Theoretical study of luminescence degradation by oxidation in Si(001) and Si(111) ultrathin films: Gap states induced by oxidation

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A possible mechanism for degradation of light emission by oxidation in Si nanostructures is proposed, on the basis of electronic state calculations by the extended Hückel-type nonorthogonal tight-binding method for possible oxygen configurations on the well-defined surfaces of Si(001) and Si(111) ultrathin films. The on-top or top-bridge site configuration of oxygen on Si(001) ultrathin films presents electronic states of a Si dangling-bond character across the fundamental band gap, suggesting the occurrence of nonradiative recombination centers and thus the luminescence degradation. In H-terminated Si(111) ultrathin films, the combination of the surface Si-H bond states and the states due to the Si-Si backbond to which oxygen attaches causes gap states, in contrast to the case of H-terminated Si(001) ultrathin films where the similar oxygen configuration does not produce any gap states. Finally, it is found that the luminescence degradation by oxidation observed in porous Si can be explained by a combination of hydrogen desorption and the following creation of the on-top or top-bridge site configuration of oxygen on the Si surfaces. [S0163-1829(99)03535-3]

I. INTRODUCTION

It is now well established that hydrogen-terminated porous Si prepared electrochemically in HF-based solutions can emit efficient visible photoluminescence (PL) at room temperature.[1] Furthermore, it has been shown that prolonged storage in the dark of luminescent porous Si in air at room temperature can lead to a significant increase in PL output, plus a shift to shorter wavelengths.[1] Thus, as-prepared porous Si, upon oxidation, exhibits an increase in PL efficiency. In particular, it has been reported that the PL efficiency of porous Si rises dramatically after anodic oxidation at a low forming current density at room temperature.[2] Fourier transform infrared (FTIR) measurements have revealed that, in anodically oxidized porous Si, the hydrogen surface coverage is preserved and the oxidation occurs on backbonds of the surface Si atoms.[3] Some other experimental studies on porous Si have also shown that oxidation results in an enhanced PL.[4,5] FTIR observations have emphasized that the PL enhancement must be caused by the incorporation of oxygen atoms in the backbond Si network on the surface of porous Si.[5] Therefore, the increase in PL intensity due to oxidation treatments of porous Si would be caused by the oxygen incorporation into Si-Si backbonds on the H-covered surface, as described in a theoretical study of luminescence enhancement in oxidized Si(001) ultrathin films.[6]

However, the PL enhancement as a result of oxidation does not always happen. It has been reported that oxidation causes significant degradation of luminescence from porous Si. Tischler *et al.*[7] and Xu, Gal, and Gross[8] have reported that, although no degradation of PL is observed in porous Si samples in O_2 in the dark, oxidation under illumination or low-temperature (200 °C) annealing substantially decreases PL output. This is in marked contrast to the above-mentioned observation in porous Si kept in air, where a reduction in PL intensity only occurs if the porous Si is annealed at higher temperatures (about 600 °C) or under stronger photoexcitation conditions.[1] Moreover, FTIR and electron paramagnetic resonance (EPR) measurements have shown a large increase in density of Si dangling bonds in degraded samples subsequent to oxidation in O_2 at temperatures as low as 300 °C or under illumination.[7,9,10] It has been ascribed to partial desorption of hydrogen from the surface of porous Si, suggesting loss of hydride passivation after oxidation and the resulting increase in density of Si dangling bonds that can behave as nonradiative recombination centers. On the other hand, Canham *et al.*[11] and Zheng, Chen, and Wang[12] have attributed the observed PL degradation to oxygen adsorption or the growth of oxide on the surfaces of porous Si samples. Suda *et al.*[13] have studied PL properties of porous Si after dry oxidation treatment using oxygen excited by electron impact and shown that the observed PL degradation is ascribed to an increase in the number of nonradiative recombination centers caused by incomplete Si oxides. Considering those experimental observations, it seems that the PL degradation and destruction of surface Si-H bonds in porous Si proceed in parallel with oxidation in O_2 under illumination or low-temperature annealing. However, the following questions still remain unexplained. (1) What could happen to oxygen, which should be adsorbed on the Si surface, following hydrogen desorption? (2) Why would oxygen adsorption or the formation of oxide on the surface following hydrogen desorption result in an increase in the density of Si dangling bonds rather than surface passivation of those dangling bonds? The latter would be a puzzle in the FTIR observation of Si-O bond vibrations enhanced after oxidation in degraded samples of porous Si.

