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Research paper

Residual nano films and patterns formed by non-volatile liquid dewetting on smooth surfaces

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ABSTRACT

It was recently reported that nano residual films could be left on smooth substrates after the dewetting of partially wetting non-volatile liquids. In this work we clarify the criteria for the residual film to form and to maintain stable on the substrate. Atomic force microscopy imaging indicated that the residual film formation was dependent on the system wettability. The residual film was investigated in molecular dynamics simulations and the results were consistent to the experiments. The disjoining pressure played an important role in determining the film stability. The results provide important guidance for long-standing puzzles about trace liquid after dewetting.

Dewetting i.e. the receding of the contact line on solid is a crucial process of many applications such as cleaning, coating, oil recovery, boiling, condensation and various biological processes [1,2]. Despite much research over years, important puzzles such as contact angle hysteresis and dynamic prediction remain under intensive debate [3]. The difficulty of direct measuring to the nanoscale contact line region has long hindered the theoretical development [4]. Tapping-mode atomic force microscopy has recently been employed to make progress. Herminghaus et al. [5], Yu et al. [6], and Ma et al. [7] measured profiles and contact angles for static liquids using this *in situ* technique. A pioneering work on dynamic wetting by Chen et al. [8] revealed that the advancing contact line follows the macroscopic profile until bending in a convex profile within 10–20 nm of the substrate and verified that the microscopic contact angle is related to the advancing velocity for the first time.

Most recently Deng et al. [9] measured receding contact line and showed that the receding interface profile extends downward as a straight line from the bulk liquid to the horizontal substrate. Meanwhile, a residual film of nanometer thickness was found on the solid after the receding contact line passed. The observation is related to the question of whether a non-zero contact angle can coexist with a molecular film, which has been extensively studied but mostly about vapor adsorption of volatile liquids [10,11]. The observed microscopic residual film modified the substrates and made dewetting far from a simple reverse of wetting. The microscopic residual film provides an essential evidence for understanding dewetting and its difference from advancing [4,12]. In this study, we further revealed the dependence of the residual film formation and its stability to the system properties. A large scale molecular dynamic simulation as well as a theoretical modeling was conducted to compare to AFM measurements.

As shown by Fig. s1 in Supporting Information, the experimental system was based on a TM-AFM (MFP-3D-BIO, Asylum Research), which had low-noise performance for high-resolution imaging of the most delicate samples like proteins or liquid surfaces [6]. The nonvolatile liquid droplets which have different Hamaker constants and wettabilities on silicon wafer and mica were used. The silicon wafer was with natural oxide layer (Micro-Nano Machining Center, Peking university, (100)-oriented, p-doped, 2–4 Ω·m). Dewetting process was achieved by vertically pulling out the solid substrate from the liquid reservoir with specific speed, or by transferring a millimeter-size liquid droplet onto the solid substrate and then sucking the droplet with a piece of filter paper in the chamber which was full of nitrogen. The residual thin film morphology was scanned using the tapping mode of the AFM about 5 min after the contact line passed. The thickness of the thin film was detected using force curve method of the AFM. Error analysis of the AFM measurements are identical to Deng et al. [9].

First as shown in Fig. 1(a), the morphology scanning on a pristine silicon wafer that has never been wetted shows sub-nanometer roughness, and the force curve measurement made on it shows two sharp valleys. Note in the force curve measurement, the AFM tip did not move across the sample surface, but approached perpendicular to the surface, pressed, and then retracted from the sample surface. The attractive and repulsive forces felt by the tip during the process were recorded versus the

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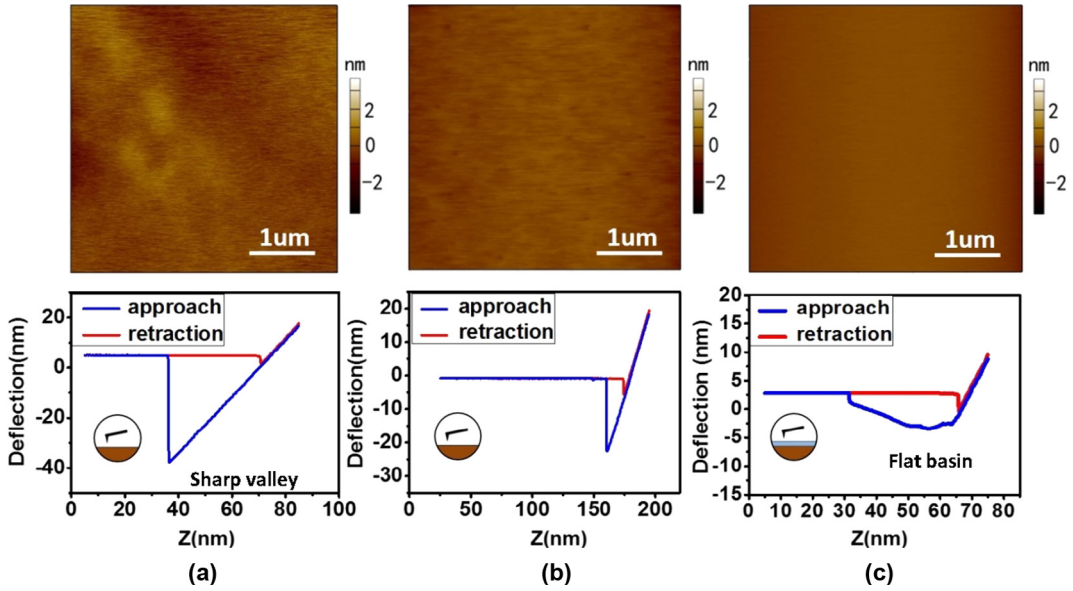

