First-Principles Studies of Er$_2$O$_3$(110) Heteroepitaxy on Si(001)

Yen-Wei Chen, Po-Liang Liu, and Chun-Hsiang Chan

Abstract—We present first-principles total-energy density functional calculations to study the heterojunction between a cubic Er$_2$O$_3$(110) film and Si(001) substrate. Using repeated free-surface terminated slabs, the relative stability of eight different models of the Er$_2$O$_3$(110)/Si(001) interface is examined as their interfacial energies and bonding analyses. The most favorable interface consists of the fourfold-coordinated Si with one Er-Si, one O-Si and two Si-Si bonds, with two Er-Si and two Si-Si bonds, and with two O-Si and two Si-Si bonds. Our findings show that the Si-Si and Er-O bond lengths immediately adjacent to the interface layer are slightly expanded and alternately released in compression and tension relative to their bulk values, respectively. Our findings agree with previously reported experimental results.

Index Terms—Er$_2$O$_3$, Si, interface, first-principles calculations.

I. INTRODUCTION

Rare earth oxides (REOs) thin films open up new doors in the development of important devices across a variety of special advantages such as the high dielectric constant, good thermodynamic stability, and wide band gap. The REOs thin films such as Y$_2$O$_3$, Pr$_2$O$_3$, La$_2$O$_3$, and Er$_2$O$_3$ films have gained great attentions and their applications have become a hot and active field in the world range wide [1], [2]. For example, R. L. Nigro et al. showed that Pr$_2$O$_3$ films grown epitaxially on Si(100) substrates were prepared via metal–organic chemical vapor deposition (MOCVD) and found to be comprised of a praseodymium silicate interfacial layer increased as the postannealing temperature rose [1]. The erbium (III) oxide (Er$_2$O$_3$) thin film is one of the most favored interface consists of the fourfold-coordinated Si with two Er-Si and two O-Si bonds in Er$_2$O$_3$ films grown on Si substrates [3]. Therefore, it is expected that the Er$_2$O$_3$ thin films could be epitaxially grown on Si substrates. S. Chen et al. demonstrated that Er$_2$O$_3$ thin films grown on Si (111) substrates show poorer thermal stability than those grown on Si(001) substrates [4]. Furthermore, R. Xu et al. reported that the epitaxial growth of Er$_2$O$_3$ films grown by molecular beam epitaxy (MBE) on Si (001) substrates are characterized by the relationship: Er$_2$O$_3$(110)/Si(001), Er$_2$O$_3$(110)/Si[110], and Er$_2$O$_3$-[110]/Si[110] [5]. However, no work has been done on theoretical mechanism for the heterojunction of the Er$_2$O$_3$(110)/Si(001). In this work, we not only present the optimized Er$_2$O$_3$(110)/Si(001) heterostructure but also provide the thermoelastic properties of the interface structure.

II. THEORETICAL APPROACH

We undertook a series of ab initio calculations to study the energetic and structural properties of various Er$_2$O$_3$(110)/Si(001) heterostructures. Our first-principles results were obtained using the Vienna Ab Initio Simulation Package (VASP) [6]-[8], which utilize Vanderbilt ultrasoft pseudopotentials (USPPs) to efficiently treat ion-electron interactions. This program employed USPPs derived from the projector augmented wave (PAW) method and the generalized gradient approximation (GGA) with the Perdew-Wang (PW91) exchange-correlation functional [9], [10]. The electronic configurations for the valence electrons are Er: 4f$^{12}$6s$^2$, O: 2s$^2$2p$^4$, and Si: 3s$^2$3p$^2$. The values of the chemical potentials of Er$_2$O$_3$ (µ$_{Er}$), Er (µ$_{Er}$), O (µ$_{O}$), and Si (µ$_{Si}$) are determined from the total energies per atom of bulk Er$_2$O$_3$ (space group: 206 Ia-3), bulk Er (space group: 194 P63/MMC), gas O$_2$ (space group: 123 P4/mmm), and bulk Si (space group: 227 Fd3-M), respectively. The adhesion energy ($E_{sub}^{Er_2O_3/Si}$) of the isolated Er$_2$O$_3$ to Si slabs is used to approximate the interface energy [11] given by

$$ E_{sub}^{Er_2O_3/Si} = n_{Er} \mu_{Er} + n_{O} \mu_{O} + n_{Si} \mu_{Si} + A \left( \sigma^{b,O}_E \mu_{Er} \right) + A \left( \sigma^{S}_S \mu_{Si} \right) + A \Gamma_m, $$

