

## Water adsorption on a BaF<sub>2</sub>(111) surface in air observed with force microscopy

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We present the dynamical behavior of water adsorption of a BaF<sub>2</sub>(111) surface in air observed with force microscopy. The profile from the BaF<sub>2</sub>(111) surface has exhibited water droplets with small contact angles on exposure to air with a relative humidity of 70%. As time passes, such droplets are plentifully formed and, as a result, turn into a uniform film showing about 1 nm in thickness. We confirm that the saturated adsorption volume of water on the surface depends on the relative humidity and increases with an increase of the relative humidity. Moreover, the force between a tip and the sample surface is measured and discussed.

The problem of molecular water adsorption on surfaces has been of great interest because water plays an important role in a surprisingly wide variety of scientific disciplines.<sup>1</sup> It has been well known that water adsorption on ionic surfaces is very important, but there has been little knowledge of the behavior of water at these surfaces. Recently, interesting studies of water aggregation on (111) surfaces of fluorite structures (CaF<sub>2</sub> and BaF<sub>2</sub>) have been reported.<sup>2,3</sup> They reveal the behavior of water adsorption on these surfaces, particularly at low coverages. In this paper, we report the behavior of water adsorption on real surfaces in air. The technique used for observing the water adsorption is essentially the same as proposed by Martin, Williams, and Wickramasinghe<sup>4</sup> which features a tip that vibrates at close proximity to a surface. The technique, accordingly, is applicable to noncontact profiling derived from an interaction potential on scales varying from tens of micrometers to a few tens of Å. Here we call this method scanning force microscopy (SFM).

The purpose of this paper is to observe the dynamical behavior of water adsorption on a BaF<sub>2</sub>(111) surface in air with SFM, and moreover to study the forces between tip and sample surfaces.

Specimens were obtained by cleaving single ionic crystals using a cutting edge in air. The apparatus of SFM is SPI-3700 (Seiko Instruments, Inc.). The tip mounted on the cantilever is silicon crystal. The profiles from ionic crystal surfaces were obtained as a function of both a tip-sample spacing  $d$  and the amplitude of the tip,  $A$ . The cantilever has a spring constant of 1.8 N/m, which corresponds to an acceptable thermal vibration of 0.7 Å at 300 K,<sup>4</sup> and a resonance frequency of 23 kHz.

Figures 1(a), 1(b), 1(c), and 1(d) display profiles obtained over the BaF<sub>2</sub>(111) surface versus elapsed time with a relative humidity of 70%, respectively ones obtained at 5, 10, 15, and 20 min after clearing in air. First, one can observe [011] edge lines formed by the (111) and  $\bar{1}\bar{1}\bar{1}$  facets. Regions  $A$ ,  $B$ , and  $C$  show the (111) facets, where surfaces  $A$  and  $B$  are parallel with a height difference  $F^- - Ba^{2+} - F^-$  ( $3.6 \pm 0.2$  Å) in Fig. 1(a). Here

we note that Fig. 1(a) is mottled in contrast, and that the mottled pattern goes out of sight forming a uniform contrast as time passes [see Figs. 1(b), 1(c), and 1(d)]. The smallest ones (droplets) of the bright parts, in contrast, appearing in Fig. 1(a) are about 20 nm in dimension and about 1 nm in thickness. The contact angle of the droplet accordingly becomes several degrees. As time passes, small droplets are plentifully formed and turn to be a uniform film about 1 nm in thickness with a slow growth rate. However, we do not observe such a mottled pattern when the relative humidity is low (0–50%). This suggests that water droplets begin to grow at some relative humidity (above 50%), and then the growth of water proceeds for formation of a uniform film. Hence it seems that the saturated adsorption volume of water on the surface depends on the relative humidity, and increases with an increase of the relative humidity. It is also known that such a small contact angle is observable when a liquid droplet attaches to a surface containing a thin physisorbed film of the same liquid, for example on mica and on graphite.<sup>5</sup> It would be reasonable to confirm that the BaF<sub>2</sub>(111) surface includes a uniform water film with a monolayer or submonolayer before the water droplets are formed [see Fig. 1(e)]. The possibility of such a uniform water film with a monolayer or submonolayer has also been discussed in our previous paper<sup>6</sup> and by Shluger, Wilson, and Williams.<sup>7</sup>

