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Structural change induced near surfaces of α-Al_2O_3 during electron irradiation

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Abstract. — A structural change produced by electron irradiation near surfaces of α-Al_2O_3 was observed through high resolution electron microscopy and electron diffraction. Initially smooth surfaces become rough during TEM observations at 200 and 400 kV and holes appear with a prefered orientation of growth. Planar defects are also produced near the surfaces; they appear as dark- or bright-lines parallel to the (001) plane when the specimen is observed along the [110] direction, and they are also visible along the [001] direction as a periodic modulation of bright dots. The defects give rise to streaks and extra spots in electron diffraction patterns along [110] and [001], respectively. A formation mechanism and model of the defects were proposed; the defects are induced by inelastic scattering on Al plane parallel to (001) through rearrangement of Al ions and Al-vacancies. Three quaters of the atomic sites of the Al plane are occupied by Al ions and one quater is vacant, while 2/3 of the sites are filled with Al ions in perfect α-Al_2O_3.

1. Introduction.

Radiation-induced structural changes of metals and ceramics have been of interest concerning with the behavior of materials in the space environment as well as with fusion reactor materials. Electron irradiation-induced structural changes in alloys and ceramics have been extensively studied so far [1-3]. Electron irradiation damages in ionic crystals occur through inelastic and elastic scattering [4]. The damage due to inelastic scattering occurs below the threshold energy for atomic displacements due to elastic collision. Structural changes have been observed even in 100 keV electron microscopes, although they have been known to be very sensitive to the nature of the system such as valency of the ion species, the crystal orientation, the degree of vacuum [5, 6]. In particular, ionic crystals are susceptible to ionization damage [7], either by radiolysis in the bulk or by desorption induced by electronic transitions at the surface [5].

A structural change induced by electron irradiation near surfaces of α-Al_2O_3 has been observed through high resolution electron microscopy and the results have been interpreted as a surface faceting, or planar defect near the surfaces [8-10]. The structure and the formation mechanism of the damages are, however, not clear. The purpose of the present paper is to characterize a new structure produced by the electron irradiation near the surfaces of α-Al_2O_3. Firstly, results of high resolution electron microscopy (HREM) at 200 or 400 keV are shown to demonstrate that the structural change occurs near the surfaces in a monolayer scale by inelastic scattering.

Secondly, a model of the new structure is proposed to explain the observed electron diffraction patterns and HREM images.

TEM observation was carried out at 200 and 400 keV by using two electron microscopes; JEM-2000FX and JEM-4000EX. The method of specimen preparation has been descrived in a previous paper [10].

2. Results and discussion.

2.1 SURFACE ROUGHENING — When the specimen is observed along [110] at 400 keV, mottled contrast appears within several minutes. The contrast becomes wavy, or like a "patchword quilt" [8, 9] with an increase in observation time. Then holes and dark-line contrast appear. A typical example is shown in figure 1 where a HREM image taken after 30 minutes of beam irradiation is given. One can see that the holes are not circular but rather ellipsoidal or rectangular, and they are aligned along directions inclined by about 40° from the (001) basal plane. It is evident that the surface roughening proceeds with a prefered orientation, namely the electron-stimulated desorption does not occur isotropically. The anisotropic hole drilling was observed in MgO too. According to Turner *et al.* [11], square cross-sectional holes appear in MgO when electrons with circular probes are irradiated. The mottled or patchword quilt-like contrast can be seen at 200 keV too, suggesting that the roughening and hole drilling are originated from desorption induced by electronic transitions at surfaces.

