

# Impact of oxidation-induced strain on microscopic processes related to oxidation reaction at the SiO<sub>2</sub>/Si(100) interface

Toru Akiyama\* and Tomonori Ito

*Department of Physics Engineering, Mie University, 1577 Kurima-Machiya, Tsu 514-8507, Japan*

Hiroyuki Kageshima and Masashi Uematsu

*NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato-Wakamiya, Atsugi 243-0198, Japan*

(Received 13 April 2007; revised manuscript received 10 February 2008; published 28 March 2008)

The reaction of oxygen molecules at the SiO<sub>2</sub>/Si(100) interface in the presence of oxidation-induced strain is investigated using total-energy electronic-structure calculations within the density-functional theory. It is found that the calculated effective barrier height for the O<sub>2</sub> reaction at the interface with strained oxide layers less than 2 monolayer (ML) thick is almost identical to that at the strain-released interface. On the other hand, it increases significantly when the strained oxide layer reaches 2 ML. This is because the energy of the O<sub>2</sub> near the strained oxide layer in the 2 ML oxidized interface is higher than that in the strain-released region. Given our result that the oxidation-induced strain should become large enough to prevent the oxidation reaction and the knowledge that oxide formation with smooth interface is continuous, we conclude that there must be some strain-release mechanism that is present during silicon thermal oxidation.

DOI: [10.1103/PhysRevB.77.115356](https://doi.org/10.1103/PhysRevB.77.115356)

PACS number(s): 68.43.Bc, 81.65.Mq, 81.15.Aa

## I. INTRODUCTION

The control of thermal oxide formation on silicon is attracting great interest due to the recent trend toward the miniaturization of silicon devices. This demand is still valid even with the recent development of high-*k* dielectrics using metal gate with strained Si channel for metal-oxide-semiconductor field-effect transistors as a replacement for conventional Si-based device structures. Satisfying this demand requires a detailed understanding of the atomic-scale processes that occur during silicon thermal oxidation, and so many experimental and theoretical investigations have been carried out.<sup>1</sup>

As evidenced by the classical theory proposed by Deal and Grove,<sup>2</sup> it is widely accepted that silicon thermal oxidation consists of the diffusion of oxidant through the SiO<sub>2</sub> already formed and its reaction at the SiO<sub>2</sub>/Si interface. The rate equations corresponding to the diffusion and reaction processes are formulated using diffusion and reaction constants whose activation energies are  $\sim 1.2$  and  $\sim 2.0$  eV, respectively.<sup>2,3</sup> They have been successful in predicting oxide growth under various oxidation conditions. However, they do not provide any atomic-scale descriptions at all.

Regarding the reaction process, first-principles calculations have revealed that the reaction barrier height to the insertion of O<sub>2</sub> into the Si-Si bonds of the Si substrate at the SiO<sub>2</sub>/Si interface is negligible<sup>4-7</sup> (0.2 eV) compared to the activation energy of the reaction constant in the Deal-Grove model. The calculated results thus imply that the activation energy used in the Deal-Grove model does not correspond to the O<sub>2</sub> insertion process. We note that the discrepancy between the calculated barrier height and the activation energy can be interpreted as indicating the importance of the structural transition layers at the interface<sup>8,9</sup> and the amorphous nature of the oxide.<sup>10,11</sup> Calculations of O<sub>2</sub> diffusion in dense SiO<sub>2</sub>, which simulated the structural transition layers, clarified that the potential energy landscape for O<sub>2</sub> diffusion is shifted significantly toward higher energies, suggesting that

