Surface Observation of MgO Single Crystal with Atomic Force Microscope and Crystallographic Orientation Dependence of Wettability of MgO by Liquid Metals[†]

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The (100), (110) and (111) surface of MgO were observed at an atomic scale using an atomic force microscope. It was identified that the line defects existed on each surface and that the surface structure of MgO was different from the bulk one. It can be inferred that all the bright spots in the AFM images correspond to the positions of the oxygen atoms in the case of MgO.

A factor affecting the wettability of MgO single crystal by liquid metals was discussed on the basis of the AFM observations. It gets cleared that the interaction between the oxygen on the surface and the magnesium or oxygen on the second layer affects the crystallographic orientation dependence of the wettability of MgO single crystal by liquid metals.

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I. Introduction

The MgO single crystal has been widely used for a substrate of superconducting thin films because of its good lattice matching⁽¹⁾. It is well known that the crystallinity and properties of films are affected by dislocations in oxide substrates⁽²⁾. Moreover, we have already reported that the wettability of MgO single crystal by liquid pure metals strongly depends on its crystallographic orientation⁽³⁾. These results suggest that the surface structure of oxides plays an important role in the properties of films and the wettability. It becomes, therefore, very important to understand the surface structure of oxides in various applications.

The scanning tunneling microscope (STM)⁽⁴⁾ has dramatically developed the surface analytical technique. It provides the surface image in real space at an atomic resolution. However, STM cannot be applied to non-conductive surface. There are very few reports about the non-conductive surface, such as MgO.

Recently, the atomic force microscope (AFM)⁽⁵⁾ was invented. The AFM can be applied to both conductive and non-conductive materials, because the AFM provides the surface topographic image by detecting force between a

tip and an atom on surface.

By using AFM, we have succeeded to observe the surface of MgO at an atomic scale for the first time. In this paper, the surface structure of MgO by AFM was compared with the bulk structure by high resolution electron microscopy. The relationship between the surface structure of solid and the wettability of solid by liquid metals was also discussed on the basis of the AFM observations.

II. Experiment

1. AFM observation

The specimens prepared for the AFM observations were as-received MgO single crystals. The surface orientations of the MgO were (100), (110) and (111). The surfaces of MgO were imaged in air at room temperature using a Nanoscope II (Digital instruments, California).

Our AFM is based on the optical lever detection technique (Fig. 1)⁽⁶⁾⁽⁷⁾. The AFM detects the vertical motion of the tip by sensing the displacement of the reflected beam with a photodiode. A feedback loop keeps the position of the reflected beam and the force on the sample constant. It is accomplished by moving the sample up and down with the xyz translator.

2. TEM observation

The MgO single crystal (the surface orientation: (100)) was observed by TEM. After the specimen was thinned to about 20 μm in thickness by polishing on SiC paper and powder, it was perforated by atom thinning.

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Fig. 1 Explanatory figure of AFM.

The specimen prepared was observed by a conventional transmission electron microscope and a high resolution electron microscope. The direction of the incident electron beam was $\langle 100 \rangle$.

III. Results

Figures 2~4 are the AFM images of the (100), (110), and (111) surfaces of MgO, respectively. Figures 5~7 are

Fig. 3 AFM image of (110) plane of the MgO surface.

Fig. 2 AFM image of (100) plane of the MgO surface.

Fig. 4 AFM image of (111) plane of the MgO surface.

Fig. 5 Schematic diagram of the (100) surface.

Fig. 6 Schematic diagram of the (110) surface.

Fig. 7 Schematic diagram of the (111) surface.

the schematic diagrams of the AFM images. The bright spots in the AFM images show the locations of the atoms.

All the AFM images were filtered. As it was confirmed that the distances and angles between atoms in the filtering data are quite the same as those in the raw data, it can be considered that the filtering data show the surface structure exactly.

