Annealing Effect of Surface Structure of MgO Single Crystal Studied by LEED

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Abstract

The annealing effect of the surface structure of MgO single crystal has been examined by low energy electron diffraction. The surface of MgO single crystal mechanically polished with 1 μm-diameter diamond paste does not recover its crystal structure by annealing at 900°C. By annealing at 1000°C, the surface of MgO has recovered partly its crystal structure. By annealing at 1200°C, the surface of MgO has recovered fully its crystal structure

Key Words: LEED, MgO, annealing, surface structure

1. Introduction

The surface crystallographic structure can be determined by low energy electron diffraction (LEED)[1]. With electron energies typically in the range from 50 eV to 200 eV, the de Broglie wavelength $\lambda = h/(2mE)^{1/2}$ (m = electron mass, h = Plank constant) varies in the range from 0.17 nm to 0.09 nm which is comparable to inter atomic distances. This leads to large diffraction angles with usually well separated diffraction spots on a fluorescent screen. Using low energy electrons, strong inelastic scattering restricts the incoming electrons to penetrate only a few layers near the surface. In this way, LEED is able to yield the structure of surface atoms.

As magnesium oxide (MgO) has low dielectric constant and is cheap, it has been widely used as a substrate for thin film deposition. The surface morphology and smoothness of the substrate strongly influence the properties of the deposited film. Ideally, the surface should be atomically smooth, free of lattice defects, and chemical impurities. Commonly used surfaces, however, include a step structure, lattice disorder, or contaminant layers[2-4]. Mechanically polished substrates also possess a damaged surface layers. Frequently used cleaning procedure for these refractory oxides is annealing at high temperatures[5-11].

LEED experiments for cleaved MgO surface have been extensively reported[12-17]. Their principal motivation was that the two species in the (100) faces of rocksalt-structure would rumple with respect to the underlying bulk solid. The annealing effect of surface structure of MgO, however, has not been examined by LEED.

In this paper, we report the annealing effect of surface structure of MgO substrates examined by LEED. Substrates are treated with five different procedures. These procedures were cleavage in air, mechanical polishing, annealing at 900°C for 24 hours, and annealing at 1000°C or 1200°C for 3 hours. We report the difference of LEED patterns between these procedures, and discuss the annealing effect of MgO single crystal.

2. Experimental

For the determination of surface structure, a surface should not be contaminated by adsorption of unwanted material, and so it was essential that LEED was carried out under ultra high vacuum (UHV) conditions, that is, pressures less than the order of 10^{-9} Torr. The UHV and LEED system used was a NEVA LEED/AES-200. The vacuum vessel (60 *l*) was pumped, first by a sorption pump, second by a 250 *l*/s turbomolecular pump while the vessel baked at 150°C, third by an 110 *l*/s ion pump and a titanium sublimation pump in parallel, and reached under pressures of 10^{-10} Torr.

Figure 1 shows the schematics of the LEED system. Electrons emitted from a cathode were

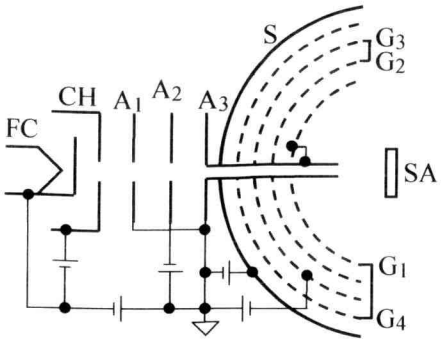

Fig. 1 Schematics of LEED system. FC denotes filament and cathode, CH cathode housing. A_1, A_2 and A_3 denote first, second and third anode, respectively. G_1, G_2, G_3 and G_4 denote first, second, third and fourth grid, respectively. S denotes fluorescent screen and SA sample.

