Comparison of interfaces, band alignments, and tunneling currents between crystalline and amorphous silica in Si/SiO$_2$/Si structures

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Abstract

Recently, to improve the performance of an integrated metal-oxide-semiconductor (MOS) device, an attempt has been made in the industry to replace the amorphous oxide with a crystalline oxide. However, various characteristics caused by the difference between amorphous and crystalline oxide in the MOS structure have not been systematically investigated. Therefore, we demonstrate the difference in atomic interface structures, electronic structures, and tunneling properties concerning varied oxide phases in a representative system, Si/SiO$_2$/Si structures, with sub-3 nm-thick silica from first-principles. We investigate two oxide phases of amorphous (a-) and crystalline (c-) SiO$_2$ with and without H passivation at the interface. Si/a-SiO$_2$ exhibits a smooth interface layer, whereas Si/c-SiO$_2$ exhibits an abrupt interface layer, resulting in the thicker interface layer of Si/a-SiO$_2$ than Si/c-SiO$_2$. Thus for a given total silica thickness, the adequate tunneling-blocking thickness, where all the Si atoms form four Si–O bonds, is thinner in a-SiO$_2$ than c-SiO$_2$, originating more tunneling current through a-SiO$_2$ than c-SiO$_2$. However, the effects of dangling bonds at Si/c-SiO$_2$ rather than Si/a-SiO$_2$ on tunneling currents are crucial, particularly in valence bands. Furthermore, when the dangling bonds are excluded by H atoms at Si/c-SiO$_2$, the tunneling current dramatically reduces, whereas the H-passivation effect on the tunneling blocking at Si/a-SiO$_2$ is insignificant. Our study contributes systematic knowledge regarding oxide phases and interfaces to promote for high performance of MOS devices.

1. Introduction

One of the recent strategies for realizing high-performance-MOS devices is using c-oxides instead of a-oxides owing to the high $k$. The relevant studies are those of Si/c-SiO$_2$ [1–3], Si/c-La$_3$O$_4$ [4, 5], Ge/c-Ge$_3$N$_4$ [6, 7], Ge/c-La$_3$O$_4$ [8] interfaces. Although many experimental and theoretical studies on interfaces between Si or Ge and a-oxide or c-oxide have been performed, systematic works investigating the general advantages or disadvantages regarding adopting a- or c-oxides in MOS structures are few. However, the fundamental characteristic comparison of varied oxide phases in MOS structures provides practical knowledge even to the currently developed high-performance devices such as the fin-field-effect transistor and the gate-all-around transistor. Therefore, intentional examination for the comparison is necessary for promoting the development of high-performance transistors.

The importance of the Si/SiO$_2$ interface for Si-based MOS applications has invoked many studies of structural [9], electronic [10], tunneling properties [11–17], and the interface is still the most used in academics and industry. Moreover, some experiments reported studies manufacturing high-quality a-SiO$_2$ [18, 19] and c-SiO$_2$ [1–3] on Si surfaces. In particular, several experiments have revealed the presence of c-SiO$_2$ clusters or metastable c-SiO$_2$ layers between a-SiO$_2$ and Si [1, 2]. Therefore, comparing a-SiO$_2$ and c-SiO$_2$ in Si/SiO$_2$/Si...
structures, from atomic structures through electronic structures up to tunneling properties, can provide insight into each oxide phase’s general strength and weakness in Si-based MOS structures.

Atomistic interface structures should be carefully treated in comparing \( a \)-SiO\(_2\) and c-SiO\(_2\). Thus, a theoretical approach describing the actual atomic structure effect on electronic structures, such as first-principle electronic structure calculations, can be a practical tool to examine the study. Meanwhile, the tunneling property through thin oxides in MOS structures is essential for realizing devices. In other words, the quantum-leakage-tunneling current through thin oxides is the critical indicator for the success of downsized MOS devices.

Historically, many semi-empirical investigations have been performed to predict the tunneling current in Si/SiO\(_2\)/poly-Si systems \([20, 21]\). However, the influence of 3D atomic interfaces on the tunneling current in Si/SiO\(_2\)/Si structures should be treated atomically using first-principle transport calculations. To the best of our knowledge, the previous first-principle tunneling studies \([11–17]\) have been conducted only for Si/c-SiO\(_2\)/Si structures, which may be due to the complexity of Si/\( a \)-SiO\(_2\) interfaces. This means that a systematic theoretical comparison of the structural, electronic, and tunneling properties of \( a \)-SiO\(_2\) and c-SiO\(_2\) in Si/SiO\(_2\)/Si structures is still not done.