the oxidation reaction process is completely dominated by diffusion phenomena.<sup>12-14</sup> A recent theoretical study,<sup>15</sup> which assumed that the diffusivity of the oxidant is decreased by the strain localized to the vicinity of the SiO<sub>2</sub>/Si interface, offered a new rate equation for the thermal oxidation of silicon; it yielded strained oxide layer thicknesses that agreed well with those estimated from x-ray reflectivity measurements.<sup>8</sup> By considering the energy penalty to transfer an oxygen molecule from a big void in amorphous bulk SiO<sub>2</sub> to the interfacial layer (1.1–1.65 eV), recent first-principles calculations<sup>7</sup> have clarified that the calculated effective barrier height for the O<sub>2</sub> reaction processes (1.8–2.05 eV) is reasonably consistent with the activation energy of the reaction constant in the Deal-Grove model. Furthermore, an alternative diffusion and reaction scenario that considers void-like regions in amorphous SiO<sub>2</sub>, in which the enthalpy of dissolution for O<sub>2</sub> incorporation is negligible,<sup>16</sup> has been proposed.<sup>17,18</sup> These calculated results inspired us to investigate the microscopic processes of the O<sub>2</sub> reaction at the interface in the presence of oxidation-induced strain; because the volume per Si atom in SiO<sub>2</sub> is 2.25 times larger than that in bulk Si, inserting oxygen into Si-Si bonds causes the formation of an oxide with large strain. Indeed, the formation of a high-density cristobalitelike oxide layer with  $\sim 2$  monolayer (ML) thickness has been observed using high-resolution transmission electron microscopy (HRTEM).<sup>19</sup> One can expect that microscopic processes such as the diffusion and reaction of O<sub>2</sub> molecules could be affected by such dense oxide regions.

In this paper, we describe first-principles total-energy calculations that clarify the atomic processes of the O<sub>2</sub> insertion into the Si substrate at SiO<sub>2</sub>/Si interfaces with *oxidation-induced strain*. Effects of strain accumulation resulting in a dense oxide layer near the interface are examined based on the incorporation energy and migration (reaction) barrier height. A possible atomic-scale process during the interfacial reaction is also suggested.

## II. CALCULATION PROCEDURE

The calculations were performed within the spin-polarized generalized gradient approximation<sup>20</sup> and ultrasoft pseudopotential scheme,<sup>21</sup> combined with the conjugate-gradient minimization technique.<sup>22,23</sup> The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 25 Ry. In the calculations, the interfacial strain induced by the oxidation is adopted by theoretically oxidizing the quartz/Si(100) interface model.<sup>24</sup> The unit cells of the interface model contain strain-released oxide layers with a thickness of 7.2 Å, oxidized layers ranging from 2.1 to 4.2 Å, and a six-atomic-layer Si substrate (8.2 Å). The lateral size of the unit cells is  $2 \times 2$  ( $a=7.73$  Å). The oxidized layer thicknesses considered in this study are 1, 1.5, and 2 ML. These layers are modeled based on HRTEM observations, in which the interface contains  $\sim 2$  ML oxidized layers with a cristobalitelike structure.<sup>19</sup> The densities of the 1, 1.5, and 2 ML oxidized interface models are 2.64, 2.76, and 2.86 g/cm<sup>3</sup>, respectively. These values are higher than the density of the structural transition layers obtained by x-ray reflectivity (2.4 g/cm<sup>3</sup>), but are comparable to the estimated density of the cristobalitelike oxide layer obtained by the HRTEM observations ( $\sim 2.8$  g/cm<sup>3</sup>).<sup>19</sup> It should be noted that x-ray reflectivity provides an averaged value over the entire interface area. Although complete high-density oxide layers have not been identified experimentally, one can consider such structures as locally oxidized interface regions. The calculations using these models also clarify the dependence of the barrier height on the strain accumulation. In addition to the calculations of the interfaces, we calculate the energies of an O<sub>2</sub> molecule in bulk SiO<sub>2</sub> in order to clarify the physical origin of the barrier height for O<sub>2</sub> diffusion near the interface. The bulk SiO<sub>2</sub> was simulated using a supercell of an  $\alpha$ -quartz crystal containing 72 atoms.<sup>25</sup> We use  $\Gamma$ -point sampling in the Brillouin zone integration. In order to determine the transition state structures, we use a constraint optimization<sup>26–28</sup> in an  $(N-1)$ -dimensional space, where  $N$  is the ionic degree of freedom (three times the number of atoms) in the unit cell.

