Direct Observation of Water Layers on Mica Surface in Water by Atomic Force Microscope

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Water film on mica surface immersed in water is directly detected and imaged by atomic force microscope. The depressions and islands indicate the existence of water layer, which preserve some solid characters of mica lattice. The observation is attributed to the inhomogeneity and disruption of water layers adjacent to mica.

Thin water film formed at interfaces between water and charged solid is important in materials, biology and heterogeneous reactions, which has received much attention for many years. The layer arrangement is postulated due to the strong interaction between the surface and water, which gives rise to bound or structurally altered water. Water molecules in the layer have lower free energy than those in bulk and extra work is required to transfer them from this layer into bulk[1].

Although water layers adsorbed onto ionic crystals can be imaged in air[2,3], direct observation of the layers in water is difficult for the small size and energetic brownian motion of individual water molecule. Previous studies in liquid focus mainly on the force interaction[4,5] or detection of the layer by other method[6,7]. Direct observations of the topographic characters in water have rarely been reported.

We show the feasibility of imaging water layers on mica surface immersed in water by atomic force microscope in this letter. The observed water layer is consistent with the results from other indirect methods[3,8] and theoretic simulation[9].

A freshly cleaved muscovite mica is first imaged in air, then in triple-distilled water by a commercial AFM (Nanoscope III, Digital Instrument, CA) with contact mode in liquid cell. The cantilever onto which Si_3N_4 tip is mounted has a reported spring constant of 0.58 N/m. The tip and the liquid cell are sonicated 10 minutes in warm ethanol and then 10 minutes in triple-distilled water to reduce the contaminants prior to the experiment. The conditions under which the images are collected include: scan rate is 5 Hz, imaging forces are ranged from 5 to 10 nN.

The layer structure of thin water film near solid wall can not be destroyed by an approaching surface due to the reduction in wetting and capillary forces in water[5]. To confirm the observation of water layers, some inhomogeneity in layer structure may be useful. It is fortunate that the movement of tip parallel to the solid surface can provide disturbance on the layer structure. So imaging water layers in water become practically possible, though water molecules above the adsorbed layer are still too mobile to be imaged. Moreover, water molecules will also adsorb and form layer structures on Si_3N_4 tip, but the direct observation does not focus on the effect.

Both islands and depressions can be discerned in figure 1 and figure 2 respectively. An interesting result of island is the boundary orientation which showed certain similarity to that formed in humid air[3]. The straight boundaries form angles of

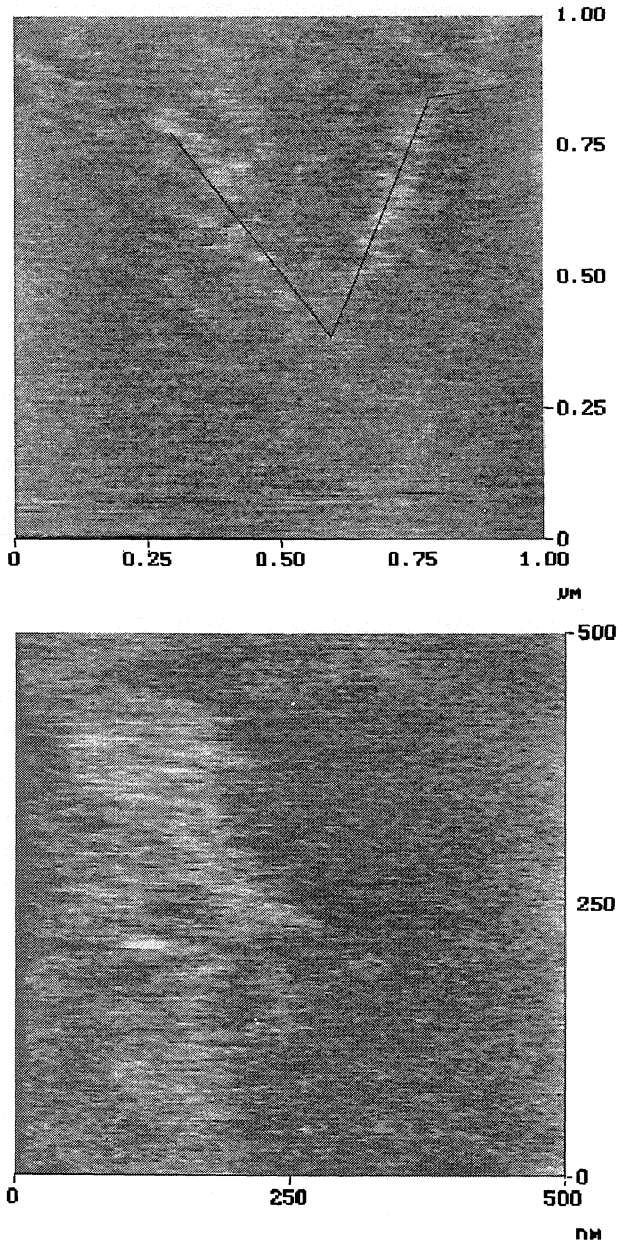

Figure 1. Water islands with straight boundary and angle of either 60° or 120°.