This study compares interface structures, bandgap alignments, and quantum-leakage-tunneling currents of sub-3 nm-thick \( a \)-SiO\(_2\) and c-SiO\(_2\) in Si/SiO\(_2\)/Si structures with varying oxide thicknesses and interface configurations by employing the first-principle calculations. In Si/SiO\(_2\)/Si structures with and without H passivation, we find out the smooth interface for \( a \)-SiO\(_2\) and the abrupt interface for c-SiO\(_2\). The different interface types cause the different interface-layer thickness, having some Si-Si bondings and exhibiting the partially formed bandgap, to be in the order Si/\( a \)-SiO\(_2\) > Si/c-SiO\(_2\). Therefore, for a given total oxide thickness, the effective oxide-barrier region, consisting only of Si\(^{3+}\) with four Si–O bonds and exhibiting the fully developed bandgap, becomes in the order Si/\( a \)-SiO\(_2\) < Si/c-SiO\(_2\). Consequently, the tunneling currents leak more through Si/\( a \)-SiO\(_2\)/Si than Si/c-SiO\(_2\)/Si structures. However, the dangling-bond states at Si/c-SiO\(_2\) interfaces critically affect the leakage current, especially for holes. But, we show that passivating dangling bonds by H atoms at Si/c-SiO\(_2\) interfaces significantly lowers the tunneling current, whereas the H passivation at Si/\( a \)-SiO\(_2\) interfaces is ineffective.

2. Methods

The atomic and electronic structures were computed using the density functional theory (DFT; SIESTA code) \([22]\), and transport properties were obtained employing the first-principles scattering-state method (SCARLET code) \([23]\). We described the ionic potential using the norm-conserving pseudopotentials \([24]\). We also employed real-space grids with a cutoff energy of 200 Ry and pseudo-atomic orbitals such as triple and double \( \zeta \) polarizations for Si and O, respectively, for expanding the electronic wave function. To integrate the Brillouin-zone, we adopted a \( 4 \times 4 \times 1 \) \( k \)-grid, a \( 12 \times 12 \times 1 \) \( k \)-grid, and an \( 8 \times 8 \) \( k \)-grid for the structural relaxation, electronic structure, and tunneling spectra, respectively.

In comparison to the experimental results, table 1 presents predicted lattice constants of bulk Si and c-SiO\(_2\) and the mass density of bulk \( a \)-SiO\(_2\). The estimated Si lattice constant is nearly identical to the experimental value, and the calculated c-SiO\(_2\) lattice constant is within 4% of the experimentally observed value. The amorphous oxides, \( a \)-SiO\(_2\), were produced using first-principles molecular dynamics, which reproduced the measured mass density of 2.2 g cm\(^{-3}\) \([25]\). For the correction of bulk Si bandgap, the LDA + \( U \) technique was applied. For the 3\( p \) of Si, \( U = 3.00 \) eV and \( J = 0.00 \) eV were selected, resulting in a bandgap of 1.1 eV, consistent with the experimental measurements. The LDA + \( U \) technique for Si corrects the bandgap in Si to a reasonable extent, although it still underestimates the bandgap in SiO\(_2\). The oxide bandgap must be precisely estimated.

| Parameter                | Method | Si       | a-SiO\(_2\) | c-SiO\(_2\) |
|--------------------------|--------|----------|-------------|-------------|
| Lattice constant (nm)    |        |          |             |             |
| Other LDA                |        | 0.543    | 0.748       |             |
| Experiment               |        | 0.543 [26]| 0.749 [26]  |             |
| LDA                      |        | 2.2      | 1.9         |             |
| Experiment               |        | 2.2 [25] | 2.2 [27]    |             |
| Density (g cm\(^{-3}\)) |        | 0.5      | 5.2         | 6.0         |
| LDA                      |        | 5.2      |             | 6.0         |
| Experiment               |        | 1.12     |             | 8.7–9.4 [28]|

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Table 1. Lattice constants, mass densities, and bandgaps of the bulk Si, \( a \)-SiO\(_2\), and c-SiO\(_2\). Bandgaps are calculated using the LDA and LDA + \( U \) methods; \( U = 3 \) eV and \( J = 0 \) eV for the LDA + \( U \) method. All calculated data are compared to the available experimental data.
using a method other than ordinary DFT, such as the GW or HSE methods. Although underestimating the bandgap in oxides may overestimate the tunneling current passing through them, the current study is still important because it analyzes the impacts of different oxide phases, including varied oxide thicknesses and interfacial structures.

