Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Adsorption Characteristics of Aliphatic Dithiols on Silver and Gold Revealed by Ellipsometry and FT-IR Spectroscopy

Sang Woo Joo [a], Sang Woo Han [a] & Kwan Kim [a]

[a] School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul, 151-742, Korea

Version of record first published: 24 Sep 2006

To cite this article: Sang Woo Joo, Sang Woo Han & Kwan Kim (2001): Adsorption Characteristics of Aliphatic Dithiols on Silver and Gold Revealed by Ellipsometry and FT-IR Spectroscopy, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 371:1, 355-358

To link to this article: http://dx.doi.org/10.1080/10587250108024759

Mol. Cryst. and Liq. Cryst., 2001, Vol. 371, pp. 355-358

Adsorption Characteristics of Aliphatic Dithiols on Silver and Gold Revealed by Ellipsometry and FT-IR Spectroscopy

SANG WOO JOO, SANG WOO HAN and KWAN KIM*

School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-742, Korea

The adsorption characteristics of (α,ω)-aliphatic dithiols on gold and silver were found to be dependent on the kind of solvent. In *n*-hexane medium, a multilayered film was readily formed not only on gold but also on silver. The infrared spectra suggested that multilayered films on gold should possess highly disordered structures regardless of the number of layers.

Keywords Self-Assembly; Aliphatic Dithiol; Gold; Silver; FT-IR; Ellipsometry

INTRODUCTION

Aliphatic as well as aromatic dithiols are known to adsorb on gold as monothiolates by forming one single Au-S covalent bond.[1] The other thiol group is pendent with respect to the gold surface. Moreover, Kohli et al.[2] recently reported that up to eight covalently attached layers could be formed on gold from solution phase (α,ω)-aliphatic dithiols. The linking chemistry between layers was claimed to be the oxidative formation of a sulfur-sulfur bond. In this work, we found evidence based on ellipsometry and infrared spectroscopy that the adsorption characteristics of (α,ω)-aliphatic dithiols on gold and silver are dependent on the kind of solvent. In a non-polar medium such as *n*-hexane, a multilayered film was readily formed not only on gold but also on silver. In a polar medium such as methanol and ethanol, at best a bilayered film could be formed on gold and silver, however.

EXPERIMENTAL

1,4-Butanedithiol (1,4-BDT), 1,5-pentanedithiol (1,5-PDT), and 1,6-hexanedithiol (1,6-HDT) were purchased from Aldrich. 1,3-Propanedithiol (1,3-PDT), 1,8-octanedithiol (1,8-ODT), and 1,9-nonanedithiol (1,9-NDT) were purchased from Lancaster. All these dithiols were used as received. Gold and silver substrates were prepared by resistive evaporation of titanium (Aldrich, >99.99%) and gold (Aldrich, >99.99%) or silver (Aldrich, >99.99%) at ~10^{-6} torr on batches of glass slides. These substrates were immersed in a solution of aliphatic dithiols in methanol or ethanol or *n*-hexane for a pre-determined period of time. After removing the substrates from the solution, they were rinsed with excess solvent and then dried in an N_2 gas stream.

The infrared spectra were obtained with a Bruker IFS 113v Fourier transform spectrometer equipped with a globar light source and a liquid N_2-cooled mercury cadmium telluride detector. The method for obtaining the reflection-absorption infrared (RAIR) spectra has been reported previously.[3] The ellipsometric thickness of the self-assembled aliphatic dithiol film was estimated using a Rudolph Auto EL II optical ellipsometer. The measurement was performed with the 632.8 nm line of an He/Ne laser incident upon the sample at 70°. The ellipsometric parameters, Δ and Ψ, were determined for both the bare clean substrates and the self-assembled films; the refractive index of the organic film was assumed to be 1.45.

RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the ellipsometric thicknesses of 1,9-NDT layers on gold and silver, respectively, versus the dipping time in two different solvents, i.e., *n*-hexane and methanol. The growth rate on silver was comparatively larger than that on gold. On the other hand, the eventual thickness was larger on silver than on gold. In 1 mM *n*-hexane solution, the thickness of the 1,9-NDT layer attained up to 9.3 nm on gold and 9.9 nm on silver. In contrast, in 5 mM methanol, the thicknesses of the 1,9-NDT layers became at most 1.8 nm on gold and 2.7 nm on silver. Quite a similar solvent dependency was observed for other dithiols, i.e., 1,3-PDT, 1,4-BDT, 1,5-PDT, 1,6-HDT, and 1,8-ODT. The measured ellipsometric thickness in *n*-hexane medium must correspond to the formation of up to nonalayers while the measured thickness in methanol indicates the formation of at best bi- or tri-layers.