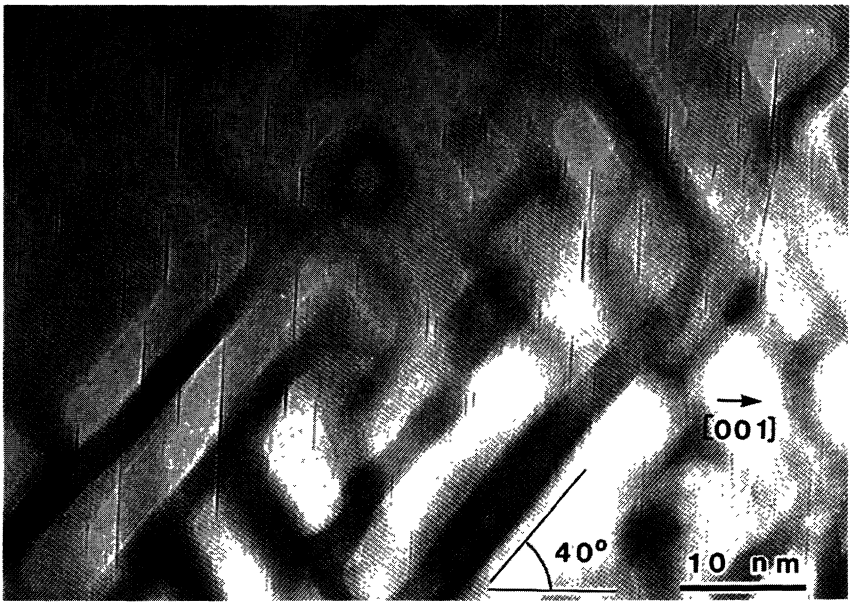

Fig. 1. — A typical example of HREM image showing electron irradiation damages in α-Al_2O_3. A specimen was irradiated along [110] at 400 keV for 30 minutes.