Two distinct heterostructures were created to explore the effects of nm-thick $a$-$\text{SiO}_2$ and $c$-$\text{SiO}_2$ oxides on the band alignment and quantum-leakage-tunneling property: Si(100)/$a$-$\text{SiO}_2$/Si(100) (SA structure) and

![Image of atomic structures and a diagram showing suboxide Si states and defects for SA and SC structures.](image)

**Figure 1.** Relaxed atomic structures of (a) $\text{Si}/a$-$\text{SiO}_2$/Si (SA) and (b) $\text{Si}/c$-$\text{SiO}_2$/Si (SC), and in the right panel, numbers of suboxide Si states and defects for (a) SA3 and (b) SC3 structures. The black, white, and red circles represent Si, O, and H, respectively. The interface layer (IL) and the dioxide area (DOX) are colored light and dark gray, respectively. The structures having the IL with H-passivation (HP IL) are shown. In (a) and (b), SA1, SA2, and SA3 structures and SC1, SC2, and SC3 structures are depicted from left to right, respectively.
Si(100)/c-SiO₂/Si(100) (SC structure). For building the SA and SC heterostructures, a silica slab was placed between two Si(100) slabs, and a 0.1 nm initial separation distance between Si and silica was chosen. The SA and SC structures have a $\sqrt{2} a_{Si} \times \sqrt{2} a_{Si}$ supercell as its in-plane dimension. The lowest energy structure was produced by relaxing the supercell size along the $z$-axis, the atoms inside silica, and two Si layers near the interface, according to our earlier study on Ge/a-GeO₂/Ge structures [29]. Consequently, this relaxation strategy is employed to generate all the systems in this study until all atomic forces are less than 0.05 eV Å⁻¹.

### 3. Results and discussion

The following aspects of heterostructures with a-SiO₂ and c-SiO₂ were compared: (i) interface atomic structures; (ii) electronic structures, i.e., bandgap and band offsets; and (iii) electron and hole quantum-leakage-tunneling properties via thin oxides. In addition, we considered different oxide thicknesses and two interfacial structures: interface layer (IL) having dangling bonds (DB IL) and IL with H passivations (HP IL). Figure 1 shows the HP IL structures.

#### 3.1. Structural properties

Figure 1 depicts relaxed SA and SC structures composed of a-SiO₂ and c-SiO₂ sandwiched between two Si(100) slabs, with Si, O, and H atoms represented by black, white, and red circles, respectively. The $\beta$-cristobalite structure for c-SiO₂ is selected to avoid a lattice mismatch. Three atomic models with different silica thicknesses are studied for each SA and SC structure, labeled ‘1’, ‘2’, and ‘3’ in the illustration from left to right. The dioxide area (DOX) and the interface layer (IL) constitute the total oxide region (TOX). DOX is a dark-gray-colored area composed entirely of the Si$^{4+}$ state (four Si–O bonds). IL, conversely, is a light gray-shaded region composed primarily of Si suboxide states with a few Si$^{4+}$ states, meaning the presence of Si–Si bondings. Si$^{1+}$, Si$^{2+}$, and Si$^{3+}$ are the suboxide states with one, two, and three Si–O bondings. The numbers of suboxide Si states and defects for SA3 and SC3 structures are drawn in the right panels of figures 1(a) and (b), respectively. The figures show that while the SA structure has smooth interfaces composed of various suboxide states from Si$^{1+}$ to Si$^{4+}$ and defects, the SC structure features abrupt interfaces composed of Si$^{3+}$ and defects.