(1)

where $\Gamma_m$ denoted by model number $m$ is the Er$_2$O$_3$-Si interfacial energy and $A$ is the surface area The number of atoms of Er, O, and Si are given by $n_{Er}$, $n_{O}$, and $n_{Si}$, respectively. The chemical potentials of Er and O in Er$_2$O$_3$ are given by $\mu_{Er}$ and $\mu_{O}$ while this of Si is given by $\mu_{Si}$. The surface energy terms, $\sigma^{b,O}_E$ and $\sigma^{S}_S$, account for two equivalent surfaces in each slab for Er$_2$O$_3$ and Si through the equation

$$ \sigma = \left( E_{sub} - \sum n_i \mu_i \right) / (2A). $$

(2)

Here, $E_{sub}$ is the total energy of the particular slab; and $n_i$
and \( \mu_i \) are the number of atoms and the chemical potential of the \( i \)th constituent of the slab. The factor of 2 accounts for two equivalent surfaces in the particular slab.

To discuss quantitatively the interface energy between \( \text{Er}_2\text{O}_3 \) and Si slabs, we have employed repeated slab geometry with separated \( \text{Er}_2\text{O}_3 \) and Si slab with free surfaces. The total energy of isolated \( \text{Er}_2\text{O}_3 \) and Si slabs (with free surfaces) can be written as

\[
E_{\text{slab}}^{P_{\text{Er3}}O_{\text{Si}}} = n_{\text{Er}} \mu_{\text{Er}} + n_{\text{O}} \mu_{\text{O}} + 2 A \sigma_{\text{Er3}}^{P_{\text{O}}} (\mu_{\text{Er}}) \tag{3}
\]

and

\[
E_{\text{slab}}^{S_{\text{Si}}} = n_{\text{Si}} \mu_{\text{Si}} + 2 A \sigma_{\text{Si}}^{O} (\mu_{\text{Si}}). \tag{4}
\]

Subtracting Eqs (3) and (4) from Eq. (1) we obtain

\[
\Delta E_{\text{slab}} = E_{\text{slab}}^{P_{\text{Er3}}O_{\text{Si}}} - E_{\text{slab}}^{S_{\text{Si}}} - E_{\text{slab}}^{0}. \tag{5}
\]

\( \Delta E_{\text{slab}} \) approximates the work of adhesion of isolated \( \text{Er}_2\text{O}_3 \) and Si slabs (with free surfaces) and is related to the interface energy \( \Gamma_m \) through the equation

\[
\Gamma_m (\mu_{\text{Er}}, \mu_{\text{Si}}) = \Delta E_{\text{slab}} / A + \sigma_{\text{Er3}}^{P_{\text{O}}} (\mu_{\text{Er}}) + \sigma_{\text{Si}}^{O} (\mu_{\text{Si}}). \tag{6}
\]

With this approach, all atomic positions are allowed to relax fully in a supercell of fixed dimensions in each of the structural models corresponding to the joined and isolated slabs, yielding \( E_{\text{slab}}^{P_{\text{Er3}}O_{\text{Si}}}, E_{\text{slab}}^{S_{\text{Si}}}, \) and \( E_{\text{slab}}^{0} \) slabs, respectively.

Eight interface models with specific bonding arrangements between \( \text{Er}_2\text{O}_3 /\text{Si}(001), \text{Er}_2\text{O}_3 /\text{Si}[110], \) and \( \text{Er}_2\text{O}_3 /\text{Si}[110] \) were first constructed using bulk crystalline configurations as shown in Fig. 1. From Fig. 1, we have examined eight types of interface: In Model 1, the interface with the fourfold-coordinated Si consists of a Si atom bonded to one Er and O atom and two Si atoms, denoted here by the Er–Si–O bonding environment; in Models 2–5, 7, and 8, the interface with the fourfold-coordinated Si consists of the Er–Si–O bonding environment, and a Si atom bonded to two Er and Si atoms, denoted here by the O–Si–O bonding environment. In Model 6, the interface with the fourfold-coordinated Si consists of the Er–Si–O and Er–Si–Er bonding environments, and a Si atom bonded to two O and Si atoms, denoted here by the O–Si–O bonding environment. To further clarify the bonding environment described in Fig. 1 we also present atomic structures of the interface in Fig. 2(a)–Fig. 2(c), for the Er–Si–Er, O–Si–O, and Er–Si–O bonding environment, respectively. Table I lists the results of our bonding analyses for 8 models in Fig. 1. The stoichiometry of eight heterostructures was fixed at \( \text{Er}_2\text{O}_3\text{Si}_{48} \).

