Bi-Stability and Orientation Change of a Thin $\alpha$-Fe$_2$O$_3$ Layer on a $\varepsilon$-Fe$_2$O$_3$ (004) Surface

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ABSTRACT: This study reports the key ingredients that influence the orientation and stability of a $\alpha$-Fe$_2$O$_3$ layer that grows on a metastable $\varepsilon$-Fe$_2$O$_3$ during pulsed laser deposition. Depending on the substrate temperature, two different $\alpha$-Fe$_2$O$_3$ orientations arise on the $\varepsilon$-Fe$_2$O$_3$ (004) surface. At 800 °C, (2−10)$_\alpha$-oriented $\alpha$-Fe$_2$O$_3$ is stabilized, whereas at 700 °C, (006)$_\alpha$-orientation occurs. The (2−10)$_\alpha$-oriented $\alpha$-Fe$_2$O$_3$ layer possesses an interface with densely packed Fe ions with presumably considerable number of oxygen vacancies. On the other hand, the (006)$_\alpha$-oriented $\alpha$-Fe$_2$O$_3$ layer is stabilized, as in the case of the YSZ (100) substrate, due to the domain pattern with an in-plane rhombic shape, which is known to become an effective nucleation site. Growth with the unexpected (2−10)$_\alpha$ orientation can be understood based on a model that takes into account the surface energy as the dominant factor, which mainly stems from the presence of dangling bonds on the surface and the atomic vibration of the surface atoms. As the surface is one of the critical elements related to the specific functionality of a material, the present study will offer valuable insights into the designs of functional devices with novel surface properties.

I. INTRODUCTION

Chemical reactions involving a solid, such as a catalytic reaction, occur on the surface.1−4 The performance of such reactions therefore strongly depends on certain surface characteristics such as the surface orientation and surface activity. Because the surface properties can depend on the presence of dangling bonds, i.e., broken chemical bonds, and given that each surface has different number of such bonds, one surface can have quite different chemical activity from another, even in the same material.5,6 Thus, engineering layer orientation is a potentially efficient method for optimizing the properties of surfaces.7−11 Controlling the surface orientation can easily be done in a single crystal by cutting a sample in the desired direction. However, this simple approach cannot be applied to a thin film because the substrate predetermines the growth direction. Under these circumstances, it is necessary to manipulate the growth itself by controlling the growth processes so that the film grows in the desired direction. However, this is not easily achieved because the parameters that determine the film orientation are not fully understood. In this study, we find that two different $\alpha$-Fe$_2$O$_3$ orientations arise on the $\varepsilon$-Fe$_2$O$_3$ (004) surface depending on the substrate temperature. The critical ingredients related to the film orientation are the number of dangling bonds on the surface and the degree of atomic vibration on the surface. The surface energy of a given surface is proportional to the number of dangling bonds per area. At low temperatures, the (006)$_\varepsilon$ surface is lower in energy compared to the (2−10)$_\varepsilon$, surface because the former has fewer dangling bonds. However, due to the atomic vibration of the atoms on the surface, the surface energy in the (2−10)$_\alpha$ case becomes comparable to that in the (006)$_\varepsilon$ case at high temperatures.

Iron(III) oxide (Fe$_2$O$_3$ or ferric oxide) is one of the suitable oxide materials that could be used in spintronic devices.12−14 To date, five crystalline polymorphs of Fe$_2$O$_3$ have been discovered. These are the naturally abundant $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ phases, the high-pressure-stabilized $\delta$-Fe$_2$O$_3$ phase, and the laboratory-synthesized $\beta$-Fe$_2$O$_3$ and $\varepsilon$-Fe$_2$O$_3$ phases.15 All of these polymorphs exhibit different crystal structures and magnetic properties.16−22 Most coexist during the phase transformation of Fe$_2$O$_3$.20,23,24 As a result, it is challenging to study the fundamental issues such as the nucleation and growth of an individual Fe$_2$O$_3$ polymorph. Owing to a lack of understanding of the influence of the growth parameters, it is a great challenge to search for the primary parameter that causes polymorphous transformations when seeking to prepare a single phase of Fe$_2$O$_3$. In particular, the preparation of a phase-pure $\varepsilon$-Fe$_2$O$_3$ has also been very challenging due to contamination with other polymorphs such as $\alpha$-Fe$_2$O$_3$. Hence, a deeper understanding of the effects of the growth parameters in relation to these Fe$_2$O$_3$ polymorphisms is required if a controllable and reliable method for the synthesis of pure $\varepsilon$-Fe$_2$O$_3$ is to be developed.