At present, the mechanism of the PL degradation due to oxidation in porous Si is still unclear. The degradation of the PL by oxidation is a serious problem concerning the application of porous Si, in that the problem of instability in porous Si should be alleviated or eliminated by oxidation approaches. An understanding of its mechanism will be essentially important, in order to cope with similar luminescence degradation issues that are likely to occur to other

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forms of Si nanostructures such as Si ultrathin films. Previously, it has been shown theoretically that light emission from the direct band gap in H-terminated Si(001) ultrathin films can be largely enhanced by oxidation, on the basis of oscillator strength calculations for some specific oxygen configurations on the film surface.[6] However, no theoretical studies on the mechanism of luminescence degradation caused by oxidation have been reported so far, in spite of its importance. Specifically, we need a theoretical study on the electronic structure of oxygen on well-defined H-terminated surfaces of Si nanostructures, because it seems that such sample-dependent phenomena as PL enhancement or degradation by oxidation observed in porous Si are ascribed to the lack of controllability for the surfaces of porous Si samples prepared. Such a theoretical study should help in understanding the confusing experimental situations in porous Si.

The aim of the present paper is to propose a possible mechanism for degradation of light emission by oxidation in Si nanostructures and to provide theoretical evidence for experimental conjectures concerning the degradation mechanism that have been reported in the past. Here, a microscopic picture of the change in electronic structure of the H-terminated Si surface by oxidation is clarified, on the basis of electronic state calculations for oxygen configurations on the well-defined surfaces of Si(001) and Si(111) ultrathin films. The calculations are carried out for specific oxygen site geometries that are closely related to emission degradation due to the occurrence of electronic states in the fundamental band gap (referred to as gap states) or nonradiative recombination centers. The present study finds that there is a great difference in oxygen configuration, which can cause luminescence degradation, between Si(001) and Si(111) ultrathin films. In particular, it is shown that, whereas surface Si hydrides backbonded to oxygen can enhance luminescence in H-terminated Si(001) ultrathin films, those species produce gap states in H-terminated Si(111) ultrathin films, suggesting the appearance of nonradiative recombination centers. The results calculated for Si(001) and Si(111) ultrathin films in this study are compared to some of experimental PL data for porous Si.

II. MODEL AND CALCULATIONS

Electronic state calculations are carried out by applying the extended Hückel-type nonorthogonal tight-binding (EHNTB) method to Si(001) and Si(111) ultrathin films or slabs. Details of electronic state calculations by the EHNTB method can be found in Ref. 6. Here, we briefly describe the EHNTB method. This is a nonselfconsistent linear combination of atomic orbitals method of the two-center approximation with no need of evaluation of the so-called multicenter integrals occurring. The basis used consists of one s and three p orbitals centered on each atom, which are approximated by Slater-type atomic orbitals. An energy matrix element between atomic orbitals is taken as proportional to an overlap matrix element between those orbitals. All distant-neighbor nonorthogonal overlaps and interactions between basis orbitals up to the sixth ones are included in all electronic state calculations and the determination of EHNTB parameters. The EHNTB parameters for Si are determined by means of an accurate fit of the bulk band structure calculated using 5.43 Å as a lattice constant to the empirical nonlocal-pseudopotential band structure for Si. The EHNTB parameters between H and Si and between H and H and those between O and Si and between O and O are respectively determined by fitting calculated surface electronic states on H- and O-covered Si(111) surfaces, which have been intensively studied in the past, to experimental data.[6]

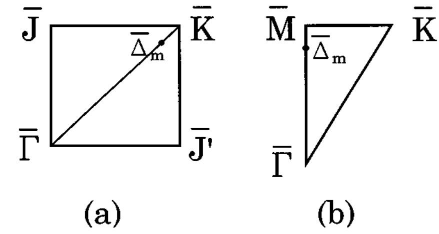

FIG. 1. The irreducible part of the surface Brillouin zone for the (a) (001) and (b) (111) thin films. The signs $\bar{\Gamma}$ and $\bar{\Delta}_m$ denote the zone center and the location where the bulk CBM occurs, respectively.