Table 2 shows the thickness comparison between SA and SC structures. The total oxide thickness, $d_{TOX}$, equals the sum of thicknesses of DOX ($d_{DOX}$) and two ILs ($d_{IL1}$ and $d_{IL2}$). The average IL thickness, $d_{IL}$, is

![Figure 2: Atomic structures (left panels) and bandgap alignments (right panels) in (a) SA3 and (b) SC2 structures with HP IL, and bandgap alignments (upper panels) and tunneling spectra per unit area $T(E)/A$ (lower panels) of (c–e) SA and (f–h) SC structures. In the band alignment in (a), the magnitudes of band offsets (VBO and CBO), band-offset widths (W_{VBO} and W_{CBO}), effective oxide bandgap ($E_{ox}$), VBM of Si$^{4+}$, and CBM of Si$^{4+}$ are indicated. (c–h) Correspond to SA1, SA2, SA3, SC1, SC2, and SC3 structures, respectively. In (c–h), the band alignments are obtained using the structures with DB IL. In (c–h), the black dashed lines in the upper panels represent $E_{ox}^{n}$, and the red (blue) lines indicate DB IL (HP IL) in the lower panels.](image-url)
Table 2. Atomic structures of Si/a-SiO$_2$/Si (SA1–SA3) and Si/c-SiO$_2$/Si (SC1–SC3) with different oxide thicknesses. Supercell information, total oxide (TOX), dioxide (DOX), interface-layer (IL) thicknesses, and numbers of suboxide Si states, defects, and H atoms are given.

| Structure | SA1 | SA2 | SA3 | SC1 | SC2 | SC3 |
|-----------|-----|-----|-----|-----|-----|-----|
| Supercell size // z (nm) | 5.021 | 5.334 | 5.765 | 5.053 | 5.757 | 6.447 |
| Number of Si/O | 138/12 | 141/19 | 148/32 | 138/16 | 146/32 | 154/48 |
| $A$ (nm$^2$) | 0.769 $\times$ 0.769 ($\sqrt{2}$ $a_{\text{Si}}$ $\times$ $\sqrt{2}$ $a_{\text{Si}}$) |
| $d_{\text{DOX}}$ (nm) | 0.736 | 1.043 | 1.495 | 0.725 | 1.465 | 2.124 |
| $d_{\text{DOX}}$ (nm) | 0.080 | 0.489 | 0.924 | 0.350 | 1.038 | 1.756 |
| $d_{\text{IL}}$ (nm) | 0.328 | 0.277 | 0.286 | 0.188 | 0.214 | 0.184 |
| Average $d_{\text{IL}}$ (nm) | 0.297 | 0.200 |
| Si$^{2+}$ | 2 | 4 | 4 | 0 | 0 | 0 |
| Si$^{3+}$ | 2 | 3 | 3 | 4 | 4 | 4 |
| Si$^{4+}$ | 2 | 2 | 1 | 0 | 0 | 0 |
| Si$^{4+}$ | 2 | 3 | 1 | 2 | 2 |
| Defect | 4 | 2 | 5 | 8 | 8 | 8 |
| H | 2 | 1 | 4 | 8 | 8 | 8 |

Table 3. Calculated $E_g^{\infty}$, VBO, CBO, $W_{\text{VBO}}$, and $W_{\text{CBO}}$.

| Structure | SA1 | SA2 | SA3 | SC1 | SC2 | SC3 |
|-----------|-----|-----|-----|-----|-----|-----|
| $E_g^{\infty}$ (eV) | 2.35 | 4.99 | 5.97 | 5.40 | 6.12 | 6.00 |
| VBO (eV) | 0.85 | 2.37 | 2.47 | 2.39 | 2.58 | 2.53 |
| CBO (eV) | 0.40 | 1.52 | 2.40 | 1.91 | 2.44 | 2.37 |
| $W_{\text{VBO}}$ (nm) | 0.00 | 0.44 | 1.05 | 0.44 | 1.17 | 1.69 |
| $W_{\text{CBO}}$ (nm) | 0.00 | 0.33 | 0.59 | 0.00 | 0.96 | 1.39 |