focused on a sample by three anodes A_1, A_2 and A_3. Inelastically scattered electrons were repelled by hemispherical grids G_2 and G_3. Only elastically diffracted electrons hit a fluorescent screen S. The radius of the fluorescent screen was 64 mm. Diffraction patterns on a fluorescent screen were photographed by a Nikon Coolpix 995 digital camera. It was assumed that the diffraction pattern $F(k_x, k_y)$ was due to the interference of electrons having a wave vector $k = (k_x, k_y)$, diffracted from the position $r = (x, y)$ of the substrate surface, where the atomic density was $D(x, y)$,

$$F(k_x,k_y) = \int D(x,y)e^{i2\pi(k_x x+k_y y)}dx\,dy. \quad (1)$$

Then the atomic density $D(x, y)$ was obtained by the inverse Fourier transformation of $F(k_x, k_y)$,

$$D(x,y) = \frac{1}{(2\pi)^2}\int F(k_x,k_y)e^{-i2\pi(k_x x+k_y y)}dk_x\,dk_y. \quad (2)$$

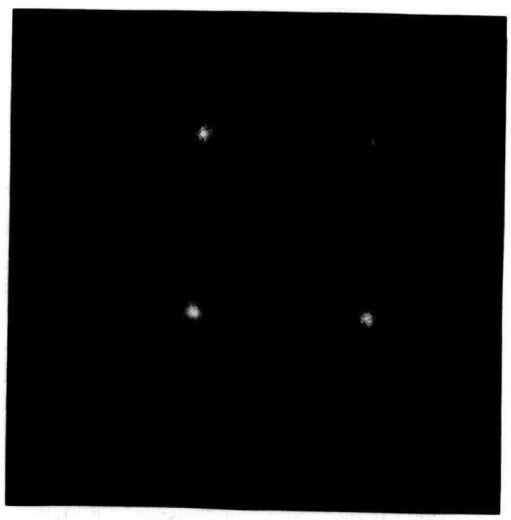

Fig. 2 Diffraction pattern of a cleaved MgO substrate. The electron energy is 100 eV.

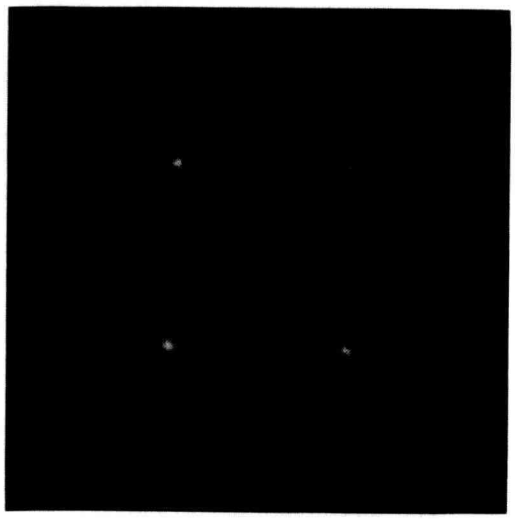

Fig. 3 Diffraction data after the rotation and the subtraction of the background in Fig.2.

Pixels of the photograph of the diffraction pattern were reduced to 256×256 pixels, in order to apply the fast Fourier transformation technique (FFT)[18]. The diffracted data after subtraction of the background intensity was Fourier transformed to obtain the atomic density $D(x, y)$ by FFT.

Single crystals of MgO substrates used in this work were commercially obtained. The cleaved substrate was cut in air from an MgO single crystal of 10 mm × 10 mm × 5 mm in size. The other substrates were 10 mm × 10 mm ×1 mm in size. The substrates were mechanically polished with 1 μm-diameter diamond paste for 10 minutes, and cleaned with acetone. The polished substrates were annealed in air at 900°C for 24 hours, at 1000°C and 1200°C for 3 hours, respectively.

