

Surface X-ray Scattering Study on Reconstruction Lifting of Au(111) Single Crystal Surface Induced by Formation of Alkylthiol Self-Assembling Monolayer

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Introduction

Self-assembled monolayers (SAMs) of alkylthiols on gold have been widely used in various fields. In order to apply the alkylthiol SAMs to modern nanotechnology, structures at electrode/electrolyte interfaces should be made clear with an atomic dimension. Although molecular arrangements of alkylthiol SAMs on Au(111) during SAM formation were investigated in details by scanning tunneling microscopy (STM) [1], structure relationship between chemisorbed alkylthiol and gold during SAM formation were not made clear because the STM measurements provide structural information of only the outermost layer.

It is well-known that the ($\sqrt{3}\times\sqrt{3}$) reconstructed structure is most stable not only in vacuum but also in solution at on Au(111) surface [2]. When atoms/molecules/ions are adsorbed on the Au(111) surface, however, the reconstructed structure of Au(111) is lifted leading to a (1 \times 1) structure. Ocko et al. reported the potential-dependent structures of the reconstructed Au(111) in the electrolyte solutions containing various halogen anions using *in situ* surface X-ray scattering (SXS), which is one of the best methods to investigate the three-dimensional (3D) interfacial structure at an atomic level.

In this report, the effect of hexanethiol (C₆SH) SAM formation on the outermost surface structure of Au(111) was investigated by *in situ* surface X-ray diffraction (SXR).

Experiments

SXR measurements were carried out at Au(111) surface in ethanol solution containing C₆SH in a beamline BL4C at Photon Factory. A wavelength of 1.100 Å was selected to avoid any fluorescence from the Au substrate [3]. After the SXR measurements, adsorbed amounts of C₆SH molecules were estimated from charge of desorbing reduction peaks in linear sweep voltammograms measured in 0.1 M KOH aqueous solutions.

Results and Discussion

Figure 1 shows SXR profiles of Au(111) surfaces without (a), with C₆SH SAM (b, c) with different coverage. Two peaks due to the ($\sqrt{3}\times\sqrt{3}$) reconstructed

and (1 \times 1) structures were observed at $q_r = 0.038$ and $q_r = 0$, respectively, before the SAM formation. However, intensity of the reconstructed peak decreased after the SAM formation with a coverage, θ , of 0.65 and this reconstructed peak was finally disappeared after the complete SAM formation ($\theta = 1$). Instead, intensity of the (1 \times 1) peak increased as increasing the adsorbed amounts. The present results suggest that the C₆SH SAM forms on Au(111)-($\sqrt{3}\times\sqrt{3}$) surface at the initial stage of the SAM formation, which means that C₆SH molecules are weakly adsorbed, and then the reconstructed structure is lifted to (1 \times 1) induced by the strong adsorption of C₆SH SAM with $\theta > 0.6$.

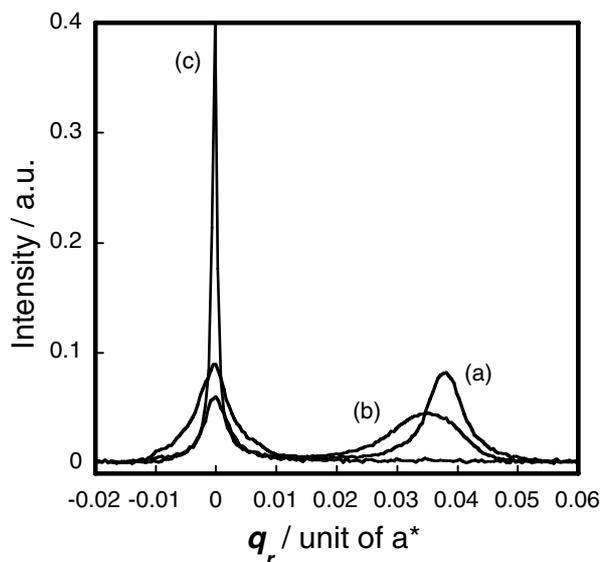


Fig. 1 SXR profiles of Au(111)/ethanol interface at $L = 0.2$ without (a) and with C₆SH SAM (b, c) with different coverage.

References

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