$\varepsilon$-Fe$_2$O$_3$ is a rare Fe$_2$O$_3$ polymorph that exists only in a nanostructure form, with low abundance.20 This polymorph is a metastable phase of iron(III) oxide, a structural intermediate.
between γ-Fe$_2$O$_3$ and α-Fe$_2$O$_3$. As the surface energy contribution stabilizes ε-Fe$_2$O$_3$, it transforms into a more stable α-Fe$_2$O$_3$ when its size exceeds a critical value. The ε-Fe$_2$O$_3$ phase has an orthorhombic crystal structure with the Pna2$_1$ space group and lattice parameters of $a = 5.095$, $b = 8.789$, and $c = 9.437$ Å. ε-Fe$_2$O$_3$ is a polar ferrimagnet that exhibits a strong magnetoelastic coupling. It is the first room-temperature multiferroic system with a single active resonance frequency in the terahertz range. Thus far, results in a large coercive field and a natural ferromagnetic resonance frequency in the terahertz range. Thus far, ε-Fe$_2$O$_3$ has been synthesized in nanoparticle form in confined nanoreactors by sol–gel-based methods, as nanowires, or as a thin film on limited substrates. As nanostructures and nanoparticles are usually randomly oriented, a textured or oriented thin film of ε-Fe$_2$O$_3$ is necessary for application of this exciting material to devices.

In this study, we mainly focus on the polymorphous transformation to α-Fe$_2$O$_3$ in a metastable ε-Fe$_2$O$_3$ thin film grown on the SrTiO$_3$ (STO)(111) surface using pulsed laser deposition (PLD). We found that the critical thickness of ε-Fe$_2$O$_3$ is approximately 17 nm, below which ε-Fe$_2$O$_3$ is stable. High-resolution X-ray diffraction (HRXRD) and transmission electron microscopy (TEM) measurements show that above this critical thickness, the α-Fe$_2$O$_3$ phase with two different orientations starts to emerge; one with the (006)/[004], relationship at 700 °C and the other with the (2−10)/[004], at 800 °C. The (2−10)$\gamma$-oriented α-Fe$_2$O$_3$ layer possesses an interface with densely packed Fe ions and with presumably considerable number of oxygen vacancies. On the other hand, the (006)-oriented α-Fe$_2$O$_3$ forms due to specific domain patterns in ε-Fe$_2$O$_3$ with an in-plane rhombohedral edge, which are known to be effective nucleation sites for α-Fe$_2$O$_3$. The unexpected growth orientation at a high substrate temperature is understood on the basis of a model in which the surface energy from dangling bonds and atomic vibration of the surface atoms plays a dominant role. It is expected that the significant strain in the (2−10)-oriented α-Fe$_2$O$_3$ layer is released by oxygen vacancies at the interface.