There are two surfaces on both sides of Si films studied and the two-dimensional periodicity parallel to the film surface is preserved. Figures 1(a) and 1(b) illustrate the irreducible part of the surface Brillouin zone (SBZ) for the (001) and (111) surfaces, respectively. The signs $\bar{\Gamma}$ and $\bar{\Delta}_m$ denote the zone center and the location where the bulk conduction-band minimum (CBM) occurs, respectively. Dispersion relations of the valence and conduction bands are calculated along the symmetry directions in the SBZ. The energies (in eV) are referred to the valence-band maximum (VBM) for Si films under study.

Not all geometries possible for atomic oxygen examined in this study lead to the occurrence of gap states serving as nonradiative recombination centers. Some of those have been found to result in luminescence enhancement, as have been reported in Ref. 6. Here, the following three characteristic oxygen configurations producing gap states are studied: the on-top and top-bridge site geometries for oxygen on Si(001) ultrathin films, and the geometry for oxygen at a Si-Si backbond on H-terminated Si(111) ultrathin films. These configurations have been claimed to be most stable theoretically and observed experimentally in the past, as described in the next section. Figure 2 shows the oxygen site geometries on Si(001). The top-layer Si (shaded circles) and second-layer Si (unshaded circles) atoms are shown, together with oxygen (small circles) at (a) an on -top site on a surface atom of Si (along the [001] direction) and (b) a top-bridge site between two top-layer Si atoms (along the [110] direction). The Si-O bond length is taken to be 1.64 or 1.76 Å for the on-top site geometry and 1.92 or 2.15 Å for the top-bridge site geometry. The above values are taken from the results of total-energy calculations using cluster and slab approaches for those oxygen configurations by Batra, Bagus, and Hermann.[14] Figures 3(a) and 3(b) illustrate geometries for oxygen at a Si-Si backbond on the H-terminated Si(001) and Si(111) surfaces, respectively. Here, the configuration for a SiH_2 surface species backbonded to oxygen on Si(001) and that for a SiH species backbonded to oxygen on Si(111) are referred to as the $OSiH_2$ and OSiH configurations, respectively. The electronic structure for the $OSiH_2$ configura-

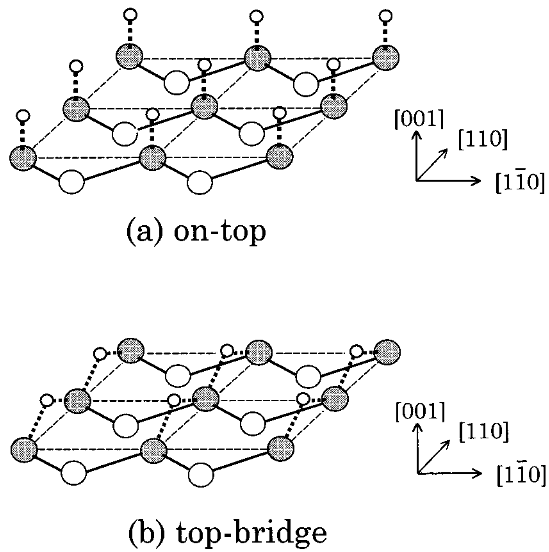

FIG. 2. (a) On-top and (b) top-bridge site geometries for oxygen on the Si(001) surface. The shaded and open circles denote the first- and second-layer Si atoms, respectively. The small open circles denote the oxygen atoms.

tion on Si(001) ultrathin films is calculated, though it presents no gap states as described later, for comparison with that for the OSiH configuration on Si(111) ultrathin films. The bond length of Si-H and Si-O are respectively taken as 1.48 and 1.64 Å.[6,15] The Si-O-Si bond angle α is 91.6°, representing the geometry for oxygen attaching to a Si-Si backbond without changing the structure of the Si skeleton of the films under study.