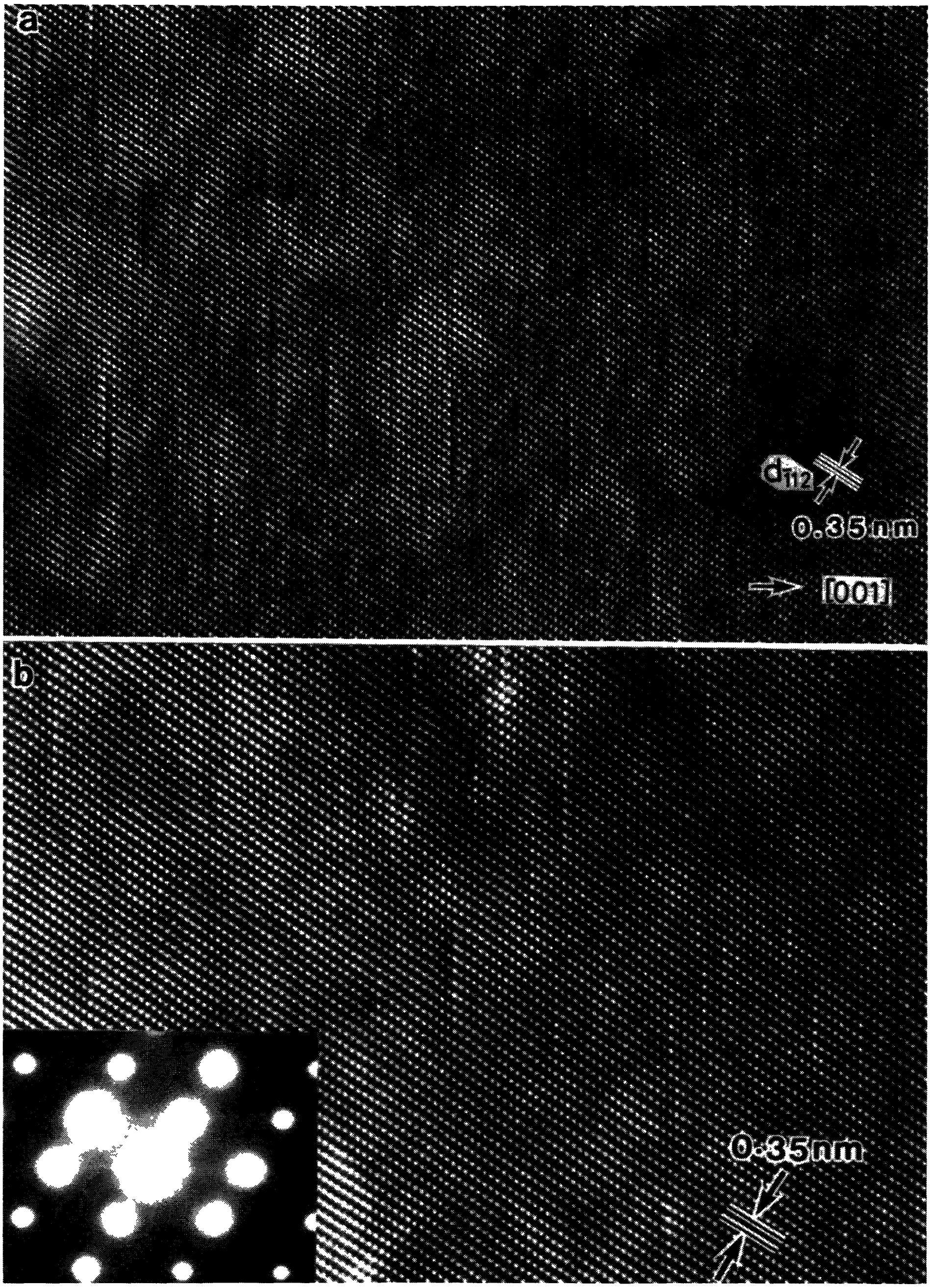

Fig. 2. — Dark-(a) or bright-(b) lines observed in a thicker region of α-Al_2O_3 specimen. Images were taken along [110] at 400 keV. Note streaking in the corresponding electron diffraction pattern in inset.

2.2 FORMATION OF PLANAR DEFECTS — During observation along [110] at 400 keV dark-line contrast appears as shown in figure 1. The number density of dark-lines increases with increasing

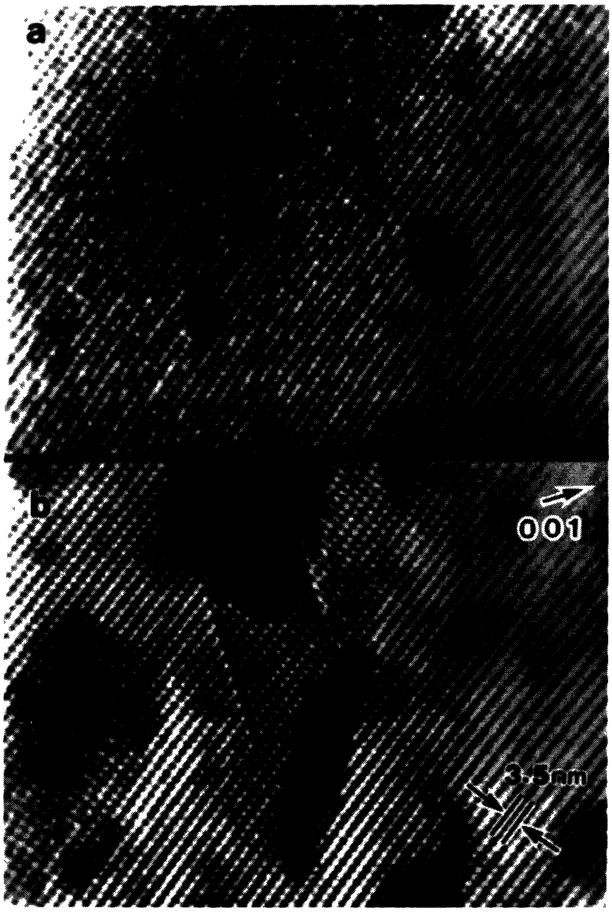

Fig. 3. — α-Al_2O_3 irradiated at 200 keV along $[\bar{1}\bar{1}0]$ for 11 minutes (a) and 16 minutes (b).

irradiation time. The dark-line contrast appears in a thicker region as well as a thin area and the contrast is not always dark. Bright-line contrast is often seen as shown in figure 2. The lines are parallel to the (001) basal plane. One can see, in the diffraction pattern shown in the iset of figure 2, streaks along the [001] direction which is perpendicular to the dark- or bright-lines. The streaks are observable when many dark- or bright-lines appear. These results suggest the presence of planar defects [10]. These dark- or bright-lines are also produced at 200 keV too, as shown in figure 3 which demonstrates a series of HREM images obtained by JEM-4000EX. One can see that bright-lines appear after irradiation for 16 minutes. Bursill and Peng Ju Lin [8] observed the similar results even at 100 keV. Thus the planar defect is apparently produced below the displacement energy for Al or oxygen ions. On the other hand, no line contrast appears even after 60 minutes of electron irradiation at 200 keV in JEM-2000FX. The actual degree of vacuum at the specimen seems to be about one order magnitude better in the JEM-4000EX than in the JEM-2000FX, because a specimen chamber in the former microscope is evacuated independently by an ion pump (evacuation speed: 150 l/s), while the one in the latter is simultaneously evacuated with a gun chamber by one ion pump (140 l/s). Above results indicate that formation of the planar defect is very sensitive to the degree of vacuum at the specimen.

