Direct Adsorption and Molecular Self-Assembly of Octylthioacetates on Au(111) in the Vapor Phase

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Self-assembled monolayers (SAMs) are a very promising construct for monomolecular thin films with various practical applications because they are very amenable to surface modification and functionalization of metal surfaces.[1-6] Alkanethiol SAMs on gold surfaces have been thoroughly studied by a number of research groups, and their structural properties have been well characterized. Organic thiols are prone to easily oxidize to disulfides or other oxidized species that can affect the formation and structure of SAMs.[7,8] The presence of disulfides or oxidized compounds in thiol samples often yields poorly ordered SAMs containing a high defect density and disordered phases. An approach that minimizes undesirable thiol oxidation is the use of a protected thiol that is deprotected *in situ* before or during SAM formation. The protection of thiol groups can be readily accomplished by acetylation. SAMs derived from acetyl protected thiols (thioacetates) on gold have usually been formed via an *in situ* deprotection process of the acetyl group in strong acidic or basic solutions.[9-11] Other deprotection techniques have also been developed that use organic compounds such as triethylamine,[12] tetrabutylammonium cyanide,[13] and 1,8-diazabicyclo[5.4.0]undec-7-ene,[8] and organic SAMs with a high degree of structural order have been successfully constructed in solutions containing these deprotection reagents.
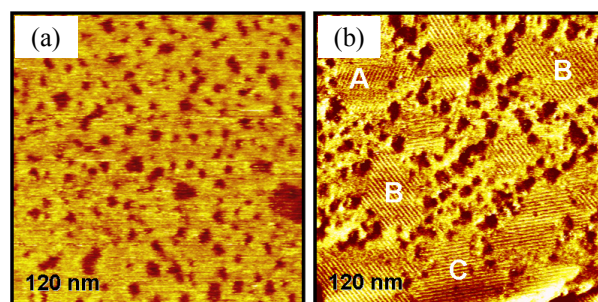
In contrast, there have been only limited reports of investigations into the direct adsorption of thioacetyl-protected organic molecules on gold in solution without any deprotection reagents.[8,9,13-15] It has been observed that the direct adsorption of alkanethioacetates (ATAs) on gold in solution generates loosely packed and disordered SAMs compared to the corresponding alkanethiols (ATs).[8,13,15] A kinetics study showed that the adsorption rate is slower for ATAs in pure solvents than for ATs.[14] Fully covered monolayers from aromatic thioacetates were formed after a longer immersion period of several days or in a concentrated 30 mM solution.[9] In general, organic thiol SAMs can be formed by both solution and vapor phase deposition, and both deposition methods yield identical SAM structures containing the hexagonal ($\sqrt{3} \times \sqrt{3}$)R30° or c(4 × 2) structure at saturation coverage.[1,3,16] To the best of our knowledge, however, there have been no reports describing organic thioacetate SAMs on gold grown by vapor deposition.

In this study, to understand the formation of thioacetate SAMs on gold depending on deposition method, we directly compared the surface structures of the acetyl-protected octylthioacetate (OTA, $CH_3(CH_2)_7SCOCH_3$), SAMs on Au(111) grown from solution and vapor phase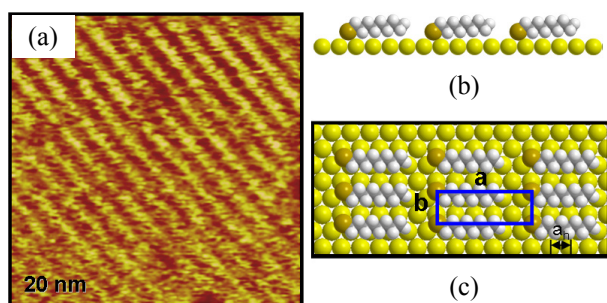 at 50 °C. Scanning tunneling micro-scopy (STM) observations clearly demonstrate that OTA SAMs grown from solution have only a disordered phase, whereas those grown from the vapor phase have an ordered 5 × $\sqrt{3}$ striped phase.

Au(111) substrates were prepared by thermal evaporation of gold onto freshly cleaved mica as has been previously reported.[3] OTA SAMs grown from solution were prepared by dipping the Au(111) substrates in a 1 mM ethanol solution of OTA at 50 °C for 24 h. OTA SAMs grown from the vapor phase were prepared by placing the substrates in a vial containing 3 μL of neat liquid OTA, and after being tightly sealed by capping, the vial was kept in a drying oven at 50 °C for 24 h. STM imaging was carried out with a NanoScope E (Veeco, Santa Barbara, CA) equipped with a commercially available Pt/Ir (80:20) tip under ambient conditions.