$d_{\text{IL}} = (d_{\text{IL,1}} + d_{\text{IL,2}})/2$. The $d_{\text{TOX}}$ values for all the structures vary from 0.725 to 2.124 nm, and the $d_{\text{DOX}}$ values extend from 0.080 to 1.756 nm. The average $d_{\text{IL}}$ values for SA and SC structures are 0.297 and 0.195 nm, respectively. The SC structure’s abrupt interface results in a narrow IL, while the smooth interface of the SA structure results in a broad IL. Consequently, for a given $d_{\text{TOX}}$, $d_{\text{DOX}}$ is thinner in SA structures than SC structures due to the thicker $d_{\text{IL}}$ in SA structures. The $d_{\text{IL}}$ values for SA and SC structures are significant compared to the $d_{\text{TOX}}$ and $d_{\text{DOX}}$ values in the sub-3 nm silica thickness range. The typical total IL thickness $(d_{\text{IL,1}} + d_{\text{IL,2}})$ values for SA and SC structures are approximately 0.594 nm and 0.390 nm, respectively, thicker than the 0.357 nm unit-cell dimension in bulk Si. The fact that the $d_{\text{IL}}$ value is significant compared to the $d_{\text{TOX}}$ and $d_{\text{DOX}}$ values prompts us to study the bandgap change at IL.

Table 2 also compares SA and SC structures’ defect and H-passivation numbers. When the maximum Si-Si and Si–O bond lengths are set to 2.81 Å and 2.29 Å, respectively, the defect number is counted by 4 — (Si–Si bond number) — (Si–Si bond number). The defects result in dangling bonds. In SA structures, the defect number in DB IL is not equal to the H-passivation number in corresponding HP IL because H atoms that cause gap states were eliminated, meaning the inclusion of only the efficiently passivating H atoms. In addition, the randomness of bondings at the Si/a-SiO$_2$ seems to cause the ineffectiveness of H passivation. On the other hand, the H atoms successfully passivated all the dangling bonds in SC structures. Therefore, the H-passivation number is equivalent to the defect number.

3.2. Bandgap alignment

The bandgap evolution along the z-axis of SA3 and SC2 structures with HP IL is shown in figures 2(a) and (b), respectively. Thus the defect effect on the bandgap evolution is not displayed. The bandgap evolution is depicted using the Si atom-projected density of states (PDOS(z, $E$)) computed by the LDA + U method. In other words, the PDOS value of 0.03 states eV$^{-1}$ determines the local VBM(z, $E$) and CBM(z, $E$) values. In reality, the wavefunction tails tunneled from the Si regions generate a low density of states inside the oxide barrier.

Consequently, $E_g^{\infty}$ and band-offset values in each structure are simply estimates. VBO + CBO + $E_g^{\infty}$ (1.1 eV) was employed to determine $E_g^{\infty}$. The VBO widths ($W_{\text{VBO}}$) and CBO widths ($W_{\text{CBO}}$), as well as the magnitude of VBO and CBO, are defined in figure 2(a).

Figures 2(a) and (b) show a progressive increase in band offsets from IL to DOX. The band offsets have their maximum values within DOX, meaning that DOX, not TOX, is the effective oxide-potential barrier. The SA1 structure in figure 2(c) illustrates this since $E_g^{\infty}$ scarcely develops because of the nearly negligible $d_{\text{DOX}}$ despite that $d_{\text{TOX}}$ is 0.74 nm. In this structure, TOX is almost identical to IL. Therefore, the magnitude of band offsets is
defined as the maximum values in the oxide center. Moreover, since VBO and CBO gradually increase from IL to DOX, the thickest band-offset widths are observed around the valence-band maximum (VBM) of the Si area (VBM\textsuperscript{dox}) and the conduction-band minimum (CBM) of the Si region (CBM\textsuperscript{dox}). Thus, W\textsubscript{VBO} and W\textsubscript{CBO} are measured at 1.0 eV below VBM\textsuperscript{dox} and above CBM\textsuperscript{dox}, respectively, for simplicity.

The upper panels of figures 2c–e and f–h compare the bandgap evolution for SA and SC structures regarding varied oxide thicknesses, respectively. The similarity in both structures is that the silica bandgap grows from a less developed state to a fully developed state as the silica thickness increases in the ultra-thin silica thickness range of less than 3 nm. Table 3 quantitatively compares the E\textsubscript{g}, VBO, CBO, W\textsubscript{VBO}, and W\textsubscript{CBO} Values between SA and SC structures. Our results show that SA structures with the smooth interface result in smaller bandgaps and offsets than SC structures with the abrupt interface for a given d\textsubscript{DOX}. For example, for a similar d\textsubscript{DOX} of 0.7 nm in SA1 and SC1 structures, E\textsubscript{g}, VBO, CBO, and W\textsubscript{VBO} in the SA1 structure are smaller than those in the SC1 structure, resulting from the thinner d\textsubscript{DOX} and thicker d\textsubscript{IL} in the SA1 structure (upper panels in figures 2c and f). Similarly, for d\textsubscript{DOX} of 1.4 nm in SA3 and SC2 structures, the thinner d\textsubscript{DOX} and thicker d\textsubscript{IL} in the SA3 structure than the SC2 structure result in smaller bandgap and offsets in the SA3 structure (upper panels in figures 2e and g).