### Table I: Bonding Analyses of Models 1–8 Shown in Fig. 1 Each Model Has Six Bonds Dominated by Three Main Analogues, Which Are Referred to as the Er–Si–Er, O–Si–O, and Er–Si–O Bonding Environments

<table>
<thead>
<tr>
<th>Model</th>
<th>Model 2</th>
<th>Model 3</th>
<th>Model 4</th>
<th>Model 5</th>
<th>Model 6</th>
<th>Model 7</th>
<th>Model 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er-Si-Er</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>O-Si-O</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Er-Si-O</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

![Fig. 1](109.png)

Fig. 1. Ball and stick structural representations of the eight interface configuration models considered in this study. The atoms are represented by spheres: Er (green, large), O (red, small), and Si (yellow, medium).

![Fig. 2](109.png)

Fig. 2. Ball and stick structural representations of (a) Er–Si–Er, (b) O–Si–O, and (c) Er–Si–O bonding environments on \( \text{Er}_2\text{O}_3 /\text{Si} \) interfaces considered in this study. The dashed line is the interface. The atoms are represented by spheres: Er (green, large), O (red, small), and Si (yellow, medium).

## III. Results and Discussion

The structurally optimized interface models relaxed to their zero force positions are shown in Fig. 3. The \( \text{Er}_2\text{O}_3 /\text{Si} \) interface energy \( \Gamma_m \) as defined by Eq. (1) is a bilinear function of the chemical potentials \( \mu_{\text{Er}} \) and \( \mu_{\text{Si}} \). The calculated interface energies for Models 1–8 are \(-0.01, -0.11, -0.01, -0.01, -0.11, -0.11, -0.01, \) and \( 0.02 \).
Models 2, 5, and 6 have the lowest overall energy of ~0.11 eV/Å², with interface structures consisting of one Er–Si–Er and five Er–Si–O bonding environments for Models 2 and 5, and two Er–Si–Er, one O–Si–O, and three Er–Si–O bonding environments for Model 6 (see Table I). Models 1, 3, 4, and 7 are the second most favorable interface structures with interfacial energies of ~0.01 eV/Å². Model 8 is unstable or metastable, with $\Gamma_8 > 0$.

Further insight into the strain relaxation near the interfaces of Er₂O₃(110)/Si(001) heterostructures can be obtained by examining the deviations of the bond length adjacent to the interface from their bulk values as shown in Table II. We carry out a detailed comparison of the bond lengths obtained from the bond lengths adjacent to the interface and their bulk values calculated from optimized unit cells. It can be observed in Table II that Model 6 has the smallest bond strains. In Model 6, the Si–Si bond lengths adjacent to the interface are slightly expanded relative to their bulk values calculated from optimized unit cells ($\Delta d_{\text{bulk-Er}}^{\text{Si-Si}} = 1.30\%$ and $\Delta d^2_{\text{Si-Si}}/d_{\text{Si-Si}}^{\text{bulk}} = 0.90\%$), while the Er–O bond lengths adjacent to the other side of the interface are alternately released in compression and tension ($\Delta d_{\text{bulk-O}}^{\text{Er}}/d_{\text{Er-O}}^{\text{bulk}} = -1.53\%$ and $\Delta d_{\text{Er-O}}^{\text{bulk}}/d_{\text{Er-O}}^{\text{bulk}} = 6.23\%$). Our results for the bond length analyses show that Model 6 is the most favorable bonding arrangement within two Er–Si–Er, one O–Si–O, and three Er–Si–O bonding environments, suggesting a possible explanation in a largest bond relaxations due to the presence of the O–Si–O bonding environments (not shown in Models 1–5, 7, and 8). Our results in Fig. 3, Tables I, and II corroborate the X-ray diffraction (XRD) observations of Er₂O₃(110) layers grown by MBE on Si(001) substrates, indicating that the surface treatment of O-exposure on the upper Si templates to form the O-Si–O bonding environments, the O-rich conditions, can degrade the Er-silicide formation, form Er- and Si-oxide in the interface, and achieve good epitaxial growth of Er₂O₃(110) films on Si(001) [5].

