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# A Rhombic Dodecahedral Honeycomb Structure with Cation Vacancy Ordering in a $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> Crystal

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TITLE RUNNING HEAD: Rhombic dodecahedral honeycomb in  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> crystal

1  
2 ABSTRACT  
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6 The crystal structure of a  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> layer grown epitaxially on an MgO substrate by a vapor phase  
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8 transport method was investigated by transmission electron microscopy, electron diffraction, and  
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10 scanning transmission electron microscopy with aberration correctors. Some forbidden reflections were  
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12 excited in electron diffraction patterns by double reflection from the vicinity of the substrate interface.  
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14 Phase boundaries are observed in atomic column images using high angle annular dark field images. A  
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16 structure model is proposed to explain the experimental results. Cation vacancy ordering is introduced in  
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18 the structure model to distort the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> crystal lattice along one axis and reduce the lattice mismatch  
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20 with the substrate. Some grains are formed and alter the directions to reduce the distortion for the other  
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22 axis. The grains are stacked with {110} phase boundaries, and form a rhombic dodecahedral  
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24 honeycomb. The rhombic dodecahedral honeycomb structure model with cation vacancy ordering is  
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26 stabilized by the lattice mismatch between the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> crystal and the MgO substrate, and it disappears  
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28 at a depth of 170 nm from the interface.  
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39 KEYWORDS:  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, defect spinel structure, Epitaxial growth, Cation vacancy ordering, rhombic  
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## Introduction

Gallium oxide ( $\text{Ga}_2\text{O}_3$ ) is one of the most attractive wide band gap materials because of its transparency, thermal and chemical stability and it is expected to find wide application to optoelectronics devices.<sup>1</sup> Five polymorphs are known for  $\text{Ga}_2\text{O}_3$ , that is, the  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\varepsilon$  forms.<sup>2</sup> The only stable form is the  $\beta$  form which has a monoclinic structure; the other forms transform into the  $\beta$  form at high temperature.<sup>3</sup> The stable  $\beta$  form has been extensively investigated, but the properties of the other forms are still poorly understood.

It has been reported that the metastable  $\gamma$  form shows some unexpected properties, that is blue light emission from nanocrystals,<sup>4</sup> room temperature ferromagnetism on Mn doping,<sup>5</sup> and selective catalytic reduction of NO in  $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$  system.<sup>6</sup> The metastable  $\gamma$  form therefore might be a more attractive material than the stable  $\beta$  form.

Basically the  $\gamma$  form has a cubic defect spinel-type structure with the lattice constant  $a = 0.822$  nm and the space group  $Fd\bar{3}m$ .<sup>7</sup> Since the  $\gamma$  form was often synthesized as nanoparticles by a sol-gel method, the crystal size was too small to investigate the structure in detail, *i.e.* surface structure, crystal defects and so on. Recently, epitaxial growth of the  $\gamma$  form has been successful on  $\text{MgO}$ <sup>8</sup> or sapphire substrates.<sup>9</sup> We have observed some forbidden reflections from the  $\gamma$  form grown on an  $\text{MgO}$  substrate by transmission electron diffraction (TED) analysis,<sup>10</sup> but their origin was unclear. In this paper, we report details of the structure investigated by high resolution transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and an *ab initio* energy calculation.

## Experimental Methods

The  $\text{Ga}_2\text{O}_3$  film was synthesized by a vapor phase transport method in a horizontal furnace.<sup>8</sup> A  $\beta\text{-Ga}_2\text{O}_3$  powder in an alumina source boat and an  $\text{MgO}$  (001) substrate coated with a thin Au layer were loaded in the furnace. The gold particles play the role of catalysts in a vapor-liquid-solid (VLS) mechanism.<sup>11</sup> The source boat was heated up to 1200 °C at a rate of 10 °C/min and the substrate