In the present study, the reaction processes of O<sub>2</sub> at the SiO<sub>2</sub>/Si interface are examined using the incorporation energy for gas-phase O<sub>2</sub> into the oxide layer of the interface,  $E_i$ , the barrier height for O<sub>2</sub> migration,  $E_d$ , the reaction barrier height for the O<sub>2</sub> insertion into the Si substrate,  $E_r$ , and the effective barrier height for the O<sub>2</sub> reaction processes,  $E_a$ , including the energy penalty to transfer the molecule from a voidlike region in amorphous SiO<sub>2</sub>. The incorporation energy  $E_i$  is given by

$$E_i = E_{tot} - E_{SiO_2} - \mu_{O_2}, \quad (1)$$

where  $E_{tot}$  is the total energy of the SiO<sub>2</sub>/Si interface with an O<sub>2</sub> molecule in the oxide layer,  $E_{SiO_2}$  the total energy of the SiO<sub>2</sub>/Si interface without O<sub>2</sub>, and  $\mu_{O_2}$  the chemical potential of an O<sub>2</sub> molecule in the gas phase. As will be explained in the next section, we find a metastable structure in addition to the stable structure in the strain-released oxide layer of the interface. Thus, there is a transition state structure and a corresponding barrier height to transfer the molecule between

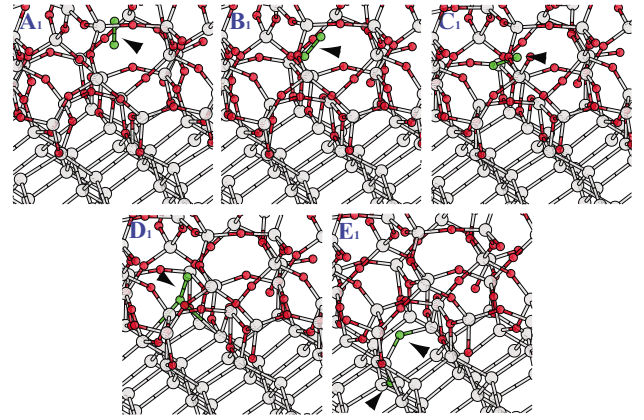


FIG. 1. (Color online) Geometries of an O<sub>2</sub> molecule located at the 1 ML oxidized interfaces. White (empty) and red (filled) circles denote Si and host O atoms, respectively, while O atoms of O<sub>2</sub> molecule are represented by green (shaded) circles. The O<sub>2</sub> molecules and inserted O atoms are indicated by arrowheads. The barrier height for O<sub>2</sub> migration  $E_d$  (O<sub>2</sub> insertion into the Si substrate  $E_r$ ) is obtained from the energy difference between A<sub>1</sub> and B<sub>1</sub> (C<sub>1</sub> and D<sub>1</sub>).

these structures. The barrier height for migration,  $E_d$ , is calculated using the energy difference between the stable structure of O<sub>2</sub> at the strain-released oxide layer and the transition state structure. The barrier height for the insertion,  $E_r$ , is defined as the energy difference between the metastable structure just before the insertion into Si and its transition state structure. Based on the experimental fact that the enthalpy of dissolution for O<sub>2</sub> incorporation is negligible,<sup>16</sup> the calculated  $E_i$  can be regarded as the energy penalty to transfer the molecule from a voidlike region in amorphous SiO<sub>2</sub>. The effective barrier height, which can be directly compared to the activation energy in the Deal–Grove model, is thus calculated using  $E_i$  and the energy difference between the stable structure of O<sub>2</sub> in the oxide layer of the interface and the transition state structure with higher energy:  $E_a$  depends on the energy landscape for O<sub>2</sub> reaction near the interface. If the energy of the transition state structure for the migration is higher than that for the insertion,  $E_a$  is given by  $E_a = E_i + E_d$ . In the opposite case, it is given by  $E_a = E_i + E_r + \Delta E$ , where  $\Delta E$  is the energy difference between stable and metastable structures.

## III. RESULTS AND DISCUSSION

Figure 1 shows the geometries of the metastable structure hosting an O<sub>2</sub> molecule around the 1 ML oxidized interface (A<sub>1</sub>, C<sub>1</sub>, and E<sub>1</sub>) and the transition state structures between these metastable structures (B<sub>1</sub> and D<sub>1</sub>). The energy variation as a function of distance measured from the position of O<sub>2</sub> located at the strain-released layer, along with the corresponding plots for the strain-released and 0.75 ML oxidized interfaces, is shown in Fig. 2. As shown in Fig. 2(A<sub>1</sub>), the O<sub>2</sub> molecule in the triplet state is stably located at open spaces in the Si-O-Si network, and the incorporation energy of gas-phase O<sub>2</sub> into this structure,  $E_i = 2.12$  eV [Fig. 2(A<sub>1</sub>)], is

