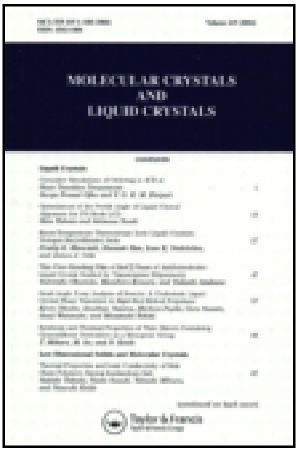

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

An STM Study on Solvent Effects in Forming Self-Assembled Cysteamine and Propanethiol Monolayers on Au(111)

Sang Yun Lee [a], Jaegeun Noh [b], Masahiko Hara [b] & Haiwon Lee [a]

[a] Department of Chemistry, Hanyang University, Seoul, 133-791, Korea

[b] Frontier Research System, RIKEN (The Institute of Physical and Chemical Research), Hirosawa, Wako, Saitama, 351-0198, Japan

To cite this article: Sang Yun Lee, Jaegeun Noh, Masahiko Hara & Haiwon Lee (2002): An STM Study on Solvent Effects in Forming Self-Assembled Cysteamine and Propanethiol Monolayers on Au(111), Molecular Crystals and Liquid Crystals, 377:1, 177-180

To link to this article: http://dx.doi.org/10.1080/713738523

Mol. Cryst. Liq. Cryst., Vol. 377, pp. 177-180
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290088834

An STM Study on Solvent Effects in Forming Self-Assembled Cysteamine and Propanethiol Monolayers on Au(111)

SANG YUN LEE[a], JAEGEUN NOH[b], MASAHIKO HARA[b] and HAIWON LEE[a,*]

[a]*Department of Chemistry, Hanyang University, Seoul 133-791, Korea and*
[b]*Frontier Research System, RIKEN (The Institute of Physical and Chemical Research), Hirosawa, Wako, Saitama 351-0198, Japan*

The morphologies of cysteamine (CA) and propanethiol (PT) self-assembled monolayers (SAMs) on Au(111) prepared in H_2O, ethanol, N,N,-dimenthylformamide (DMF), and toluene solution were imaged by scanning tunneling microscopy (STM). The STM measurements showed that the formation of domains like dendrites in CA SAMs was dependent on a type of solvent. On the other hand, a pit size in PT SAMs was controlled by a type of solvent without such a domain formation. These results clearly revealed that the solvent plays an important role in SAM formation.

Keywords: STM; SAM; alkanethiol; cysteamine; solvent effect

INTRODUCTION

SAMs prepared by sulfur-containing molecules on metal surfaces have been of great interests because of potential applications such as sensors, nanolithography, molecular electronic devices, corrosion inhibition, and nanoparticle formation[1]. It is generally believed that the formation of SAMs is a result of interplay between substrate-molecule interactions and intermolecular interactions. It is also considered that pit-like defects in the SAMs are created from the lateral displacement of gold atoms on the surface rather than traditional chemical etching. On the other hand, in the case of NH_2-terminated alkanethiols, especially, cysteamine (CA) is widely used as a linking agent at metal surfaces, because the amino groups can provide a favorable surface for adsorption of biomolecules such as proteins. To fabricate well-organized SAMs, it is essential to understand their fine structure and growth process. The recent STM investigations revealed that the size of etch pits and domain in alkanethiol SAMs were affected by a type of solvent[2] and the solvent was an important factor in determining the surface structure of SAMs[3]. In this study, we have examined and compared solvent effects in the formation of CA and PT SAMs on Au(111)

EXPERIMENTAL

Cysteamine (CA, >98%) was purchased from Tokyo Chemical. The compound was purified by recrystallization with diethylether and ethanol before use. Propanethiol (PT, 99%) was purchased from Aldrich and used as received. All solvents but DMF were obtained from Tedia company, Inc. DMF (99.9+%) was obtained from Aldrich. All solvents were used in HPLC/spectro grade without further purification. The gold substrates were prepared by thermally evaporating gold onto freshly cleaved mica sheets prebaked to 300 °C for 2h under a vacuum pressure of 10^{-7}-10^{-8} Torr. After depostion, the substrates were annealed at 460 °C in a furnace for 4 h to obtain a large flat single-crystal surface. SAMs were prepared by dipping the gold substrates into 1 mM CA and PT solutions prepared from appropriate solvents for 2h. After the substrates were removed from the solutions, the SAM samples were immediately rinsed with the corresponding solvents. All STM images were obtained in air using a constant current mode or a constant height mode. The bias voltage and tunneling current were 500 mV and 300 pA for all samples, respectively.