1 temperature rose to 640 °C. A gas mixture (95% N<sub>2</sub> and 5% H<sub>2</sub>) was flowed from the source to the  
2 substrate during the heating process. The film thickness was controlled by the processing time.  
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5 When the source boat was cooled after arriving at the maximum temperature, thin  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>  
6 nanocolumns had grown on the substrate. The growth direction was identified as the [001] orientation  
7 by TEM and TED analysis.<sup>10</sup> The  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> layer could be obtained by keeping the system at the  
8 maximum temperature for 3 hours. The  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> layer was formed at the interface with the substrate,  
9 while thick  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanorods grew on the surface.  
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17 A thin specimen for TEM observation was prepared by a focused ion beam (FIB) technique with  
18 a Hitachi FB-2000A. A small 10  $\mu$ m wide piece was picked up from the specimen and was attached on a  
19 metal lift-out grid. Initially the piece was thinned to 70 nm by FIB with 30 keV Ga ions. It was thinned  
20 additionally by low energy Ar ion milling with a Fischione Model 1040 (NanoMill). A surface damage  
21 layer introduced by the FIB process was completely removed by Ar ion milling at a low energy of 500  
22 eV.<sup>12</sup>  
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31 TEM and TED observation was performed using a JEOL JEM-3100FEF with a 300 keV  
32 acceleration voltage,<sup>13</sup> and STEM observation was performed with a FEI Titan<sup>3</sup> with aberration  
33 correctors and a monochromator.<sup>14</sup>  
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## 41 Results

42 Fig. 1(a) shows a TEM image of a specimen thinned by FIB and low energy Ar ion milling and  
43 Fig. 1(b)-(d) are selected area electron diffraction patterns taken from the areas shown by circles in Fig.  
44 1(a). The diffraction spots in Fig. 1(b) and 1(d) can be assigned to  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> with a space group  $Fd\bar{3}m$   
45 and the MgO substrate, respectively. On the other hand, some forbidden reflections, for example (001),  
46 (002), (003), (~~012102~~), (~~023204~~) and so on, were excited in Fig. 1(c), but (~~011101~~), (~~031301~~) and  
47 (~~033303~~) are not seen. Furthermore, streak lines were observed along the <110> reflection in Fig. 1(c).  
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58 These suggested the presence of stacking faults or twins on the {110} planes.  
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1 Such a faulted structural phase is clearly differentiated from the usual  $Fd\bar{3}m$  structure at the  
2 interface shown by an arrow in Fig. 1(a). It is not that the faulted structure fades out gradually on  
3 moving away from the substrate interface. The thickness of the faulted structure was 170 nm. This type  
4 of faulted structure has not been reported for the  $\gamma$  form grown on a sapphire substrate.<sup>9</sup>  
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9 Fig. 2(a) shows a high magnification TEM image of the faulted structure. This area was thinned  
10 by Ar ion and high energy electron beam and its width was 16 nm. The thickness in this area was  
11 probably equivalent to, or a little thicker than, the width, and thus it can be estimated as about 20 nm. To  
12 clarify the features, the image contrast was emphasized and shown with pseudo colors in Fig. 2(b).  
13 Some distinctive contrast can be seen in Fig. 2(b); high contrast column image areas indicated by H in  
14 Fig. 2(c) and low contrast areas L that surround the H areas. The square lattice in the H areas can be  
15 assigned to  $\{022\}$  reflections from the  $\gamma$  form. On the other hand, long periodic fringes appear in the L  
16 areas as shown by arrows in Fig. 2(b), and the periodicity corresponds to  $\{001\}$  reflections that are  
17 forbidden reflections for the usual  $\gamma$  form. The distinctive contrast suggests that small grains of 4-5 nm  
18 are connected with twin boundaries. Since the  $\{110\}$  twin boundary in a  $Fd\bar{3}m$  structure corresponds to  
19 a phase boundary, long periodic fringes may appear when two grains connected by the twin boundary  
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38 Fig. 3 shows high angle annular dark field (HAADF) images taken by STEM with two kinds of  
39 incidence,  $[010]$  and  $[110]$  respectively. These images were taken using a multiple fast acquisition with  
40 drift tracking technique to improve the signal to noise ratio,<sup>15</sup> and a random noise was reduced by a local  
41 2D difference filter.<sup>16</sup> The HAADF images can be interpreted as incoherent images, and thus every  
42 atomic column appears with bright contrast. The insets show gallium sites in a  $\gamma$ - $\text{Ga}_2\text{O}_3$  crystal structure.  
43 The yellow and green spheres indicate tetragonal and octahedral positions, respectively. The atomic  
44 arrangements in a unit cell are shifted from the lower regions to the upper regions. The images in the  
45 intermediate region can be interpreted as overlaps of both atomic arrangements in the lower and upper  
46 regions. This also supports the thesis that phase boundaries formed at the grain boundaries in the faulted  
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## Discussion

