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Atomic force microscopy images of MgO(100) and $TiO_2(110)$ under water and aqueous aromatic molecule solutions

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Abstract

In situ atomic force microscopy (AFM) observations at atomic level of the surface structures of MgO(100) and $TiO_2(110)$ under water and aqueous aromatic molecule solutions are reported. Under deionized water the MgO(100) surface showed slow dissolution initiated by pitting, whereas the $TiO_2(110)$ surface did not show any surface dissolution. At atomic level, MgO(100) gave AFM images of very low contrast, indicating very small force variations on its surface under aqueous environment. $TiO_2(110)$ showed images with rows whose intervals correspond to those of Ti^{4+} rows. Addition of an aqueous ammonium benzoate solution onto MgO(100) surface produced structures attributable to adsorbed molecule overlayers, similar to the ones observed on zeolite surfaces. The $TiO_2(110)$ surface under aqueous aromatic solutions gave images similar to those obtained under deionized water, indicating no or very slow adsorption of these molecules on the surface. © 1997 Elsevier Science B.V.

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1. Introduction

Scanning probe microscopy such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) enabled us to observe molecules adsorbed on solid surfaces at atomic resolution under various environments such as vacuum, ambient and underwater. The earliest example is the observation of a benzene ring arrays on a Rh single crystal surface with STM under ultrahigh vacuum (UHV) conditions [1]. The resolution of AFM reached that level only recently, and the reports on AFM observations of adsorbed species are scarce.

Recently we successfully obtained atom-resolved AFM images of natural zeolite surfaces, stilbite(010) and heulandite(010), and in situ molecular images of liquid-phase-adsorbed pyridine and picoline on these surfaces [2–5]. From these AFM data we were able to determine the array and orientation structures of the adsorbed molecules. Here we report in situ obser-

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vations of the surface structures of $TiO_2(110)$ and MgO(100) under water and under aqueous aromatic molecule solutions.

2. Experimental

Polished $TiO_2(110)$ and MgO(100) samples were used as substrates. They were placed in a sealed AFM liquid cell which is then filled with either deionized water or 1 vol% aqueous solutions of phenol, pyridine or 1 wt% ammonium benzoate. Contact-mode AFM examinations of the surfaces were performed in the repulsive force regime with a tip load of ca. 5 nN. Type NP cantilevers (Digital Instruments) were employed, which have Si_3N_4 tips and force constant equal to 0.38 kN/m. The recorded images are presented with or without filtering, as noted in the captions.

3. Results and discussion

3.1. MgO(100)

The solubility of MgO into cold water is known to be very small (0.62 mg/100 cc of water), which makes us to anticipate relatively stable observation of its surface structure under aqueous environments. Fig. 1 shows a series of AFM images of a polished MgO(100) surface under deionized water. Immediately after its immersion, AFM showed a flat surface with a small number of pits as found in Fig. 1(a). After 12 min the number and the size of the pits increase while other part of the surface seems unaffected, as shown in (b). Three hours and 26 min later the surface gives an AFM image found in (c). It appears that the dissolution of MgO(100) is initiated first by pit formation, then proceeds from the pits expanding the dissolved area into the undissolved region. Microscopic process of MgO dissolution has not been studied in detail to our knowledge, and the present work constitutes its first in situ AFM observation.

Fig. 2 compares narrow-area, 8 nm × 8 nm AFM images taken under (a) deionized water, (b) a phenol solution and (c) an ammonium benzoate solution. Each image was taken with a new sample, since the above observation indicated slow and gradual deterioration of the MgO(100) surface under aqueous environment. Under deionized water, MgO(100) surface gave very low-contrast AFM images as found in Fig. 2(a). It does show faint square structures, although the contrast is too low to extract any periodic structure even with two-dimensional fast Fourier transform. This is in contrast to UHV or ambient AFM observations of other ionic surfaces such as NaCl(001) [6] and LiF(100) [7], in which square lattices of bulky anions are observed. The low contrast of the present underwater image indicates very small force variation on the surface, possibly due to the hydration of the surface atoms and screening of the ionic charges by the water molecules.