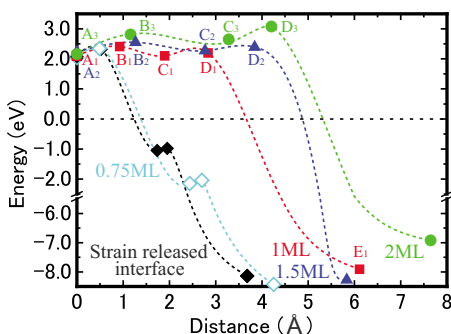


FIG. 2. (Color online) Energy profile as a function of distance measured from the position of O<sub>2</sub> located in the strain-released oxide layer in the 1 ML (squares), 1.5 ML (triangles), and 2 ML (circles) oxidized interfaces. The calculated results for the strain-released (solid diamonds) and 0.75 ML oxidized (open diamonds) interfaces (Refs. 4 and 5) are also shown. The incorporation energy  $E_i$  corresponds to the energy difference between the O<sub>2</sub> in the oxide layer at the interface and the gas-phase O<sub>2</sub>.

comparable to that in the strain-released interface.<sup>4,5</sup> This structure is the most stable location of O<sub>2</sub> in the oxide layer, so that it is reasonable to take it as the starting point of the atomic processes in the 1 ML oxidized interface. We note that this structure does not correspond to the stable structure in the oxide. As pointed out in permeation experiments on fused silica,<sup>16</sup> the solubility of the O<sub>2</sub> molecule is independent of temperature, indicating that oxygen molecules are trapped in voidlike regions without enthalpy of dissolution. The calculations for the transition state structures demonstrate that the O<sub>2</sub> in Fig. 2(A<sub>1</sub>) moves toward the strained oxide layer through the transition state structure shown in Fig. 2(B<sub>1</sub>). The analysis of these structures clarifies that the distances between the O atom of the O<sub>2</sub> molecule and surrounding O atoms in the transition state structures are  $\sim 0.08$  Å shorter than those in the stable structures. The difference in the atomic distances implies that the energy deficit in the transition state structure originates from the interaction between nonbonding  $2p$  orbitals of surrounding O atoms and  $\pi$  orbitals of O<sub>2</sub>. Indeed, we found that the distances in the transition state structure of O<sub>2</sub> diffusion in bulk SiO<sub>2</sub> are shorter than those in the stable structure by  $\sim 0.05$  Å. Considering that similar transition state structures are formed both in the oxide layer near the interface and in bulk SiO<sub>2</sub>, it is reasonable to conclude that the atomic process for the O<sub>2</sub> migration with barrier height  $E_d = 0.3$  eV (energy difference between A<sub>1</sub> and B<sub>1</sub>) corresponds to the diffusion process through bulk SiO<sub>2</sub>.<sup>25,29,30</sup>

The calculations also demonstrate that the O<sub>2</sub> in the metastable structure [Fig. 1(C<sub>1</sub>)] reacts with the Si substrate through another transition state structure, that shown in Fig. 1(D<sub>1</sub>). The calculated barrier height for O<sub>2</sub> insertion  $E_r$  (energy difference between C<sub>1</sub> and D<sub>1</sub>) is 0.2 eV. This transition state is due to the interaction between  $3p$  orbitals of interfacial Si atoms and partially occupied  $2p$  orbital of one of the O<sub>2</sub> molecule, resulting in the dissociation of  $\pi$  orbitals in O<sub>2</sub>.<sup>4</sup> However, the energy of the transition state structure for O<sub>2</sub> migration is higher than that for O<sub>2</sub> insertion. The higher

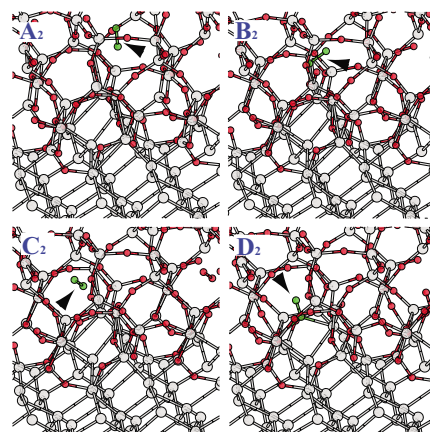


FIG. 3. (Color online) Geometries of an O<sub>2</sub> molecule located in the 1.5 ML oxidized interfaces. The barrier height for O<sub>2</sub> migration  $E_d$  (O<sub>2</sub> insertion into the Si substrate  $E_r$ ) is obtained from the energy difference between A<sub>2</sub> and B<sub>2</sub> (C<sub>2</sub> and D<sub>2</sub>). Same notations as in Fig. 1.

