

# Annealing Effect of MgO Substrates Studied by Atomic Force Microscope

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## Abstract

The annealing effect of MgO substrates is studied by means of an atomic force microscope. Annealing at temperatures above 1260°C results in the formation of atomic steps on the substrate surface. The heights of steps are multiples of 0.354 nm. As the bulk lattice parameter is 0.421 nm, this result shows that the surface structure is different from the bulk crystal.

**Key Words:** MgO, annealing, AFM, atomic step

## 1. Introduction

Since the discovery of high-temperature superconductivity in cuprate oxides by Bednorz and Muller<sup>1)</sup>, there have been many efforts to prepare them as high-quality thin films<sup>2)</sup>. The physical properties of superconducting thin films are known to depend on the substrate used. The choice of substrates is dictated by various requirements, such as compatibility of lattice parameters and thermal-expansion coefficients, chemical inertia and low microwave losses. Single-crystalline substrates have been used for the epitaxial superconducting thin film growth. These crystals are SrTiO<sub>3</sub>, LaAlO<sub>3</sub>, LiNbO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, Y-stabilized ZrO<sub>2</sub> (YSZ), BaF<sub>2</sub> and, in particular, MgO. The MgO crystal has been widely used as a substrate for the high-temperature superconducting thin films, because of low chemical reactivity with them, despite the more than 9 % lattice mismatch<sup>3)</sup>.

The surface morphology and smoothness of the substrate strongly influence the growth and electric properties of the deposited superconducting film<sup>4)</sup>. Ideally, the surface should be atomically smooth, free of lattice defects, and chemical impurities. Commonly used surfaces, however, comprise a step structure, lattice disorder, or physisorbed and chemisorbed contaminant layers, respectively. Mechanically polished single crystals also possess a damaged surface layer. MgO is also known as a typical basic oxide being able to adsorb dissociatively or reactively species from the ambient air. For example, H<sub>2</sub>O and CO<sub>2</sub> are chemisorbed to form hydroxide<sup>5)</sup> and carbonate<sup>6)</sup>, respectively. An effective cleaning procedure for refractory oxides is firing at temperatures above 1000°C<sup>3,7-12)</sup>. In addition to the hydroxide or carbonate decomposition, formation of vacancies and thermal etch pits can also occur. The dehydration reaction of Mg(OH)<sub>2</sub> is observed to result in formation of very small crystallites of MgO<sup>13)</sup>. Consequently, study of the effect of annealing on the MgO substrate is quite important for the high-quality superconducting film deposition.

In this paper, we report the effect of annealing on the surface morphology of the MgO substrate by means of an atomic force microscope (AFM). Annealing of the substrate at temperatures above 1260°C results in the formation of atomic steps on the substrate surface.

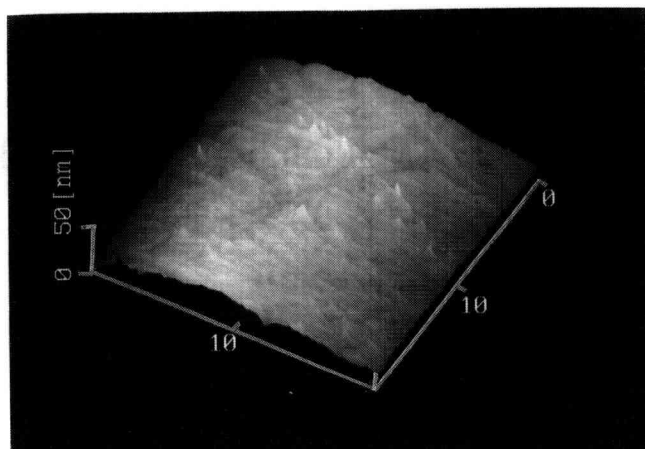


Fig. 1. AFM image of mechanically polished MgO surface (scan area:  $20 \times 20 \mu\text{m}^2$ , z scale: 50 nm /div. ).