III. RESULTS AND DISCUSSION

Figure 4 shows the surface energy-band diagram for the on-top site model in the Si four-layer film (the Si-O bond length is 1.64 Å). In this configuration, as expected, the oxygen atom mainly combines with the p_z and s orbitals of the underlying surface Si atom. Electronic states appear in the band gap as shown by the dashed curves. These are p_y-like nonbonding states on the first-layer Si atom along the [110] direction (see Fig. 2) and have the character of the component of the two Si(001) dangling bonds parallel to the film surface. These states are dispersive along the SBZ because of their interactions through the underlying Si atoms. When the Si-O bond length is increased to 1.76 Å or reduced to 1.5 Å the situation does not change substantially. This occurs in all Si(001) films under study, irrespective of the Si film thickness as well as the bond length of Si-O. Thus, the on-top site oxygen on Si(001) fails to passivate the component of the Si dangling bond along the film surface, leading to the occurrence of the gap states. Likewise, the surface energy-band diagram for the top-bridge site model also presents electronic states localized on the first-layer Si atoms in the band gap as depicted by the dashed curves in Fig. 5 (the Si-O bond length is 2.15 Å). It is found that this is similar in situation to a result of first-principles calculations for a similar oxygen configuration on Si(001) in that surface states appear in the band gap.[16] In this configuration, these gap states are mainly Si p_z states perpendicular to the film surface and have a dangling-bond character. The oxygen atom at the top-bridge site mainly combines with the p_y and s orbitals of the underlying Si surface atoms. This implies that the component of the Si dangling bond perpendicular to the surface is not passivated by oxygen at the top-bridge site. The situation does not change at all when the Si-O bond length is reduced to 1.92 Å. It is found that these states appear in the band gap, regardless of the thickness of the Si films under study as well as the bond length of Si-O. These are also dispersive along the SBZ owing to their interactions through the underlying Si atoms. According to total-energy calculations performed in

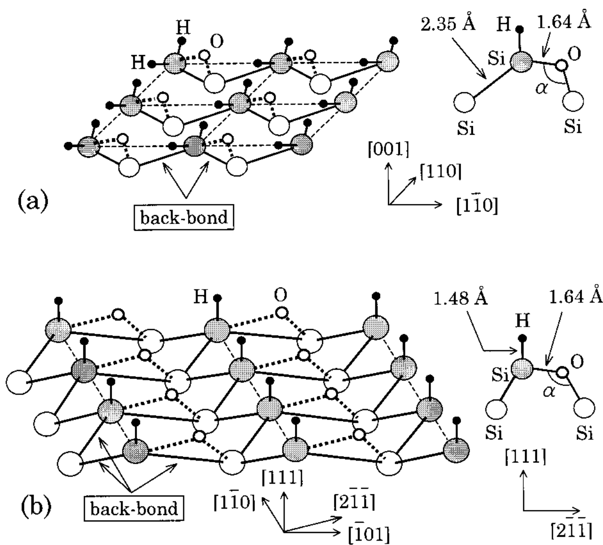

FIG. 3. Geometry for oxygen at a Si-Si backbond on the (a) Si(001) and (b) Si(111) surfaces. The shaded and open circles denote the top- and second-layer Si atoms, respectively. The small open and closed circles denote the oxygen and hydrogen atoms, respectively. The Si-O-Si bond angle α is taken as 91.6°.

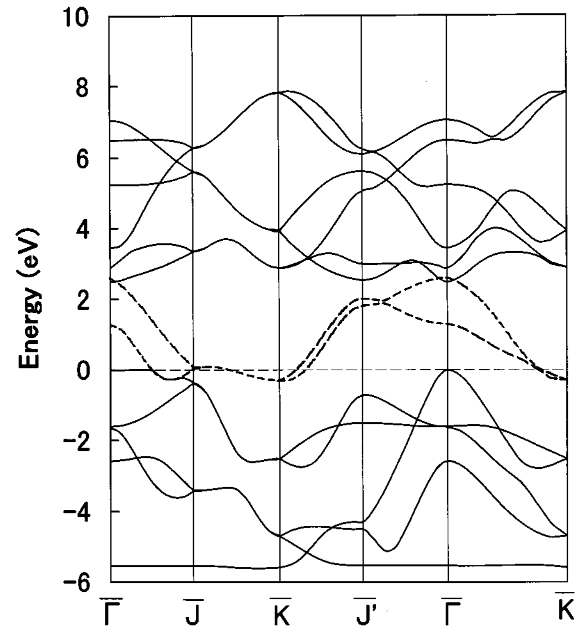

FIG. 4. Surface energy band diagram for the on-top site model in the Si(001) ultrathin film. The number of Si layers in the film is four. The gap states are shown by the dashed curves.