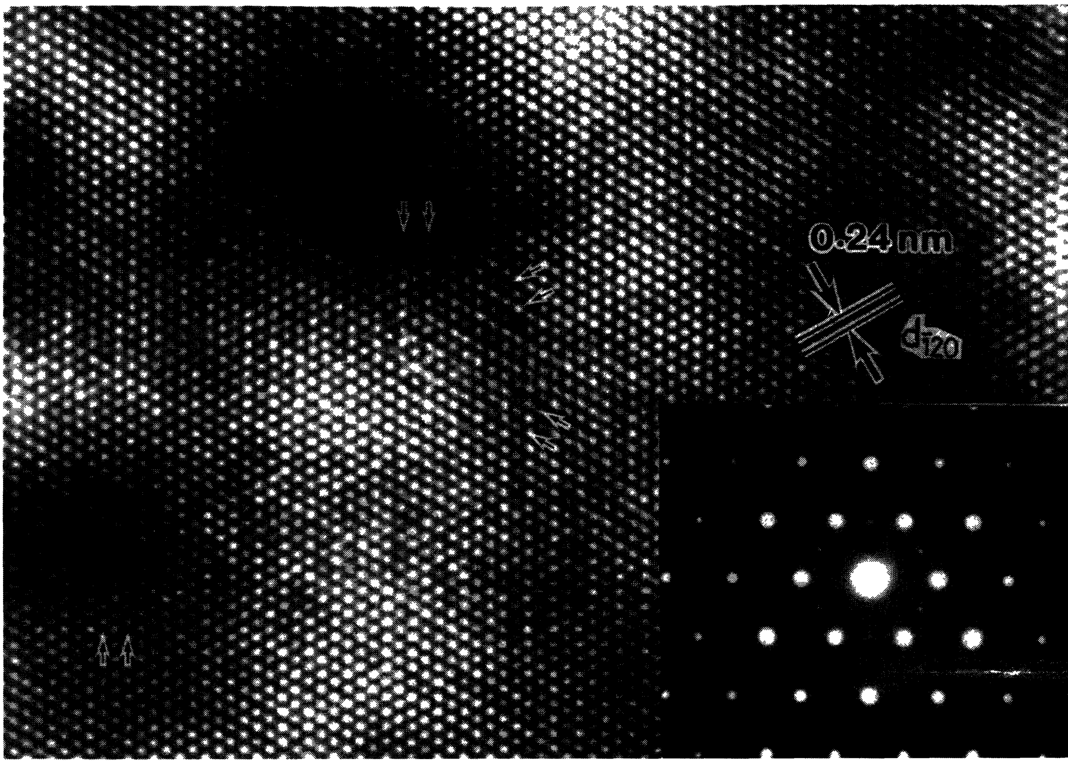

Fig. 4. — A HREM image of α-Al_2O_3 and the corresponding electron diffraction pattern taken along [001] at 400 keV. Note periodic modulation of bright dots in intensity and extra spots in the diffraction pattern.

In order to investigate the origin of the line contrast, HREM images were observed along the [001] direction. Figure 4 shows an example obtained at 400 keV. One can see no clear contrast which may correspond to edges of the dark- or bright-lines. A periodic modulation in the intensity of bright dots can, however, be seen along three directions. Brighter dots appear every other lattice plane along the (110), ($\bar{1}20$) or ($\bar{2}10$) plane. Namely the configuration of the brighter dots has a sixfold symmetry. This periodic modulation can not be seen at an initial stage of electron irradiation but appears with increasing irradiation time. A size of the modulated region is comparable with a length of the dark- or bright-line. Extra spots are evident in the diffraction pattern shown in figure 4. They appear at 1/2 (110), 1/2 (300) and the identical position, indicating the presence of an ordered structure with a double period. These extra spots were also reproduced well by the optical diffraction of the image of figure 4. A key diagram for the diffraction pattern is shown in figure 5 along with the one for [110] diffraction pattern in figure 2. The extra spots can not be also seen at the initial stage, and the intensity of the spots becomes strong with an increase in irradiation time. It is clear therefore that the line contrast in figure 2 and the periodic modulation in figure 4 are due to the same planar defect, and has a double period ordered arrangement of atoms in a plane parallel to the (001) basal plane.