II. RESULTS AND DISCUSSION

II.I. Influence of Substrate Temperature and Laser Energy Density. As the laser energy density and the substrate temperature are two major growth parameters during the PLD synthesis process, their effects on the growth of ε-Fe$_2$O$_3$ thin films were initially explored. We systematically investigated the ε-Fe$_2$O$_3$ thin films grown on the STO(111) surfaces at temperatures of $T = 600$, 700, and 800 °C at an approximate energy density of $F = 2.0$ J/cm$^2$. We could confirm the formation of the ε-Fe$_2$O$_3$ phase by means of in-house X-ray diffraction measurements, as shown in Figure 1a,b. These data show only the (001)$_{\gamma}$, reflections (i = 2n, n is an integer) of the ε-Fe$_2$O$_3$ phase. However, these in-house measurements are incapable of detecting tiny diffraction peaks of impurity phases and other Fe$_3$O$_4$ polymorphs. Thus, synchrotron X-rays measurements were carried out to identify such small signals, as will be shown later. The three main peaks at $2\theta = 38.2, 58.7,$ and $81.4$° correspond to the (004)$_n$, (006)$_n$, and (008)$_n$, reflections of the ε-Fe$_2$O$_3$ structure, respectively. From these peak positions, the out-of-plane lattice parameter is estimated to be about $c = 9.465$ Å, which is in agreement with the reported bulk value. This demonstrates a strain relaxation of the ε-Fe$_2$O$_3$ layer. In fact, the values of the in-plane lattice mismatch between ε-Fe$_2$O$_3$ and STO(111) substrate are $(\sqrt{3}\alpha_{\text{STO}} - 2\alpha)_{/2}\alpha_{\text{STO}}$ −6% and $(3\sqrt{2}\alpha_{\text{STO}} - 2\beta)_{/2}\beta -6%$ for [100]$_n$/[1−21]$_{\text{STO}}$ and [010]$_n$/[303]$_{\text{STO}}$ directions, respectively. Large strain is released by forming dislocations at the interface. Indeed, we observed dislocations at the interface in our preliminary scanning TEM experiments. Figure 1a,b compares the ε-Fe$_2$O$_3$ thin films grown at $F = 1.7$ and 2.0 J/cm$^2$, respectively. At each energy density level, deposition at different temperatures was done for identical periods, ensuring that the film thicknesses were also identical. Using X-ray
reflectivity (XRR) measurements, we estimated the thickness of the films shown in Figure 1a,b, revealing a value of approximately 15 nm.

To quantify the crystallinity of the films at different temperatures with the given energy density, we calculated the integrated intensity of the (006) peaks. To do this, the (006) peaks were fit with the Gaussian profile. First, the data were normalized according to the STO(111) peak to remove the scale factor. The width of the (006) peaks was observed and found to be larger than the instrumental resolution due to the finite size effect. It is well known that a small grain size results in the line broadening of a peak. This line broadening is expressed by the Scherrer equation $\theta = K\lambda/\beta \cos(\theta)$, where $\theta$ is the angle of reflection. The width of the (006) reflection is approximately 0.6°, giving rise to a grain size of ~16 nm according to the Scherrer equation. This value is in excellent agreement with the thickness ~15 nm of the films. This result implies that the line width of the (006) reflection is indeed broadened by the finite size effect, as expected. As shown in Figure 1c,d, the (006) peaks are quite well fitted to the Gaussian profile. At $F = 1.7$ J/cm², the integrated intensity of the peak increases with an increase in the growth temperature, while the full width at half-maximum (FWHM) decreases, as shown in Figure 1f, respectively. On the other hand, at $F = 2.0$ J/cm², the film grown at 700 °C has the highest integrated intensity, suggesting the best crystallinity at this temperature.

II.II. Stability of the ε-Fe₂O₃ Phase and Its Polymorph Transition to α-Fe₂O₃. We also systematically studied the stability of the ε-Fe₂O₃ thin film grown on the STO(111) surface and its polymorph transition to α-Fe₂O₃ at different laser energy densities and substrate temperatures. We focus on two substrate temperatures: 700 and 800 °C. The growth conditions used in the present study are summarized in Table 1. Under these conditions, we grew several thin films with different thicknesses for different deposition times to determine the critical thickness, beyond which a minor Fe₂O₃ polymorph emerges. We could detect tiny X-ray signals from the minor polymorph by obtaining the measured synchrotron HRXRD data. Figure 2a shows the synchrotron HRXRD data of the ε-Fe₂O₃ thin film sample synthesized at $T_s = 800$ °C. These data indicate the growth of the single ε-Fe₂O₃ phase up to 10 nm, as there are no additional peaks other than those from the ε-Fe₂O₃ structure. On the other hand, additional peaks emerge in the film with a thickness of 17 nm. These additional peaks are identified as (2−10)α, and (4−20)α from the α-Fe₂O₃ structure, and they have epitaxial relationship of (2−10)α/004. This result suggests that the critical thickness below which the ε-Fe₂O₃ phase is stable without any second phase is <17 nm in our growth condition. In samples thicker than 17 nm, the α-Fe₂O₃ phase eventually becomes stabilized because ε-Fe₂O₃ is unstable in this thickness range.