The structure of the  $\gamma$  form is usually described as a defect spinel structure like  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a lattice constant  $a = 0.822$  nm. A spinel cubic cell has 32 oxygen atom sites and 24 cation sites in tetrahedral and octahedral positions, but  $2\frac{2}{3}$  cation vacancies must be introduced to satisfy the Ga<sub>2</sub>O<sub>3</sub> stoichiometry. If the vacancies occupy the specific positions regularly, the crystal symmetry is reduced from  $Fd\bar{3}m$  and forbidden reflections like as (002) and (~~024204~~) might be excited.

From *ab initio* calculations, it has been reported for both  $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>17</sup> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub><sup>18</sup> that the total energy is minimized when all the vacancies are located at specific octahedral positions that are furthest from each other. However, the energy difference between the possible vacancy configurations is too small after the structure optimization to conclude that the minimum energy structure is formed in the actual crystals at a finite temperature. Generally it is thought that the vacancies occupy both the tetrahedral and octahedral positions randomly to form the  $Fd\bar{3}m$  symmetry.

There is some room created for the vacancies to occupy the specific positions when the crystal is distorted by the lattice mismatch between the crystal and the substrate. Since the substrate MgO has a cubic rock salt structure with the lattice constant of 0.421 nm that is 2.4% longer than one half of the lattice constant of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, some distortion should be introduced in the vicinity of the interface.

An optimized structure has been evaluated by an *ab initio* calculation for the minimum energy vacancy configuration that was predicted from the previous theoretical studies.<sup>17, 18</sup> Following the previous studies, we also used a supercell that is three times the size of the primitive cell of the cubic spinel structure. The supercell contains 24 oxygen atoms, 16 gallium atoms, and two cation vacancies, and the cation vacancies occupy the octahedral positions that are furthest away from each vacancy. The distance between the vacancies is 0.769 nm before the structure optimization. The calculation was performed with the ABINIT code<sup>19</sup> and a pseudo potential based on the generalized gradient approximation.<sup>20</sup>

1 The optimized supercell after the minimum energy calculation was converted into a cubic like  
2 unit cell, and the optimized lattice constants were obtained as  $a = b = 0.8211$  nm,  $c = 0.840$  nm,  $\alpha = \beta =$   
3  $89.75^\circ$ , and  $\gamma = 91.42^\circ$ . The value of  $a$  and  $b$  are almost unchanged from the original cubic lattice  
4 constant of  $0.822$  nm, but  $c$  is expanded by  $+2.1\%$ , a value that is quite close to twice the lattice constant  
5 for MgO. The lattice mismatch between the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> and the MgO substrate can be relaxed for one axis  
6 by setting the elongated  $c$  axis parallel to the MgO [100] or [010] axis, though the lattice is still  
7 mismatched along the other axis normal to the  $c$  axis.  
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10 To reduce the distortion caused from the lattice mismatch, some grains could be formed. The  
11 elongated  $c$  axes of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> grains are directed along the MgO [100] and [010] axes alternately, and  
12 these grains are connected with {110} interfaces. The structure model is schematically drawn in Fig. 4.  
13 The black square mesh in Fig. 4(a) represents an MgO (001) surface where oxygen atoms arrange in a  
14 square lattice. Oxygen atoms in a  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> crystal also form a face-centered cubic arrangement, and the  
15 (001) surface can be represented by the red or blue lattices in Fig. 4(a). Here, the red square mesh is  
16 expanded toward the [010] direction of the MgO substrate and the lattice distance is matched to the  
17 MgO lattice; the blue square mesh is expanded toward the [100] direction similarly. These square  
18 meshes are arranged on the MgO substrate with alternate tiling, as shown in Fig. 4(b). The MgO and  $\gamma$ -  
19 Ga<sub>2</sub>O<sub>3</sub> lattices match each other in the four areas shown by red circles in Fig. 4(b) and on vertical and  
20 horizontal bands connecting the red circles, while they mismatch around areas shown by green circles.  
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43 While the grains in this structure model are connected with {110} interfaces, {110} twin  
44 boundaries are also suggested by the TED pattern, the high resolution TEM image and the HAADF  
45 image. There are 12 equivalent {110} planes in a cubic structure, and a crystal grain truncated by these  
46 equivalent {110} planes forms a rhombic dodecahedron, as shown in Fig. 5(a). The rhombic  
47 dodecahedron is one of the polygons that can fill a 3D space without any gaps. The space tessellation is  
48 known as a rhombic dodecahedral honeycomb, where rhombic dodecahedrons are stacked on each other  
49 with face-centered cubic packing (see Fig. 5(b)).  
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1 According to the rhombic dodecahedral honeycomb structure model with cation vacancy  
2 ordering, the TEM images and TED patterns were simulated by the multi-slice method<sup>21</sup>. The supercell  
3 size used in the simulation was 11.6 nm x 11.6 nm and the thickness was 16.4 nm that was divided into  
4 thin slices 0.82 nm in thickness. In the simulated image shown in Fig. 6(a), some square high contrast  
5 regions are surrounded by lower contrast boundary regions, and long periodic fringes are seen in the  
6 lower contrast boundary regions. These features correspond to those observed in the TEM image in Fig.  
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2. In the simulated diffraction pattern shown in Fig. 6(b), some forbidden (001), (002), (003), and (~~012~~102) reflections and the streak lines along the <110> reflection were reproduced. This rhombic dodecahedral honeycomb model with cation vacancy ordering explains all the experimental results.