roughly either 60 ° or 120 ° as showed by lines, which is consistent with the hexagonal lattice of mica surface. Such angles suggest the preservation of solid characters and the lattice-dependent crystalline structure of water layers. The step height of island and depression indicate an integral character roughly with 0.24, 0.44, 0.7, 1.04 nm. The minimal height is

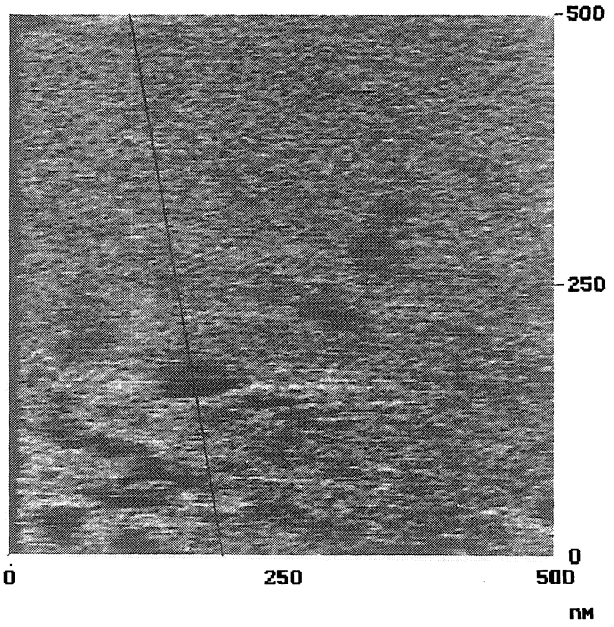

Figure 2. Depression in the layer structure of water film.

usually less than the diameter of a water molecule (0.28 nm), perhaps due to the compression from the tip. The section analysis of the depression in figure 3 clearly indicate water layer. This ordering of waters into immobile layers will increase their shear resistance by restricting motion in the direction parallel to mica surface. But the islands still can not endure elongated scan and disappear or transform quickly.

The formation of thin liquid film depends on the property of the liquid as well as that of the surface. Electric interaction and hydrogen bond determine the dipolar attraction of water[7]. Water molecule next to negatively charged mica is unequivalent to the bulk water by intrinsic electrostatic attraction, which will lead to the oxygen-up orientation and a greater density than that in bulk[8,10]. Hydrogen bond network in bulk water is also affected and not maintained in first layer, because water form hydrogen bond with oxygen atoms on mica surface[5,9]. All these factors favor the formation of layer structures and the tight binding of water on mica surface.

But the observation of the layers by AFM requires more than their formation. Three factors may contribute to the observation. First, the attractive restriction increase the local density of water on mica and the crystalline structure of first layer formed as a result. The further extended to bulk water, the less the attraction between water molecules. Such difference in water density which is created either by intrinsic inhomogeneity or disturbance can be detected by AFM; Second, the dielectric constants of water layers depend on the distance away from mica surface. Negatively charged Si_3N_4 tip will response to the difference in dielectric constant as that of charged conductive tip in

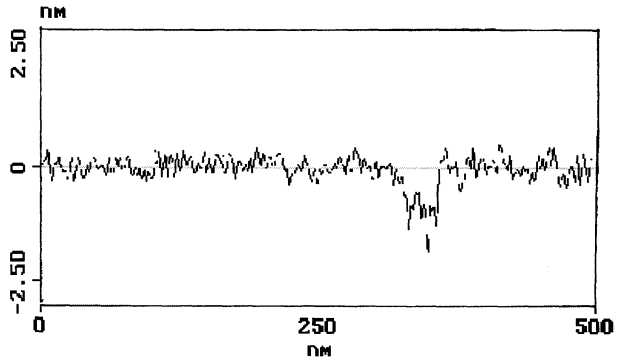

Figure 3. Layer structure found in the cross section of depression.

polarization force microscope[3]. Images taken from a new tip or thoroughly cleaned tip strongly confirm the influence of tip, because the removal of contaminants will make the tip more easily to be charged. Third, the disturbance from tip to the layer may faciliate the displacement of randomly distributed K^+ on mica[5]. This will induce the formation of depression, which usually disappear or transform in following image for the rapid diffusion of water.

The competition of adsorption and desorption, together with variations in nucleation centers determined the inhomogeneous adsorption strength of waters on mica surface. Owing to the adsorptive restriction and disturbance of water layers, the film on mica surface in water can be directly imaged by AFM. Because epitaxial phase is less strongly adsorbed than that of intrinsic adsorbed layers[3], we concluded the water layers of epitaxial phase are imaged in the experiment.

The possibility of imaging water layer in water reflects an intrinsic property in general. More work is needed to get comprehensive knowledge on the role of water.

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