The STM images in Figure 1 clearly show considerable structural differences between OTA SAMs on Au(111) grown from solution and vapor deposition at 50 °C for 24 h. OTA SAMs grown from solution were mainly composed of disordered phases containing many vacancy islands (VIs, dark holes), as shown in Figure 1a. The surface structures of these OTA SAMs were nearly identical to those obtained from OTA and decylthio-acetate SAMs formed in 1 mM solutions at room temperature.[8,13] It has been found that high quality AT SAMs containing large well-ordered domains and low density VIs were formed at an elevated solution temperature.[5,16,17] Contrary to AT SAMs, however, the structural quality of OTA SAMs did not improve after increasing the solution temperature to 50 °C, which suggests that solution temperature is not an important factor in the formation and structure of ATA SAMs on gold. Previous work from us and other groups has shown that the direct adsorption of

Figure 1. STM images of OTA SAMs on Au(111) grown from (a) solution and (b) vapor phase at 50 °C for 24 h. All scan sizes were 120 nm × 120 nm.

40   *Bull. Korean Chem. Soc.* **2011**, Vol. 32, No. 1

Communications to the Editor

Figure 2. (a) 20 nm × 20 nm STM image showing the striped phase of OTA SAMs on Au(111) grown from vapor phase at 50 $^{\circ}$C for 24 h, (b) side view, and (c) structural model of the striped phase for OTA SAMs on Au(111). Note that a_h corresponds to the distance between gold atoms.

ATAs on gold in a pure solvent does not create any closely packed well-ordered SAMs irrespective of solution temperature. We speculate that the different structural behavior of ATAs compared to ATs in SAM formation derives from a lower adsorption activity of the sulfur atoms due to the direct attachment of electron-withdrawing acetyl groups. This suggestion is supported by the fact that the growth kinetics of ATA SAMs on gold surfaces is slower than that of the corresponding alkanethiols.[14] On the other hand, it has been suggested that highly ordered SAMs of thioacetates could be obtained from solutions containing thiols formed by *in situ* deprotection processes.[9-13] Recently, it was found that the degree of structural order of thioacetate SAMs increased with increasing amounts of thiols derived from *in situ* deprotection just prior to or during SAM formation.[8]

Unlike the formation of disordered OTA SAMs on Au(111) grown from solution, we observed that OTA SAMs grown from the vapor phase were composed of well-ordered phases surrounded by multiple VIs, as shown in Figure 1b. The ordered domains have three domain orientations (regions A, B, and C) with domain angles of 60° or 120°, which reflects the growth of OTA SAMs being influenced by the three-fold Au(111) symmetry. Most of the disordered phases existed in regions consisting of a high density of VIs, which seem to greatly hamper the formation and growth of ordered phases. From this STM observation, we demonstrated that OTA SAMs with a high degree of structural order can be obtained by vapor phase deposition.

The magnified STM image (20 nm × 20 nm) in Figure 2a clearly shows an ordered row structure of OTA SAMs grown from vapor deposition. The distance between molecular rows was measured to be 15.0 ± 0.5 Å (a = 5a_h), which is slightly larger than the molecular length of octanethiol (13.3 Å).[18] Although we do not clearly observe individual molecules in the rows, a number of STM observations reveal a molecular distance of approximately 5.0 Å (b = $\sqrt{3}a_h$) in the ordered row. Therefore, it is reasonable to assign the observed structure as (5 × $\sqrt{3}$) striped phase where the alkyl chains of the OTA molecules are oriented parallel to the surface, as shown in the adsorption model for OTA SAMs on Au(111) (Figures 2b and c). The rectangular unit cell contains one adsorbed molecule. We

recently observed the same type of surface structure from OT SAMs formed in 1 mM toluene solution at 50 $^{\circ}$C. A similar striped phase with low density surface coverage has often been observed at the initial stages of SAM growth[19] and after thermal annealing at high temperature.[20] At present, it is very difficult to rationalize the vapor phase deposition of OTA molecules preferentially forming a lying-down striped phase rather than a standing-up, densely packed, ordered phase.

In summary, we demonstrate that the direct adsorption of OTA on Au(111) in ethanol solution led to the formation of a disordered phase, whereas OTA SAMs grown from the vapor phase have an ordered 5 × $\sqrt{3}$ striped phase. Thus, vapor deposition was found to be a more effective technique, as compared to solution deposition, for improving the structural order of SAMs by direct adsorption of thioacetates on gold.

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