In order to clarify the origin of the forbidden reflection excitation crystallographically, electron diffraction patterns were simulated for two structure models; (1) a cation vacancy ordering model with lattice distortion predicted from the *ab initio* calculation described above and (2) a rhombic dodecahedral honeycomb model without the cation vacancy ordering. The simulated patterns are shown in a supplemental data and the results are summarized here.

From the first structure model, (002) and (204) forbidden reflections are reproduced. These reflections can be categorized as systematic absences and they could be excited if the space group is reduced from  $Fd\bar{3}m$ . The cation vacancy ordering reduces the crystal symmetry, and thus the systematic absences could be excited.

On the other hand, (001), (003), (102) and so on are reproduced by the second structure model. These forbidden reflections are lattice absences that could not be excited if the crystal system remains cubic. However they can be excited by double reflections in grains that are connected with phase boundaries.

It is seen from these simulation results that the rhombic dodecahedral honeycomb model with the cation vacancy ordering is essential to reproduce the excitation of both lattice absences and systematic absences like the experimental results shown in Fig. 1(c).

## Conclusions

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3 A structural model was proposed to explain the forbidden reflections observed from the vicinity  
4 of the interface between a  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> layer and an MgO substrate. Cation vacancy ordering is introduced to  
5 reduce the lattice mismatch for one axis and some grains are formed in alternating 90° directions to  
6 reduce the distortion in the other axis. The grains are surrounded by {110} twin boundaries and form a  
7 rhombic dodecahedron. Finally, the rhombic dodecahedral grains are stacked to form a honeycomb. This  
8 structure model consistently explains all the experimental results. The structure is formed to reduce the  
9 2.4% lattice mismatch between the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> crystal and the MgO substrate, and thus it is only stable on  
10 the substrate.  
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27 [Electron diffraction patterns for some structure models are seen in a supplemental data to analyze the](#)  
28 [origin of the forbidden reflections. This information is available free of charge via the Internet at](#)  
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Figure captions

