MRT Letter: Real Time and In Situ Imaging the Reversible Evolution of Ethanol Vapor Condensed on Mica Surface

DONGHUA ZHANG,* CHEN ZHANG, FUCHUN ZHANG, AND JUN HU
Laboratory of Physical Biology, Shanghai Institute of Applied Physics, Chinese Academy of Science, Shanghai 201800, People's Republic of China

KEY WORDS in situ; real time; ethanol vapor; nanoclusters; mica; VSPFM

ABSTRACT The reversible adsorption and desorption of ethanol vapor on mica surface at ambient temperature were investigated in situ with time-evolution by Vibrating Scanning Polarization Force Microscopy (VSPFM). At temperature 20°C and relative humidity 20%, ethanol vapor condensed and formed clusters on the freshly cleaved mica. These clusters expanded to a network structure and later formed a full film shown by continuous VSPFM imaging. The film broke into pieces and desorbed completely if in unsaturated condition. The film showed different apparent heights when different biases were used in VSPFM study, indicated polarized orientation of the ethanol molecules on the mica surface. It is a process of hours for the clusters or network structures to form a film on mica, which demonstrated that vapor ethanol molecule is not so easy to precipitate on mica as ethanol molecule in liquid stage. *Microsc. Res. Tech. 74:481–483, 2011.*

INTRODUCTION

Nanofilms on solid surfaces play important roles in many interfacial processes, including wetting and dewetting, lubrication, adhesion, and molecular biological recognition (Allara, 2005; Chandler, 2005). On the other hand, because of the thin-thickness nature, nanofilms are strongly influenced by the substrate and the air and show different properties from bulk.

Nanofilms of volatile molecules on surfaces can be easily obtained from vapor adsorption and condensation. Mica is one of the best substrates for thin film study because it is easy to be cleaved into atomically smooth sheets. Early research on gas adsorption and condensation on mica surface was carried out by Langmuir dated back to 1918 (Langmuir, 1917). The isotherms of adsorption and condensation from volatile organic molecule vapor on mica were investigated by Bangham and Mosallam (1938). However, prior works were limited to average results of the adsorption on solid surface, while the microscopic details about the adsorption and condensation of the volatile molecules vapor on surfaces could not be studied because of the lack of appropriate techniques at that time. Recently, with the development of new scientific instruments and techniques, the microscopic characteristic of thin films and molecules adsorption on solid surfaces could be investigated in real time and in situ.

Ethanol is one of the typical volatile molecules. Ethanol molecule also has hydroxyl group, which is easy to interact with hydrophilic surface by liquid phase similar to water. But as a volatile molecule, ethanol molecule was easier to interact with other solid surface as gas molecule. Did ethanol molecule in vapor state easily absorb and condensate on a super hydrophilic surface? Is it a homogeneous film or not? To the best of our knowledge, no report has been presented so far about the microscopic details of condensation and adsorption of organic vapors on solid surfaces. The answers to these questions would help to further understand gas/solid interactions.

A method termed vibrating scanning polarization force microscopy (VSPFM), which is an alternative from atomic force microscope (AFM), has been proven to be a powerful technique to image soft material surfaces (Hu et al., 1995). VSPFM is based on the measurement of electrostatic forces between the tip and the sample surface to perform noncontact imaging in tapping mode AFM apparatus. The typical advantages of VSPFM were imaging soft materials stably under a force (<0.5 nN) which is much smaller than that of imaging in tapping mode AFM (typically 1–10 nN). Small perturbation is helpful for soft thin film imaging.

MATERIALS AND METHODS

Relative humidity and temperature were controlled with a chamber. Temperature was set to 20°C and relative humidity was controlled to 20% by filling in the chamber with nitrogen gas. Ethanol in container was put in the chamber before the experiment.

All the AFM experiments were carried out with a NanoScope IIIA AFM system (Veeco, Santa Barbara) equipped with a J scanner. The detailed mechanism of VSPFM was described in the previous work (Wang et al., 2007). Conductive rectangular cantilevers (NSC18/TiPt, with 10 nm Pt layer on a 20-nm Ti sublayer, MikroMasch) with a spring constant of about 3.5 N/m and a resonant frequency of around 69 kHz were used here.

*Correspondence to: Donghua Zhang, Shanghai Institute of Applied Physics, Chinese Academy of Science, P. O. Box 800-204, Shanghai 201800, People's Republic of China. E-mail: zhangdonghua@sinap.ac.cn

Received 1 March 2011; accepted in revised form 27 March 2011
DOI 10.1002/jemt.21022
Published online 29 April 2011 in Wiley Online Library (wileyonlinelibrary.com).

