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COMPOSITION AND SURFACE STRUCTURE OF THE (0001)-FACE OF  $\alpha$ -ALUMINA BY LOW ENERGY ELECTRON DIFFRACTION

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Composition and Surface Structure of the (0001)-Face  
of  $\alpha$ -Alumina by Low Energy Electron Diffraction

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Abstract

The (0001) crystal face of  $\alpha$ -alumina undergoes a change of surface structure upon heat treatment in vacuum above 1250°C. This order-order phase transformation [(Al(0001) - (1 x 1)  $\rightarrow$  rotated ( $\sqrt{3} \times \sqrt{3}$ ))] is accompanied by a change in the chemical composition of the surface, i. e. by the loss of oxygen. The structural change is reversible and either surface structure can be obtained alternately by heat treatment of the samples in oxygen ( $>10^{-4}$  torr) or in the presence of excess aluminum on the surface. The large unit cell which characterizes the high-temperature oxygen-deficient surface structure is indicative of a marked mismatch between the surface layer and the underlying (0001) crystal orientation. Evidence is presented to show that the aluminum cation in the high temperature surface structure is in a reduced valence state and that the structure is composed of a cubic overlayer on the hexagonal  $\alpha$ -alumina substrate. It appears that compounds with unusual oxidation states which would not be stable in the solid state may be stabilized in the surface environment.

## Introduction

Low energy electron diffraction (LEED) studies have revealed that the structure of single crystal surfaces can be correlated with the chemical bonding properties which characterize the solid. Semiconductors (Si, Ge, GaAs, InSb, diamond, etc.) have surface structures which are characterized by unit mesh which are integral multiples of the bulk unit cell.<sup>1</sup> These surface structures have well-defined temperature ranges of stability and can undergo order-order phase transformations as a function of temperature. It has been suggested<sup>2</sup> that the surface structures are due to small, periodic displacements of atoms out of the surface plane (surface buckling) to optimize the overlap of localized electron orbitals of the covalently bonded atoms. Metal surfaces with some notable exceptions (Au,<sup>3</sup> Pt,<sup>4</sup> Bi<sup>5</sup> and Sb<sup>5</sup>), largely appear to have the same periodicity at the surface which also characterized the bulk structure. If there is only scanty experimental information available on the structure of a few semiconductor and metal surfaces, large band gap insulators have been investigated to even a lesser extent. Only  $\alpha$ -alumina,  $Al_2O_3$ ,<sup>6,7</sup> and some of the alkali halides<sup>8,9</sup> have been the subject of low energy electron diffraction studies. It has been reported that different crystal faces of  $\alpha$ -alumina assume surface structures after heating to high temperatures which are different from that predicted by the bulk unit cell.<sup>6,7,10</sup> Alkali halides, on the other hand, maintain their bulk structure up to the surface although the freshly cleaved surface may be stabilized by halogen evolution (excess anion vacancies) or precipitation of the alkali metal (excess cation vacancies).<sup>11</sup>

We have studied the (0001) surface of  $\alpha$ -alumina under a variety of experimental conditions in the temperature range of 25° - 1700°C. It is the purpose of this paper to show that changes of the surface structure are accompanied by changes in the chemical composition of the surface. The ordered alumina surface transforms into a new surface structure upon heating the solid, with simultaneous evolution of oxygen. The transition between this oxygen-deficient, high-temperature surface structure and the simple, low-temperature, bulk-like surface is reversible and depends on the oxygen pressure and/or the presence of excess aluminum on the surface. Arguments will be presented to show that the aluminum cation in the high temperature surface structure is in a reduced, lower oxidation state. Such a change in the chemical surface composition as a function of temperature may not be restricted to alumina alone but could well be detectable for many compounds with similar bonding characteristics as well.

### Experimental

The crystals were the best grade available from the Union Carbide Corporation. An analysis by the supplier of typical boules showed impurity levels of --(in ppm) Mg < 2, Si < 4, Fe < 2, Ca < 2, Ga < 2, Cu < .5. The samples which were cut the size 5 x 7 x 1 mm, were supplied already oriented to the (0001) face and polished. The crystals were chemically etched using potassium persulfate and boric acid mixed in equal parts by volume. The crystals were heated in the etching mixture to approximately 750°C in a gold covered combustion boat for about 30 minutes. Using this procedure, weak diffraction beams were often observed

without further treatment. Varian LEED apparatus was used for all these experiments.

The crystal was mounted in a star shaped piece of 1 mil tungsten foil. The points of the star were bent around the sample to hold it securely. There was minimum contact of the points with the front surface. The tungsten foil was spot welded to tantalum supports which were attached to the crystal holder and manipulator.

The crystal was heated by radiation from the resistively heated tungsten foil. The temperature was measured by an optical pyrometer focused on the tungsten which had been vacuum evaporated on the back of the sample.

Vacuum evaporation by heating the crystal to high temperatures ( $>1200^{\circ}\text{C}$ ) was used most frequently to clean the surface. Ion bombardment could also be used for surface cleaning. Ion bombardment using 1-2 keV argon ions disordered the alumina surface and eliminated the diffraction features. Heating, above about  $900^{\circ}\text{C}$  after ion bombardment, would restore the surface order. The minimum conditions of ion bombardment to disorder the diffraction pattern were  $10^{-5}$  torr argon, 2 keV accelerating potential, 4 ma ionizing electron flux for 10 minutes.

Bulk aluminum oxide has a hexagonal structure. The hexagonal unit cell has 6 layers of close packed oxygen as shown in Fig.(1a). In between these layers in the octahedral holes are placed the aluminum atoms.<sup>12</sup> In each aluminum layer there are as many sites as there are oxygen atoms. In order to maintain the stoichiometry characteristic of  $\text{Al}_2\text{O}_3$ , only  $2/3$  of the aluminum sites are filled. The sites that contain aluminum atoms are of two kinds as shown in Fig. (1b).