The calculated bandgap tendencies in all SA and SC structures are presented as a larger VBO than CBO and a thicker W\textsubscript{VBO} than W\textsubscript{CBO}. The larger VBO than CBO appears to be linked to the thicker W\textsubscript{VBO} than W\textsubscript{CBO}. There is also a tendency for VBO to be larger than CBO in the experiments. CBO for the Si/α-SiO\textsubscript{2} surfaces is reported to be 3.1 eV for d\textsubscript{SiO\textsubscript{2}} ≥ 1.0 nm [30] and 4.49 eV for d\textsubscript{SiO\textsubscript{2}} ≥ 1.5 nm [31]. The computed CBO and VBO values for the SA3 structure with d\textsubscript{DOX} = 0.924 nm are 2.40 and 2.47 eV, respectively. In the SA3 structure, the estimated band offsets are significantly smaller than the experimental values. Thus, our predicted tunneling results for SA and SC structures below may be higher than the actual values.

An experimental study [32] showed that the smallest thickness where the silica prevents tunneling in Si/α-SiO\textsubscript{2}/Si structures is 0.7 nm, which is in reasonable agreement with those in SA and SC structures in our work. When d\textsubscript{DOX} is below 0.7 nm, E\textsubscript{g}, VBO, CBO, W\textsubscript{VBO}, and W\textsubscript{CBO} steadily increase with the increasing d\textsubscript{DOX}, as shown in figure 2. When d\textsubscript{DOX} is thicker than 0.7 nm, only W\textsubscript{VBO} and W\textsubscript{CBO} increase with the growing d\textsubscript{DOX}, while the fully formed E\textsubscript{g}, VBO, and CBO remain unchanged. For example, since E\textsubscript{g}, VBO, and CBO in the SC2 structure with d\textsubscript{DOX} of 1.0 nm are already entirely created, the SC3 system with d\textsubscript{DOX} of 1.8 nm merely increases W\textsubscript{VBO} and W\textsubscript{CBO}.

### 3.3. Quantum-leakage-tunneling properties

First-principles transport simulations employing the first-principles scattering-state approach are utilized to examine the quantum-leakage-tunneling features of charge carriers in SA and SC structures. The first-principles scattering-state method [23] is a companion to the non-equilibrium Green’s function (NEGF) method, and it provides a foundation for studying the electrical transport features of infinite systems with no periodic boundary constraints, such as nanometer-scale quantum structures. The z-length where the semi-bulk Si areas are removed at both ends and the numbers of Si and O atoms in these areas are summarized in table 4. The tunneling spectra per area, T(E)/A, are shown in lower panels of figures 2c–e and f–h. Here, A is the cross-sectional area of the supercell. The average tunneling probabilities, T(E), at the charge-carrier energy, E, are obtained by summing T\textsubscript{c}(E, k\textsubscript{f}) over all the bands, n, and averaging them over the wave vector parallel to the interface, k\textsubscript{f}. The red color in the lower panels represents DB II, whereas the blue color represents HP II. The tunneling spectra values are zero since there is no propagating state inside the Si bulk bandgap.
The lower panels of figures 2(c)–(h) compare the tunneling spectra between SA and SC structures. The similarity of tunneling spectra between SA and SC structures is the tunneling-spectra asymmetry, which means the more reduction of tunneling spectra in valence bands rather than conduction bands. The tunneling-spectra asymmetry is induced from the thicker \( W_{VBO} \) than \( W_{CBO} \) and the bigger VBO than CBO in valence bands than conduction bands. Another similarity is the tunneling-spectra change with the increase in \( d_{DOX} \). As \( d_{DOX} \) increases, \( W_{VBO} \), \( W_{CBO} \), VBO, and CBO increase, and, consequently, the energy range of decreased tunneling spectra becomes wider up to the fully developed \( E_g^{ox} \), and the reduction degree increases.