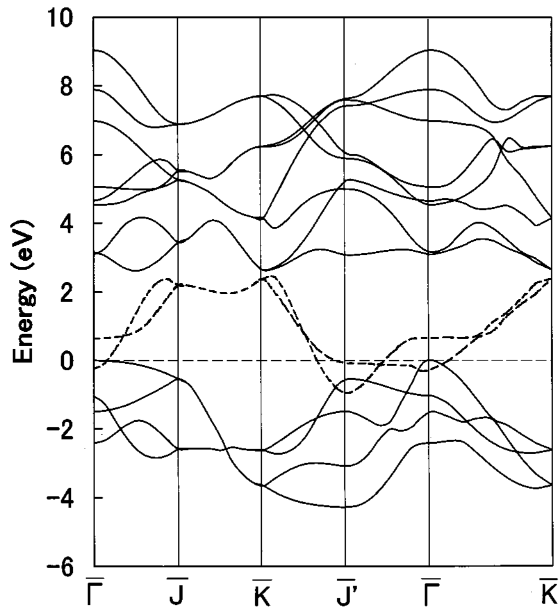

FIG. 5. Surface energy-band diagram for the top-bridge site model in the Si(001) ultrathin film. The number of Si layers in the film is four. The gap states are denoted by the dashed curves.

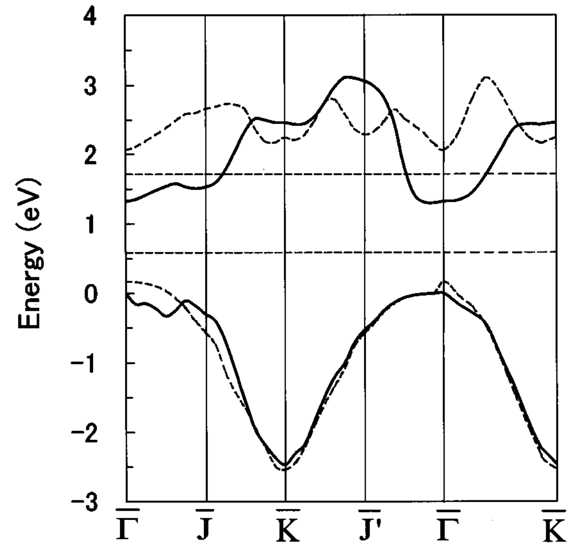

FIG. 6. Dispersion relation of the valence- and conduction-band edges for the $OSiH_2$ configuration on the Si(001) ultrathin film (solid curves). The number of Si layers in the film is eight. The band-edge dispersions for the H-terminated case are presented by the dashed curves for comparison. The VBM and CBM in the infinite Si bulk are shown by the horizontal dashed lines.

the past for oxygen chemisorption on the unreconstructed Si(001) surface, both the on-top and top-bridge sites are most stable in chemisorption of oxygen.[14,17,18] Thus, from the present calculations, it follows that in either case atomic oxygen at the most stable sites on the topmost layer of Si(001) cannot fully passivate the Si dangling bonds. Those unpassivated components of the Si dangling bonds (p_y-like for the on-top site and p_z-like for the top-bridge site) in both geometries cause electronic states in the band gap, despite the presence of Si-O bonds on the Si surface, and can act as nonradiative recombination centers for light emission. Finally, the oxygen states in the Si-O bonds for both geometries occur in energy away from the fundamental gap and do not contribute to the gap states.

Figure 6 shows the surface valence- and conduction-band edge dispersions near the fundamental band gap for the $OSiH_2$ configuration in the eight-layer Si(001) film (solid curves), in comparison with the case of the H-terminated eight-layer film (dashed curves). The VBM and CBM in the infinite Si bulk are shown by the horizontal dashed lines. It is found that, while the band gap of the H-terminated eight-layer film is direct at $\bar{\Gamma}$, as shown by the dashed curves, that of the $OSiH_2$ configuration is quasidirect at $\bar{\Gamma}$ (the real CBM lies slightly away from $\bar{\Gamma}$ along the $\bar{\Gamma}-\bar{J}'$ direction in Fig. 6). The latter situation is caused by the occurrence of p-like Si-O-Si bond states at the conduction-band edge near $\bar{\Gamma}$, leading to the lowering in energy below the bulk CBM. These Si-O-Si bond states are not localized on the surface and behave as part of the conduction band. In addition, the conduction-band edge near $\bar{\Gamma}$ moves in energy up to the level of the bulk CBM with an increase in the number of Si layers in the film and up to the same level as in the H-terminated case with an increase in $\alpha\,(\leqslant 180°)$.[19] In this configuration, thus, no gap states appear.