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The octahedral holes are large enough so that the aluminum ions can occupy different positions. An octahedral site can either have an aluminum in A' position or in B' position or the site can be empty. If only the aluminum sites are considered in the successive layers there is a progression of A', B', empty site, A', B', empty site, etc. Since the oxygen ions are hexagonally close packed, the oxygen atoms in successive layers occupy alternating positions which may be labeled A, B, A, B. Therefore the successive layers of the crystal could be labeled A, A', B, B', A, empty, B, A', A, B', B empty, A, A', etc. Hence we have six oxygen layers in the bulk unit cell.

The vapor pressure over  $\alpha$ -alumina has been measured as a function of temperature. The vapor of aluminum oxides contains both  $AlO$  and  $Al_2O$  molecules in addition to aluminum and oxygen species.<sup>13,14</sup> Figure (4) shows the vapor pressure curves as reported by Searcy and Brewer.<sup>13</sup> The melting point of aluminum oxide is  $2050^\circ C$ .

Elimination of Space Charge at Insulator Surfaces  
During LEED Studies

When electrons in the energy range 5-100 eV strike the aluminum oxide surface, a space charge builds up rapidly such as to repel the incident electron flux before it can penetrate the crystal or be scattered by the periodic atomic potential at the surface. Thus, under usual operating conditions which are employed in LEED studies of metal surfaces, no diffraction pattern can be obtained from an  $Al_2O_3$  surface below a certain voltage, usually 100eV. This negative space charge build-up poses serious limitation to structural studies of insulator surfaces



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since most of the experimental information about the surface structure is obtained in the electron energy range 30-120 eV. Above these energies a larger fraction of the electrons penetrate below the surface and the back-scattered beam contains more information about the bulk than about the topmost atomic layer. Therefore, in LEED studies of insulator surfaces it is imperative that this negative space charge layer be removed from the studied surface.

We have been successful in removing the negative space charge layer from the (0001) face of alumina by the simultaneous application of two electron guns; one, operating at 1-2 kvolts at grazing angle of incidence ( $15^\circ$ ) was continuously discharging the surface while the usual LEED gun, operating in the range 10 - 350 eV, was used to obtain the diffraction pattern.

This technique should be applicable for the elimination of negative space charge from all those insulator surfaces which a) have a secondary electron emission flux above a given incident electron energy which is larger than the incident electron flux and which b) do not decompose or otherwise interact chemically with the high energy electron beam. It is well known that for many insulators the yield of secondary electrons which leave the solid during electron bombardment is greater than the incident electron flux, above a certain threshold energy of the incident electron beam.<sup>15</sup> The incident electron energy at which the ratio of the secondary electron emission current and the incident electron beam current becomes larger than unity is often called the "secondary emission crossover." By continuously spraying the insulator surface with electrons with energies above the secondary crossover the

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surface can be discharged or a small positive space charge may be established. Since this positive space charge attracts electrons toward the crystal it does not effect the diffraction process although it may change the energy of the incident electrons to a small extent.

The secondary emission crossover for the clean (0001) face of alumina which exhibits a (1x1) surface structure appears to be in the range 80 - 100 eV. The crossover energy varied within this range from sample to sample and was found to be dependent on the purity of the surface. Slight contamination of the surface by tantalum which was often used at first as a crystal holder could increase the crossover to over 200 eV.

The secondary emission crossover may also depend on the chemical surface composition. When the surface structure was changed to an ordered, oxygen-deficient surface structure (to be discussed later) the crossover energy decreased to approximately 50 eV. Since heat treatments were necessary to produce this new structure and the accompanying changes in surface composition, the possibility of unwanted impurities diffusing to the surface and aiding reduction of the crossover cannot be eliminated. Auger spectroscopy experiments have not revealed the presence of impurities however. It is likely therefore that the lowering of the secondary emission crossover is caused by the change in the surface composition of the (0001)- face of alumina.

Since the electrons from the high energy electron gun which is used to eliminate the negative space charge are energetic enough to pass through the grid system of the electron optics and reach the fluorescent screen, the background intensity is increased. This, however, does not prevent the detection of diffraction spots from a fairly

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ordered alumina surface to as low as at 25 eV incident electron beam energy from the LEED electron gun. The high energy electron flux which is used to discharge the surface was cut back to a minimum in order to minimize the background intensity on the fluorescent screen. Figure(3) gives the secondary electron emission crossover as a function of the ratio of the current from the high energy gun ( $I_2$ ) and the LEED electron gun ( $I_{LEED}$ ) for two different electron energies of the discharging gun. The crossover decreases with increasing  $I_2/I_{LEED}$  ratio at first but above  $I_2/I_{LEED} = 2$ , the ratio remains constant. The crossover appears to be independent of the discharging gun energy in the range 1000-2000 eV. No studies have been made with the discharging gun below this energy range.

Although our technique, i.e. the simultaneous use of two electron guns, was successful in removing the space charge, other techniques might also be employed in studies of insulator surfaces. For alkali halide crystals which are known to interact with the electron beam LEED surface studies may be carried out at elevated temperatures using thin samples in order to sufficiently increase <sup>the ionic conductivity.</sup> For crystals which exhibit photo-conductivity, illumination by light of suitable wavelength might be employed to increase the surface conductance and thereby eliminate the surface space charge. Pulsing the grazing angle electron gun and the grids at a well-chosen frequency and energies could also be considered. This would minimize the high background intensity common in experiments with the continuous application of a discharging electron gun.

Surface Structures of Alumina

It is well known that the structure of alumina surfaces is different from that which is expected by projection of the bulk unit cell to the various crystal surfaces.<sup>7,10</sup> The (0001) crystal face exhibits its (1 x 1) bulk-like structure up to ~ 1250°C in vacuum. It rearranges above this temperature to give a weak ( $\sqrt{3} \times \sqrt{3}$ )-(rotated 30°) surface structure, and upon further heating to the final rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure which is stable to the highest studied temperature of 1700°C. Schematic representations of the resultant diffraction patterns are shown in Fig. (4)

It is customary to designate the complex surface structures by the coefficients of its transformation matrix which generate the structures with the unit cell vectors of the bulk-like substrate.<sup>3</sup> This is given, for the rotated ( $\sqrt{31} \times \sqrt{31}$ ) pattern by

$$A = \begin{pmatrix} 11/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & 11/2 \end{pmatrix} \quad B = \begin{pmatrix} 11/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & 11/2 \end{pmatrix}$$

These matrices generate the two domains which must be present on the surface simultaneously in order to generate the observed diffraction pattern. These domains are formed from the original unit mesh by expanding the unit vectors by a factor of  $\sqrt{31}$  and by rotating them either +9° or -9°. We shall show evidence that the alumina surface which exhibits the rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure is oxygen deficient.

