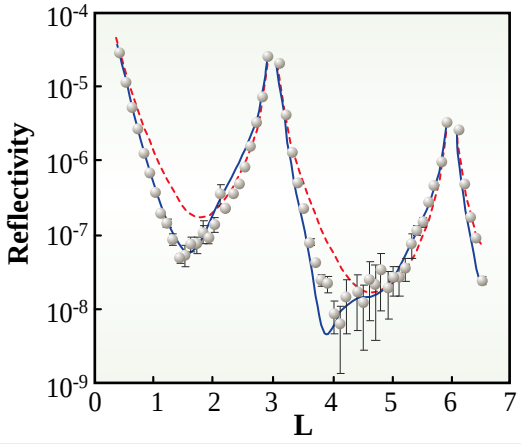

Fig. 2. Specular X-ray reflectivity from the Te UPD layer on the Au(111) substrate. The data collection was performed between 39 to 59 hours after the UPD potential had been applied. The dashed red line shows the reflectivity expected for a Te layer immediately above the Au(111) substrate. The solid blue line shows the reflectivity expected for the top layer consisting of the UPD Te atoms and Au atoms which diffuse from the Au(111) substrate.

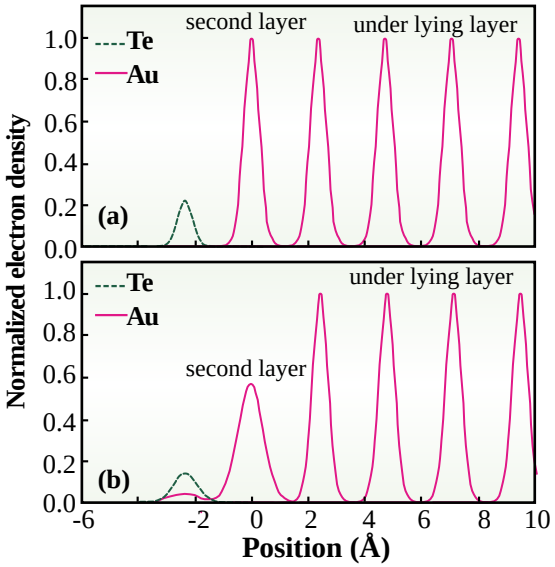

*Fig. 3. Normalized electron density profile normal to the surface for fit to the observed specular X-ray reflectivity. A negative value of position means that a layer is out of the ideally terminated Au surface. **(a)** Model for the top layer consisting of 0.33 ML Te. **(b)** Model for the top layer consisting of 0.33 ML Te and 0.08 ML Au, and the second layer consisting of 0.92 ML Au.*

References

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