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4 **Figure 1.** A transmission electron microscope image (a) of a  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> layer grown epitaxially on an  
5 MgO substrate. Selected area electron diffraction patterns (b)-(d) taken from areas circled in (a).  
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10 **Figure 2.** A high resolution transmission electron microscope image of a faulted  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> layer (a). The  
11 contrast was emphasized and shown with pseudo colors in (b), and some distinctive contrast areas are  
12 shown schematically in (c).  
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18 **Figure 3.** High angle annular dark field images of a faulted  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> layer seeing from a [010] (a) and a  
19 [110] axis. The insets show gallium sites in a  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> crystal structure. The green and yellow spheres  
20 indicate octahedral and tetragonal sites, respectively. The crystal lattices between upper and lower sides  
21 are shifted, and there is a phase boundary.  
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29 **Figure 4.** The grain stacking structure model. The black mesh represents the MgO substrate, and blue  
30 and red meshes represent a  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> layer, which are expanded respectively along one axis in (a). The  
31 red and blue meshes are tiled alternately on the black mesh in (b).  
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37 **Figure 5.** A rhombic dodecahedron (a), and a rhombic dodecahedral honeycomb (b).  
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40 **Figure 6.** A simulated electron microscope image (a) and a simulated electron diffraction patterns (b)  
41 for a rhombic dodecahedral honeycomb with cation vacancy ordering.  
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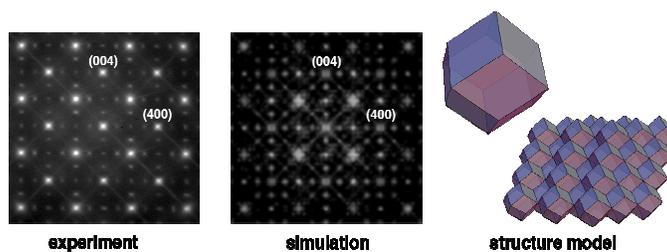
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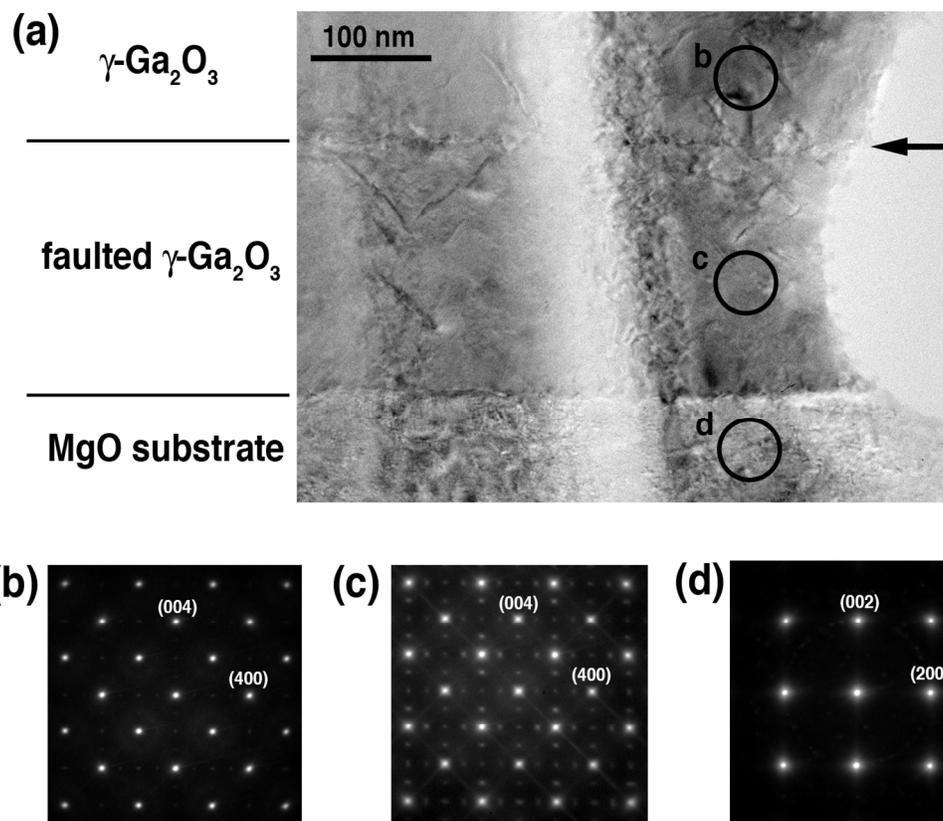
Title: A Rhombic Dodecahedral Honeycomb Structure with Cation Vacancy Ordering in a  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>

Crystal

Authors: Masanori Mitome, Shigemi Kohiki, Takuro Nagai, Keiji Kurashima, Koji Kimoto, Yoshio