Unlike the case above, the ε-Fe₂O₃ films grown at $T_s = 700$ °C show completely different features, as presented in Figure 2f. The films in the vicinity of the critical thickness exhibit both ε-Fe₂O₃ and α-Fe₂O₃ peaks with the epitaxial relationship of (006)α/004. This epitaxial relationship is in sharp contrast to the case discussed above. Upon increasing the thickness of the film, the ε-Fe₂O₃ peaks vanish completely, which indicates the instability of the ε-Fe₂O₃ films on the STO(111) surfaces when the film is thick. In the thick-film region, α-Fe₂O₃ grows epitaxially. How such an epitaxial α-Fe₂O₃ layer grows without the ε-Fe₂O₃ layer is an interesting issue because it is likely that ε-Fe₂O₃ first nucleates and subsequently grows before the α-Fe₂O₃ layer. This absence of ε-Fe₂O₃ in a thick film implies that the interface energy between the ε-Fe₂O₃ layer with the (004)α orientation and α-Fe₂O₃ with (006)α is positive and that it becomes more positive with an increase in the thickness of α-Fe₂O₃. Hence, a α-Fe₂O₃ layer in contact with a thick α-Fe₂O₃ cannot survive, transforming into α-Fe₂O₃. This will also be the case for the (2−10)α orientation. Of course, the stability problem depends on the growth kinetics as well. For instance, if the deposition rate is very high or if the thermal energy is not sufficient, the activation barriers will not be overcome. In such cases, a metastable phase, which nucleates initially but cannot fully relax, can grow to a certain thickness. However, this is not the case here. Therefore, our growth conditions are considered as quasi-thermodynamic because the α-Fe₂O₃ phase grows with no ε-Fe₂O₃ when the film is thick. On the other hand, ε-Fe₂O₃ becomes thermodynamically stable when its thickness is below the critical value. This is possible owing to the surface energy contribution at the domain boundaries in a specific domain pattern. Moreover, the absence of a correlation between the layer orientation and the laser energy that determines the energy of the plume particles also indicates the relative unimportance of the kinetic factors in our growth condition. Table 1 summarizes the growth conditions with the orientation of the α-Fe₂O₃ layer. This table shows that the substrate temperature is the main control parameter of the layer orientation. The above picture might not be valid if ε-Fe₂O₃ is formed during the cooling down period. However, this cannot happen in the present case because α-Fe₂O₃ is thermodynamically more stable. Thus, it is not thermodynamically preferable that α-Fe₂O₃ transforms into ε-Fe₂O₃ at temperature range below 800 °C. As explained before, the most important stabilizing factor of ε-Fe₂O₃ on STO(111) is the domain wall energy.

Next, consider the structural relationship between the ε-Fe₂O₃ and α-Fe₂O₃ layers. α-Fe₂O₃ has a rhombohedral structure with lattice parameters of $a_\alpha = b_\alpha = 5.03$ Å and $c_\alpha = 13.74$ Å, while ε-Fe₂O₃ is orthorhombic with $a_\varepsilon = 8.78$, and $c_\varepsilon = 9.47$ Å. Figure 2c illustrates a ε-Fe₂O₃ (004) plane with planar unit cells whose cell parameters are $a_\varepsilon$ and $b_\varepsilon$. Above, the two-dimensional (2D) units of (2−10)α planes are displayed. As highlighted in Figure 2b, the (2−10)α plane is shown inside the conventional hexagonal unit cell of α-Fe₂O₃ by the red lines with short and long lengths of $\sqrt{3}/2a_\varepsilon$ and $c_\varepsilon$, respectively. The short length of $\sqrt{3}/2a_\varepsilon$ of this rectangle approximately matches the $a_\alpha$ parameter or one half of the $b_\alpha$ lattice parameter. Therefore, there are two possibilities for this rectangle to cover the (004)α plane, as shown in Figure 2d,e. The first case is that the short length $\sqrt{3}/2a_\varepsilon$ and the long length $c_\varepsilon$ are aligned along the $a_\varepsilon$ and $b_\varepsilon$ directions.