RESULTS AND DISCUSSION

Figure 1 shows STM images of PT SAMs on Au(111) prepared from various solutions. The SAMs consist of $(\sqrt{3} \times \sqrt{3})$ R30° domains and many pits with monatomic step height of 0.25 nm as reported before[4]. Interestingly, pit formation with larger size from the SAM samples prepared in DMF and toluene solutions was observed than in SAM samples made from H_2O and Ethanol solutions. On the other hand, it was found that the fraction of the integrated pit area to the total area was almost identical. This result indicates that the solvent strongly affects the migration rate of adsorbate-gold complex[5].

STM images in Fig. 2 display the surface structure of CA SAMs on Au(111) prepared from various solutions. The surface structure of CA SAMs is quite different from that observed in PT SAMs. The dendrite-like domains and pit-like defects in Figs. 2a and b were observed in the SAMs prepared from H_2O and ethanol solution. It may be due to the hydrogen bond between amino groups and coadsorbates such as H_2O or solvent. However, the size of pits in SAMs prepared from DMF (Fig. 2c) and toluene (Fig. 2d) tends to be decreasing regardless of their polarities.

The quantitative analysis on the domain and pit sizes was carried out as summarized in Table 1. From these results, it is considered that the size of pits in both SAMs is affected by the type of solvents. In the comparison of DMF with ethanol, the dendrite-like domains are likely

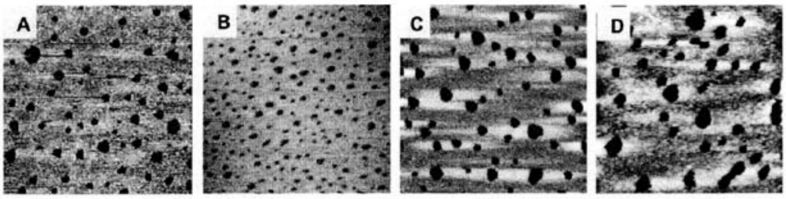

FIGURE 1 STM images of PT SAMs on Au(111) prepared from 1mM solution in (a) H_2O, (b) ethanol, (c) DMF and (d) toluene for 2h.

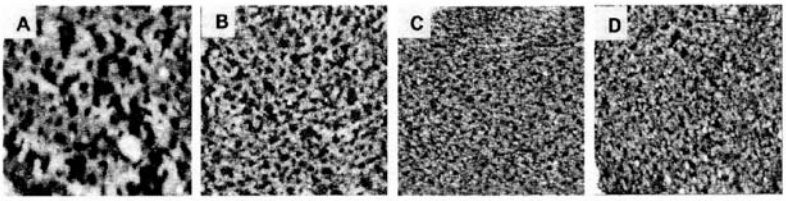

FIGURE 2 STM images of CA SAMs on Au(111) prepared from 1mM solution in (a) H_2O, (b)ethanol, (c)DMF and (d) toluene for 2h.

TABLE 1 Size of pits integrated from STM images and dielectric constants of the solvents.

Solvent	PT		CA		Dielectric constant ε (25℃)	Type of solvent
	Pit size / nm^2	Fraction / %	Pit size / nm^2	Fraction / %		
H_2O	7	10	-	25	78.5	Polar protic
Ethanol	8	9	-	16	24.3	Polar protic
DMF	11	7	5	13	37.6	Polar aprotic
Toluene	14	7	4	11	2.37	Nonpolar

due to electrostatic interactions (hydrogen bond) rather than polarity-based interaction[6].

CONCLUSIONS

We have observed that solvent strongly affects the surface structure of SAMs. The size of the pits in PT SAMs increase with decreasing the polarity of solvent except in DMF solution. In the case of CA SAMs, the morphological change was significant in the SAMs prepared from polar protic solvents. These results indicate that proticity of solvent is prior to the polarity in determining the morphology of hydrophilic group-terminated monolayers.

Acknowledgment

This work was supported by the National Program for Tera-level Nanodevices of the Ministry of Science and Technology as one of the 21st century Frontier Programs.

References

[1] A. Ulman, *Chem. Rev.*, **96**, 1533 (1996).

[2] R. Yamada, H. Sakai, and K. Uosaki, *Chem. Lett.*, 667 (1999).

[3] K. Umemura, K. Fujita, T. Ishida, M. Hara, H. Sasabe, and W. Knoll, *Jpn. J. Appl. Phys.*, **37**, 3620 (1998).

[4] G. E. Poirier, *Chem. Rev.*, **97**, 1117 (1997).

[5] G. E. Poirier and M. J. Tarlov, *J. Phys. Chem.*, **99**, 10966 (1995).

[6] M. Sprik, E. Delamarche, B. Michel, U. Röthlisberger, M. L. Klein, H. Wolf, and H. Ringsdorf, *Langmuir*, **10**, 4116 (1994).