

## Structural Transition of Alkylthiol/Au(111) Interface During Self-assembly Process

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Construction of well-ordered organic molecular layers on solid surfaces has been the subject of numerous studies because of their importance both in fundamental science and for a wide range of applications such as molecular and bio-electronic devices. Self-assembly (SA) technique is proved to be one of the best methods to construct ordered molecular layer on solid surfaces to provide functional surface. Self-assembled monolayers (SAMs) of alkylthiols on gold have been extensively studied because stable monolayers with high packing density, stability, and orientational order can be very easily formed by soaking a substrate in solution containing alkylthiol molecules. Surface properties can be controlled by forming SAMs of alkylthiols with terminal functional groups.<sup>1-3</sup>

In order to construct the highly efficient molecular devices using SAMs, we have to construct the well-ordered SAMs on Au(111) and it is essential to understand and to control the SA process of the alkylthiol on a Au(111) surface.<sup>1-7</sup> Not only the structure of the SAM of full coverage but also formation processes of the alkylthiol SAMs on Au(111), which are grown both from solution or from the gas-phase, have been extensively studied experimentally and theoretically but there are many discrepancies between experimental results and theoretical models. Furthermore, alkylthiol SAMs on Au(111) have some defects such as a missing row (boundary defect) and vacancy island (etch pit) and their formation mechanisms have not been made clear completely yet.

Surface X-ray scattering (SXS) technique is one of the best methods to precisely determine the interfacial atomic arrangements with a high spatial resolution and has been employed to monitor the change of the surface atomic arrangements of the Au(111) surface from the  $(23 \times \sqrt{3})$  reconstructed structure to the  $(1 \times 1)$  structure under electrochemical condition *in situ*.<sup>8,9</sup>

Here, the transition of the atomic arrangement of Au(111) surface from the reconstructed  $(\sqrt{3} \times 23)$  to the  $(1 \times 1)$  structure during the hexylthiol ( $C_6SH$ ) SAM formation was investigated by monitoring in-plane SXS, i.e., surface X-ray diffraction (SXRD), profiles of the  $C_6SH$  SAM modified Au(111) with various surface densities of the SAM,  $\Gamma$ , which were determined by the electrochemical reductive desorption of the SAM.<sup>10</sup>

Detailed electrochemical and surface X-ray diffraction measurements shows that the Au(111)- $(23 \times \sqrt{3})$  reconstructed structure is converted to the Au(111)- $(1 \times 1)$  structure upon the formation of a hexylthiol SAM but the degree of the lifting of the Au(111) reconstructed structure non-linearly depends on the surface concentration of the thiol SAM,  $\Gamma$ . The reconstruction lifting seems to be induced by the formation of the

condensed phase of the SAM on the Au(111) surface with  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure, which takes place when the surface concentration of the adsorbed thiol on the Au(111)- $(23 \times \sqrt{3})$  reconstructed structure reached the full coverage in the lying-down phase.<sup>11</sup>

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