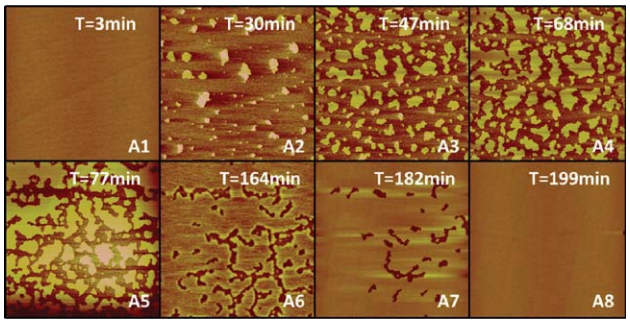

Fig. 1. VSPFM images (5 μm × 5 μm × 2 nm) showing the evolution of clusters formed by adsorption and condensation from ethanol vapor on a surface of freshly cleaved mica. During imaging, the tip is biased to AC5V and scans at VSPFM Mode with scan rate of 1 Hz. The relative humidity in the chamber is 20% ± 2, temperature is 20°C. The images from A1 to A8 were acquired as soon as opening the ethanol container cover [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

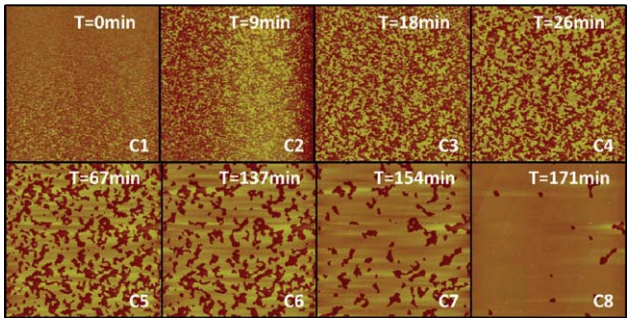

Fig. 3. VSPFM images (5 μm × 5 μm × 2 nm) show the re-evolution of clusters to form a film by adsorption and condensation from vapor. During imaging, the tip is biased to AC 5V and scans at VSPFM Mode with scan rate of 1 Hz. The relative humidity in the chamber is 20% ± 2, temperature is 20°C. The images from C1 to C8 were acquired as soon as open the ethanol container cover [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

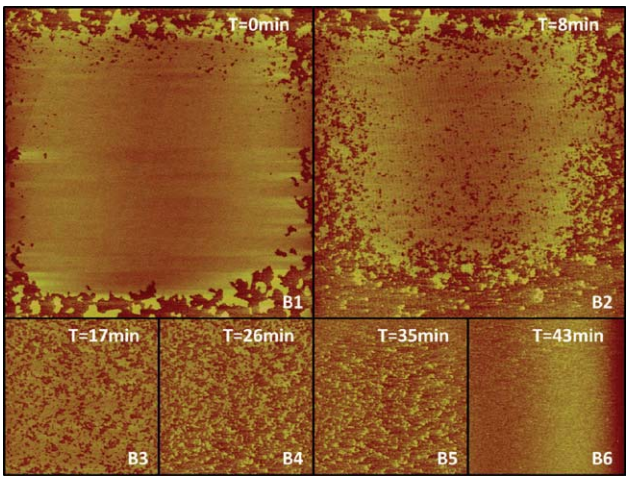

Fig. 2. VSPFM images show desorption of the ethanol film and nanostructures. VSPFM images were obtained with AC 5V bias. Scan size: 10 μm × 10 μm × 2 nm (B1 and B2), 5 μm × 5 μm × 2 nm (B3–B6), respectively [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

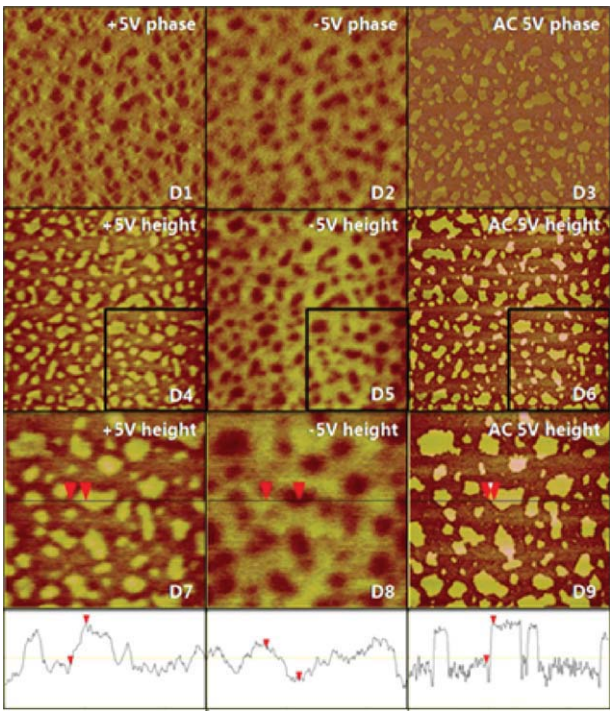

Fig. 4. VSPFM images (5 μm × 5 μm × 2 nm). D1, D2, and D3 are VSPFM phase imaging obtained with tip bias of +5V, −5V, and AC 5V, respectively. D4, D5, and D6 are VSPFM height imaging, respectively. Height measurements were showing in D7, D8, and D9, respectively [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

RESULTS

Images show typical VSPFM images of the dynamic evolution of the condensation of ethanol vapor on the freshly cleaved mica surface. Opening the ethanol container released ethanol molecules to evaporate into the air and fulfilled the chamber immediately. At the beginning of ethanol evaporation, it was difficult for the VSPFM to image stably. Several minutes later, the VSPFM started to work stably (Fig. 1, A2). As hours went by, film-like structures formed (Fig. 1, A3), which were expanding on the surface (Fig. 1, A4-A7), indicating that more ethanol molecules condensed on the mica surface. At last, the ethanol structures coalesced with each other and formed a homogenous film in the scanning area (Fig. 1, A8).