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The other two crystal faces, the  $(\bar{1}012)$  and  $(11\bar{2}3)$  orientations which have been studied, give  $(2 \times 1)$  and  $(4 \times 5)$  surface structures, respectively at high temperatures ( $> 900^\circ\text{C}$ ).<sup>10</sup>

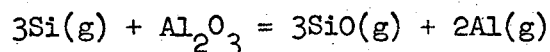
We have been able to confirm the presence of the surface structures on the (0001)-face of  $\alpha$ -alumina which have also been reported by Charig and Chang.<sup>6,10</sup> Due to the reproducibility of these surface characteristics there can be little doubt that these structures are the property of the clean alumina. We have not employed electron bombardment heating of the samples in our experiments to avoid difficulties in interpreting our results which are due to the well-documented interaction of the high energy electron beam with the crystal surface.<sup>6</sup>

#### Properties of the Rotated ( $\sqrt{31} \times \sqrt{31}$ ) Surface Structure

Heating, by radiation, the freshly etched (0001) alumina surface which exhibits the  $(1 \times 1)$  surface structure in vacuum, above  $1250^\circ\text{C}$ , readily produces the rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure (Fig. 5). During its formation oxygen evolution is detectable by mass spectrometer. Oxygen evolution was also detected by Charig during the formation of the rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure by electron bombardment heating above  $900^\circ\text{C}$ .<sup>10</sup> Ion bombardment using high energy (2 kev) argon ions disorders the surface structure. It is readily regenerated, however, by annealing the surface at approximately  $800^\circ\text{C}$ . Thus, once it forms upon heat treatment at high temperatures this surface structure is extremely stable and reproducible under various experimental conditions.

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Its stability is clearly shown by the silicon deposition studies which have been made to investigate the epitaxy of silicon on the (0001) alumina surface. Silicon is known to etch the alumina surface by removing both aluminum and oxygen according to the overall reaction<sup>7</sup>:



Chang has detected all of the gaseous species in their proper atomic ratios by mass-spectrometer.<sup>7,16</sup> Heating the alumina surface above 900°C, after deposition of silicon at lower temperatures either on the (1 x 1) or rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface of alumina, has regenerated the rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure. Heating the (0001) face below 900°C after silicon deposition, yields the (1 x 1) bulk-like surface structure.

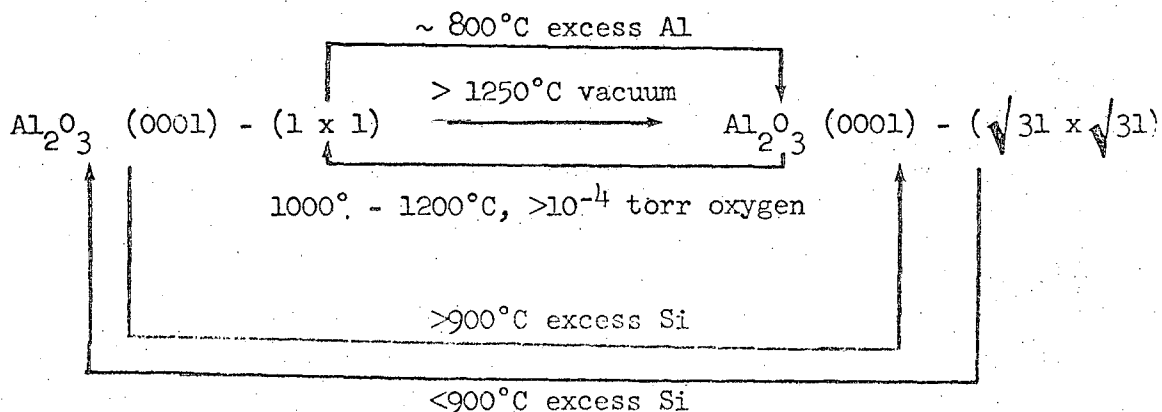
In order to establish that the stable high temperature rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure has a chemical composition which is different from that of the low temperature (1 x 1) surface structure and to establish its stoichiometry we have heated the (0001) face in excess oxygen and aluminum vapor.

When the rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure is heated in oxygen at pressures  $> 10^{-4}$  torr (these pressures considered to be high in ultra high vacuum LEED studies) at 1200°C the (1 x 1) surface structure was obtained. Removal of the oxygen and heating to a slightly higher temperature (1250°C or higher) in vacuum caused the reappearance of the rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure. This reversible phase transformation could be induced at will upon introduction or removal of oxygen.

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Pressures lower than  $10^{-4}$  torr did not induce detectable changes in the high temperature surface structure during the usual heat treatment times (15 minutes).

When aluminum metal was condensed on the (0001) alumina surface which exhibits the (1 x 1) surface structure, the rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure is formed with heating to  $800^\circ\text{C}$ . In the absence of excess aluminum on the surface, the (1 x 1) surface structure would have been stable. Thus, the structural changes which occur in vacuum (mass spectrometric detection of oxygen while the rotated ( $\sqrt{31} \times \sqrt{31}$ ) structure forms), in oxygen (the (1 x 1) surface structure is regenerated in a temperature range,  $\sim 1200^\circ\text{C}$ , where the rotated ( $\sqrt{31} \times \sqrt{31}$ ) structure is stable), and with aluminum (the rotated ( $\sqrt{31} \times \sqrt{31}$ ) structure is formed in a temperature range,  $\sim 800^\circ\text{C}$ , where the (1 x 1) surface structure is stable) indicate that the (0001) face of alumina undergoes a surface phase transformation from a (1 x 1) surface structure to an oxygen-deficient, rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure which is stable at high temperatures. This phase transformation can be made reversible by variation of the chemical surface composition using excess oxygen or aluminum. The transformations which have been found to occur under the various experimental conditions may be summarized by the following diagram:



Discussion

The following statements summarize those results of our experiments which can be used to interpret the surface structures of  $\alpha$ -alumina.