transition state structure seen in the O<sub>2</sub> migration path indicates that O<sub>2</sub> migration into the strained oxide layer is rate limiting in the 1 ML oxidized interface. In addition, since there is an energy penalty to transfer the molecule from the stable voidlike region of amorphous SiO<sub>2</sub> to the oxide layer near the interface shown in Fig. 1(A<sub>1</sub>), the effective barrier height for the reaction,  $E_a$ , should be estimated using  $E_i$  and  $E_d$ . The value of  $E_a = E_i + E_d = 2.4$  eV in the 1 ML oxidized interface is similar to that in the strain-released case (2.3 eV), implying that these atomic processes are basically unaffected by the formation of the thin strained oxide layer.

Similar atomic processes are also found in the 1.5 ML oxidized interface case, as shown in Fig. 3. The O<sub>2</sub> molecule located in the open spaces in the Si-O-Si network [Fig. 3(A<sub>2</sub>)], with  $E_i = 2.23$  eV, moves toward the strained oxide layer through the transition state structure shown in Fig. 3(B<sub>2</sub>) with  $E_d = 0.3$  eV, which is identical to that in the 1 ML oxidized case. After the transition state structure, the metastable structure near the strained oxide layer [Fig. 3(C<sub>2</sub>)] is formed. Next, the O<sub>2</sub> insertion occurs through another transition state structure [Fig. 3(D<sub>2</sub>)] with  $E_r = 0.2$  eV, which is identical to that in the 1 ML oxidized interface case. The energy profile shown in Fig. 2 demonstrates that each calculated energy in the 1.5 ML oxidized interface is similar to its counterpart in the 1 ML oxidized interface. Therefore, strain accumulation yields an insignificant increase in  $E_a$  (less than 0.2 eV).

Although each O<sub>2</sub>-reaction process in the 2 ML oxidized interface case shown in Fig. 4 is similar to its counterpart in the 1 and 1.5 ML oxidized interfaces, the energy profile shown in Fig. 2 demonstrates that the energies are significantly altered by the accumulated strain. In particular, the energy deficits of the metastable and transition state structures [Figs. 4(B<sub>3</sub>), 4(C<sub>3</sub>), and 4(D<sub>3</sub>)] compared to the 1 and 1.5 ML oxidized cases are more than 0.5 eV. Consequently, the rate-limiting process in the 2 ML oxidized interface is different from that in the 1 and 1.5 ML oxidized interfaces.

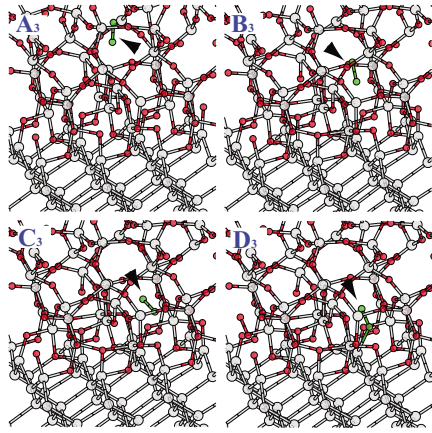


FIG. 4. (Color online) Geometries of an  $O_2$  molecule located in the 2 ML oxide layer. The barrier height for  $O_2$  migration,  $E_d$  ( $O_2$  insertion into the Si substrate,  $E_r$ ), is obtained from the energy difference between  $A_3$  and  $B_3$  ( $C_3$  and  $D_3$ ). Same notations as in Fig. 1.