Fig. 1. Morphology scanning and force curve measurements on pristine as well as prewetted substrates (dewetting rate around 0.1 mm/s): (a) Pristine silicon wafer that has never been wetted; (b) Silicon wafer after glycerol dewetting. The force curve is similar to (a) indicating no film left; (c) Mica after glycerol dewetting. The sharp retraction valley is now replaced by a flat basin in the force curve due to the existence of the residual nano film. The static contact angles θ_a of glycerol on the silicon wafer and mica were 46° and 15° respectively.

perpendicular distance Z. The negative and positive values in the curve represent the attractive and repulsive forces, respectively. In Fig. 1(a) both the approaching (indigo) and retracting (red[1]) curves are straight with sharp valleys, which is a typical result for stiff surfaces without soft films. The force curve on pristine mica surface is similar.

Then we tested the silicon wafer after glycerol droplet dewetting with the receding velocity of about 0.1 mm/s, as shown in Fig. 1(b). Note the static contact angle of the glycerol droplet on the wafer was $\theta_a = 46°$. Two sharp valleys were still there which means no residual film left. The morphology scanning also shows no sign of film patterns. For glycerol dewetting on mica ($\theta_a = 15°$) with the same receding velocity, Fig. 1(c), the morphology measurement still shows a smooth surface, however the sharp retraction valley in the force curve measurement has been replaced by a flat basin, which means the prewetted substrate has been covered by a soft film.

The above results indicated that better wettability facilitated the formation of the residual film. More results are shown in Table 1 using different solids and non-volatile liquids. For example, hexadecane left a residual film on silicon wafer ($\theta_a = 7°$), while didn't leave on fluoridization-treated silicon wafer ($\theta_a = 58°$). Ionic liquid 1-Butyl-3-methylimidazolium tetrafluoroborate did not leave film on silicon wafer ($\theta_a = 70°$), while left on plasma-treated silicon wafer ($\theta_a = 9°$). The residual film formation was inevitable when the contact angle was less than about 20°, while may not occur when the contact angle was larger than about 40°. See Supporting Information for details.

We also tested at higher speed i.e. about 10 mm/s. Previous experiments [13–15] have shown that if a critical speed is exceeded, the contact line is no longer visible and a macroscopic film with optically detectable thickness is deposited on the solid. The macroscopic film is not in this work's scope. During the experiment after pulling out the substrate from the liquid pool we kept it vertical for two minutes and the macroscopic film, if any, removed by the gravity. After that we found nano residual film was still evi-

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

Table 1
Static contact angles, residual nano films, and Hamaker constants for partially wetting non-volatile systems at room temperature.

System	Static angle	Residual nano film	Hamaker constant ($\times 10^{-20}$ J)
PEG400 on silicon wafer	17°	Flat	−0.34
PEG400 on mica wafer	12°	Flat	−1.88
Phosphoric-acid on silicon wafer	19°	Ruptured	0.23
Polystyrene on silicon wafer [24]	8°	Ruptured	1.8
Glycerol on mica wafer	15°	Flat	−1.49
Glycerol on silicon wafer	46°	No residual	0.20
Glycerol on fluoridization-treated silicon wafer	70°	No residual	N/A
PEG400 on fluoridization-treated silicon wafer	50°	No residual	N/A
Hexadecane on silicon wafer	7°	Flat	−0.57
Hexadecane on fluoridization-treated silicon wafer	58°	No residual	N/A
1-Butyl-3-methylimidazolium tetrafluoroborate on plasma-treated silicon wafer	9°	Flat	N/A
1-Butyl-3-methylimidazolium tetrafluoroborate on silicon wafer	70°	No residual	N/A

table for those $\theta_a < 20°$, and still no residual film left for those $\theta_a > 40°$.

A large-scale molecular dynamic simulation was performed to confirm the relationship between the residual film formation and the wettability. An argon droplet with diameter of 20 nm was placed on a platinum substrate with crystal constant of 3.92 angstroms. The system consisted of 99,072 atoms. Interactions between atoms adopted the Lenard-Jones potential:

$$\varphi_{ab} = 4\varepsilon_{ab}\left[\left(\frac{\sigma_{ab}}{r}\right)^{12} - \left(\frac{\sigma_{ab}}{r}\right)^{6}\right] \quad (1)$$

where the subscripts a and b denote different atom types, which can be substituted by l (liquid) or s (solid). To realize different wettabilities, ε_{ab} was set to be $\varepsilon_{ls} = c \cdot \varepsilon_{ll}$, where c was chosen to be 0.30, 0.40 or 0.85. The parameters in the LJ potential were listed in Table s1 in