1. Upon heating the (0001) face of alumina, which exhibits a (1 x 1) surface structure, in vacuum ( $>800^\circ\text{C}$ ) new ordered surface structure which can be characterized as  $\sqrt{3} \times \sqrt{3}$  rotated  $30^\circ$  appears. Subsequent heating to even high temperatures produces the ordered rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure. Simultaneously, there is oxygen evolution from the surface. This surface structure, once formed, is extremely stable under a variety of experimental conditions.

2. Heating the high temperature rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure in oxygen at pressures greater than  $10^{-4}$  torr at  $1000 - 1200^\circ\text{C}$ , restores the low temperature (1 x 1) surface structure  $[(\sqrt{31} \times \sqrt{31}) \xrightarrow{\text{O}_2} (1 \times 1)]$ . Excess aluminum on the (0001) face on the other hand, catalyzes the reverse  $[(1 \times 1) \xrightarrow{\text{Al}} (\sqrt{31} \times \sqrt{31})]$  order-order transformation at  $\sim 800^\circ\text{C}$ .

These results would indicate that the ordered surface structures which appear at high temperature are oxygen deficient with respect to the bulk structure of alumina. The transient ( $\sqrt{3} \times \sqrt{3}$ ) surface structure can be explained to form by the removal of oxygen atoms or by the addition of aluminum atoms to the (0001) surface. A possible model of the rearranged surface which would give rise to the observed diffraction pattern is shown in Figure 5. Other explanations are also possible: in all of the proposed models however, the substrate serves as a template for the arrangement of the surface atoms.



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Many of the diffraction patterns which exhibit fractional order diffraction beams can be rationalized in a straightforward manner. The extra spots appear at positions which are some fraction of the distance between the integral order diffraction beams and they indicate the appearance of a new surface periodicity which is integral multiple of, and is parallel to the bulk unit cell. Such a surface structure can be generated by periodic buckling of the surface or by the result of partial occupation of the available surface sites. The surface structure thus formed retains the symmetry of the underlying substrate and there is little reason to postulate any marked change in the chemical bonding of surface atoms with respect to the atoms in the bulk.

It is however, difficult to explain the appearance of large surface unit cells which are also rotated with respect to the bulk unit cell without invoking significant chemical rearrangements in the surface layer. The rotated ( $\sqrt{3}l \times \sqrt{3}l$ ) unit mesh signifies marked mismatch between the newly formed surface structure and the underlying hexagonal substrate. The surface atoms which are built into the new structure can no longer adjust to the symmetry of the substrate, and the observed diffraction pattern is likely to be due to the coincidence of lattice sites between the rearranged surface layer and the hexagonal substrate.

Let us assume that, along with the change of chemical composition, the aluminum cation,  $Al^{3+}$ , is reduced in the oxygen-deficient surface layer to the  $Al^+$  (or  $Al^{2+}$ ) oxidation state. The ionic radius would be expected to increase as the valency is decreased. Let us estimate the ionic radius of  $Al^{+1}$  ion. This ion may be more stable than the  $Al^{+2}$  ion because it has a pair of s electrons in the outer shell. It can be assumed that the radii of isoelectronic atoms and ions are inversely

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proportional to the effective nuclear charges.<sup>17</sup> Using this rule and using the interatomic distance of Mg and Na in the solid, we have  $\sim 0.8 \text{ \AA}$  for the radius of  $\text{Al}^{+1}$ , and  $\sim 0.7 \text{ \AA}$  for the  $\text{Al}^{+2}$  radius. It is clear that ions of this size will be unable to pack the same way as the small ( $0.5 \text{ \AA}$ )  $\text{Al}^{+3}$  ions pack in the  $\alpha$ -alumina. It seems unlikely that the larger ions will be able to fit in the "holes" in a close packed oxygen lattice at all. If the valency of the aluminum cation is reduced in the aluminum-rich surface layer whose chemical composition should be closer to  $\text{Al}_2\text{O}$  or  $\text{AlO}$  than to  $\text{Al}_2\text{O}_3$  what kind of surface structure would be expected to form? It is instructive to compare several oxides of the  $\text{M}_2\text{O}_3$  type which have the same structure as  $\text{Al}_2\text{O}_3$  such as  $\text{V}_2\text{O}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Ti}_2\text{O}_3$ .<sup>12</sup> These cations form stable oxides in their +2 oxidation states as well ( $\text{VO}$ ,  $\text{FeO}$  and  $\text{TiO}$ ).<sup>18</sup> The oxides of the  $\text{MO}$  type however, have face centered cubic structure. The ratio of the ionic radii  $\text{M}^{3+}/\text{O}^{2-}$  and  $\text{M}^{2+}/\text{O}^{2-}$  are very similar for all these compounds to that which is found for  $\text{Al}_2\text{O}_3$  and is expected for  $\text{AlO}$ .

Both,  $\text{Al}_2\text{O}$  (vapor) and  $\text{AlO}$ (vapor) are stable, were detected in the vapor composition over  $\alpha$ -alumina in equilibrium and also during vaporization into vacuum. The other group III elements are also known to form stable oxides in their higher (3+) oxidation states ( $\text{Ga}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Tl}_2\text{O}_3$ ) while their vapors contain the monovalent oxides ( $\text{Ga}_2\text{O}$ ,  $\text{In}_2\text{O}$  and  $\text{Tl}_2\text{O}$ ) in large concentrations.<sup>14,20</sup> The monovalent oxides in group III of the periodic table,  $\text{M}_2\text{O}$ , appear to be much more stable\* than the divalent

\*  $\text{Tl}_2\text{O}$  is a stable solid whose thermodynamic properties have been measured although only an X-ray powder pattern is reported. <sup>19</sup>

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oxides of the MO type. Other stable monovalent oxides such as  $\text{Li}_2\text{O}$  and  $\text{Na}_2\text{O}$  which should have similar ion ratios as in  $\text{Al}_2\text{O}$  form cubic structures of the fluorite ( $\text{CaF}_2$ ) type.