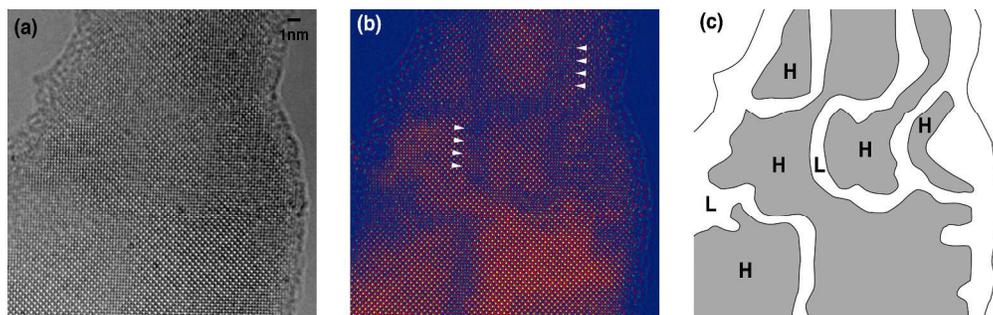
Bando

We analyzed a crystal structure of a faulted  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> layer grown on an MgO substrate by TEM, STEM, and *ab initio* calculations. A rhombic dodecahedral honeycomb structure model with cation vacancy ordering is proposed, and it is confirmed by simulations of electron diffraction patterns.



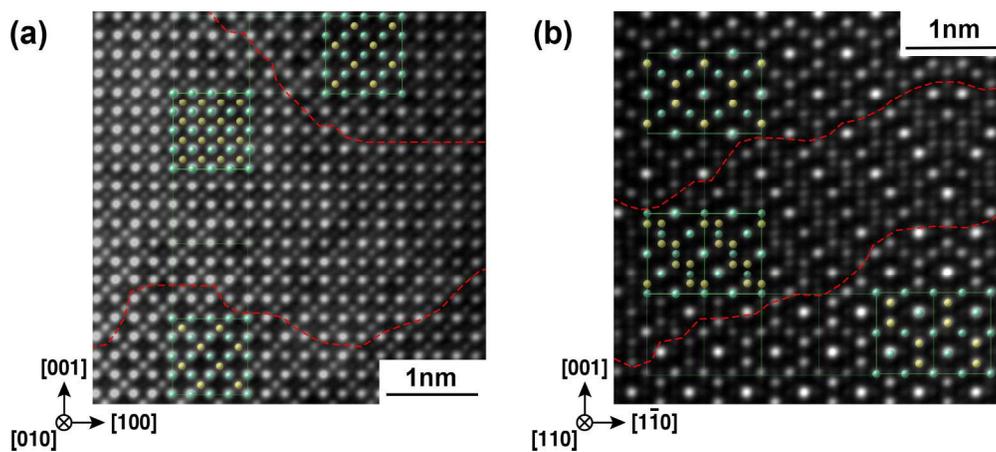
34 A transmission electron microscope image (a) of a  $\gamma\text{-Ga}_2\text{O}_3$  layer grown epitaxially on an MgO substrate.  
35 Selected area electron diffraction patterns (b)-(d) taken from areas circled in (a).  
36 136x111mm (300 x 300 DPI)

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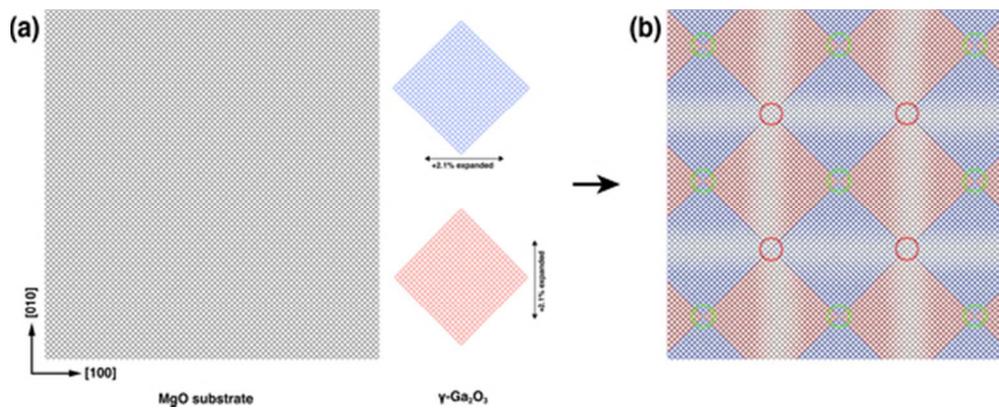


A high resolution transmission electron microscope image of a faulted  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> layer (a). The contrast was emphasized and shown with pseudo colors in (b), and some distinctive contrast areas are shown schematically in (c).