| sample batch number | $E$ (J/cm²) | $T_s$ (°C) | oxygen pressure (Torr) | orientation of α-Fe₂O₃ |
|---------------------|-------------|-------------|------------------------|------------------------|
| 1                   | 2.0         | 700         | $3 \times 10^{-3}$     | (006)                  |
| 2                   | 2.2         | 700         | $3 \times 10^{-3}$     | (006)                  |
| 3                   | 1.7         | 800         | $3 \times 10^{-3}$     | (2−10)                 |
| 4                   | 2.2         | 800         | $3 \times 10^{-3}$     | (2−10)                 |
respectively. Figure 2d shows such a pattern. The second is that the short length $\sqrt{3}/2a_\alpha$ and the long length $c_\alpha$ are aligned in opposite directions relative to the first case, as illustrated in Figure 2e. In the interface structure in Figure 2d, compressive strains with $(2\alpha-10)/3b_\alpha$ and $(7\sqrt{3}/2a_\alpha-6a_\alpha)/6a_\alpha \approx 4.3\%$ exist along the $b_\alpha$ and $a_\alpha$ directions, respectively. In the case shown in Figure 2e, $(2 \sqrt{3}/2a_\alpha-b_\alpha)/b_\alpha \approx -0.77\%$ and $(9c_\alpha-24a_\alpha)/24a_\alpha \approx 1.42\%$ imply tensile and compressive strains of $-0.77$ and $1.42\%$ along the $b_\alpha$ and $a_\alpha$ directions, respectively. For the release of such large strains, a certain strain relaxation mechanism should exist. One strain relaxation mechanism is the formation of misfit dislocations at the interface. Another possibility is the formation of oxygen and iron vacancies. Lighter oxygen anions are more easily separated from the structure in metal oxides.$^{30,41}$ Oxygen vacancies are formed particularly near the dislocations and in interface regions in which stress is high. By emptying oxygens, the strain is released locally. When such oxygens accumulate, a considerable amount of strain can be released.$^{42}$ Thus, the $(2\alpha-10)$-oriented $\alpha$-Fe$_2$O$_3$ layer is considered to possess a disordered interface structure with considerable numbers of oxygen and iron vacancies. In contrast to the above case, the X-ray data shown in Figure 2f can be understood based on the interface structure illustrated in Figure 2g, as reported on the YSZ (100) surface in earlier work.$^{38}$ Three domains of $\epsilon$-Fe$_2$O$_3$ form $120^\circ$ patterns on the STO(111) surface, as depicted on the right-hand side of Figure 2g. As $a_\alpha \approx a_\alpha$, this pattern becomes an effective nucleation site for $\alpha$-Fe$_2$O$_3$. The $\alpha$-Fe$_2$O$_3$ layer will grow on top of $\epsilon$-Fe$_2$O$_3$ along the [004]$_\alpha$ direction.