Figures 8~10 are the bulk structures of MgO. Figure 11 is the image obtained by the high resolution electron microscope. It can be seen that the distances between atoms on each surface obtained by the AFM are different from those of bulk. These results indicate that the surface structures differ from the bulk ones.

It has been reported that the STM image of graphite correspond to the bulk structure⁽⁸⁾. One of the authors have also clarified that the AFM image of graphite is quite similar to the bulk structure⁽⁹⁾. It can be considered from these results that the AFM gives the real surface structure. There was little effect of drift on the AFM images in our observations. It suggests that the difference between the surface structure and the bulk one is quite

Fig. 8 Schematic diagram of the (100) bulk structure of MgO.
(○: Oxygen, ●: Magnesium) Fig. 9 Schematic diagram of the (110) bulk structure of MgO.
(○: Oxygen, ●: Magnesium) Fig. 10 Schematic diagram of the (111) bulk structure of MgO.
(○: Oxygen, ●: Magnesium)

Fig. 11 HREM micrograph of MgO.

reasonable. Some researchers have reported that the surface structures of the (100) plane of ionic crystals⁽¹⁰⁾ correspond to the each bulk structure. This result differs from our results. Further investigations are required to clarify the differences.

The line defects (black dots in Figs. 2~4) are observed in any MgO plane. The surface structure of (111) plane is more irregular than those of (100) and (110) ones. The adsorbants on the surfaces must be considered because the AFM observations were carried out in air. However, physical adsorbants could be removed in the AFM observations, because the tip always contacts the surface when the tip scans on the surface. It can be expected that the AFM images are free of physical adsorbants.

IV. Discussion

1. Surface structure of MgO single crystal

As mentioned in Section 3, the line defects were observed on every surface. They (or their extended lines) intersected with a constant angle on the surfaces of the (100) and (110) planes. On the contrary, the angle between the line defects are not constant on the (111) plane. Moreover, the surface structure of the (111) plane was more irregular than those of the (100) and (110) planes.

(1) Surfaces of the (100) and (110) planes of MgO

Low energy electron diffraction (LEED) and X-ray diffraction (XRD) have been widely used to analyze surface. Previously, Henrich observed the structure of MgO surfaces by LEED⁽¹¹⁾. However, he has never reported defects on the first surface layer. LEED and XRD, which utilize the diffraction phenomena, cannot inform us the structure of the first surface layer, because incident electron beam or X-ray pass into the bulk, and the information of the bulk structure in the vicinity of the first surface layer must be obtained. Accordingly, the AFM is the only technique to analyze the outermost surface layer of non-conductive material.

In general, dislocations in ionic crystals are composed of two extra atom rows (Fig. 12)⁽¹²⁾ to retain the electric charge balance. If the line defects are introduced only on

the surfaces, the line defects must consist of two extra atom rows to retain the electric charge balance. It is very important that the line defects are composed of one atomic row in the present observation.

On a surface of ionic crystal, the atoms are rearranged (Fig. 13). Negative ions appear at the surface and positive ions are retracted into the bulk⁽¹²⁾. The AFM may not identify positive ion because the vertical resolution of AFM is not good enough. It can be concluded from these results that all the bright spots in the AFM images of MgO correspond to the positions of the oxygen atoms.

Figure 14 is the TEM micrograph which shows the highest dislocation density in MgO sample. It is apparent that the density of extra atomic row (the dislocation density) is much lower than that on the surface observed by the AFM. These results mean that all the extra atomic rows on the surface of MgO are introduced due to the surface reconstruction to retain the electric charge balance. From our results of the AFM and TEM observations, it is quite reasonable that almost all the extra atomic rows on the surface are not the dislocations but the line defects introduced only on the outermost surface layer in the case of MgO. However, there is a possibility that some extra atomic rows may be the cores of dislocations. It is also reported that the lattice defects (edge dislocation) are identified on the surface of the LiF(100)⁽¹⁰⁾.