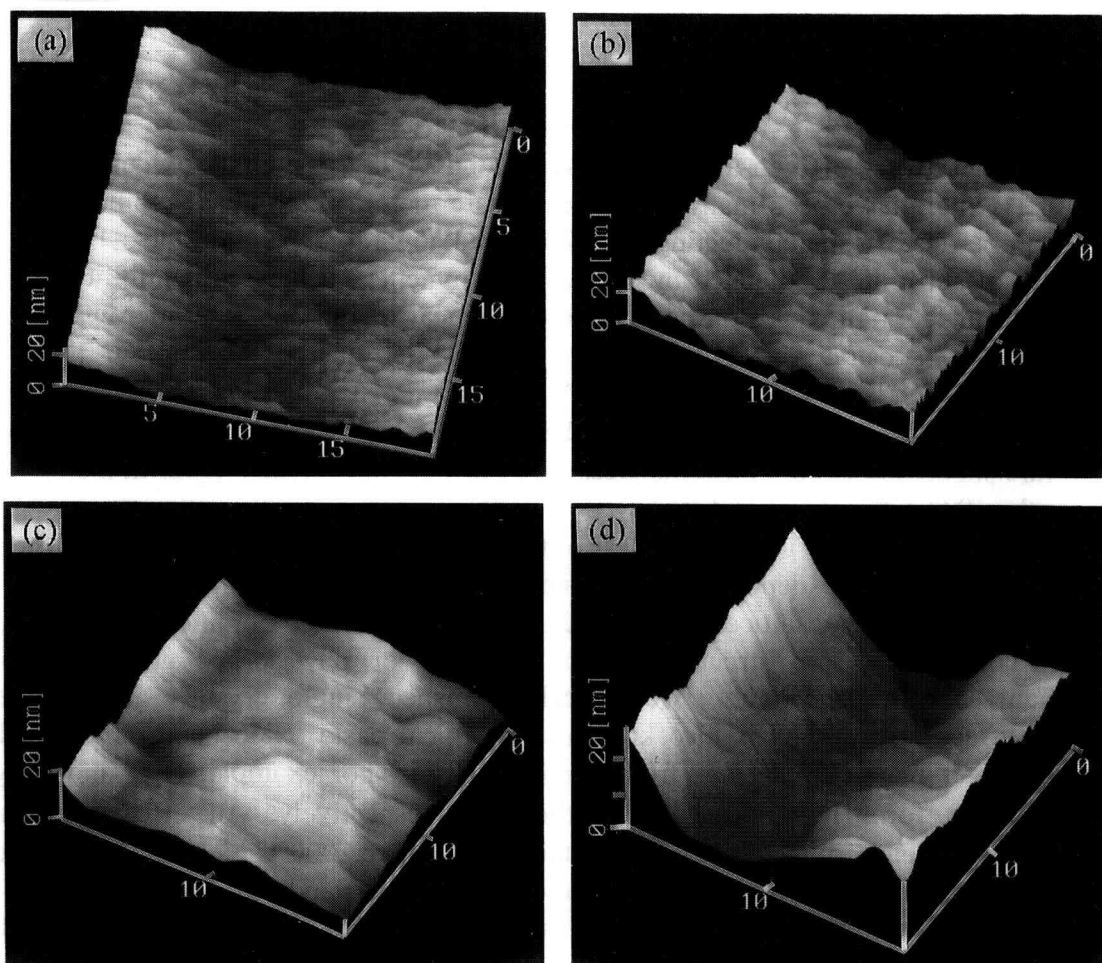


Fig. 2. AFM image of MgO surface annealed for 24 h (a) at 870°C, (b) at 970°C, (c) at 1070°C and (d) at 1160°C, respectively. (scan area:  $20 \times 20 \mu\text{m}^2$ , z scale 20 nm /div. ).