3. Experimental results and discussion

3.1 Air-cleaved MgO substrate

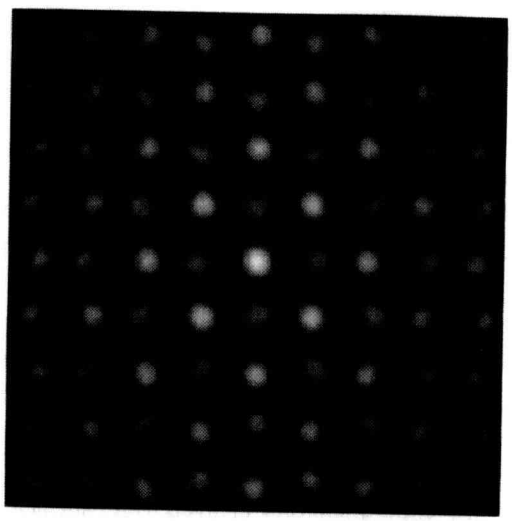

Fig. 4 FFT image of diffraction pattern of Fig.3. Plotted area is 2 nm × 2 nm.

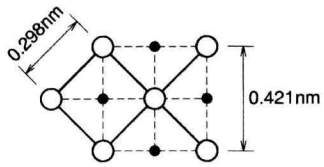

Fig. 5 Shematic structure of the bulk MgO. Open and close circles represent oxygen and magnesium atoms, respectively.

The thickness of the cleaved sample was about 1.5 mm. After the cleavage, the sample was immediately mounted to a sample holder and inserted into a vacuum vessel. After the pressure of the vessel was reduced below 10^{-10} Torr, the filament of LEED was turned on. The pressure of the vessel increased to about 10^{-9} Torr during the heating. As MgO was an insulator, the surface of the substrate charged by the bombardment of low energy electrons. No diffraction spots were observed at an electron energy of 60 eV.

Figure 2 shows the LEED pattern observed for an electron energy of 100 eV. The LEED pattern shows that the surface structure of MgO has a four-fold symmetry. By the restriction of the sample manipulator employed, the sample surface could not be positioned normal to the electron beams. The LEED pattern was photographed by a digital camera. These data were transferred to a personal computer. The coordinates of data were rotated to make the sample surface normal to the electron beams and the background signal was subtracted. Figure 3 shows the LEED data after the rotation and the subtraction of the background in Fig.2.

Figure 4 shows the FFT image of the diffraction pattern of Fig.3. Plotted area is 2 nm × 2 nm. The lattice constant in Fig. 4 is 0.439 nm, which is 4 % larger than the bulk lattice constant 0.421 nm of MgO.

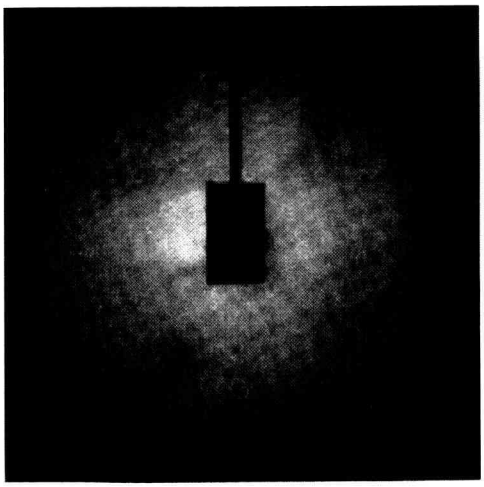

Fig. 6 Diffraction pattern of a mechanically polished MgO substrate. The electron energy is 100 eV.

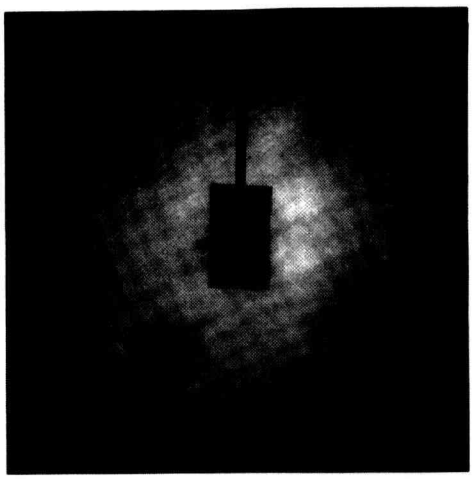

Fig. 7 Diffraction pattern of MgO annealed at 900°C for 24 hours. The electron energy is 100 eV.