474x147mm (300 x 300 DPI)



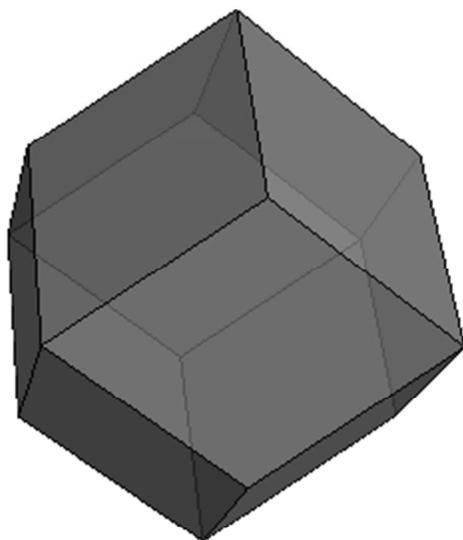
High angle annular dark field images of a faulted  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> layer seeing from a [010] (a) and a [110] axis. The insets show gallium sites in a  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> crystal structure. The green and yellow spheres indicate octahedral and tetragonal sites, respectively. The crystal lattices between upper and lower sides are shifted, and there is a phase boundary.  
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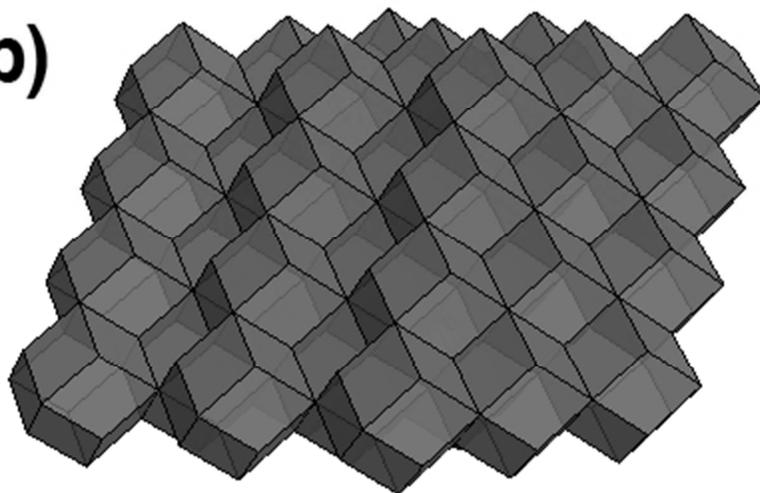
The grain stacking structure model. The black mesh represents the MgO substrate, and blue and red meshes represent a  $\gamma\text{-Ga}_2\text{O}_3$  layer, which are expanded respectively along one axis in (a). The red and blue meshes are tiled alternately on the black mesh in (b).  
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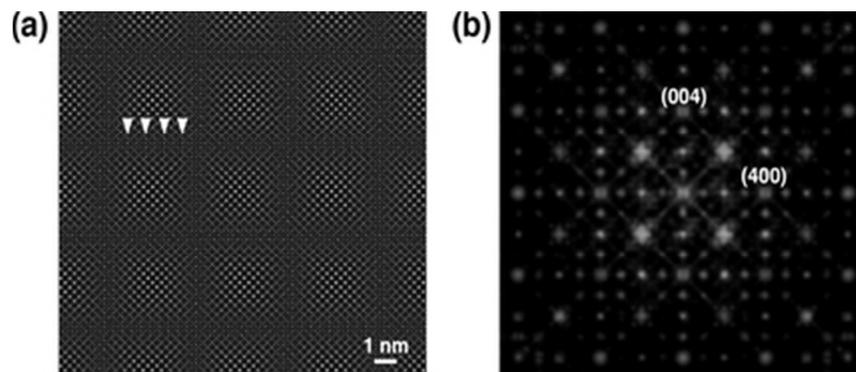
**(a)**



**(b)**



A rhombic dodecahedron (a), and a rhombic dodecahedral honeycomb (b).  
34x49mm (300 x 300 DPI)



A simulated electron microscope image (a) and a simulated electron diffraction patterns (b) for a rhombic dodecahedral honeycomb with cation vacancy ordering.  
36x15mm (300 x 300 DPI)