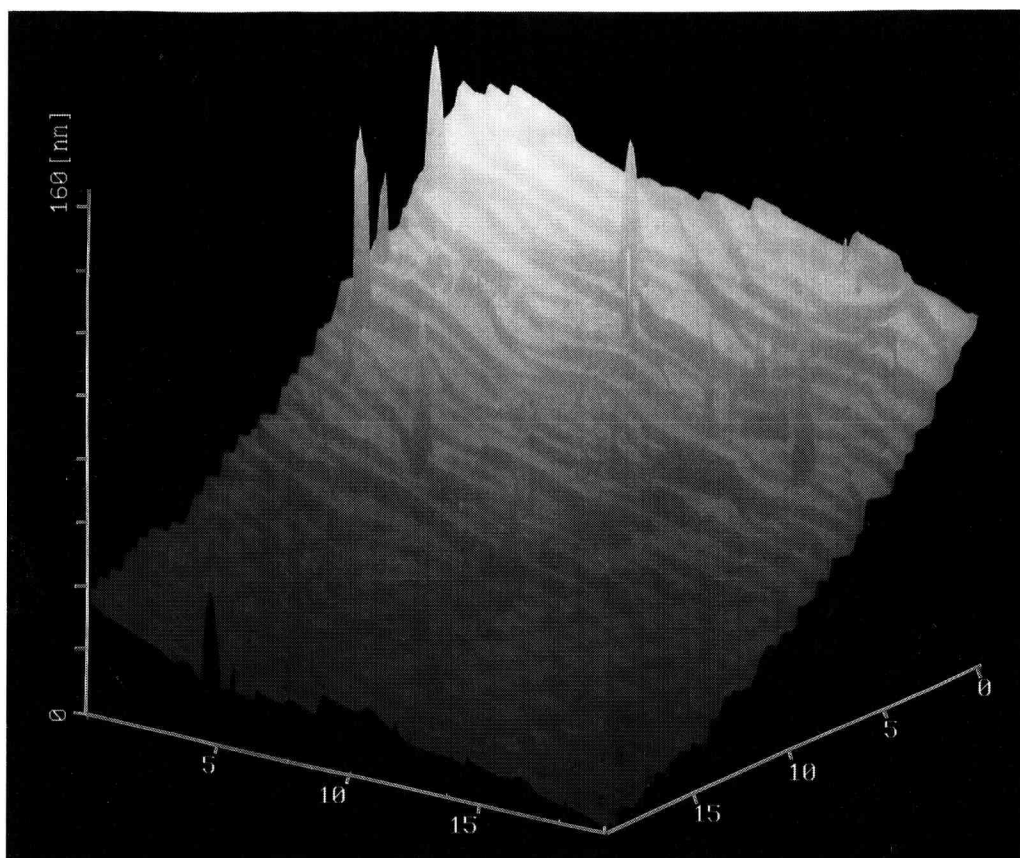


Fig. 3. AFM image of MgO surface annealed at 1260°C for 24 h (scan area:  $20 \times 20 \mu\text{m}^2$ ,  $z$  scale 20 nm/div). Something like a needle is due to dust.

The analysis of the step height shows that a unit layer thickness at the surface is 0.354 nm. As the distance of oxygen and magnesium atoms in the bulk MgO crystal 0.21 nm, this result shows that the surface structure is different from the bulk structure.

## 2. Experimental

Single crystals of MgO substrates used in this work were commercially obtained. Their size was  $10 \times 10 \text{ mm}^2$  and 1 mm thick. The (100) surface of the MgO substrates was mechanically polished at first with 6  $\mu\text{m}$  diamond paste for 3 minutes, second with 3  $\mu\text{m}$  diamond paste for 5 minutes, third with 1  $\mu\text{m}$  diamond paste for 10 minutes, at last with 1/4  $\mu\text{m}$  diamond paste for 30 minutes. The polished substrates were cleaned with acetone. Then the substrates were heated in air for 24 h at 870, 970, 1070, 1160, 1260 and 1360°C, respectively. The surface morphology was investigated in air at room temperature by an atomic force microscope (AFM) SEIKO MODEL SPI 3700. All surface images were obtained in a constant force mode with force of 87 pN. The material of the cantilever used in this experiment was  $\text{Si}_3\text{N}_4$ . Data were recorded with a computer and surface morphology was displayed as 64 color gray scale.