The attractive force between a silicon tip and BaF<sub>2</sub>(111) was measured over a wide range of tip-sample spacings. Figure 2 shows the typical curve of the amplitude  $A$  versus the tip-sample spacing  $d$ , when the tip is moved at constant speed toward the surface. The origin of the tip-sample spacing has been determined approximately in the following way. Assuming that the  $A$ - $d$  curve has a crease at the value of  $d_e$  when the vibrating tip contacts the sample surface, and that  $A$  at  $d_e$  is  $A_e$ , then the tip-sample spacing  $d$  at  $d_e$  becomes  $A_e$ . The origin of the tip-sample spacing accordingly has been shifted by  $A_e$  from the  $d_e$  position to the left. We have computed the values of  $f'$  and  $f$ , deduced from  $A$  in accordance with Martin's method,<sup>4</sup> which are shown respectively in

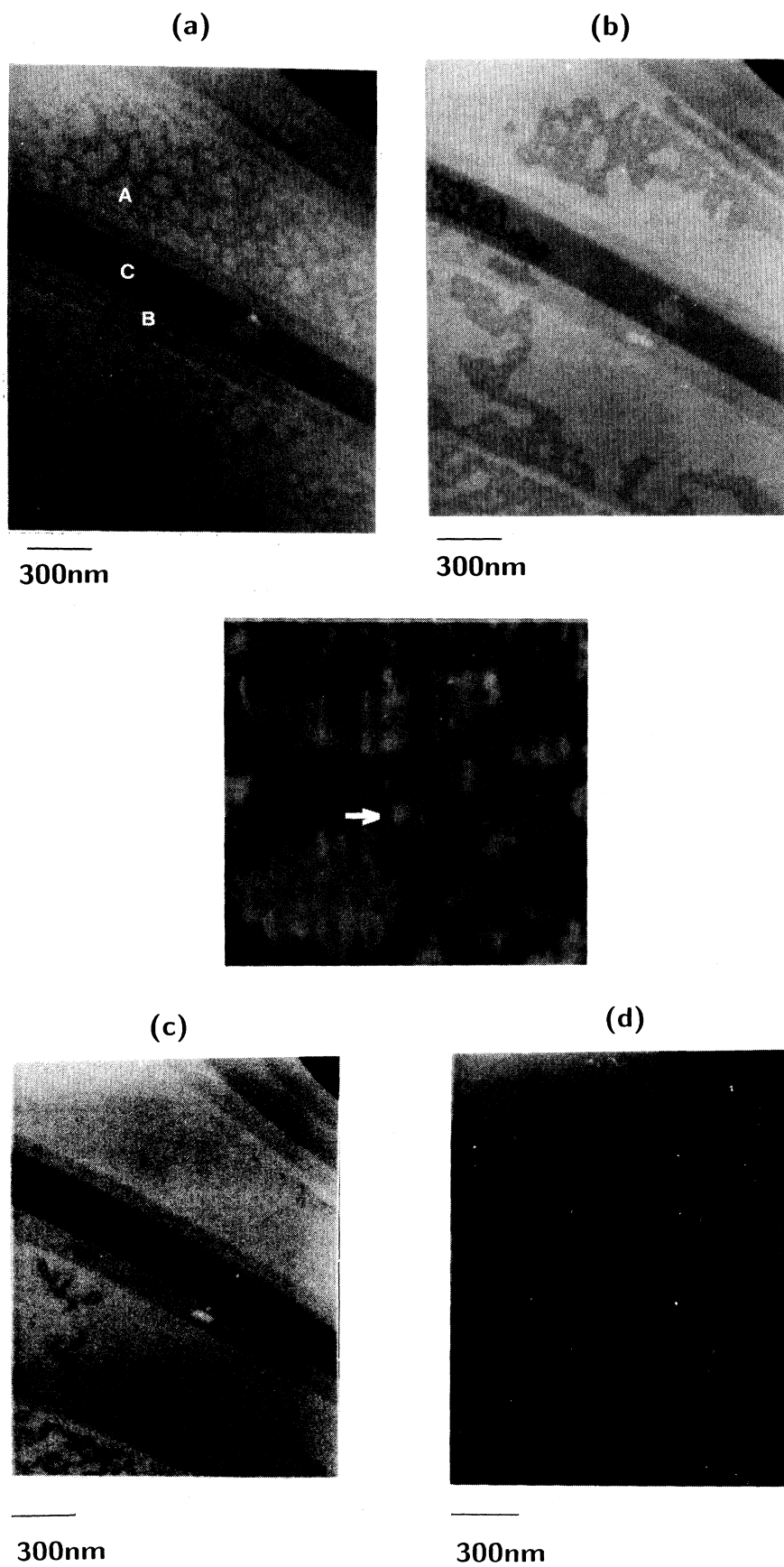


