

***In situ* SXR D Study of Electrochemical Formation/Desorption Processes of Self-Assembled Monolayer (SAM) on Au(111) Electrode Surface**

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Introduction

Self-assembled monolayers (SAMs) of alkanethiols on gold have attracted many research groups because they have a wide variety of potential applications such as sensors, corrosion inhibition, wetting control, and molecular electronic devices. To construct well-designed SAMs, it is essential to understand their fine structure and formation/desorption processes. The various molecular arrangements of the SAMs of alkanethiols on gold, depending on their coverage, have been revealed mainly by SPM [1, 2], however, the surface atom arrangements of the underlying gold electrode have been still unclear. Here we investigated the structural change of Au(111) electrode surface *in situ* during electrochemical formation/desorption processes of hexanethiol (C6SH) SAM by surface X-ray diffraction (SXR D) technique.

Experimental

SXR D measurements were carried out in a spectroelectrochemical cell developed by our group [3]. The Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. Prior to each measurement the Au(111) disk was flame annealed using a Bunsen burner and slowly cooled in air. It was then transferred to the spectroelectrochemical cell with the surface being covered with a drop of pure water to avoid any surface contamination. The electrolyte solution was 0.1 M KOH ethanol containing 100 mM C6SH. The Au(111) electrode was placed in contact with the electrolyte solution while the electrode potential was held at -0.3 V. Next, the potential was scanned from -0.3 V in the negative direction at a scan rate of 10 mV/s to -1.05 V and held at -1.05 V for 1 h, so that the clean reconstructed phase covered on the surface. After the potential was scanned positively and held at -0.6, -0.4 V and 0V for 1 h or 10 min, the electrode surface was pushed to the Mylar window. And then SXR D measurements were performed. The thin layer configuration of the electrolyte has an advantage in avoiding X-ray scattering by the solution.

Results and Discussion

Figure 1 shows a typical cyclic voltammogram (CV) of an Au(111) electrode in 0.1 M KOH ethanol containing 100 mM C6SH [4, 5]. Cathodic peak corresponding to reductive desorption of C6SH SAM was observed at -0.85 V, and anodic peak corresponding to oxidative adsorption of thiolate at -0.75 V. Figure 2 shows the potential dependence of the in-plane scattering through the (01) bulk reflection along the [11] direction at $L = 0.2$.

We labeled it as q_r axis, where $q_r = 0$ corresponds to the (01) reflection, i.e., (1x1) substrate symmetry and $q_r = 0.038$ to reconstructed $\sqrt{3} \times 23$ periodicity. As shown in Fig.2, the intensity of the (1x1) peak grew while that of the reconstruction peak concomitantly decreased as the potential became more positive, showing that oxidative adsorption of thiolate induced the lifting of reconstructed phase into (1x1) at the Au(111) electrode surface. The peak position of the reconstruction shifted to smaller q_r , i.e., smaller compression, as the potential became more positive increased. It is interesting to note that the reconstructed phase still remained on the surface at -0.4 and -0.6 V, which were more positive than the oxidative adsorption peak. To understand the kinetic aspect of the formation/desorption processes, the holding time dependencies of these peak intensities at constant potentials are now under investigation.

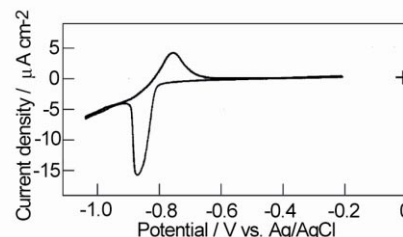


Fig. 1 Cyclic voltammogram of an Au(111) electrode measured in 0.1 M KOH ethanol solution containing 100 mM C6SH. Scan rate 10mV/s

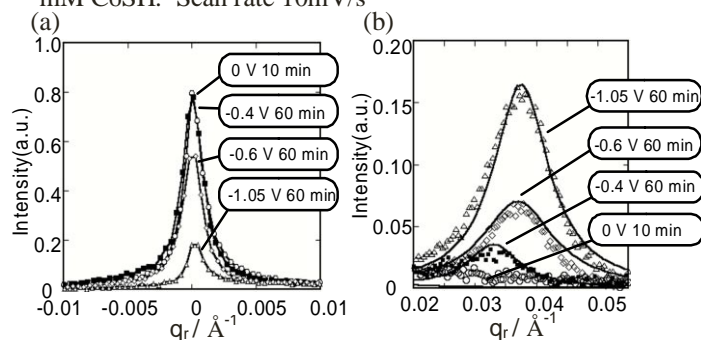


Fig. 2 Potential dependence of the in-plane X-ray scattering intensity along q_r axis around (a) the (1x1) peak and (b) the reconstruction peak.

References

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