## 3. Experimental Results and Discussion

Figure 1 shows the AFM image of the mechanically polished MgO surface. The scan area is  $20 \times 20 \mu\text{m}^2$  and the  $z$  scale is enlarged to 50 nm/division. The surface roughness is 7 nm root mean square. Deep grooves are due to scratches caused by large-sized diamond grit.

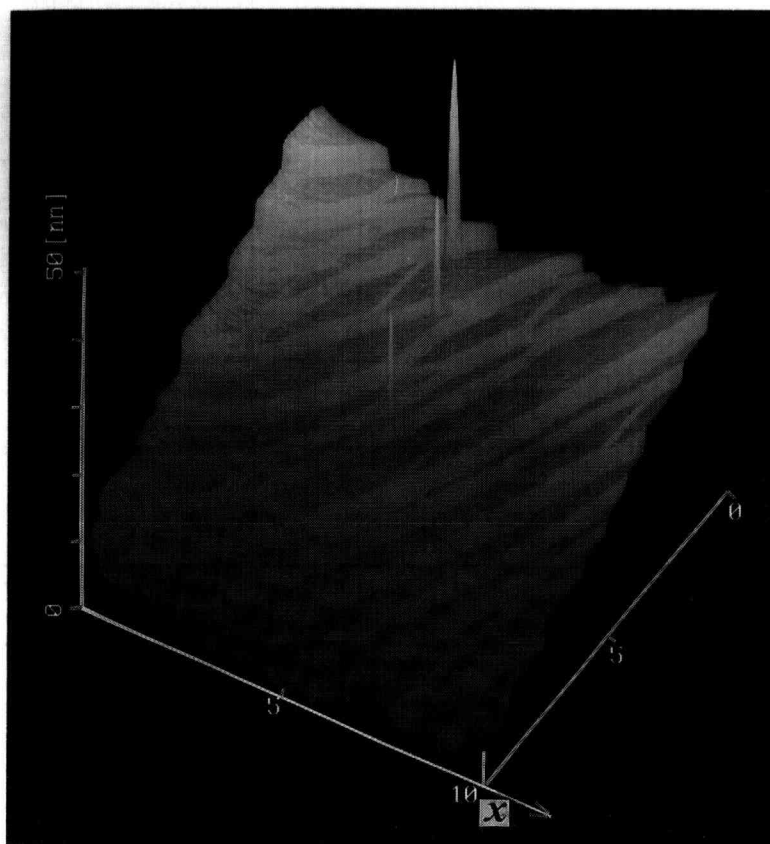


Fig. 4. AFM image of MgO surface annealed at 1360°C for 24 h (scan area:  $10 \times 10 \mu\text{m}^2$ ,  $z$  scale 10 nm /div ). Something like a needle is due to dust.

Figures 2 (a), (b), (c) and (d) show the AFM images of the MgO surface annealed at 870, 970, 1070 and 1160°C, respectively. These annealing temperatures are relatively low, compared to the melting point 2852°C of MgO<sup>14</sup>). As the annealing temperature increases from 870 to 1160°C, however, the smoothness of the surface increases. This result shows that atoms at the surface can move around at temperatures above 1000°C.