When the surface is contacted with aqueous phenol solution, it produces an AFM image shown in Fig. 2(b). Higher image contrast under phenol solution is attributed to the presence of phenol molecules in the proximity of the surface. The structure appears

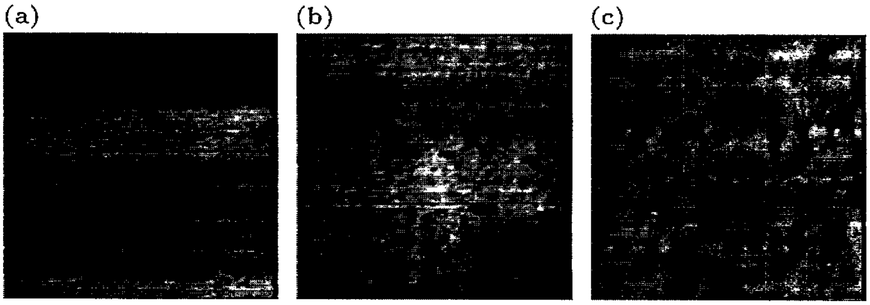

Fig. 1. Wide-area, 0.9 μm × 0.9 μm AFM images of a MgO(100) surface observed under deionized water. Images were taken (a) immediately, (b) 12 min and (c) 3 h and 26 min after the immersion. Gray scales are (a) and (b) 2 nm and (c) 12 nm full scale. Images are presented without any filtering.

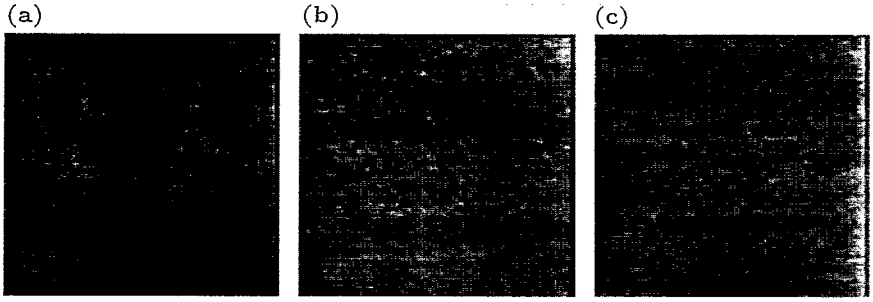

Fig. 2. Narrow-area, 8 nm × 8 nm AFM images of a MgO(100) surface taken under (a) deionized water, (b) a phenol solution and (c) an ammonium benzoate solution. Gray scales are (a) 0.4 nm and (b) and (c) 0.5 nm full scale. Images are flattened and low-pass-filtered.

to indicate a cubic symmetry, with its periodicity being ca. 3 Å. Magnesium oxide takes NaCl crystal structure with the unit length a_0 of 4.21 Å. The observed periodicity in Fig. 2(b) is in good agreement with the MgO(100) anion (or cation) nearest neighbor distance of 2.98 Å. Thus the image shown in Fig. 2(b) could be interpreted in two ways: it may be the anion (or cation) array, or it may be the adsorbed phenol overlayer. In the former case, added phenol may prevent water molecules to hydrate the surface and screen the surface charges, thus restoring the original substrate surface corrugation. In the latter case the observed image may indicate that the adlayer is in registry with the surface structure. It is not possible at this moment to determine which case is more likely. If it is the latter case, higher resolution images should provide the inner structure of the adsorbed molecules, as observed in the case of pyridine base molecule adsorption on zeolite surfaces [3–5]. Efforts to attain such a high resolution in the present system have not been successful to date.

When the surface is contacted with aqueous ammonium benzoate solution, an ordered structure was also observed, as shown in Fig. 2(c). This structure is different from the one observed under a phenol solution, and shows a rhombic unit cell with cell length of ca. 4 Å and an inclined angle of ca. 75°. The difference of the observed 2D crystal structure with that expected for MgO(100) indicates that the observed structure is due to the adsorbed overlayer of benzoate. Like the case of phenol, it has not been possible to observe the inner structure of the adsorbed benzoate molecules.

3.2. $TiO_2(110)$

The (110) surface of rutile TiO_2 is known to be the most stable one among the TiO_2 crystallographic surfaces. A clean (110) surface is expected to have Ti^{4+} ions aligned along the [001] direction with the interval between them being 3.25 Å, and every other Ti^{4+} row is covered with oxygen atoms. Thus topo-