Figure 3 shows a cross-sectional TEM image of the sample grown at $T = 800^\circ$C with a stacking sequence of $\alpha$-Fe$_2$O$_3(2-10)/\epsilon$-Fe$_2$O$_3(004)/$STO(111). The TEM image reveals the existence of two layers with a somewhat blurred interface, suggesting a disorder at the interface. Because both layers contain the same elements, the density difference is negligible. However, the atomic arrangements in each layer differ from each other, as can be seen in Figure 3a. Moreover, the Fourier transforms of the real space image clearly distinguish the structures of the two layers, as shown in Figure 3b,c. These findings confirm that the upper layer is rhombohedral and the lower one is orthorhombic, in good agreement with the XRD results. Notably, the planar distances estimated from these Fourier transforms are consistent with the reported bulk values, indicating a strain relaxation. The strain is released possibly due to misfit dislocations and oxygen vacancies at the interface, which may be the origin of the blurred interface.
We can view the matching of the \( \alpha \)-Fe\(_2\)O\(_3\) and e-Fe\(_2\)O\(_3\) layers from a more microscopic viewpoint. Figure 4b shows the top and side views of the (004), plane in e-Fe\(_2\)O\(_3\). The 2D unit cell of this plane consists of four octahedrally coordinated Fe ions (Fe 1, 3, 4, and 5) and two tetrahedrally coordinated Fe ions (Fe 2 and 6). The FeO\(_6\) octahedrons are located on the same plane, whereas the FeO\(_4\) tetrahedrons are above this plane. All of these polyhedrons are connected by edge-sharing. On the other hand, the (2−10)\(_a\) plane, displayed in Figure 4a, is composed of two chains of the FeO\(_6\) octahedron dimers formed via face-sharing (Fe 1 and 2). The dimers and the intervening gaps between the dimers, which are aligned along the c-direction, constitute a chain. The second chain, which is displaced by one octahedral unit along the c-direction, is linked to the first one along the direction. Here, an interchain connection is made via corner-sharing (between Fe 1 and 3, and between Fe 1 and 4) and edge-sharing (between Fe 2 and 4). These atomic arrangements of the (004) and (2−10) planes provide a better hint about how the (004) and (2−10) planes are combined. For the case shown in Figure 2d, the tetrahedron-coordinated Fe ions on the (004)* plane can occupy the gaps in the (2−10)* plane, as schematically illustrated in Figure 4c. This is a structure that reduces the repulsive interaction between the Fe in the FeO\(_4\) tetrahedrons and the Fe in the lower (004)*. In contrast, in the case shown in Figure 2c, there is no match by which the FeO\(_4\) tetrahedrons in the (004)* plane regularly fill the gaps in the (2−10)* plane. In this combination, some of the FeO\(_4\) tetrahedrons are inevitably positioned at sites with no gap. This configuration increases the interaction energy because the distance between the Fe ions is too short. Therefore, it is unlikely that the (2−10)* plane will be stabilized following the configuration in Figure 2e. Even in the former interface structure, oxygen and iron ions are displaced and even detached from their equilibrium positions due to high levels of strain, dislocations, and symmetry mismatches. According to Kelm et al., e-Fe\(_2\)O\(_3\) and \( \alpha \)-Fe\(_2\)O\(_3\) structures indeed have a strong distortion in the arrangement of oxygen ions in the polyhedral coordination, which may cause oxygen ions to shift and become detached from the ideal sites, whereas the Fe ions move toward empty sites. As the oxygen vacancies can have an impact on the phase formation and orientations of the \( \alpha \)-Fe\(_2\)O\(_3\) layer, it is necessary to know the contents of oxygen vacancies in the sample. In the present study, the samples were synthesized at a relatively high oxygen pressure (10\(^{13}\) Torr) and postannealed at a high oxygen atmosphere (30 Torr). Thus, the investigated samples are thought to have relatively small concentrations of oxygen vacancies and to be almost stiochiometric. It will be interesting to investigate how the oxygen vacancies affect the phase formation and orientations of the \( \alpha \)-Fe\(_2\)O\(_3\) layer (Figure 5).

Figure 5. Temperature dependence of the renormalized surface energies \( \sigma^*(hkl) \) for \( n_\text{hkl} \). \( T_c \) denotes the critical temperature at which the \( \sigma^*(006) \) and \( \sigma^*(2−10) \) curves intersect.

II.III. Effects of Substrate Temperature and Surface Energy on the \( \alpha \)-Fe\(_2\)O\(_3\) Layer Orientation. The orientation of the \( \alpha \)-Fe\(_2\)O\(_3\) layer on the metastable e-Fe\(_2\)O\(_3\) is affected by different energy contributions, such as the surface, interface, and strain energies. Among these, the surface energy is believed to be dominant in the present case for the following reasons. First, the top layer is very thin and thus possesses a large surface-to-volume ratio. Second, as discussed above, the strain is almost entirely relaxed. Therefore, the contribution by
the strain energy must be minimal. Finally, as argued earlier, the surface energy values of both α-Fe₂O₃ (2−10)/ε-Fe₂O₃ (004) and α-Fe₂O₃ (006)/ε-Fe₂O₃ (004) are positive and thus destabilize these bilayer structures. In fact, it is the surface energy and the domain wall energy in ε-Fe₂O₃ that make these natural heterostructures stable.