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### TABLE II: PERCENT DEVIATIONS OF NEAR-INTERFACE BOND LENGTHS FROM THEIR CORRESPONDING BULK VALUES FOR MODELS 1–8

<table>
<thead>
<tr>
<th>Model</th>
<th>$\Delta d_{\text{Si-Si}}^{\text{Si-Si}}^{\text{bulk}}$</th>
<th>$\Delta d_{\text{Si-O}}^{\text{Si-O}}$</th>
<th>$\Delta d_{\text{Er-O}}^{\text{Er-O}}$</th>
<th>$\Delta d_{\text{Si-Er}}^{\text{Si-Er}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1</td>
<td>1.60%</td>
<td>1.03%</td>
<td>5.21%</td>
<td>7.76%</td>
</tr>
<tr>
<td>Model 2</td>
<td>1.45%</td>
<td>0.93%</td>
<td>9.86%</td>
<td>13.2%</td>
</tr>
<tr>
<td>Model 3</td>
<td>1.06%</td>
<td>0.82%</td>
<td>9.85%</td>
<td>9.99%</td>
</tr>
<tr>
<td>Model 4</td>
<td>1.03%</td>
<td>0.99%</td>
<td>11.79%</td>
<td>9.99%</td>
</tr>
<tr>
<td>Model 5</td>
<td>1.54%</td>
<td>1.01%</td>
<td>10.56%</td>
<td>9.91%</td>
</tr>
<tr>
<td>Model 6</td>
<td>1.30%</td>
<td>0.90%</td>
<td>-1.53%</td>
<td>6.23%</td>
</tr>
<tr>
<td>Model 7</td>
<td>1.31%</td>
<td>0.74%</td>
<td>2.26%</td>
<td>6.65%</td>
</tr>
<tr>
<td>Model 8</td>
<td>5.64%</td>
<td>3.89%</td>
<td>1.14%</td>
<td>3.01%</td>
</tr>
</tbody>
</table>

Fig. 3. Ball and stick structural representations of the eight optimized interface configuration models considered in this study. The atoms are represented by spheres: Er (green, large), O (red, small), and Si (yellow, medium).

The Superscripts “1” and “2” in the ratios $\Delta d/d$ denote bond lengths within the first and second layers on either side of the interface. $\Delta d_{\text{Si-Si}}^{\text{Si-Si}}/d_{\text{Si-Si}}^{\text{bulk}}$, $\Delta d_{\text{Si-O}}^{\text{Si-O}}$, $\Delta d_{\text{Er-O}}^{\text{Er-O}}$, and $\Delta d_{\text{Er-Si}}^{\text{Er-Si}}$ are the innermost and second Si–Si and Er–O bond lengths, respectively.
(Δd\text{Er}_2\text{O}_3/Δd\text{Er}_2\text{O}_\text{bulk} = 5.64\% and Δd\text{Er}_2\text{O}_3/Δd\text{Er}_2\text{O}_\text{bulk} = 3.89\%).

From our ab initio calculations, we have determined that the most favorable interfacial bonding geometry (Model 6, Fig. 2) contains two Er–Si–Er, one O–Si–O, and three Er–Si–O bonding environments. To compare the interfacial bonding arrangement of Models 1–8, Er\text{Si}_7\text{O}_8 and Er\text{Si}_2 were calculated to elucidate a mechanism for mismatch accommodation between the Er\text{O}_2\text{Si}(110) films and Si(001) templates. We obtained relaxed lattice constants \(a = 4.68\ Å, b = 5.56\ Å, \) and \(c = 10.79\ Å\) for the equilibrium structure of Er\text{Si}_7\text{O}_8 (space group: 14 \(P2\text{1}c\)), while \(a = b = 3.79\ Å\) and \(c = 4.08\ Å\) are determined from the equilibrium structure of Er\text{Si}_2 (space group: 191 \(P\bar{6}mm\)). Table III represents the ratio between the Si-O (Er-Si) bond lengths immediately adjacent to the interface in Models 1–8 and the Si-O (Er-Si) bond lengths of Er\text{Si}_7\text{O}_8 (Er\text{Si}_2). From Table III, it can be seen that Model 6 has the smallest bond strains, which show that the Si-O and Er-Si bond lengths immediately adjacent to the interface layer are expanded \((6.64)\%\) and compressed \((0.30)\%\) relative to those of Er\text{Si}_7\text{O}_8 and Er\text{Si}_2, respectively.