Table 1 shows the crossing angle between the atomic rows in the bulk structure and that in the AFM images. These values on the (100) and (110) planes of AFM images are quite the same as those between atomic rows in the bulk structure. This implies that the surface struc-

Fig. 13 Ionic rearrangement near an ionic crystal surface⁽¹²⁾. (○: Anion, ●: Cation)

Fig. 12 Schematic diagram of edge dislocation in NaCl⁽¹²⁾. (○: Chlorine, ●: Sodium)

Fig. 14 TEM micrograph of MgO single crystal.

Table 1 Comparison of the crossing angle of the atomic rows between in the bulk and at the surface.

	In the bulk (degree)	At the surface (degree)
(100)	0, 45, 90	0, 90
(110)	0, 55, 71, 90	0, 68

tures of the (100) and (110) planes are strongly affected by the bulk structure, although the line defects are introduced on the surfaces.

Figure 6 shows a schematic diagram of the (110) plane of MgO. All the bright spots in the AFM images are assumed as oxygens (Mg atoms cannot be observed by AFM because they exist inside rather than at the surface). The MgO(110) surface structure (Fig. 6) has the similar configuration to the bulk one (Fig. 9), that is, the angles between atomic rows at the (110) surface are the same as those in the bulk. However, the kind of the atoms at some positions do not correspond to the bulk one.

In the case of NaCl type structure such as MgO, the (100) plane is the most stable structure⁽¹³⁾. Figure 15 is the schematic diagram, assuming that the surface structure of (110) changes to the one similar to (100). The atomic arrangement in Fig. 15 is close to that of the (100) plane, although the distances between atoms differ from those on the (100) plane. It can be considered that the structure of the (110) plane changes to the one similar to the (100) when the surface reconstruction occurs.

Henrich has reported that the surfaces of the annealed (111) and (110) planes show the LEED pattern of the (100) plane⁽¹¹⁾. It can be considered from this report that the bulk structure in the vicinity of the surface changes to the most stable structure from the viewpoint of atomic arrangement. This report does not conflict with our conclusion that the surface structure of the (110) surface changes to that of the (100) surface by surface reconstruction. Moreover, it is also reported that the as-received (110) surface shows the LEED pattern of the (110) bulk structure⁽¹¹⁾. It suggests that the bulk structure in the vicinity of the surface layer must be obtained by LEED.

Fig. 15 Schematic diagram of the rearranged (110) surface structure of MgO. (○: Oxygen, ●: Magnesium)

(2) Surface of the (111) plane of MgO

It is observed from AFM images that the surface structure of the (111) plane is more irregular than those of (100) and (110), and that the atomic arrangement and the distance between atoms on the surface of the (111) plane are not the same as those of the bulk. Moreover, the extra atomic rows do not cross with a constant angle. It can be considered that the surface structure of the (111) plane is not affected by the bulk structure. It can be considered that the structural change on the (111) surface occurs only at the outermost surface layer.

The polarity of the surface might contribute to this difference in the surface structural change among planes. The electric charge balance at the surface of (111) plane is unstable, because the (111) plane consists of anions (or cations). On the contrary, the electric charge balance of (110) and (100) is very stable. Therefore, it can be considered that the surface of the (111) plane changes to balance the electric charge. From the results of surface structure of (110), it is inferred that the surface structure of (111) surface may be similar to that of the (100) plane.

2. Important factor affecting the wettability of oxide by liquid metals

We have already reported that the wettability of MgO single crystal by liquid pure metals strongly depends on the crystallographic orientation of the MgO single crystal⁽³⁾. For example, the work of adhesions between liquid Sn and MgO single crystals at 873 K are $121(\times 10^{-3} \text{ J/m}^2)$ for (100) plane, $84(\times 10^{-3} \text{ J/m}^2)$ for the (111) plane and $8(\times 10^{-3} \text{ J/m}^2)$ for the (110) plane, respectively.

In the liquid Sn-MgO system, no reaction is expected at 873 K. When the interaction between an atom of liquid metal and an oxygen at the MgO surface dominates the value of work of adhesion, it can be expected that the value of work of adhesion becomes larger in accordance with an increase in the number of oxygen atoms at the MgO surface.