To understand the change of growth orientation of the α-Fe₂O₃ layer with temperature quantitatively, we apply the surface-energy model.⁴₄,⁴₅ We consider a nucleus with the radius \( r \) and the center angle 2\( θ \), as shown in Figure 4d. The free-energy change accompanying the formation of such a nucleus is given by

\[
ΔF = 4πf(θ)\{σ(006)rr - \frac{1}{3}g_r r^3\}
\]

where \( f(θ) \) is an angular factor, \( σ(006) \) is the surface energy of the nucleus surface with the [006] orientation, and \( g_r \) is the bulk condensation energy. A thermodynamic equilibrium is achieved when \( ΔF/dr = 0 \). This condition gives rise to the critical nucleus size \( r = r* \) and activation barrier \( ΔF* \). With the value of \( ΔF* \), the growth probability \( p(hkl) \) of a cluster with the [hkl] orientation is expressed as

\[
p(hkl) = \exp\left[-\frac{1}{k_BT_s}\left(\frac{Kσ(hkl)^2}{g_r}\right)\right]
\]

where \( K \) is a function of \( θ \) and \( T_s \) is the substrate temperature. This expression implies that the (hkl) surface with the lowest surface energy tends to grow more readily.

The surface energy is approximately proportional to the number of dangling bonds.⁴₅⁻⁴⁷ Therefore, it is necessary to compare the number of dangling bonds per unit area to determine the lowest surface energy. Table 2 presents the number of dangling bonds and the surface energy levels of the (006)\(_α\) and (2−10)\(_α\) surfaces.⁴₅⁻⁴⁸ We define the bonding energy per bond as \( ε \) and assume it to be independent of the surface orientation, as the first approximation. Even if breaking a given bond may redistribute the charges in the remaining bonds, the energy related to this charge redistribution is lower than the energy spent on breaking the bond itself. This dangling bond model suggests that the surface energy of the (006)\(_α\) surface is lower than that of the (2−10)\(_α\) surface. This is in quite good agreement with the experimental observation at a lower substrate temperature. However, this simple model cannot explain the change of the layer orientation at an elevated substrate temperature.

Experimentally, the (2−10)\(_α\) surface was observed and found to be more stable at 800 °C. The change of the stable surface at a higher substrate temperature can be understood by considering the vibration of the surface atoms,⁴⁵ which becomes more enhanced with an increase in the substrate temperature. Within harmonic approximation, this vibration renormalizes the surface energy, which increases drastically with \( T_s \). The renormalized surface energy \( σ^*(hkl) \) is expressed by

\[
σ^*(hkl) = σ(hkl)\left[1 - \exp\left(\frac{α}{C_0} \exp\left(-\frac{n_i(hkl)ε}{k_BT_s}\right)\right)^{1/3}\right]
\]

where \( ε \) is the bonding energy per bond and \( C_0 \) is a force constant between the nearest-neighbor atoms. The constant \( α \) is a renormalization factor of the bonding energy caused by atomic vibration. The bonding energy is more renormalized by the vibration of the surface atoms and the \( α \) value is larger. \( n_i(hkl) \) represents the number of dangling bonds per atom on the (hkl) plane.

Using eq 3, we calculated the temperature dependences of the renormalized surface energy for the (006)\(_α\) and (2−10)\(_α\) layers as a function of \( k_BT_s/ε \). Figure 4 shows the calculated renormalized surface energy plotted by assuming \( \left(\frac{α}{C_0}\right) = 3.5 \).

Upon an increase in the temperature, the surface of the upper layer undergoes an orientation change from \( σ^*(006) \) to \( σ^*(2−10) \) at substrate temperature \( T_s \). The existence of this crossover temperature indicates that the \( α-Fe₂O₃ \) layer could be stabilized with a different surface orientation depending on the substrate temperature. We acquired finite \( T_s \) values when \( \left(\frac{α}{C_0}\right) > 0 \), suggesting that \( σ^*(006) \) and \( σ^*(2−10) \) always cross at a specific temperature only if the above condition is satisfied.