After being scanned at the same area by the AFM tip with AC 5V for 3 h, the scanned area was enlarged, which revealed a flat and homogenous film (Fig. 2, B1). Outside of the previously scanned region, the condensed ethanol nanostructures did not form a homogeneous film. We suppose that the growth of ethanol film was accelerated by the AFM scanning probably because the electric field near the sharp tip enhanced the formation of ethanol meniscus which facilitated ethanol condensation on the mica surface (Sacha et al., 2006). If the ethanol container was covered and the chamber was opened a little for a while to decrease the

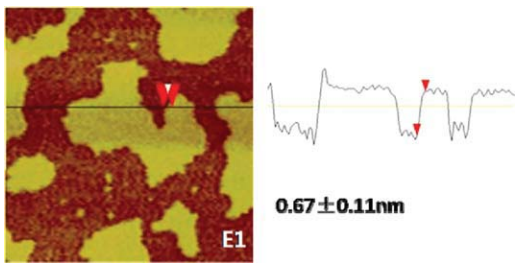

Fig. 5. Height measurement of ethanol nanostructures with tapping mode AFM (1 μm × 1 μm × 2 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

saturated ethanol vapor pressure, the homogeneous film broke into pieces dispersedly and desorbed completely at last (Fig. 2, B2∼B6).

When the ethanol film was evaporated completely, recharging the testing chamber with saturated ethanol resulted in a regrowth of ethanol nanostructures on the mica surface. Ethanol evaporated and fullfilled the chamber again, and the process of nanostructure growing to form a film could be imaged again (Fig. 3). From the reversal condensation and evaporation process, we conclude that the film on the mica imaged by VSPFM was developed from ethanol vapor.

To investigate the characteristic of the film on mica surface, we employed positive, negative, and alternative current biases for VSPFM to image the ethanol nanostructures condensed on the mica surface (Fig. 4), which enable VSPFM to work like electrostatic force microscopy (EFM). The VSPFM phase images (Fig. 4, D1, D2, and D3) were obtained with biases +5V, −5V, and AC5V, respectively. The corresponding height images (Fig. 4, D4, D5, and D6) show different apparent heights of the condensed ethanol nanostructures with different biases. The reverse height contrasts of the nanostructures in D7 and D8 obtained with VSPFM working with opposite biases indicated repulsive tip-surface interaction in positive tip bias and attractive tip-surface interaction in negative tip bias. So, we supposed that the ethanol nanostructures on mica were polar and oriented. From experiment results, we speculate that the OH group of the ethanol orients to surface while its ethyl group orients to air, because the ethyl group should show positive charge characteristic (He et al., 2009; Kim and Dunn, 2010).

Advantage of VSPFM is that it is convenient to shift from VSPFM mode to tapping Mode. In tapping mode, as shown in Figure 5, the height of the nanostructures was 0.67 ± 0.11 nm, which was almost the length of an ethanol molecule.

DISCUSSION

It is important to emphasize that AFM only images the contrast on surfaces. Therefore, a question arises: is the film we observed the first ethanol layer on mica? One possibility is that mica surface was covered by a homogeneous film of water because we cannot exclude all the water molecules out of the experimental environment. In this case, the ethanol films we observed were the second layer on mica. However, it is known that water vapor in the air could not form a homogenous film cover on mica surface at RH < 50% (Miranda et al., 1998), which eliminates this possibility since our experiments were carried out under RH 20%.

So, the film we imaged was the first layer on mica surface, which developed from ethanol gas molecules. But the development of film was almost 3 h.

CONCLUSIONS

A method in situ and real time observation of ethanol gas molecule adsorption/desorption on mica has been presented. Images clearly show that the film we image was the first molecular layer of ethanol absorbed on mica surface. It was interesting that ethanol vapor was not easy absorbed on mica surface to form a film like ethanol in liquid stage.

ACKNOWLEDGMENTS

The authors thank Prof. Zhang Yi and Prof. Yan Long for helpful discussions. This work was Supported by the National Basic Research Program of China (973 Program No. 2007CB936000), the Ministry of Health of China (No. 2009ZX10004-301), National Natural Science Foundation of China (No.10874198, 90923002 and 10975175), the Chinese Academy of Sciences (No. KJCX2.YW.H06, KJCX2.YW.M03), and the Science and Technology Commission of Shanghai Municipality (No. 0952nm04600).

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