The highest energy configuration in the 2 ML oxidized interface is the transition state for  $O_2$  insertion into the Si substrate [Fig. 4( $D_3$ )], whereas it is the transition state for  $O_2$  migration in the 1 and 1.5 ML oxidized interfaces. Due to a large energy increase in the transition state structure of  $O_2$  insertion, the effective barrier height in this atomic process,  $E_a = E_i + E_r + \Delta E = 3.1$  eV, is higher than that in the strain-released interface by  $\sim 0.7$  eV. The main contributor in the 2 ML oxidized interface is  $\Delta E = 0.6$  eV, which is caused by the energy increase in the metastable structure near the strained oxide layer [Fig. 4( $C_3$ )]. This energy increase is attributed to the enhanced repulsion between nonbonding O  $2p$  orbitals of surrounding O atoms and  $\pi$  orbitals of the  $O_2$  molecule. In the 2 ML oxidized case, the O atom of the  $O_2$  molecule is closer to the surrounding O atoms in the metastable structure, by  $0.02$ – $0.17$  Å, than is true in the 1 and 1.5 ML cases. On the other hand, the energy increase in  $E_r$  ( $=0.3$  eV, energy difference between  $C_3$  and  $D_3$  in Fig. 4) is as small as  $0.1$  eV, indicating that  $O_2$  insertion is, *per se*, virtually independent of the strain accumulation. These energy-profile characteristics indicate that  $O_2$  diffusion is mainly determined by the highly strained oxide layer, as predicted by Bongiorno and Pasquarello.<sup>12–14</sup>

Figure 5 shows the calculated barrier height as a function of oxide density, along with the equivalent plots taken from previous studies.<sup>4,5</sup> We find that  $E_r$  always takes small values, implying that the  $O_2$  reaction process *per se* is not rate limiting at all, even if dense oxides form at the interface. In contrast,  $E_d$  and  $E_a$  are almost constant if the oxide layer thickness is under 2 ML, but both increase significantly when the thickness reaches 2 ML. As explained above, the energy difference  $\Delta E$  strongly contributes to the energy increase in the 2 ML case. Since the net reaction energy is strongly exothermic with an energy gain of more than  $9.1$  eV (energy differences between initial and final states shown in Fig. 2) for all interface models, it is inferred that the oxidation reaction at the interface with oxide layer less than 2 ML

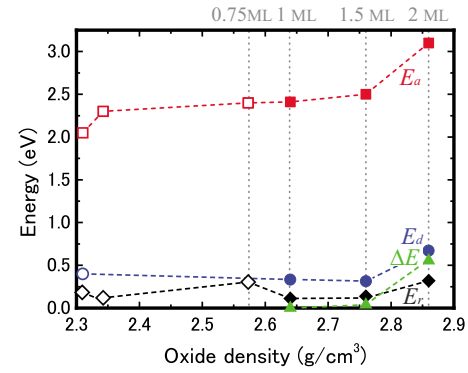


FIG. 5. (Color online) Calculated barrier height for  $O_2$  diffusion near the interface [ $E_d$  (circles)] and  $O_2$  insertion into the Si substrate [ $E_r$  (diamonds)], energy difference between stable and metastable structures of  $O_2$  in the oxide layer of the interface [ $\Delta E$  (triangles)], and effective barrier height for the reaction process taking account of the  $O_2$  transfer from a big void in bulk  $SiO_2$  [ $E_a$  (squares)] as a function of the oxide density. Open symbols represent the values obtained in previous studies (Refs. 4, 5, and 7). The vertical dotted lines indicate the oxidized layers. Note that the result of Bongiorno and Pasquarello (Ref. 6) is not shown due to the uncertainty of the incorporation energy  $E_i$  and oxide density (the density range is  $2.3$ – $2.4$   $g/cm^3$  in Ref. 39).

thick proceeds in the same way as the reaction at the strain-released interface, whereas with the oxide layer thickness of 2 ML, the oxidation reaction should be suppressed. Considering that oxide formation is continuous under thermal oxidation, if the interface is smooth, the  $E_a$  dependence on strain implies that there actually is a transition from the strained crystalalitelike oxide to the quartzlike unstrained oxide.<sup>31</sup> Although this transformation is not found in our calculations, the results obtained for the  $O_2$  reaction with strained layers support some form of strain-release mechanism, one of which was advanced in theoretical studies<sup>17,32–35</sup> and verified theoretically<sup>7,36</sup> and experimentally.<sup>37,38</sup>