### III. CONCLUSIONS

In summary, we found that depending on the substrate temperatures, a polymorph \( α-Fe₂O₃ \) layer grown on a \( ε-Fe₂O₃ \) film changes its orientation. At 800 °C (700 °C), \( α-Fe₂O₃ \) grows along the (2−10)\(_α\) [(006)\(_α\)] directions on the \( ε-Fe₂O₃ \) (004)\(_α\) surface. In addition, \( α-Fe₂O₃ \) with the (006)\(_α\) orientation is stabilized due to the domain patterns with an in-plane rhombic shape in \( ε-Fe₂O₃ \), creating effective nucleation sites for \( α-Fe₂O₃ \). On the other hand, \( α-Fe₂O₃ \) with the (2−10)\(_α\) orientation forms a disordered interface with significant numbers of oxygen vacancies. The main factor to control the orientation of the \( α-Fe₂O₃ \) layer was the surface energy, which is proportional to the number of dangling bonds per area. At low temperatures, the surface energy of the (006)\(_α\) surface is lower because that surface has fewer dangling bonds. However, due to the vibration of the surface atoms, crossover in the surface energy occurs; the (2−10)\(_α\) surface energy becomes lower above the crossover temperature. The present results demonstrate that the orientation of a thin layer grown on another can be engineered, for instance by changing the substrate temperature, when the strain and interface energy do not dominate. As some important chemical reaction occur on the surface, the present study will provide important insights into the optimal ways to design catalysts, sensors, fuel cells, and other components involved in surface reactions.

### IV. EXPERIMENTAL SECTION

The \( ε-Fe₂O₃ \) films of different thicknesses were grown on the STO(111) substrates using a PLD technique. We investigated

| thin film orientation | number of dangling bonds per atom: \( n_i \) (hkl) | number of atoms contained in (hkl) plane per unit area | surface energy \( σ/ε \) |
|-----------------------|-----------------------------|---------------------------------|-----------------|
| \( α-Fe₂O₃ \)         | (006)                       | 2                               | \( \frac{4}{a^2\pi} \) |
|                       | (2−10)                      | 4                               | \( \frac{16}{a^2\pi} \) |

Table 2. Surface Energy Levels Depending on the Specific Orientation of the \( α-Fe₂O₃ \) Layer (\( ε \) is the Bonding Energy Per Bond and \( α \) and \( c \) are the Lattice Constants)
the effects of the laser energy density and substrate temperature, with focus on the two substrate temperatures of 700 and 800 °C. Although we also examined the film growth at 600 °C, the crystallinity of the samples grown at this temperature was inferior. The 248 nm wavelength from a Kr excimer laser was used at a repetition rate of 2 Hz. A sintered α-Fe2O3 pellet was used as a target, placed at a distance of 45 mm from the substrate. The oxygen pressure was maintained at 3.0 × 10−3 Torr during the sample growth process and was increased to 30 Torr at a substrate temperature of 600 °C for postannealing. The postannealing was carried out to minimize the oxygen vacancies in the films and to maintain their stoichiometry. The crystal structure of the films was investigated by X-ray diffraction (XRD) using a Cu Kα radiation in a Rigaku diffractometer (λ = 1.54 Å) and with synchrotron X-rays (λ = 1.10898 Å) at the 3A beamline of the Pohang Accelerator Laboratory (PAL). X-ray reflectivity (XRR) data were also collected to estimate the thickness, the growth rate, and the surface/interface roughness of the films. Transmission electron microscopy (TEM) measurements were taken to characterize the microstructures, the thickness of the thin film, and the structures on an atomic scale. To determine the α-Fe2O3 orientation, we utilized a 3A beamline of PAL. As the reflections from the minor α-Fe2O3 phase are at least 1 order of magnitude smaller than those from ε-Fe2O3, the α-Fe2O3 peaks were undetectable in an in-house diffractometer.

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**Notes**
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