Thus, it appears that if the high temperature oxygen deficient rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure has a composition which corresponds to  $\text{Al}_2\text{O}$  (or  $\text{AlO}$ ) it would be likely to form a cubic overlayer in which the cation is appreciably larger than in the underlying hexagonal (0001) substrate. Strong mismatch due to the differences in structure and ion sizes in the two layers should be expected.

We have been able to generate the rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure by placing a cubic overlayer in which the interatomic distance was increased to adjust for the increased cation radius on top of the (0001) substrate. There are several cubic structures which can generate the rotated ( $\sqrt{31} \times \sqrt{31}$ ) unit mesh by coincidence with the (0001) substrate. One of these surface structures are given in Figure (6).

Additional evidence that the ( $\sqrt{31} \times \sqrt{31}$ ) structure is due to a reduced aluminum oxide overlayer comes from studies of the epitaxial deposition of silicon on the (0001) face. Silicon was found to etch the  $\alpha$ -alumina surfaces efficiently. Silicon however, is also a reducing agent which can remove oxygen from the surface by the reaction,<sup>10</sup>

$\text{Al}_2\text{O}_3 + 2\text{Si}(\text{vapor}) \rightarrow \text{Al}_2\text{O} + \text{SiO}(\text{vapor})$ . It was found that silicon catalyzes the formation of the rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure at  $800^\circ\text{C}$ , a temperature too low for this phase transformation in vacuum.<sup>6</sup>

Additional evidence that the rotated ( $\sqrt{31} \times \sqrt{31}$ ) surface structure is composed of a cubic overlayer on the hexagonal (0001) substrate comes

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from studies of aluminum oxide structures which are formed on the aluminum metal surface. The oxide has a cubic structure in this aluminum rich environment.<sup>21</sup>

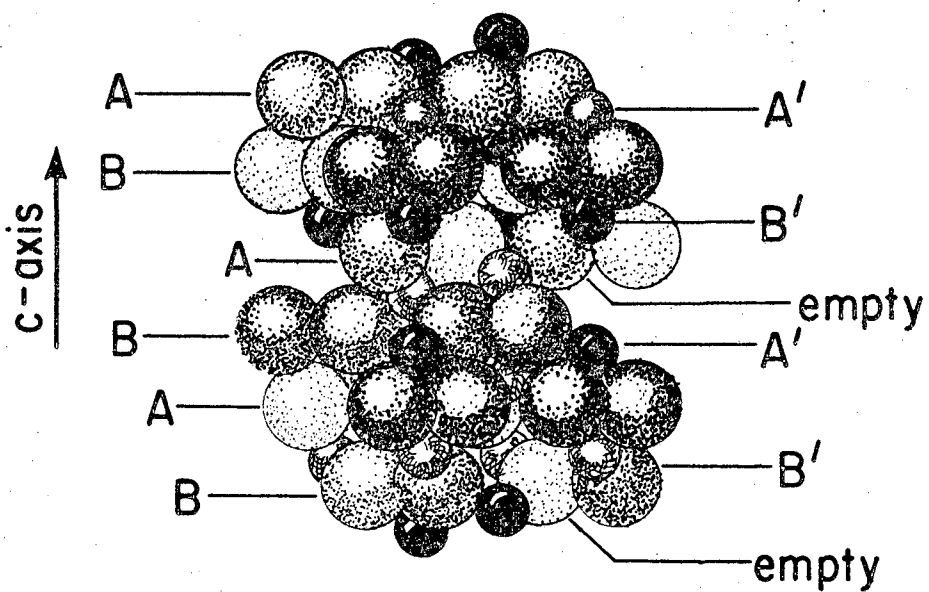
If the reduced oxides of aluminum,  $Al_2O$  or  $AlO$ , are stable in the  $\alpha$ -alumina surface at elevated temperatures, it is likely that the other group III oxides of the  $M_2O$  type might also be stable in the surface environment. Investigation of the surface structures of  $Ga_2O_3$  and  $In_2O_3$  would be of interest. It is also likely that oxides of other metals ( $MgO$ ,  $BaO$  for example) may have unusual oxidation states which are stabilized in the surface environment. It should be noted that vanadium pentoxide,  $V_2O_5$  has been reported recently<sup>22</sup> to undergo a change of surface composition (accompanied by loss of oxygen) upon heating in vacuum with a corresponding order-order transformation of its surface structure.