FIG. 1. (a), (b), (c), and (d) display the profile obtained over the  $\text{BaF}_2(111)$  cleavage surface vs elapsed time with a relative humidity of 70%, respectively ones obtained at 5, 10, 15, and 20 min after cleaving in air. The enlarged version of the inset indicated by the black-colored arrow in (a) is given below (a), and the one indicated by the white-colored arrow in the enlarged version is the highlight one of the smallest droplets about 20 nm in dimension and about 1 nm in thickness. (e) shows the formation process of the water adsorption, where the smeared part is the  $\text{BaF}_2$  crystal and the arrow shows the passage of time.

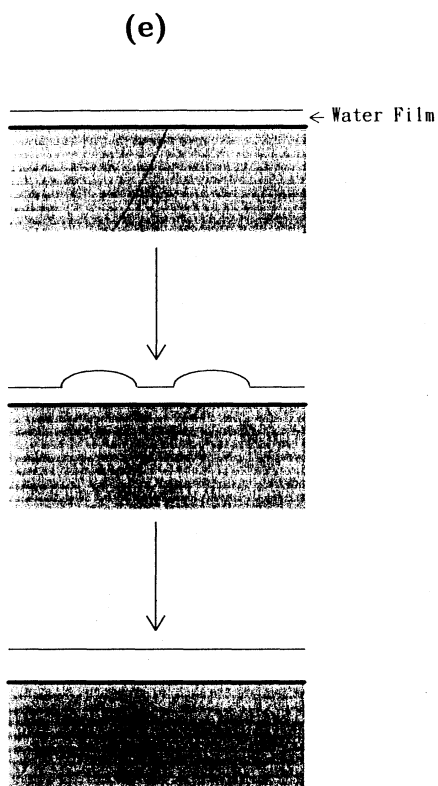


FIG. 1. (Continued).

Figs. 3(a) and 3(b) for the  $\text{BaF}_2(111)$  surface, where  $f'$  and  $f$ , respectively, are the force derivative and the force between the tip and surface. It is found that the  $f$  for the sample varies from  $10^{-11}$  to  $10^{-10}$  N, when the tip is brought from 10 nm to about 1 nm.

To study the tip-sample interaction potential form, the result in Fig. 3(b) has been logarithmically scaled, which

