Adsorption of Alkanethiol Self-Assembled Monolayers on Sputtered Gold Substrates for Atomic Nanolithography Applications

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Self-assembled monolayers (SAMs) of thiol-functionalized molecules on single-crystal Au surfaces have been studied by numerous groups since their discovery [1]. Such organosulfur monolayers now have numerous technological applications, the most recent of which involves their use as positive resists in atomic nano-fabrication [2]. In the light of recent technological advances in atom beam nanolithography, a detailed understanding of the quality of coverage of the Au surface by the alkanethiol monolayer is necessary to determine its limitations as a uniform resist for feature definition on the order of $5 \sim 25$ nm.

Si(100) substrates were used with a 4 nm Cr adhesion layer deposited prior to Au sputtering. After cleaning, the samples were incubated for 24 h in an ethanol based 1-nonanethiol solution.

The work has delineated the true structure of 1-nonanethiol self-assembled monolayers on sputtered Au surfaces by using molecular resolution STM and AFM imaging. The monolayer self-assembles on an extremely smooth Au surface that is composed of predominantly $\{111\}$ oriented grains with a typical size of $25 \sim 40$ nm. An AFM image of this surface can be seen in Fig. 1. Domains of the alkanethiol monolayer are observed with sizes typically of $5 \sim 25$ nm and multiple molecular domains can exist within one Au grain. STM imaging shows that the $(4 \times 2)$ superlattice structure reverts back to a $(3 \times 2\sqrt{3})$ structure when imaged under non-contact AFM conditions. An STM image of the monolayer is shown in Fig. 2 and the inset shows the hexagonal packing arrangement when imaged using non-contact AFM. These high resolution studies have not only clarified the true structure of 1-nonanethiol on Au$\{111\}$ but have resolved the debate on whether domain boundaries are bounded by monoatomic depressions. We have showed that this is not the case. The first direct evidence that the 1-nonanethiol molecules must reside in the three-fold hollow sites of the Au lattice is also presented. The 1-nonanethiol molecules residing in the three-fold hollow sites of the Au$\{111\}$ lattice are aligned along the Au[112] lattice vectors. The SAM monolayer contains many non-uniformities and discontinuities such as pin-holes, domain boundaries and monoatomic depressions. It has also been established that these depressions exist on the Au surface prior to and during the adsorption of alkanethiols. The observation of a high density of domain boundaries, pin-holes and monoatomic depressions may limit the applicability of 1-nonanethiol as a resist in atomic nanolithography experiments for features sizes $< 20$ nm.

References