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References

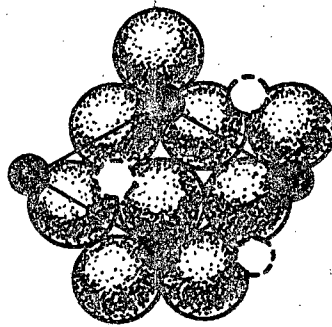
1. J. J. Lander, Progr. Solid State Chem. 2, 26 (1965); and J. W. May, Ind. and Eng. Chem. 57, 19 (1965).
2. D. Haneman and D. L. Heron, Proc. Conf. "The Structure and Chemistry of Solid Surfaces" ed. G. A. Somorjai (Wiley Publ. N. Y. 1969); J. J. Burton and G. Jura, *ibid.*
3. P. W. Palmberg and T. N. Rhodin, Phys. Rev. 161, 586 (1967).
4. A. E. Morgan and G. A. Somorjai, Surface Sci. 12, 405 (1968).
5. F. Jona, Surface Sci. 8, 57 (1967).
6. J. M. Charig, App. Phys. Letters 10, 139 (1967).
7. C. C. Chang, J. App. Phys. 39, 5570 (1968).
8. I. Marklund and S. Andersson, Surface Sci. 5, 197 (1966).
9. H. Tokutaka and M. Prutton, Surface Sci. 11, 216 (1968).
10. J. M. Charig and D. K. Skinner, Proc. Conf. "The Structure and Chemistry of Solid Surfaces" ed. G. A. Somorjai (Wiley Publ. N. Y. 1969).
11. M. Prutton, private communication.
12. R. W. G. Wycoff, "Crystal Structure" Vol. II. Interscience (1964).
13. L. Brewer and A. W. Searcy, J. Am. Chem. Soc. 73, 5315 (1951).
14. R. P. Burns, J. Chem. Phys. 44, 3307 (1966).
15. A. J. Decker, Sol. State Phys. 6, 251 (1958) (ed. F. Seitz & D. Turnbull)
16. C. C. Chang, Proc. Conf. "The Structure and Chemistry of Solid Surfaces" ed. G. A. Somorjai, (Wiley Publ. N. Y. 1969).
17. L. Pauling "The Nature of the Chemical Bond" Cornell Univ. Press (1960).
18. R. W. G. Wycoff, Crystal Structure, Vol I. Interscience (1963).
19. F. Halla, H. Tompa, L. Zimmerman, Z. für Kristallographie 86, 304 (1933).
20. Natl. Bur. Standard Circ. 500 (1961).

21. F. A. Cotton and G. Wilkinson, "Adv. Inorganic Chem." Interscience  
N. Y. (1966).
22. L. Fiermans and J. Vennik, Surface Sci. 9, 187 (1968).



XBL 701-1

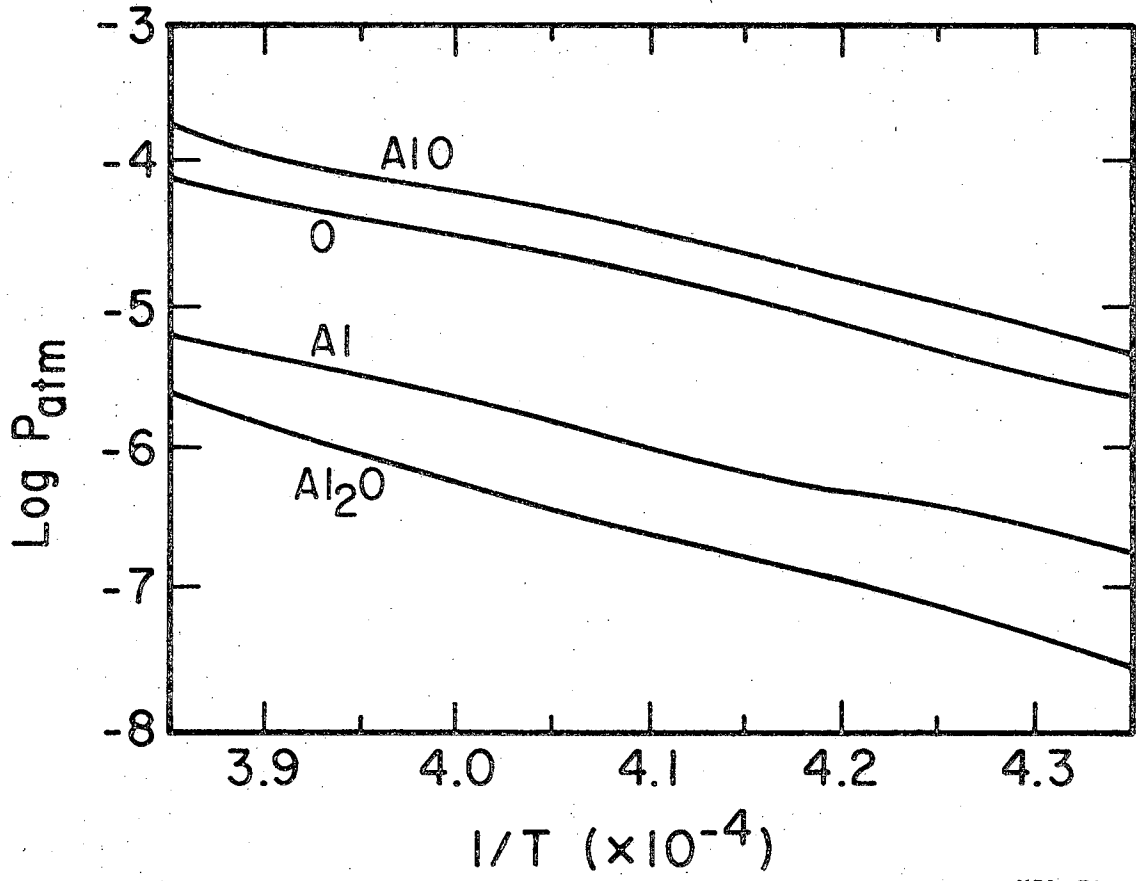
Fig. 1a. Bulk structure of  $\alpha\text{-Al}_2\text{O}_3$  as viewed along the c-axis. Large balls are oxygen ions and the small balls show the position of the aluminium ions.