The smaller bond strains in Model 6 are consistent with its more favorable bonding arrangement. Apart from Model 6, the other five models, i.e., Models 2, 3, 4, 5, and 7, are similar except that the Si-O and Er-Si bond lengths exhibit a larger tensile and compressed strain (see Table III), respectively. In the case of Model 2, the Si-O and Er-Si bond lengths immediately adjacent to the interface layer are expanded \((8.04)\%\) and compressed \((6.92)\%\) relative to those of Er\text{Si}_7\text{O}_8 and Er\text{Si}_2, respectively. Similarly, in Model 5, the Si-O and Er-Si bond lengths immediately adjacent to the interface layer are expanded \((7.64)\%\) and compressed \((8.37)\%\) relative to those of Er\text{Si}_7\text{O}_8 and Er\text{Si}_2, respectively. In contrast to Models 2–7, Model 1 exhibits the largest bond strains, which show that the Si-O bond lengths immediately adjacent to the interface layer are expanded \((16.16)\%\) relative to those of Er\text{Si}_7\text{O}_8. In the bond length analysis for Models 2–5, 7, and 8 as seen in Table I and III, it can be clearly seen that Si-O bond strains increase with decreasing the number of interfacial Er–Si–O bonds and Er-Si bond strains undergo a transition from compressed to tensile strain with increasing the number of interfacial Er–Si–Er bonds. Our results indicate that interfacial Er–Si–O bonds are more desirable than Er–Si–Er that cause degradation of key thermoelastic properties at the film/substrate interfaces, in excellent agreement with recent experimental evidence of erbium oxide films grown by laser MBE on Si(001) surfaces[12].

### TABLE III: PERCENT DEVIATIONS OF NEAR-INTERFACE Si-O AND Er-Si BOND LENGTHS FROM THE CORRESPONDING BOND LENGTHS OF BULK Er\text{Si}_7\text{O}_8 AND Er\text{Si}_2, RESPECTIVELY

<table>
<thead>
<tr>
<th></th>
<th>Si-O</th>
<th>Er-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1</td>
<td>16.16%</td>
<td>-</td>
</tr>
<tr>
<td>Model 2</td>
<td>8.04%</td>
<td>-6.92%</td>
</tr>
<tr>
<td>Model 3</td>
<td>8.24%</td>
<td>-4.36%</td>
</tr>
<tr>
<td>Model 4</td>
<td>8.27%</td>
<td>-8.15%</td>
</tr>
<tr>
<td>Model 5</td>
<td>7.64%</td>
<td>-8.37%</td>
</tr>
<tr>
<td>Model 6</td>
<td>6.64%</td>
<td>-0.30%</td>
</tr>
<tr>
<td>Model 7</td>
<td>8.83%</td>
<td>-2.57%</td>
</tr>
<tr>
<td>Model 8</td>
<td>9.201%</td>
<td>2.22%</td>
</tr>
</tbody>
</table>

### IV. CONCLUSIONS

The interface energies of Er\text{O}_2\text{Si}(110) films grown epitaxially on the Si(001) substrates were studied by first-principles calculations. By studying the thermodynamic stability of eight interface structural models with a fixed Er\text{O}_2\text{Si}_{32} stoichiometry and comparing their interface energies, we found that Models 2, 5, and 6 have the lowest interface energy. By comparing the bond lengths adjacent to the Er\text{O}_2\text{Si}(110)/Si(001) interface, we found that Model 6 has the largest bond relaxations within two Er–Si–Er, one O–Si–O, and three Er–Si–O bonding environments. Our result agrees with recent MBE experiments on Er\text{O}_2\text{Si}(110) films epitaxially grown on Si(001) substrates.

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### REFERENCES


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