Figure 7 shows the surface energy-band diagram near the fundamental band gap for the OSiH configuration in the 12-layer Si(111) film. The H-terminated Si(111) ultrathin films are indirect transition semiconductors with the VBM at $\bar{\Gamma}$ and the CBM at $\bar{\Delta}_m$, as found from the solid curves in Fig. 7. Hence, we expect that the efficiency of luminescence from the H-terminated Si(111) ultrathin films would be controlled by phonon-assisted transitions of carriers spatially confined along the [111] direction and surface passivation phenomena as in H-terminated porous Si.[1] It is noted in Fig. 7 that elec-

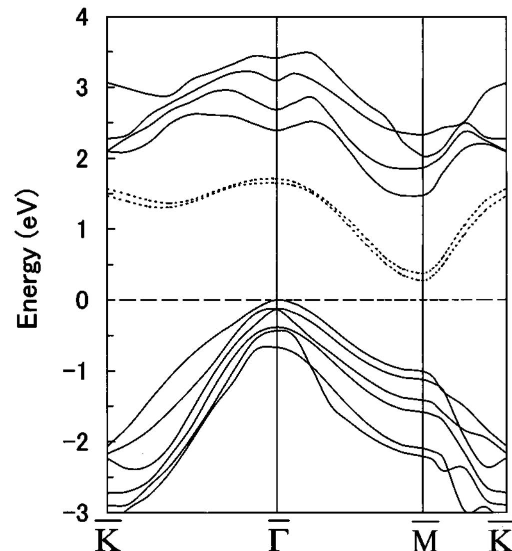

FIG. 7. Surface energy-band diagram near the fundamental gap for the OSiH configuration on the Si(111) ultrathin film. The number of Si layers in the film is twelve. The solid curves show the valence- and conduction-band states. The gap states are shown by the dotted curves.

tronic states appear in the fundamental band gap after an oxygen atom just attaches to one of the three backbonds of a Si surface atom, as shown by the dotted curves. These gap states are not ones due to Si dangling bonds which are fully passivated by hydrogen, but the Si-H bond (s- and p_z-like) states combined with the Si-Si backbond (p-like) states localized on the surface of the film, as described in more detail below. In this configuration, an oxygen atom attaching to a Si-Si backbond can partly isolate electronically a Si-H bond on the surface from the rest of the Si layers.[6] At the same time, an oxygen atom extracts electrons from the Si-Si backbond to which it attaches, resulting in a weakening of the Si-Si backbond and thus the creation of a Si-O-Si bond. Thus, the antibonding states between hydrogen and the underlying Si atoms fall in energy below the conduction-band edge because of the electronic isolation of the surface Si-H bonds from the rest of the Si skeleton, while the electronic states due to the weakened Si-Si backbonds, emerging from the valence band, rise in energy above the VBM. Both states mix in the band gap and form the gap states mentioned above. This situation is the same for all film thicknesses and Si-O-Si bond angles under study.

On the Si(001) ultrathin films, however, the aforementioned antibonding states associated with the Si-H bonds do not affect electronic states near the conduction-band edge, leading to no occurrence of gap states. The difference in situation of the antibonding states related to the Si-H bonds between the H-terminated Si(001) and Si(111) ultrathin films can be explained as follows. Because the antibonding states due to the Si-H bonds are located far above the CBM (about 2.3 eV above the CBM),[6] in the Si(001) ultrathin films, those states still remain above the CBM in spite of their downshifting in energy by the attachment of oxygen to one of the two backbonds of a Si surface atom. In contrast, those antibonding states associated with the Si-H bonds are located just above the conduction-band edge (about 2.8 eV above the VBM or 0.5 eV above the conduction-band edge at $\bar{\Gamma}$, which is a projection from the L_{1c} state at 2.26 eV in bulk Si) (Ref. 6) in the Si(111) ultrathin films. Therefore, those states can be downshifted in energy to levels in the band gap by the attachment of oxygen to one of the three backbonds of a Si surface atom.