Figure 5 shows the schematic structure of the (100) plane of the bulk MgO. The large gray circles in Fig. 4 represent oxygen atoms, and the small white circles represent magnesium atoms.

3.2 Mechanically polished MgO substrate

The substrate of MgO single crystal was 10 mm × 10 mm × 1 mm in size. The substrate was mechanically polished with 1 μm-diameter diamond paste for 10 minutes, and cleaned with acetone. The sample was mounted to a sample holder and inserted into a vacuum vessel.

Figure 6 shows the LEED pattern of the mechanically polished MgO observed for an electron energy of 100 eV. The LEED pattern has no diffraction spot. It shows that the surface of this surface has no periodic structure. This indicates that the surface layers have been damaged by mechanical polishing.

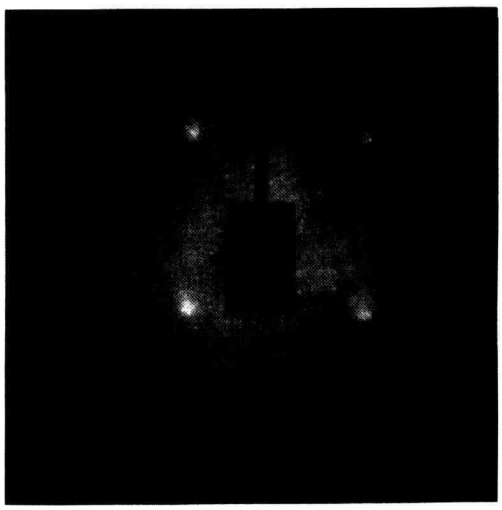

Fig. 8 Diffraction pattern of MgO annealed at 1000°C for 3 hours. The electron energy is 100 eV.

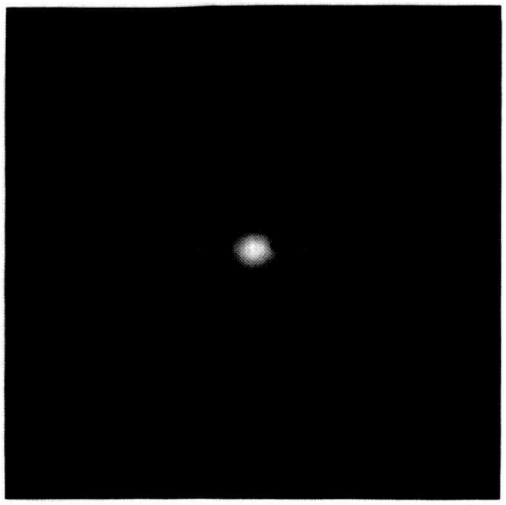

Fig. 9 FFT image of diffraction pattern of MgO annealed at 1000°C for 3 hours. Plotted area is 2 nm × 2 nm.

3.3 MgO substrate annealed at 900°C for 24 hours

The substrate of MgO was mechanically polished with 1 μm-diameter diamond paste for 10 minutes, and cleaned with acetone. The polished substrate was annealed in air at 900°C for 24 hours. Figure 7 shows the LEED pattern of MgO annealed at 900°C for 24 hours for an electron energy of 100 eV. The LEED pattern shows that the damaged surface layer did not recover by annealing at 900°C.

3.4 MgO substrate annealed at 1000°C for 3 hours

The MgO substrate was mechanically polished with 1 μm-diameter diamond paste for 10 minutes, and cleaned with acetone. The polished substrate was annealed in air at 1000°C for 3 hours. Figure 8 shows the LEED pattern for an electron energy of 100 eV. The LEED pattern has weak diffraction spots which indicate the four-fold symmetry of surface structure.