2.3 MODEL OF THE PLANAR DEFECT — It is worth while to recall a structure of perfect α-Al_2O_3 before interpreting the contrast shown in the preceding section. Alpha Al_2O_3 is well known to have a corundum structure (a_0 = 0.4758, c_0 = 1.2991 nm) in which oxygen ions have a close packed

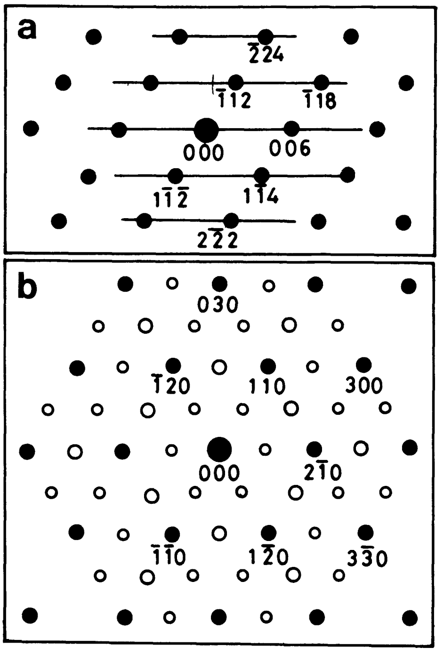

Fig. 5. — Key diagrams of the diffraction patterns shown in figures 2 and 4. a): [110] zone axis; b): [001] zone axis, closed circle; normal spot, open circle; extra spot.

hexagonal arrangement, and aluminum ions occupy two third of octahedral interstices formed by the oxygen ions. One third of the octahedral interstices are vacant (The vacant site is reffered as an Al-vacancy). A sequence of layers of oxygen ions is expressed as ABABAB..., while the one of aluminum ions as $\alpha\beta\gamma\alpha\beta\gamma$ .... Aluminum ions are actually displaced from the ideal positions along the c-axis and oxygen ions are displaced within the (001) plane because of the presence of Al-vacancies. An ideal structure [12] of the unit cell is shown in figure 6a where the displacement of aluminum ions are ignored and oxygen ions are omitted. Figure 6b shows a [110] projection of the ideal structure.

It is apparent from comparison of figures 2b and 6b that the bright dots in the HREM image correspond to columns of Al-vacancies. The distortion of image around the dark- or bright-line is quite small and limited to a narrow region as seen in figure 2. Furthermore any shift of ($\bar{1}12$) lattice fringes can not be observed at the planar defect. Hence, it is unlikely that the planar defect is a stacking fault consisting of excess or deficient (001) planes [13]. An Al column along the [001] direction consists of 2/3 of Al ions and 1/3 of Al-vacancies as shown in figure 6a. The Al columns are visible as bright dots in a [001] HREM image of figure 4. The periodic modulation in bright dots seems to be due to the change of atomic arrangements in an Al layer of the basal plane.

We assume from above discussion that the planar defect is a result of rearrangements of Al ions and Al-vacancies in the (001) basal plane. A model of the rearrangement is shown in figure 7. In the [110] projection of the planar defect, columns of Al-vacancies alone are lost and those consisting of 50% of Al ions and Al-vacancies are present, whereas columns of Al-vacancies (open circles) are arranged with every other two columns of Al ions (closed circles) in the perfect structure. This means that the ratio of the number of vacancies to the one of Al ions in the defect plane changes to 1/3 from 1/2 in a perfect plane. An atomic arrangement in the defect plane is shown