Now we analyze the mechanism of luminescence degradation in more detail, on the basis of the calculated electronic states for the Si(001) and Si(111) ultrathin films presented above. On H-terminated Si surfaces, generally, dangling bonds on the surface are passivated by hydrogen and thus O_2 molecules reaching the surface would not be dissociated into oxygen atoms nor adsorbed on the surface at room temperature or in the dark.[20] Thus, the oxidation of H-terminated Si surfaces can be suppressed, compared to that of clean Si surfaces.[20] However, we expect that, when the H-terminated Si surfaces are annealed at low temperatures or illuminated, hydrogen desorption from the surface would be promoted under the influence of interactions between Si-H bonds and oxygen, as described later with respect to porous Si. This can lead to the promotion of the dissociation of O_2 molecules into oxygen atoms by an increase in density of dangling bonds on the Si surface.[18,20] On the other hand, as stated above, both the on-top and top-bridge sites are the most stable positions for atomic oxygen adsorbed on the unreconstructed Si(001) surface, with the top-bridge site being the more energetically favorable, judging from the adsorption energies calculated for both configurations in the past.[14,17,18] This is consistent with experimental findings that oxygen atoms take the top-bridge sites between the first-layer Si atoms on the Si(001) surface.[21] Therefore, the surface configuration of oxygen at the on-top or top-bridge sites on the Si(001) ultrathin films studied here can be realized as a result of chemisorption of atomic oxygen at those sites on the surface, which would occur immediately after or during hydrogen desorption from the surface. As stated earlier, these oxygen configurations produce electronic states of a Si dangling-bond character across the fundamental band gap of the Si(001) ultrathin films, regardless of their thickness, suggesting the appearance of nonradiative recombination centers and thus the luminescence degradation.

Here, it is worth while describing some of results calculated for on-top and top-bridge oxygen site geometries on Si(111) ultrathin films,[22] though those geometries on Si(111) are not shown in the present paper. As expected, both the on-top and top-bridge oxygen configurations could also be created on the Si(111) surface following or during hydrogen desorption under oxygen atmosphere. It is found that electronic states near the band gap calculated for the on-top site geometry on Si(111) ultrathin films are almost the same in behavior as those for the molecular oxygen chemisorption site geometry on Si(001) ultrathin films.[6] Specifically, atomic oxygen at the on-top sites, saturating dangling bonds on Si(111), presents electronic states due to mild π bonds between the nonbonding p orbitals of oxygen and the p orbitals of the underlying Si atoms just above the VBM, independent of the film thickness. Those π-bond states are not localized on the surface, behaving as part of the valence band. Thus, this configuration does not produce localized gap states. On the other hand, the behavior of the top-bridge site configuration of atomic oxygen on Si(111) is also similar to that on Si(001). Oxygen at the top-bridge sites does not fully passivate Si dangling bonds on the surface, resulting in the occurrence of p_z-like states of a dangling-bond character. These states are strongly localized on the surface as expected, serving as nonradiative recombination centers. However, a MO cluster model total-energy calculation has provided no evidence for any top-bridge site chemisorption of oxygen on Si(111), though the on-top site chemisorption would be possible.[23] Another cluster model calculation has indicated that both the on-top and top-bridge sites on Si(111) are not as stable as those on Si(001).[17] In either case, the top-bridge site configuration could be much less probable on Si(111).

On the other hand, the surface Si hydrides backbonded to oxygen ($OSiH_2$ configuration), which is the most probable configuration of atomic oxygen on the H-terminated Si(001) surfaces observed in experiment at an initial stage of oxidation,[24] tend to change the band gap of the Si(001) ultrathin films from the direct one to quasidirect one, but never produce gap states, as shown in Fig. 6. On the contrary, this oxygen configuration can increase oscillator strength for light emission, compared to the H-terminated films. For example, the values of oscillator strength calculated for the Si eight-12-, and 40-layer films are 7.5×10^{-2}, 6.8×10^{-2}, and 6.7×10^{-3}, respectively, in this oxygen configuration, compared to the H-terminated case (4.4×10^{-3}, 1.6×10^{-3}, and

5.6×10^{-6} for the Si eight-, 12-, and 40-layer films, respectively).[6,19] In addition, the band gap returns back to the direct one and the calculated oscillator strength is largely intensified by an increase in $\alpha\,(\leqslant 180°)$.[19]

In contrast, the similar oxygen configuration (OSiH configuration) produces the gap states in the H-terminated Si(111) ultrathin films, as shown in Fig. 7. The oxidation of a Si-Si backbond with surface hydride has been observed experimentally at an early oxidation stage of the H-terminated Si(111) surfaces.[25] Moreover, MO cluster model calculations have shown that oxygen insertion into Si-Si backbonds occurs more favorably than into Si-H bonds.[15,26] Thus, we believe that this configuration of a Si hydride backbonded to oxygen can occur at an initial stage of oxidation on Si(111), leading to the appearance of the gap states shown in Fig. 7.