On the other hand, the tunneling-spectra difference between SA and SC structures with DB IL is prominent in valence bands, especially near VBMSi. Tunneling spectra of SC structures with DB IL have sharp peaks near VBMSi, while those of SA structures with DB IL have no peaks. The sharp peaks of SC structures with DB IL come from the dangling-bond states near VBMSi, caused by the defects at Si/c-SiO\(_2\) interfaces. The sharp peaks in SC structures with DB IL are removed effectively by passivating dangling bonds by H atoms, as shown in figures 2(f)–(h). On the contrary, tunneling spectra for DB IL and HP IL in SA structures are similar, as illustrated in figures 2(c)–(e). The similarity implies that the H passivation at the Si/a-SiO\(_2\)/Si interface has a negligible effect on the tunneling spectra. The irregular bonding at the interface is most probably responsible for the ineffectiveness. Finally, when the interface states are removed by H atoms in SA and SC structures with HP IL, the lowest tunneling-spectra characteristic is observed around VBM\(_{Si}\) and CBM\(_{Si}\), caused by the thickest oxide-potential-barrier width near VBM\(_{Si}\) and CBM\(_{Si}\).

The quantum-leakage-tunneling-current density per unit area, \( J_{QLT} \), is the leakage-current density caused by the quantum-mechanically tunneling wave functions passing through the ultrathin oxide barrier, even without the externally applied voltage. \( J_{QLT} \) for electrons, \( J_e \), and holes, \( J_h \), can be estimated using tunneling spectra.
assuming electron \( n_e \) and hole concentrations \( n_h \) [29]. Since tunneling spectra are integrated mostly along the Si band-edge boundaries to estimate \( J_{\text{QLT}} \), tunneling spectra near VBM\(^9\) or CBM\(^8\) are the most essential. Since \( J_e \) and \( J_h \) are related to the quantum tunneling from the channel to the gate in modern nMOS or pMOS devices, \( n_e \) or \( n_h \) can be considered the semiconductor channel-doping concentration \( 10^{18} \) or \( 10^{20} \text{ cm}^{-3} \). Using the bulk Si density of states (DOS\(n_0\)), the theoretical local chemical potentials, \( \mu_c \), corresponding to \( n_e \) and \( n_h \) are calculated. The \( \mu_c \) is located at 0.010 eV above the CBM for \( n_e = 10^{18} \text{ cm}^{-3} \) (at 0.199 eV above CBM for \( n_e = 10^{20} \text{ cm}^{-3} \)) and at 0.022 eV above the VBM for \( n_h = 10^{18} \text{ cm}^{-3} \) (at 0.163 eV below the VBM for \( n_h = 10^{20} \text{ cm}^{-3} \)) in DOS\(n_0\).

For \( n_e = 10^{18} \text{ cm}^{-3} \), figures 3(a) and (b) show the predicted log-scale \( J_e \) and \( J_h \) with respect to \( d_{\text{DOX}} \) for SA and SC structures, respectively. DB IL is shown by the red color, whereas the blue color indicates HP IL. Our experimental electron tunneling current densities of Si\(n\) structures were summarized in table 4 in terms of \( J_e \) and \( J_h \). H-atoms significantly lower than that of SC structures with DB IL, owing to the large reduction in the peak intensities near VBM\(^9\) in the tunneling spectra, as observed in the lower panels of figures 2(f)–(h). H-atoms’ effective passivation is responsible for this decrease. Consequently, Our results show that the c-SiO\(_2\)/Si interface without H-passivation causes higher tunneling currents than the a-SiO\(_2\)/Si interface, especially for holes, due to the dangling bond states near the valance band top, resulting from the defects. However, once the dangling-bond states at the c-SiO\(_2\)/Si interface are passivated by H-atoms, the c-SiO\(_2\)/Si interface with H-passivation results in lower tunneling currents than the a-SiO\(_2\)/Si interface.

Furthermore, our results eventually show the effects of smooth or abrupt interface types on tunneling currents. As a reminder, \( d_{\text{DOX}} \) in SA structures with the smooth interface was thinner than that in SC structures with the abrupt interface for a given \( d_{\text{TOX}} \), resulting in the smaller bandgaps and offsets of SA structures than SC structures. In comparing \( J_{\text{QLT}} \) of table 4 between SA1 and SC1 structures having HP IL, despite a similar \( J_{\text{QLT}} \), the former value for SA1 structure is larger than that in the SC1 structure, resulting from the thinner \( d_{\text{DOX}} \) and the smaller bandgap and offsets in the SA1 structure. Similarly, despite a similar \( d_{\text{TOX}} \) of 1.4 nm, the thinner \( d_{\text{DOX}} \) and the smaller bandgap and offsets in the SA3 structure with HP IL than the SC2 structure with HP IL results in the bigger \( J_{\text{QLT}} \) in the SA3 structure with HP IL.