XBL 701-2

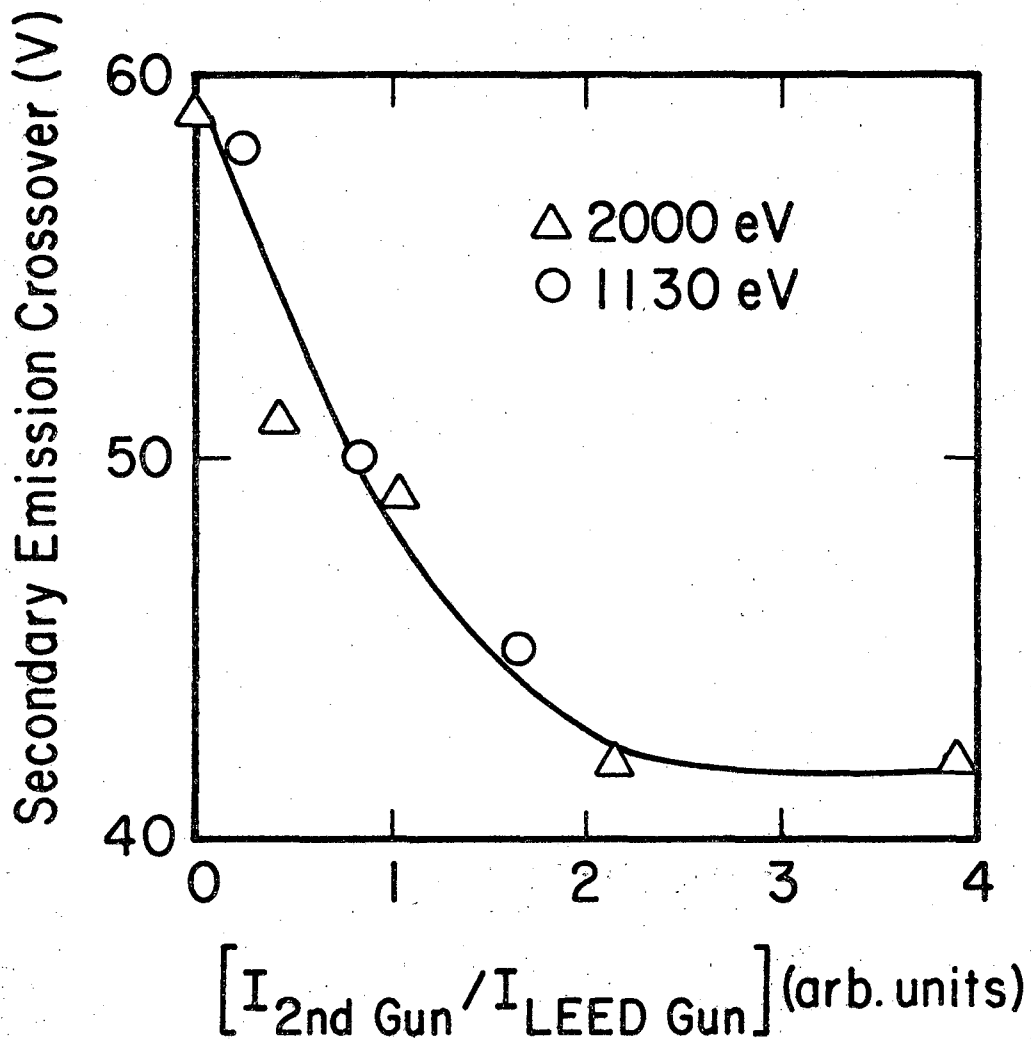
Fig. 1b. Top view of the  $\alpha\text{-Al}_2\text{O}_3$  structure from the direction of the c-face. The dotted balls are underneath the oxygen layer.





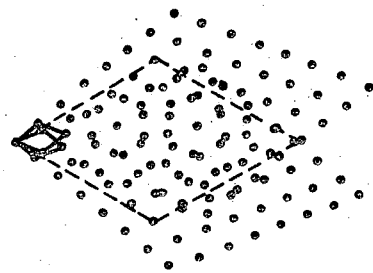
XBL 701-3

Fig. 2. The vapor composition over aluminum oxide.

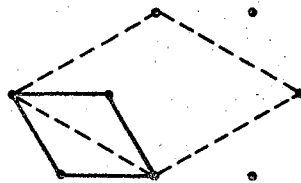


XBL 701-4

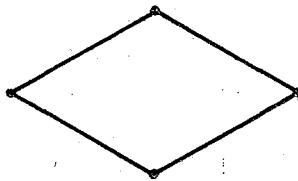
Fig. 3. The secondary emission crossover as a function of the gun current ratio,  $I_2/I_{LEED}$  scaled by an arbitrary factor, for two different electron energies of the second gun.



$(\sqrt{31} \times \sqrt{31})$   
Rotated  $\pm 9^\circ$



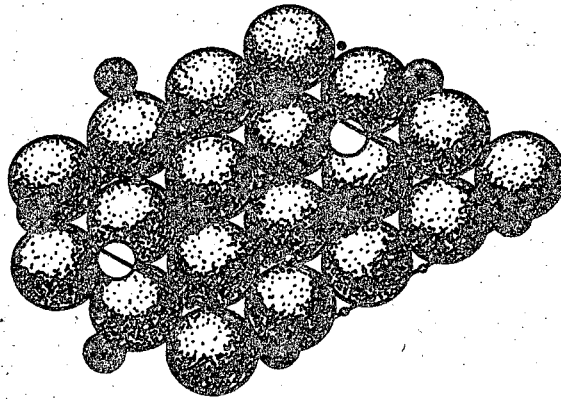
$(\sqrt{3} \times \sqrt{3})$   
Rotated  $\pm 30^\circ$



$(1 \times 1)$

XBL 701-5

Fig. 4. Schematic representation of three aluminum oxide diffraction patterns which are due to the appearance of different surface structures on the (0001) crystal face.



- Al Atoms
- Additional Al Atoms
- Unfilled Site

XBL 701-6

Fig. 5. One of the possible unit cells to generate the rotated  $(\sqrt{3} \times \sqrt{3})$  aluminum oxide surface structure.