Figures 3 and 4 show the AFM images of the MgO surface annealed at 1260 and 1360°C, respectively. Something like a needle in the Figures is due to dust at the surface. The surface morphology is quite different from those of Fig. 2. A series of steps is observed at the surface. The step height of the substrate annealed at 1360°C is measured. The step heights are measured at  $x = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9$  and  $10 \mu\text{m}$  in Fig. 4. Observed step heights are as follows: 0.35, 0.71, 1.06, 1.41, 1.77, 2.12, 2.48, 2.83, 3.18, 3.54, 3.89, 4.24, 4.60 and 4.95 nm. Figure 5 shows the histogram of the step heights. The most frequent step heights are from 2.12 nm to 3.89 nm. If these steps are due to atomic steps, the observed step height corresponds to a multiple of a unit layer thickness. The lowest step height of 0.35 nm is assigned to the first order, the next step height of 0.71 nm to the second order and so on. Figure 6 shows the relation between the observed step height and the order. The step height is proportional to the order. This clarifies that the steps observed in Fig. 4 are due to atomic steps. These steps are formed as a result of the lowering of the total free energy of the system<sup>15</sup>). The dashed line in Fig. 6 is the least-square-fitting curve, and the fitting value of the unit layer thickness is 0.354 nm.

The bulk lattice parameter of the MgO crystal, however, is 0.421 nm<sup>16</sup>) as shown in Fig. 7.

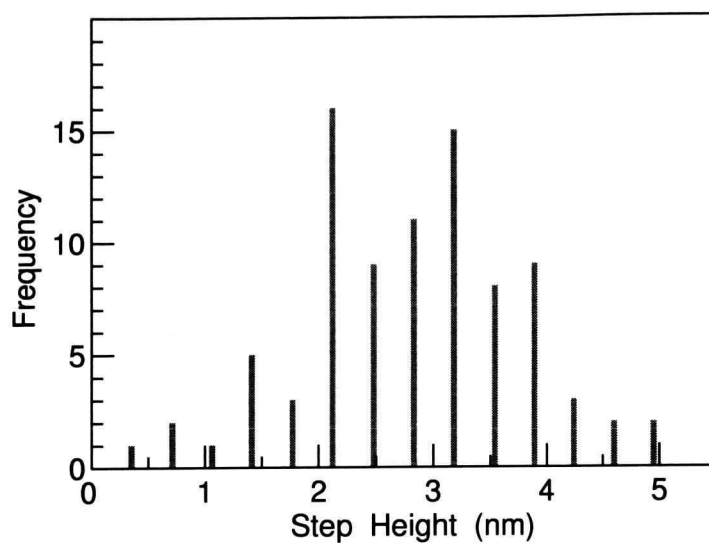


Fig. 5. Histogram of the step height observed in the MgO substrate annealed at 1360°C for 24 h.

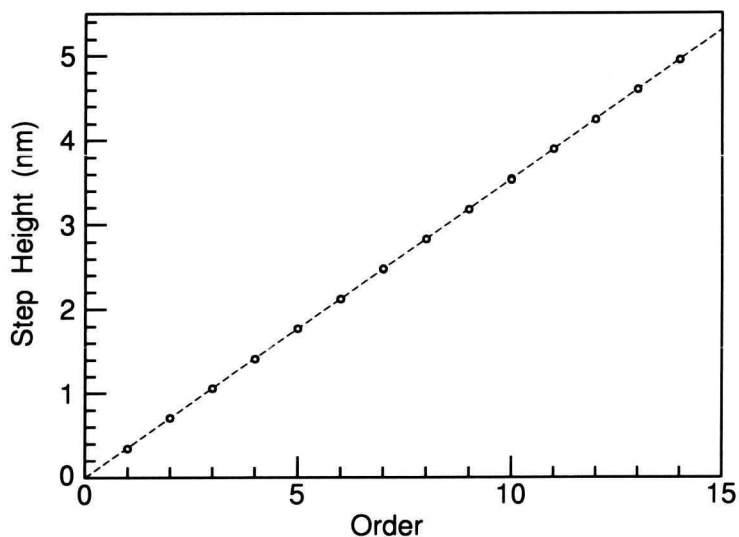


Fig. 6. The relation between the step heights observed at the annealed MgO and the order. The dashed line is the least-square-fitting curve.