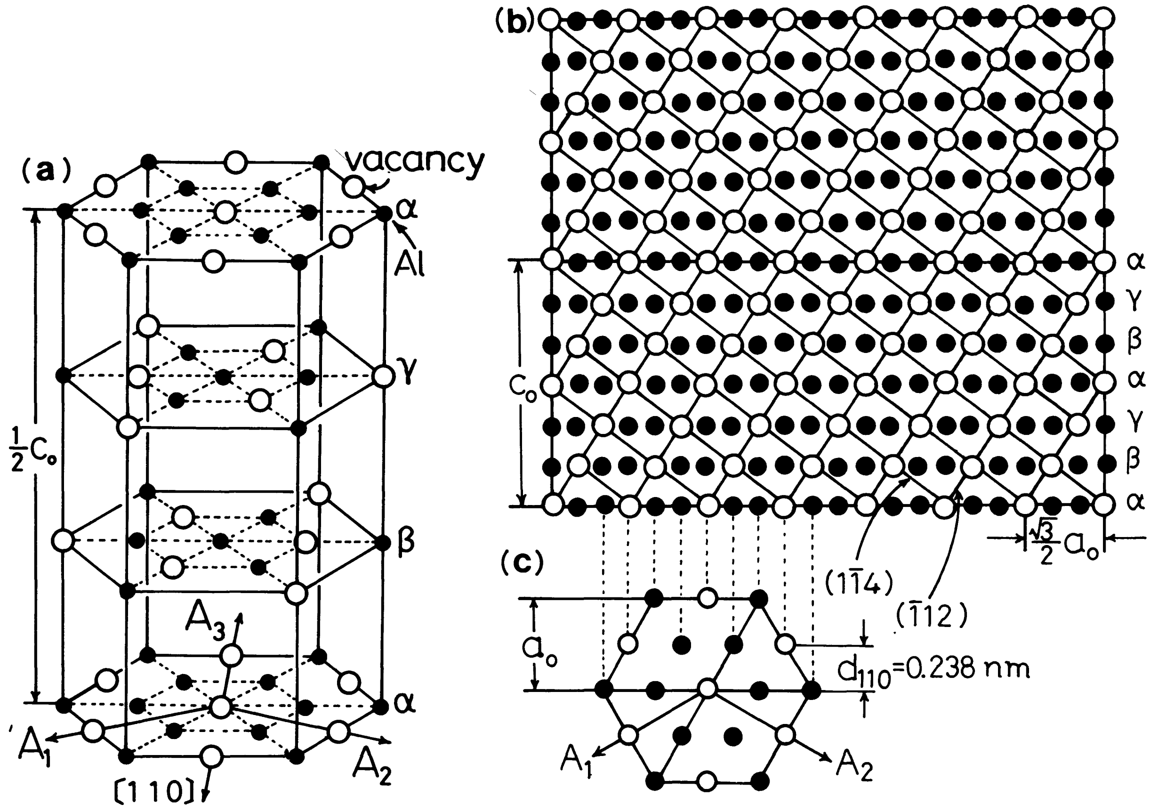

Fig. 6. — Ideal structure of α-Al_2O_3. The arrangements of Al ions (closed circles) and vacancies (open circles) are shown but the displacement of Al ions along c-axis is ignored. Oxygen ions are omitted. a) three dimensional view; b) projection view along [110] and c) Al layer of the (001) basal plane.

in figure 7b along with the one in the perfect plane. A row of Al ions alone appears along [110] and the identical directions with every other one row which consists of 50% of Al ions and 50% of Al-vacancies. Al ions and Al-vacancies are arranged so that the structure may have a six-fold symmetry and a double period compared with the original structure. The model of the planar defect shown here can qualitatively account for the streaking and extra spots in figure 5. It should be pointed out that the ratio of the number of Al-vacancies to the atomic sites in the defect Al plane is equal to one fourth which corresponds to the composition of Al_3O_4, while the ratio in the perfect Al-plane in α-Al_2O_3 is one third. The rearranged structure shown in figure 7b is actually the same as the one of (111) layers of γ-Al_3O_4 (spinel-type). It is noticeable that Bursill and Peng Ju Lin [14] interpreted, from computer simulation of [110] HREM images, the dark-lines as being due to the facets terminated with a monolayer γ-Al_3O_4 structure. These results suggest the local reduction of Al_2O_3 in a monolayer scale. We have, however, not detected any sign in HREM image and diffraction pattern to indicate the presence of Al_3O_4 phase or metallic Al phase. On the other hand, Bonevich and Marks [9] observed small crystallites of Al at surfaces of α-Al_2O_3 instead of the dark-lines when the specimen was irradiated under ultra-high vacuum. This result also indicates that the damage process is very sensitive to the degree of vacuum at the specimen.