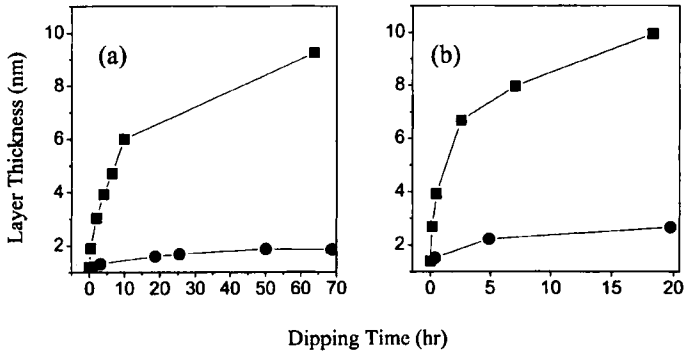

FIGURE 1. Ellipsometric thickness of 1,9-NDT layers on (a) gold and (b) silver versus the dipping time in two different solvents, i.e., in 1 mM *n*-hexane solution (-■-) and in 5 mM methanol solution (-●-).

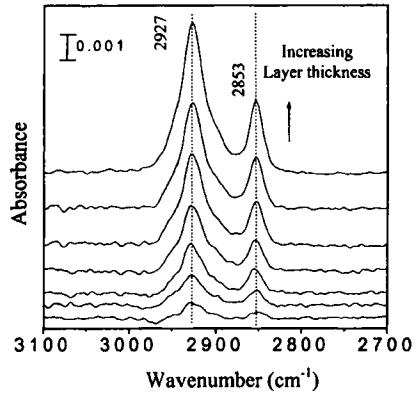

FIGURE 2. RAIR spectra in the C-H stretching region taken after self-assembly of 1,9-NDT on gold in 1 mM *n*-hexane solution for a certain period of time; each spectrum corresponds to one of the square data points in the ellipsometry data in Figure 1(a).

Figure 2 shows a series of RAIR spectra in the C-H stretching region taken after self-assembly of 1,9-NDT on gold in 1 mM *n*-hexane solution for a certain period of time. The peak positions of the symmetric as well as the antisymmetric stretching modes of the methylene groups were found to

be rather insensitive to the growth of 1,9-NDT layers. That is, the $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ bands appeared at 2853 and 2927 cm^{-1}, respectively, in all RAIR spectra. This indicates that the overall structure is independent of the layer thickness. Using the fact that the peak positions of the $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ modes can be used as a sensitive indicator of the ordering of the alkyl chains, the above positions suggest that the alkyl chains of 1,9-NDT on gold should be highly disordered in the form of *gauche* defects. The proposition that the overall structure of the 1,9-NDT layer is independent of the layer thickness is also supported by the absorbances of the $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ bands. Although not shown here, the $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ bands also appeared at 2853 and 2927 cm^{-1}, respectively, in the RAIR spectra of 1,9-NDT self-assembled on the silver substrate, regardless of the layer thickness. The relative absorbances of the $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ bands were also invariant for all 1,9-NDT layers assembled on silver.

In the RAIR spectra of the 1,6-HDT and 1,8-ODT layers on gold, the $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ bands were observed at 2854 and 2928 cm^{-1}, respectively, regardless of the layer thickness. However, for the layers assembled on the silver substrate, the peak positions seemed to be dependent on the number of layers. Namely, for a film corresponding to a near monolayer, the $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ bands were identified, respectively, at 2853 and 2927 cm^{-1}. When a film close to a trilayer was formed, those bands were observed at 2849 and 2920 cm^{-1}, respectively. This may indicate that multilayered 1,6-HDT and 1,8-ODT films on silver assume quite close-packed structures. Recalling that the multilayered 1,9-NDT film on silver has a disordered structure, this may be regarded as a kind of even-odd effect of (α,ω)-aliphatic dithiols on silver.

Acknowledgement

This work was supported in part by KOSEF through the Center for Molecular Catalysis and by KRF through the BK21 program.

References

[1] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **278**, 252 (1997)

[2] P. Kohli, K. K. Taylor, J. J. Harris, G. J. Blanchard, *J. Am. Chem. Soc.* **120**, 11962 (1998)

[3] S. H. Kim, S. J. Ahn, K. Kim, *J. Phys. Chem.* **100**, 7174 (1996)