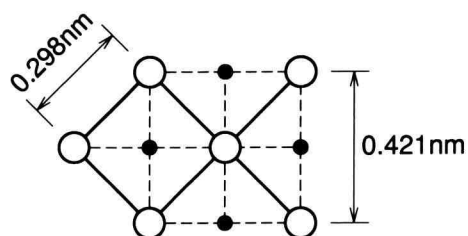


Fig. 7. Schematic structure of the (100) plane of the bulk MgO. Open and closed circles represent oxygen and magnesium atoms, respectively.

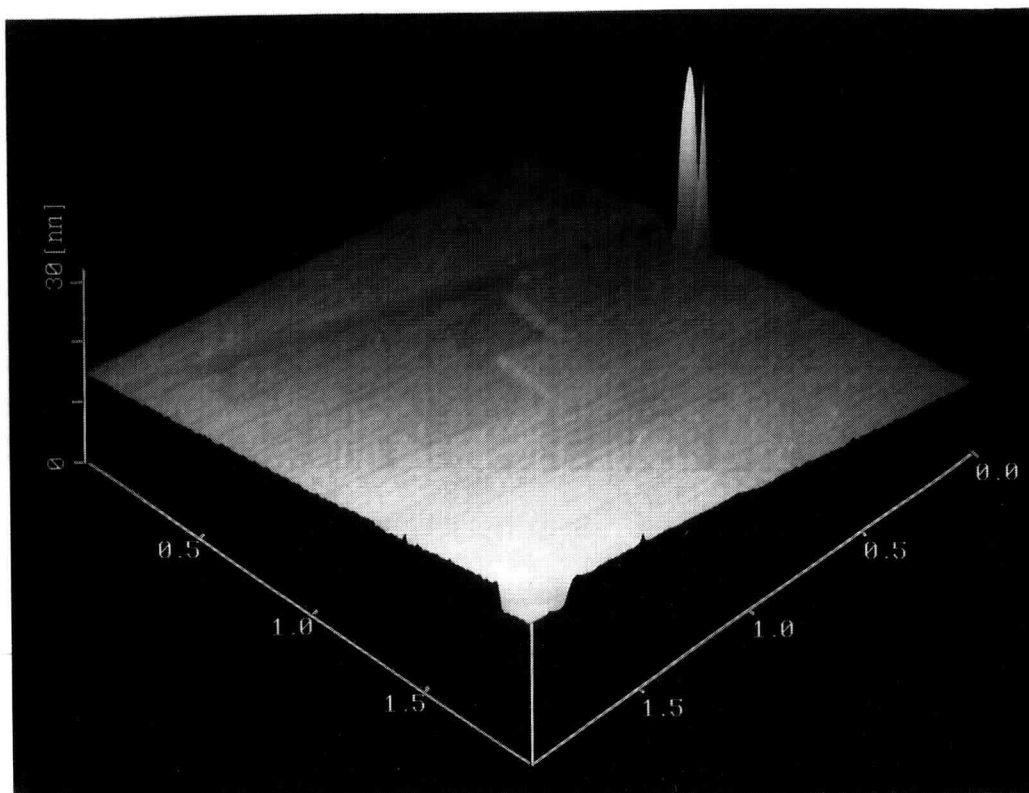


Fig. 8. AFM image of the cleaved MgO surface (scan area:  $2.0 \times 2.0 \mu\text{m}^2$ , z scale 10 nm /div ).