#### IV. CONCLUSION

We have investigated the reaction pathways of an oxygen molecule at the  $SiO_2/Si(100)$  interface in the presence of oxidation-induced strain based on total-energy electronic-structure calculations within the density-functional theory. We found that the calculated barrier height for  $O_2$  insertion into the Si substrate takes a small value ( $\sim 0.3$  eV) that is independent of the strain accumulation at the interface. The calculated barrier height including an energy penalty to transfer the  $O_2$  molecule from a voidlike region in amorphous  $SiO_2$  to the oxide layer (thickness less than 2 ML) of the interface is virtually identical to that in the strain-released interface, whereas it drastically increases when the oxide layer thickness reaches 2 ML. The energy increase in the barrier height can be interpreted in terms of an energy deficit within the strained oxide layer. Our results indicate that there must be some process that relaxes the oxidation strain.

## ACKNOWLEDGMENTS

This work was supported in part by Grant-in-Aid for Scientific Research (Grants No. 18560020 and No. 18560027) from the Japan Society for the Promotion of Science. Codes

used in this work are based on Tokyo *Ab initio* Program Package (TAPP). Computations were performed at RCCS (National Institutes of Natural Sciences) and ISSP (University of Tokyo).

\*akiyama@phen.mie-u.ac.jp

- <sup>1</sup>M. L. Green, E. P. Gusev, R. Degraeve, and E. L. Garfunkel, *J. Appl. Phys.* **90**, 2057 (2001).
- <sup>2</sup>B. E. Deal and A. S. Grove, *J. Appl. Phys.* **36**, 3770 (1965).
- <sup>3</sup>H. Z. Massoud, J. D. Plummer, and E. A. Irene, *J. Electrochem. Soc.* **132**, 1745 (1985).
- <sup>4</sup>T. Akiyama, H. Kageshima, and T. Ito, *Jpn. J. Appl. Phys., Part 1* **43**, 7903 (2004).
- <sup>5</sup>T. Akiyama and H. Kageshima, *Surf. Sci.* **576**, L65 (2005).
- <sup>6</sup>A. Bongiorno and A. Pasquarello, *Phys. Rev. Lett.* **93**, 086102 (2004).
- <sup>7</sup>L. Tsetseris and S. T. Pantelides, *Phys. Rev. Lett.* **97**, 116101 (2006).
- <sup>8</sup>N. Awaji, S. Ohkubo, T. Nakanishi, Y. Sugita, K. Takasaki, and S. Komiya, *Jpn. J. Appl. Phys., Part 2* **35**, L67 (1996).
- <sup>9</sup>S. D. Kosowsky, P. S. Pershan, K. S. Krisch, J. Bevk, M. L. Green, D. Brasen, L. C. Feldman, and P. K. Roy, *Appl. Phys. Lett.* **70**, 3119 (1997).
- <sup>10</sup>J. F. Shackelford, *J. Non-Cryst. Solids* **253**, 231 (1999).
- <sup>11</sup>R. H. Dremus, *Diffusion of Reactive Molecules in Solids and Melts* (Wiley, New York, 2002).
- <sup>12</sup>A. Bongiorno and A. Pasquarello, *J. Phys.: Condens. Matter* **15**, S1553 (2003).
- <sup>13</sup>A. Bongiorno and A. Pasquarello, *Phys. Rev. B* **70**, 195312 (2004).
- <sup>14</sup>A. Bongiorno and A. Pasquarello, *J. Phys.: Condens. Matter* **17**, S2051 (2005).
- <sup>15</sup>T. Watanabe, K. Tatsumura, and I. Ohdomari, *Phys. Rev. Lett.* **96**, 196102 (2006).
- <sup>16</sup>F. J. Norton, *Nature (London)* **191**, 701 (1961).
- <sup>17</sup>H. Kageshima, M. Uematsu, T. Akiyama, and T. Ito, *Jpn. J. Appl. Phys., Part 1* **45**, 7672 (2006).
- <sup>18</sup>H. Kageshima, M. Uematsu, T. Akiyama, and T. Ito, *ECS Trans.* **6**, 449 (2007).
- <sup>19</sup>N. Ikarashi, K. Watanabe, and Y. Miyamoto, *Phys. Rev. B* **62**, 15989 (2000).
- <sup>20</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>21</sup>D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- <sup>22</sup>J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino, *Phys. Rev. B* **54**, 5586 (1996).