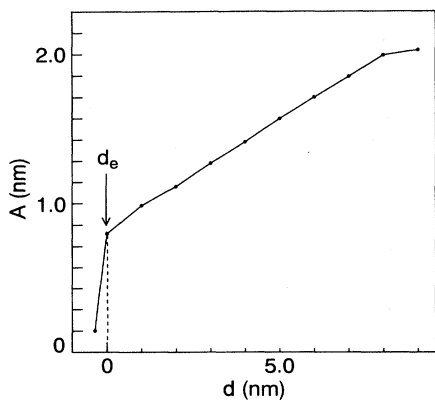
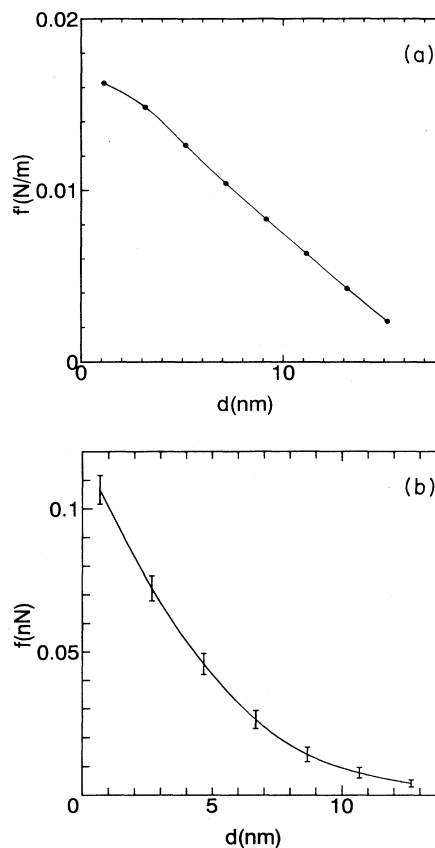
FIG. 2. The typical curve of amplitude  $A$  vs the tip-sample spacing  $d$ .

FIG. 3. (a) and (b) display the values of  $f'$  and  $f$  for the  $\text{BaF}_2(111)$  surface deduced from  $A$  in accordance with Martin's method, where  $f'$  and  $f$ , respectively, are the force derivative and the force between the tip and sample surface.

is shown in Fig. 4. Suppose that the attractive force between the tip and sample surface is of the general form  $f = -K/d^n$ , where  $d$  is the separation of tip and sample surfaces and  $K$  the constant. Then the power-law index  $n$  in case of the  $\text{BaF}_2(111)$  surface can be chosen to be 2–4

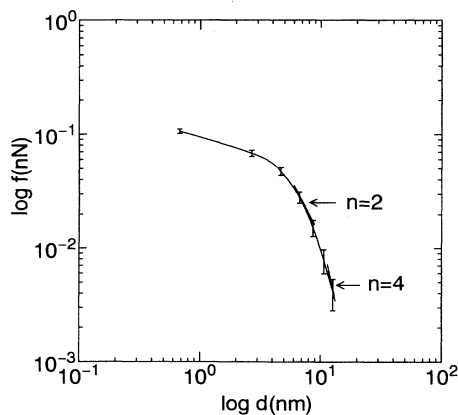


FIG. 4. The logarithmically scaled force-distance curve which is derived from results in Fig. 3(b). The power-law indices and slopes of the force-distance curve are indicated in the figure.

at above 4 nm, and in contrast to that to be below 2 at below 4 nm. Here, assuming that the interaction between the tip and sample surface is the van der Waals force, and that the tip shape is the sphere,<sup>5</sup> the interaction potential form between them is noted to transform from  $1/d$  into  $1/d^3$  with respect to the separation  $d$  between the sphere and sample surface, thereby producing force exponents of  $1/d^2$  to  $1/d^4$  in the direction perpendicular to the sample surface. The behavior of the exponents of the force-distance curve above 4 nm obtained in this experiment can hence describe the pictures stated above. However we cannot account for the exponents smaller than 2 on the inside, which would be expected to

be induced by adsorbed water on the  $\text{BaF}_2(111)$  surface and tip, since at this stage we cannot obtain experimental data to elucidate such a force. In the future we shall study the interaction force at close proximity to a surface in detail for a more perfect understanding.

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<sup>6</sup>K. Miura and Y. Shukuya, *Jpn. J. Appl. Phys.* **32**, 4752 (1993).

<sup>7</sup>A. L. Shluger, R. M. Wilson, and R. T. Williams, *Phys. Rev. B* **49**, 4915 (1994).