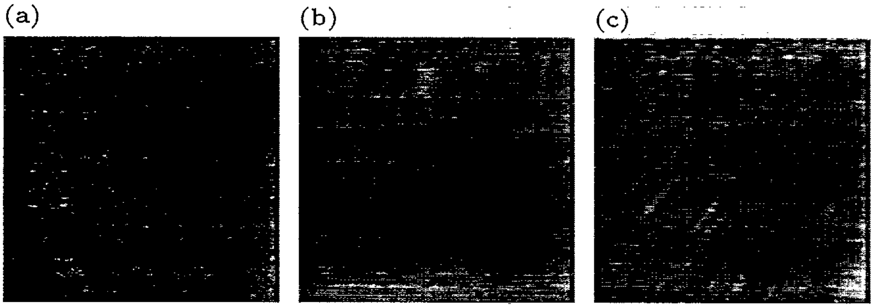

Fig. 3. Narrow-area, 8 nm × 8 nm AFM images of a $TiO_2(110)$ surface obtained under (a) deionized water, (b) a phenol solution and (c) a pyridine solution. Images are presented without any filtering. Gray scales are all 0.5 nm full scale.

graphically the surface should consist of oxygen rows separated by titanium trenches, with the interval of 6.5 Å. With UHV-STM rows extending along the [001] direction with the interval of 6.5 Å are typically observed [8,9]. In this case, however, observed rows are attributed to that of Ti^{4+}, since the tunnel current flows into the Ti^{4+} 3d orbitals. When gas-phase formic acid is contacted on the surface, each molecule is adsorbed on two Ti^{4+} ions, producing (2 × 1) surface periodicity [8,9].

The present study is aimed at obtaining a $TiO_2(110)$ surface topography under an aqueous environment. Immersed in deionized water, no dissolutions of the surface were observed under the present examination conditions. Fig. 3 compares narrow-area, 8 nm × 8 nm AFM images taken under (a) deionized water, (b) a phenol solution and (c) a pyridine solution. All of them show similar row structures, with the interval among the rows being about 3 Å, half of that expected for (1 × 1) clean surface periodicity. In contrast to STM, AFM images are expected to reflect actual surface topography, and the observed row structure could be explained if we assume that the Ti^{4+} trenches are filled with adsorbed molecules, bringing their height comparable to that of the oxygen rows of the clean surface along the [001] direction. Most likely, the molecules to fill the Ti^{4+} trenches are the water molecules adsorbed on Ti^{4+}, which would have the molecular size about the same to that of the lattice oxygen. Then the row images found in Fig. 3 could be interpreted as alternating lattice oxygen and adsorbed water rows.

The addition of a phenol or pyridine aqueous solution onto the $TiO_2(110)$ surface did not change the observed AFM images significantly, as found in Fig. 3(b) and (c), indicating that the adsorption of these aromatic molecules is very slow on this surface, if it happens at all. The effects of the presence of these molecules on the AFM images are noted, however, in the enhanced contrast of the row structure as may be found by comparing three images shown in Fig. 3.

4. Summary

In situ observation of MgO(100) and $TiO_2(110)$ surfaces under water and under aqueous aromatic molecule solutions were attempted by AFM. Slow dissolution of the MgO(100) surface was observed, initiated by pitting. MgO(100) gave AFM images of very low contrast at atomic level under deionized water. Addition of an aqueous phenol solution onto MgO(100) surface appeared to enhance the MgO atomic images, whereas ammonium benzoate solution produced a structure attributable to adsorbed molecule overlayers. $TiO_2(110)$ showed an image that corresponds to the Ti^{4+} rows under deionized water, possibly produced by water molecule adsorption on empty Ti^{4+} rows. Under aqueous aromatic solutions AFM images were similar to those obtained under deionized water, indicating no or very slow adsorption of these molecules on the surface.

References

[1] H. Ohtani, R.J. Wilson, S. Chiang, C.M. Mate, Phys. Rev. Lett. 60 (1988) 2398.

[2] M. Komiyama, Scanning 18 (1996) 244.

[3] M. Komiyama, M. Gu, Jpn. J. Appl. Phys. 35 (1996) 3775.

[4] M. Komiyama, T. Koyama, T. Shimaguchi, M. Gu, J. Phys. Chem. 100 (1996) 15198.

[5] M. Komiyama, M. Gu, J. Vac. Sci. Technol. B, in press.

[6] G. Meyer, N.M. Amer, Appl. Phys. Lett. 56 (1990) 2100.

[7] E. Meyer, H. Heinzelmann, D. Brodbeck, G. Overney, R. Overney, L. Howald, H. Hug, T. Jung, H.-R. Hidber, H.-J. Guntherrodt, J. Vac. Sci. Technol. B 9 (1992) 1329.

[8] H. Onishi, Y. Iwasawa, Surf. Sci. 313 (1994) L783.

[9] H. Onishi, K. Fukui, Y. Iwasawa, Bull. Chem. Soc. Jpn. 68 (1995) 2447.