- <sup>23</sup>H. Kageshima and K. Shiraishi, *Phys. Rev. B* **56**, 14985 (1997).
- <sup>24</sup>The density of SiO<sub>2</sub> in the initial quartz-SiO<sub>2</sub>/Si interface used to model the strained interface is 2.34 g/cm<sup>3</sup>, which is reasonably consistent with those used in previous studies and experimental findings. See Refs. 6–8.
- <sup>25</sup>It has been found that the barrier height of O<sub>2</sub> diffusion is almost independent of the crystal structure of SiO<sub>2</sub> [see T. Akiyama, K. Kawamoto, H. Kageshima, M. Uematsu, K. Nakamura, and T. Ito, *Thin Solid Films* **508**, 311 (2006), and references therein]. We thus employ an  $\alpha$ -quartz crystal as a representative of crystalline bulk SiO<sub>2</sub>.
- <sup>26</sup>S. Jeong and A. Oshiyama, *Phys. Rev. Lett.* **81**, 5366 (1998).
- <sup>27</sup>M. Otani, K. Shiraishi, and A. Oshiyama, *Phys. Rev. Lett.* **90**, 075901 (2003).
- <sup>28</sup>The reaction coordinate in our approach is defined using the initial and final atomic configurations, while that in more elaborate techniques such as the elastic band method is estimated from the two adjacent images. The deficiency due to the fixed reaction coordinate might cause overestimation in the barrier height. However, the barrier height of the O<sub>2</sub> reaction in the strain-released interface using our method (0.2 eV) is identical to that in the elastic band method. We thus believe that the overestimation in this case is small and does not disturb our conclusion.
- <sup>29</sup>W. Orellana, A. J. R. da Silva, and A. Fazzio, *Phys. Rev. Lett.* **87**, 155901 (2001).
- <sup>30</sup>Although the calculated barrier height for O<sub>2</sub> diffusion in bulk SiO<sub>2</sub> (0.2 eV) is similar to those in the previous calculations (e.g., Ref. 29), the value is much lower than the activation energy extracted from the diffusion constant in the Deal–Grove model (~1.2 eV). This implies that a simple picture for the O<sub>2</sub> diffusion, in which O<sub>2</sub> molecules transfer between Si-O-Si cages with similar incorporation energy, is not appropriate in amorphous SiO<sub>2</sub>. Reference 17 discusses the issue in detail.
- <sup>31</sup>H. Kageshima, M. Uematsu, K. Akagi, S. Tsuneyuki, T. Akiyama, and K. Shiraishi, *e-J. Surf. Sci. Nanotechnol.* **4**, 584 (2006).
- <sup>32</sup>H. Kageshima and K. Shiraishi, *Phys. Rev. Lett.* **81**, 5936 (1998).
- <sup>33</sup>H. Kageshima, K. Shiraishi, and M. Uematsu, *Jpn. J. Appl. Phys., Part 2* **38**, L971 (1999).
- <sup>34</sup>M. Uematsu, H. Kageshima, and K. Shiraishi, *Jpn. J. Appl. Phys., Part 2* **39**, L699 (2000).
- <sup>35</sup>H. Kageshima, M. Uematsu, K. Akagi, S. Tsuneyuki, T. Akiyama, and K. Shiraishi, *Jpn. J. Appl. Phys., Part 1* **45**, 694 (2006).
- <sup>36</sup>Y. Tu and J. Tersoff, *Phys. Rev. Lett.* **89**, 086102 (2002).
- <sup>37</sup>S. Fukatsu, T. Takahashi, K. M. Itoh, M. Uematsu, A. Fujiwara, H. Kageshima, Y. Takahashi, K. Shiraishi, and U. Gösele, *Appl. Phys. Lett.* **83**, 3897 (2003).
- <sup>38</sup>Z. Ming, K. Nakajima, M. Suzuki, K. Kimura, M. Uematsu, K. Torii, S. Kamiyama, Y. Nara, and K. Yamada, *Appl. Phys. Lett.* **88**, 153516 (2006).
- <sup>39</sup>A. Bongiorno, A. Pasquarello, M. S. Hybertsen, and L. C. Feldman, *Phys. Rev. Lett.* **90**, 186101 (2003).