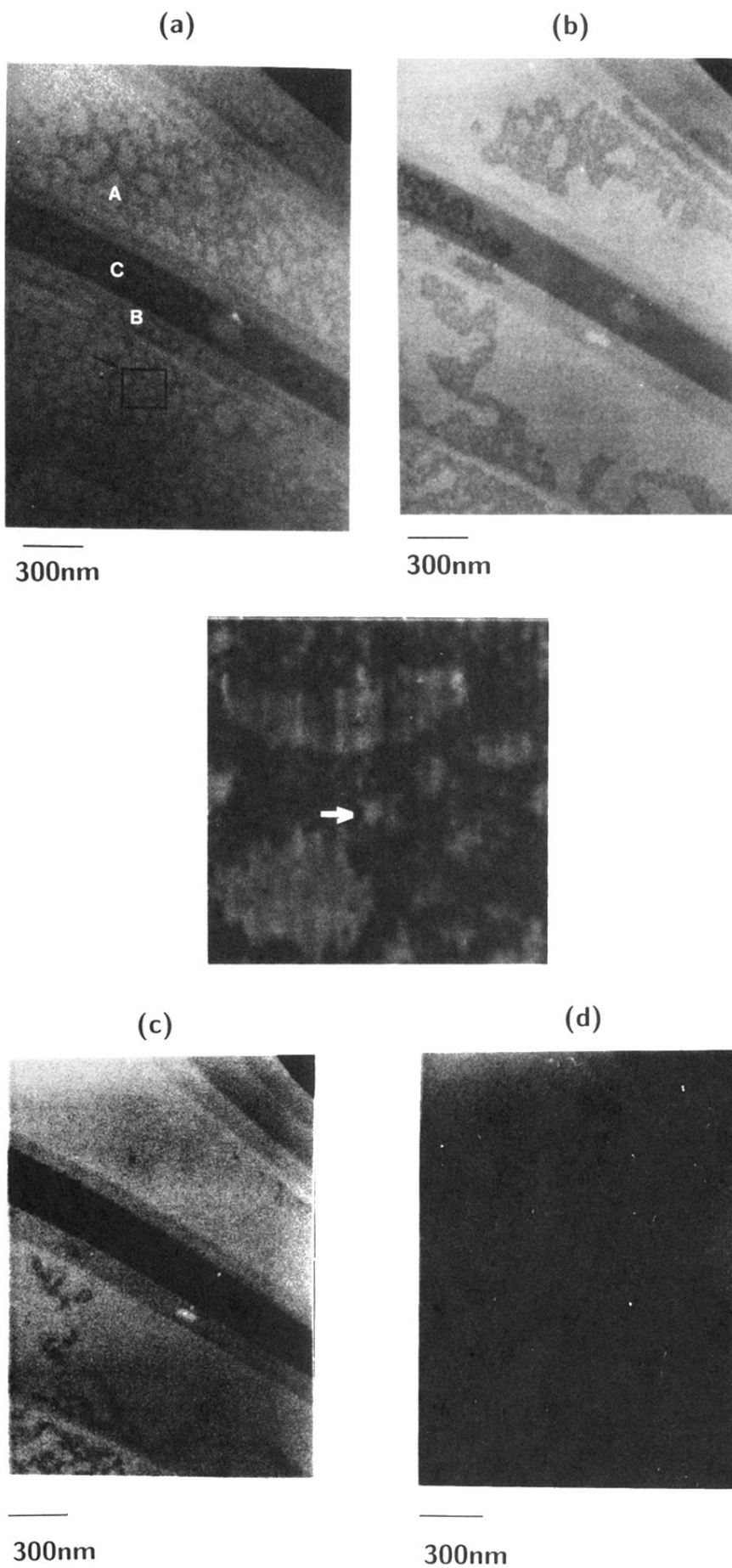


FIG. 1. (a), (b), (c), and (d) display the profile obtained over the  $\text{BaF}_2(111)$  cleavage surface vs elapsed time with a relative humidity of 70%, respectively ones obtained at 5, 10, 15, and 20 min after cleaving in air. The enlarged version of the inset indicated by the black-colored arrow in (a) is given below (a), and the one indicated by the white-colored arrow in the enlarged version is the highlight one of the smallest droplets about 20 nm in dimension and about 1 nm in thickness. (e) shows the formation process of the water adsorption, where the smeared part is the  $\text{BaF}_2$  crystal and the arrow shows the passage of time.