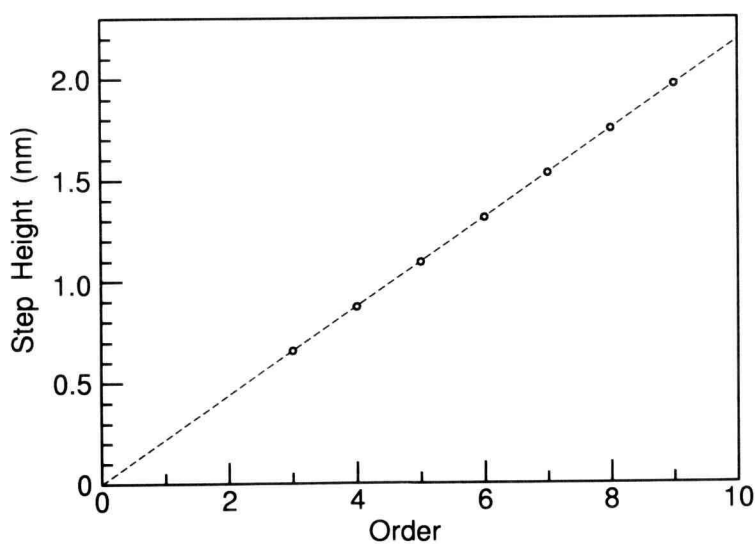


Fig. 9. The relation between the step heights observed at the cleaved MgO and the order. The dashed line is the least-square-fitting curve.

The unit layer thickness of 0.354 nm at the annealed surface is quite large, compared to 0.21 nm, the distance of oxygen and magnesium atoms in the bulk MgO crystal. H. Takeda *et al.*<sup>17)</sup> observed surface morphology of the (100) surface of MgO by means of AFM. They obtained AFM images of spots arrayed rectangularly with a interval of 0.22 nm long and 0.24nm wide.



On a surface of ionic crystal, atoms are rearranged so that negative ions appear at the surface and positive ions are retracted into the bulk<sup>18)</sup>. They assigned that all the spots in the AFM images correspond to the positions of the oxygen atoms. Then the surface structure of cubic MgO crystal is not a square and the distance between the oxygen atoms is reduced to 74 % or 81 % of that of the bulk crystal. They concluded that the surface structure of MgO was different from the bulk one. We have tried to obtain atomic images of the annealed surface of the MgO crystal, but could not distinguish individual atoms at the surface. If the tip of the cantilever is obtuse, the force measured by AFM is the sum of the force acted between many atoms. The measured step heights are the average values of the atoms at the surface.

We also measured cleaved surfaces of MgO crystals, to compare with those of annealed MgO. MgO crystals were cleaved in air at room temperature. Observed step heights of the cleaved MgO surfaces are for example, 22.80, 23.33, 49.44, 62.23, 64.43, 67.60 nm and usually larger than those observed at the annealed surface. Figure 8 shows one of the AFM images of the cleaved MgO crystals. The step heights observed in Fig. 8 are relatively small. The observed step heights in Fig. 8 are 0.657, 0.875, 1.095, 1.313, 1.532, 1.752 and 1.971 nm. The lowest step height of 0.657 nm is assigned to the third order, the next step height of 0.875 nm to the fourth order and so on. Figure 9 shows the relation between the observed step height and the order. The step height is proportional to the order. The dashed line in Fig. 8 is the least-square-fitting curve, and the fitting value of the unit layer thickness is 0.219 nm which is very close to the distance of oxygen and magnesium atoms in the bulk MgO crystal.

The surface structure of annealed MgO substrate has a different structure from the bulk crystal, but the structure of the unit layer thickness of 0.354 nm is unknown.

### Conclusions

In this paper, we have studied the effect of annealing on the surface morphology of the MgO substrate by means of an atomic force microscope. Annealing of substrates at temperatures above 1260°C results in the formation of atomic steps on the substrate surface. The unit layer thickness at the surface is 0.354 nm. As the distance of oxygen and magnesium atoms in the bulk MgO crystal 0.21 nm, this result shows that the surface structure is different from the bulk structure.

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