From all of the foregoing we expect that the difference in situation of electronic states due to the similar oxygen configurations between the Si(001) and Si(111) ultrathin films may be a reason for controversial experimental results for the PL intensity, which increases in some cases and decreases in other cases with oxidation in porous Si,[27] since surfaces of porous Si could be of different crystallographic orientations. However, it should be noted that the proposed degradation mechanism based on the on-top or top-bridge site configuration of oxygen on the Si(001) ultrathin films is able to explain the experimentally observed results in porous Si, where oxidation does not degrade luminescence in the dark or at room temperature, but decreases PL output under illumination or low-temperature annealing (200 °C).[7,8] In fact, thermal annealing studies[28] have shown that hydrogen is desorbed from Si dihydride species on porous Si at low temperatures (~300 °C). Also, photoinduced hydrogen desorption from porous Si with a threshold at 2–3 eV in illumination energy has been observed in FTIR measurements.[29] Thus, it is quite probable that hydrogen desorption in oxygen atmosphere is largely promoted through interactions between Si-H bonds and oxygen under thermal annealing or illumination, as stated above. This would be followed by the creation of the on-top or top-bridge site configuration of oxygen on the surface of porous Si as in Si(001), producing dangling-bond-like gap states.[30] The proposed mechanism described above explains the FTIR and EPR observations that the degradation of PL by oxidation in porous Si is accompanied by a large decrease in the total number of Si-H bonds and an increased amount of Si dangling bonds, despite the observed increase in Si-O bond vibrations accompanying oxidation.[7,9,10]

Finally, when hydrogen at the on-top site of a surface Si atom in the OSiH configuration on Si(111) is replaced by an oxygen atom or OH species, as expected at higher oxygen coverages and temperatures, calculations (the Si-O bond length is 1.64 Å) show that the Si(111) ultrathin films with oxygen at a Si-Si backbond produce no gap states for all film thicknesses and Si-O-Si bond angles under study.[22] The surface configuration of one oxygen atom occupying the on-top site and the other being at the backbond site has been claimed to be possible on the Si(111) surface by electron spectroscopy measurements[31] and the MO cluster model calculation.[23] Moreover, this configuration on the Si(111) ultrathin films is quite similar in situation to SiO_4 terminated Si(001) ultrathin films, in that all Si dangling bonds on the film surface are fully passivated by oxygen.[6,32] The latter have been found to present enhanced oscillator strength for light emission at direct band gaps at $\bar{\Gamma}$ compared to the H-terminated counterparts.[6,32] Thus, further oxidation or oxide formation, where oxygen replaces hydrogen on the Si surface, can remove gap states and recover light emission in the Si(111) ultrathin films. Similar situations have been observed in porous Si oxidized thermally at high temperatures (~1000 °C).[1,33]

IV. CONCLUSIONS

A possible mechanism for degradation of light emission by oxidation in Si nanostructures has been proposed, on the basis of electronic state calculations by the EHNTB method for the specific oxygen configurations on the well-defined surfaces of the Si(001) and Si(111) ultrathin films. The conclusions of the present study can be summarized as follows:

(1) The on-top or top-bridge site configuration of oxygen on the Si(001) ultrathin films can be realized as a result of oxygen chemisorption at those sites on the surface, which would occur immediately after or during hydrogen desorption from the surface under oxygen atmosphere. Both oxygen configurations present electronic states of a Si dangling-bond character across the fundamental band gap of the Si(001) ultrathin films, suggesting the occurrence of nonradiative recombination centers and the luminescence degradation.

(2) In the H-terminated Si(111) ultrathin films, the combination of the surface Si-H bond states and the states due to the Si-Si backbond to which oxygen attaches causes gap states, resulting in the occurrence of nonradiative recombination centers. This is in contrast to the case of the H-terminated Si(001) ultrathin films where the similar oxygen configuration does not produce any gap states.

(3) Finally, it is found that the luminescence degradation due to oxidation observed in porous Si can be explained by a combination of hydrogen desorption and the following creation of the on-top or top-bridge site configuration of oxygen on the Si surfaces, causing gap states of a Si dangling-bond character.

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