Compared with experiments, the experimental electron tunneling current density of the Si\(a\)/a-SiO\(_2\)/Si structures was only found. The experimental electron tunneling current densities of Si\(a\)/a-SiO\(_2\)/Si structures with the interface passivated by H-atoms at zero gate voltage are \( 7.2 \times 10^{-6} \text{ (A cm}^{-2}\)) for \( d_{\text{TOX,exp}} \) of 1.2 nm and \( 6.0 \times 10^{-6} \text{ (A cm}^{-2}\)) for \( d_{\text{TOX,exp}} \) of 2.0 nm [33]. The Si’s experimental electron doping concentration is \( 5 \times 10^{15} \text{ (cm}^{-2}\)) [33]. When \( d_{\text{TOX,exp}} \) is assumed to be comparable with \( d_{\text{DOX,exp}} \), the former value for \( d_{\text{TOX,exp}} \) of 1.2 nm is smaller than our calculated \( J_e \) for the SC2 structure with \( d_{\text{DOX,exp}} \) of 1.0 nm in table 4. Similarly, the latter value for \( d_{\text{TOX,exp}} \) of 2.0 nm is smaller than our calculated \( J_e \) for the SC3 structure with \( d_{\text{DOX,exp}} \) of 1.8 nm in table 4. The smaller theoretical \( J_e \) than experiments may originate from the smaller experimental Si doping concentration and the smaller theoretical \( d_{\text{DOX,exp}} \).

When comparing \( J_{\text{QLT}} \), tunneling spectra, particularly in all SC structures with HP IL, including the SA3 structure, it is clear that \( J_e \) is always greater than \( J_h \), owing to the thicker \( W_{\text{VBO}} \) than \( W_{\text{CBO}} \) and the larger VBO than CBO. However, the trend of \( J_e > J_h \) is not clearly observed in the remaining structures due to interface states, despite the tendency of the band offsets of VBO > CBO remains unchanged. For example, the calculated \( J_e \) < \( J_h \) in SC structures with DB IL is caused by the sharp tunneling-spectra peaks near VBM\(^9\), induced by the interface-dangling-bond states. This finding also highlights the importance of the interface state in determining \( J_{\text{QLT}} \).

### 4. Conclusion

We systematically compared interface structures, bandgap alignments, and tunneling properties between Si\(a\)/a-SiO\(_2\)/Si and Si\(c\)/c-SiO\(_2\)/Si structures with sub-3 nm-thick silica considering different oxide thicknesses and two interface types with and without H passivation. Our findings revealed that the smooth Si\(a\)/SiO\(_2\) interface and abrupt Si\(c\)/SiO\(_2\) interface determine the thicker interface-layer thickness of Si\(a\)/SiO\(_2\) than Si\(c\)/SiO\(_2\), resulting in the thinner oxide-potential-barrier thickness of Si\(a\)/SiO\(_2\)/Si than Si\(c\)/SiO\(_2\)/Si for a given total silica thickness. Thus, c-SiO\(_2\) can play a tunneling-blocking role more effectively than a-SiO\(_2\) in MOS structures, inducing lower leakage-tunneling currents through c-SiO\(_2\) than a-SiO\(_2\). However, the defect effect at the Si\(c\)/SiO\(_2\) interface on tunneling currents is more significant than the Si\(a\)/SiO\(_2\) interface, particularly near Si VBM. Fortunately, the defect effect at the Si\(c\)/SiO\(_2\) interface on the tunneling current can be removed effectively by H-passivation. In contrast, H-passivation at the Si\(a\)/SiO\(_2\) interface is ineffective in lowering the
tunneling current. Our research provides fundamental and systematic knowledge for interface engineering in MOS devices.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Author contributions

E K performed and analyzed all the calculations. J H C arranged and supervised all the calculations and took charge of the manuscript preparation. All the authors discussed and reviewed the manuscript. All the authors contributed to the writing of the manuscript.

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