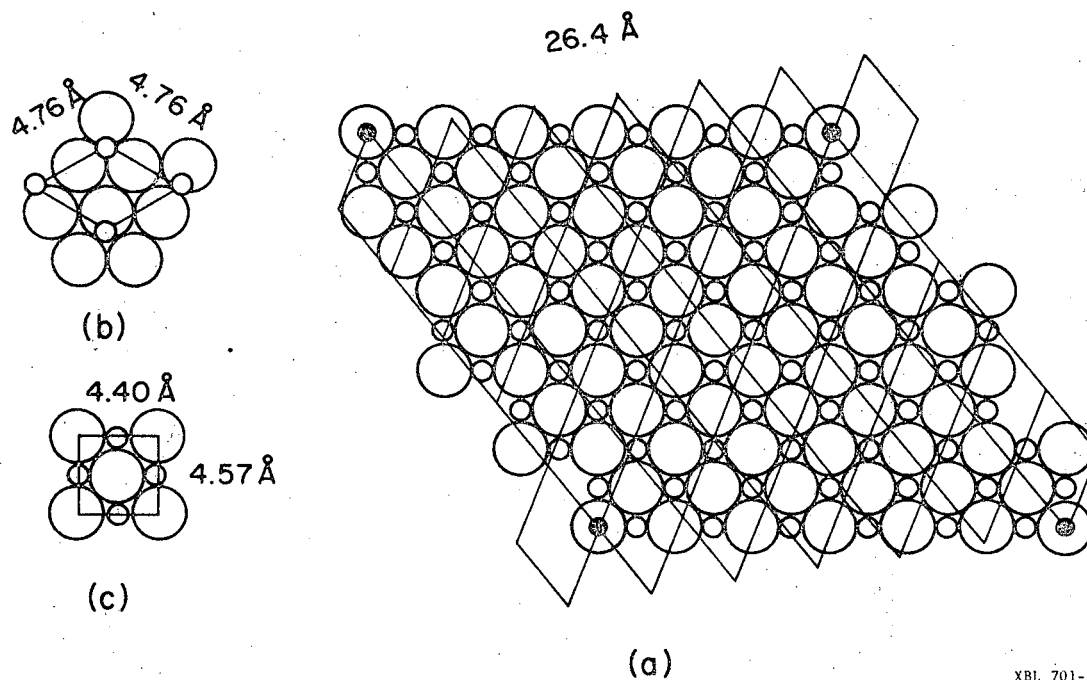
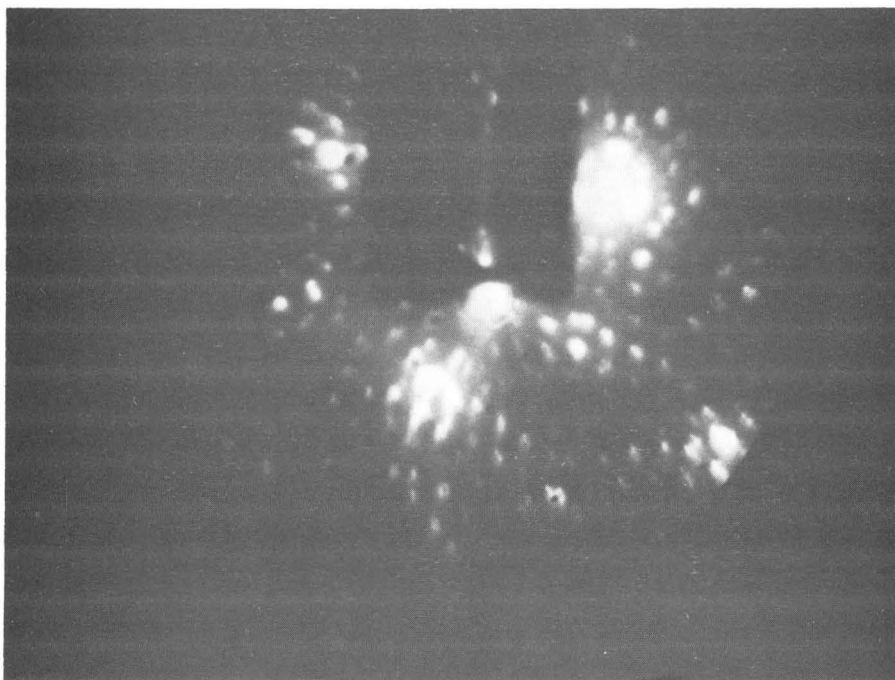
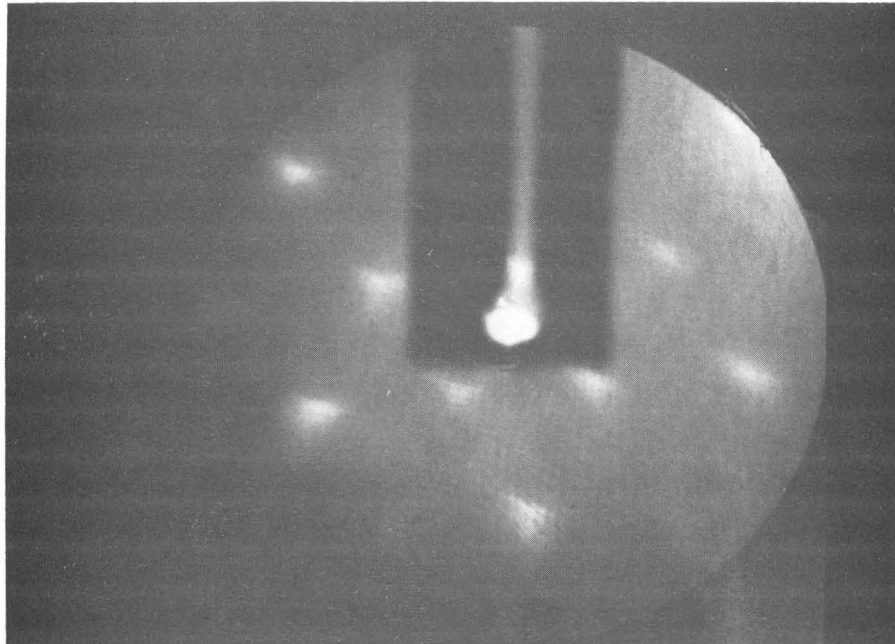


Fig. 6. (a) the hexagonal unit cell of the (0001) substrate and the (b) square unit cell of the oxygen deficient overlayer which together generate the (c) unit cell corresponding to the rotated ( $\sqrt{31} \times \sqrt{31}$ ) by coincidence.

XBL 701-7



XBB 6910-7008

Fig. 7. The diffraction patterns which correspond to the (a)  $(1 \times 1)$  and to the high temperature (b) rotated  $(\sqrt{3}1 \times \sqrt{3}1)$  surface structures.

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