Figure 9 shows the FFT image of the rotated and background-subtracted data from Fig.8. Plotted area is 2 nm × 2 nm. The lattice constant obtained from Fig. 9 is 0.436 nm. Electron beams hit the sample would be 1 mm in diameter. The LEED pattern is due to the average of the surface area bombarded by electron beams. It shows that the surface structure recovers partly by annealing at 1000°C.

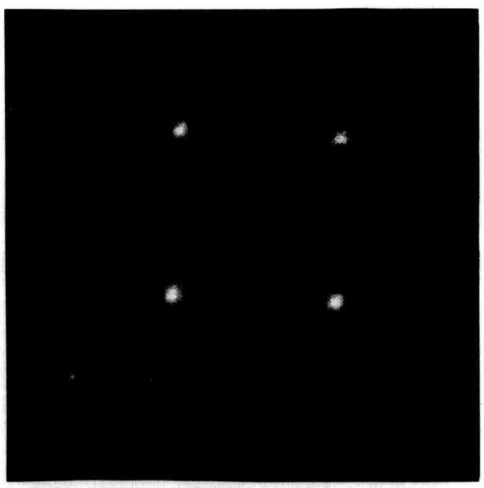

Fig. 10 Diffraction pattern of MgO annealed at 1200°C for 3 hours. The electron energy is 100 eV.

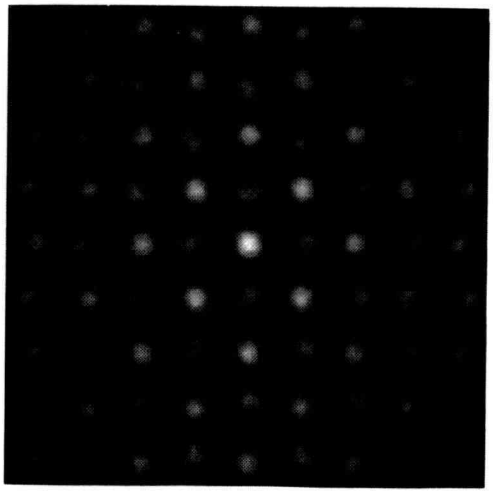

Fig. 11 FFT image of diffraction pattern of MgO annealed at 1200°C for 3 hours. Plotted area is 2 nm × 2 nm.

3.5 MgO substrate annealed at 1200°C for 3 hours

The MgO substrate was mechanically polished with 1 μm-diameter diamond paste for 10 minutes, and cleaned with acetone. The polished substrate was annealed in air at 1200°C for 3 hours. Figure 10 shows the LEED pattern for the electron energy of 100 eV. The LEED pattern reveals clearly four-fold symmetric diffraction spots.

Figure 11 shows the FFT image of the rotated and background-subtracted data from Fig. 10. Plotted area is 2 nm × 2 nm. The lattice constant obtained from Fig. 11 is 0.446 nm, which is 6 % larger than the bulk lattice constant. It shows that the surface structure recovers fully by annealing at 1200°C.

Conclusion

The annealing effect of the surface structure of MgO substrate has been examined by low energy electron diffraction. Substrates are treated with five different procedures. The surface of cleaved MgO substrate has four-fold symmetry with the lattice constant of 0.439 nm. The surface of mechanically polished MgO substrate has fully damaged layers. The surface of MgO single crystal mechanically polished with 1 μm-diameter diamond paste did not recover its crystal structure by annealing at 900°C. The surface of MgO single crystal mechanically

polished with 1 μm-diameter diamond paste recovered partly its crystal structure by annealing at 1000°C. The substrate of MgO single crystal mechanically polished with 1 μm-diameter diamond paste recovered fully its crystal structure by annealing at 1200°C.

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