Table 2 shows the number of oxygen at the (100) and (110) surfaces. These values were calculated utilizing AFM observations. The number of oxygen at the (100) surface is almost the same as that at the (110) surface. However, the work of adhesion on (100) plane was much larger than that on the (110) surface. Furthermore, in Section IV.1, it got cleared that the atomic arrangement on the (110) surface of MgO is quite similar to that on the (100) surface. These results imply that the wettability is not dominated by the interaction between an atom of liq-

Table 2 Number of oxygen on surface and work of adhesion between MgO and liquid metal.

	(100)	(110)
Number of oxygen on surface of MgO ($\times 10^{-5} \text{ mol/m}^2$)	7.1	8.9
Work of adhesion between MgO and liquid metal ($\times 10^{-3} \text{ J/m}^2$)	121	8

liquid metal and an oxygen at the MgO surface and the atomic arrangement of the MgO surface.

Table 3 shows the coulomb force between oxygen ion on the surface of MgO and the nearest neighbor ions (magnesium ion and oxygen ion) on the second layer. The coulomb force was calculated on the assumption that the surface structure is the same as the bulk one. Then, it is assumed that the surface structure of the (110) plane changes to the one similar to the of (100). In Table 3, the positive value means that the coulomb force acts towards the exterior of bulk.

In the case of the (100) plane, all the oxygens on the surface are easy to be separated from the surface, because all the oxygens on the surface are pushed towards the exterior of bulk (Fig. 16). On the contrary, the half of oxygens on the surface are pushed towards the exterior of the bulk (Fig. 17(a)) and the others are pulled towards the interior of the bulk (Fig. 17(b)) in the case of the (110) surface. This fact means that the number of oxygen at the (110) surface which can be separated from the surface is less than that at the (100) surface, although the total number of the oxygen at the (110) surface is almost the same as that at the (100) surface.

The interaction between an oxygen at the surface of MgO and the nearest neighbour ions in the bulk are different between (100) and (110), by which can be qualitatively explained the difference of the wettability. This result suggests that the interaction between the surface and the second layer is the very important factor for the value of work of adhesion, that is, the wetting phenomena.

The work of adhesion on the (111) plane is close to that on the (100) plane. This result also suggests that the structure in the vicinity of the (111) surface was similar to the (100) structure.

Table 3 Coulomb force between oxygen on surface and the nearest-neighbor ions on the second layer.

Coulomb force ($\times 10^{-18} \text{ C}^2/\text{m}^2$)		
(100)		2.32
(110)	(a)	2.32
	(b)	-2.32

Fig. 16 Schematic diagram of the atomic arrangement in the vicinity of (100) surface. (○: Oxygen, ●: Magnesium)

Fig. 17 Schematic diagram of the atomic arrangement in the vicinity of (110) surface. (○: Oxygen, ●: Magnesium)

V. Conclusion

The surface of MgO was observed by a newly developed atomic force microscope (AFM). New information on the wettability of oxide by liquid metals was obtained from the AFM observation.

The results can be summarized as follows:

- (1) The surface structure of the (100), (110) and (111) planes of MgO are different from those of bulk structure but the surface structures of (100) and (110) surfaces are still strongly affected by bulk.
- (2) The surface structure of the (110) plane is quite similar to the atomic arrangement of (100) plane which is the most stable one in view of the surface energy.
- (3) The line defects are identified on each plane of MgO and the surface structure of (111) plane is more irregular than those of (100) and (110).
- (4) The bright spots in the AFM images of MgO correspond to the locations of oxygen atoms.
- (5) In spite of the similarity of the surface structure between (100) plane and (110) plane, the wettability of them quite differs.
- (6) The interaction between the oxygen on the surface and the magnesium or oxygen on the second layer affects the crystallographic orientation dependence of the wettability of MgO single crystal by liquid metals.

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