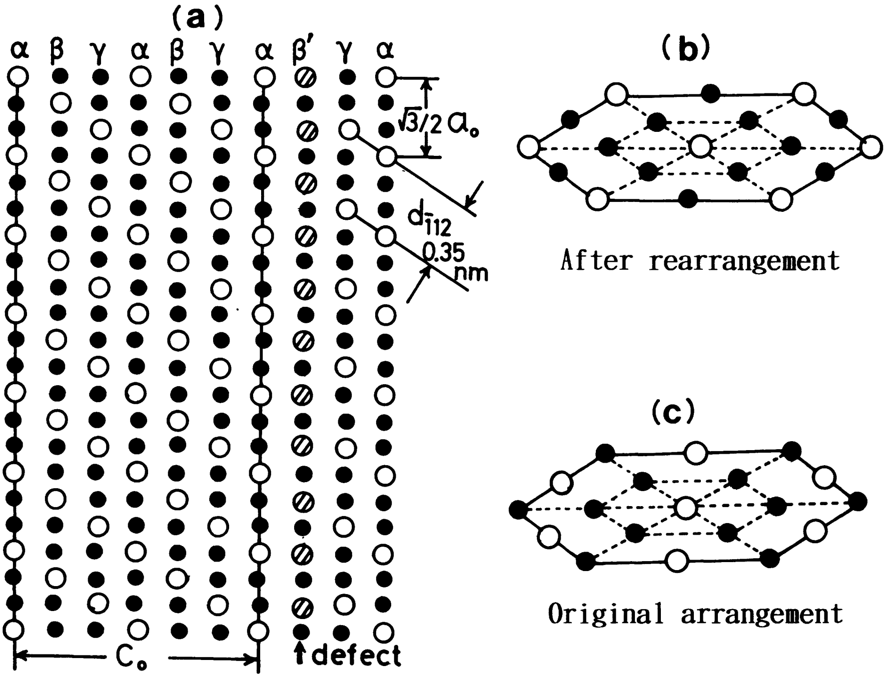

Fig. 7. — A model of the planar defect in α-Al_2O_3. a) [110] projection, • column consisted of Al ions alone, o column consisted of Al-vacancies alone, ⊘ column of 50% Al ions and 50% Al-vacancies; b) rearranged structure in the defect plane and c) original arrangement in the perfect plane; • Al ion, o Al-vacancy.

3. Concluding remarks.

As already pointed out in the preceding section, surface roughening occurs with a preferred orientation and holes are rectangular when they are projected along the [110] direction. A comparison of figure 1 and figure 6b shows that one of the edges of the rectangular hole is parallel to $(1\bar{1}4)$ planes which include layers of Al-vacancies. It would consequently seem that bonding between Al and oxygen ions tends to be destroyed along $(1\bar{1}4)$ plane of Al-vacancies.

The dark- or bright-line contrast and the periodic modulation in intensity observed in the HREM image were interpreted in terms of the planar defect produced at or near the surfaces by inelastic scattering of electrons. The planar defect is formed on the basal plane through a rearrangement of Al ions and Al-vacancies. The rearrangement in an Al plane seems to be easy because 1/3 of the atomic sites are originally vacant and consequently, Al ions can easily migrate *via* the vacancies without largely disturbing the electrical neutrality. This interpretation corresponds well to the result that the planar defect does not grow along a direction perpendicular to the plane, although it grows along the plane [10]. The rearrangement is presumably initiated by surface desorption caused by inelastic scattering of electrons, because the planar defect is produced after surface roughening at 200 keV as well as 400 keV.

The concentration of Al-vacancies in the planar defect is 1/4, whereas that in the perfect crystal is 1/3, suggesting the occurence of local reduction in a monolayer scale. This can explain well the result that the formation of planar defects depends sensitively on the degree of vacuum in a specimen chamber of TEM.

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