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Structure and formation mechanism of blue-light-emitting centers in silicon and silica-based nanostructured materials

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We propose a model of the blue-light-emitting center in silicon and silica-based materials on the basis of the density functional theory calculations. It has been shown that the dehydroxylation reaction involved in the annealing process of surface hydroxyl groups results in the formation of a defect pair consisting of a dioxasilirane, $=\mathrm{Si}(\mathrm{O}_2)$, and a silylene, $=\mathrm{Si}:$, center. The resulting defect pair has the allowed electronic transition energies of ~3.5 and ~5 eV, in agreement with the peak positions of the photoluminescence excitation spectra of the blue-light-emitting materials.

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Visible light emission from Si-based nanostructures, including porous and nanocrystalline silicon, has generated tremendous interest in view of the intriguing emission features and the possible application of optoelectronics.[1] The visible photoluminescence (PL) bands from Si-related nanostructured materials are commonly classified into two groups depending on their characteristics decay times. One is the so-called "slow band (*S* band)," which is characterized by the decay times of the order of several microseconds at room temperature. It has been demonstrated that the position of the *S* band is affected by the dimensions of Si nanocrystals, extending from about 1.3 eV (950 nm) to 2.1 eV (590 nm). This provides the possible experimental evidence that quantum confinement plays a vital role in showing the *S* band.[1,2] The other widely-studied PL from Si-based materials is a blue-green band with decay times in the nanosecond regime and is hence termed the fast band or "*F* band." In contrast to the *S* band, there has been no clear experimental evidence that links the *F* band to any Si nanostructures;[3] rather, defective oxide structures are likely to be responsible for the *F* band because this type of PL is observed exclusively from oxidized porous silicon and the relevant silicon oxide-based materials.[1] Some researchers suggest that carbonaceous contaminations, e.g., carbonyl-related chromophores, are responsible for the *F* band.[4] However, these organic chromophores are not necessarily needed to show the *F* bandlike output; for example, as will be shown below, high-purity nanometer-sized amorphous silica (SiO_2) particles called fumed silica, which has been shown to have unique structural characteristics as compared to bulk amorphous silica,[5] also exhibit a similar blue PL band in the nanosecond time domain. Thus far, the complexity of microscopic details has not allowed us to perform reasonable theoretical investigations of the *F* band, and the physical origin of the blue emission is still unclear and a matter of controversy.

Although there has been no accepted model of the *F* band, the experimental evidence is provided for a surface-related defect model.[6] One possible candidate of the surface emission center is the silanol groups (Si–OH) adsorbed on the surface of silicon and/or silicon-oxide structures.[7] Since the blue PL can be generally stimulated by immersion of the oxidized porous silicon into water or by a long-term aging in air,[7,8] it is quite likely that the adsorbed silanol groups are responsible, directly or indirectly, for the *F* band. However, there appears to be several drawbacks of the silanol model as follows. One is that a heavily hydrated material does not show an efficient blue PL, but it generally requires an annealing process between about 100 to 400 °C to generate the substantial PL output.[7] The annealing process normally induces the dehydroxylation reaction between silanol groups and will hence reduce the number of surface silanol groups. The other critical point we would like to note is that the silanol groups in the silicon oxide network do not show an absorption band below ~7.3 eV (~170 nm),[9,10] whereas the blue emission is normally observed under excitation of ~330–~360 nm light.[4–8] These considerations strongly suggest that the blue PL does not result from the surface silanaol groups as they are but from their derivatives generated during the annealing process. It should be noted, however, that the common temperature-driven condensation reaction of silanol groups, namely, $2\equiv\mathrm{Si{-}OH}\rightarrow\equiv\mathrm{Si{-}O{-}Si}\equiv+\mathrm{H}_2\mathrm{O}$, will not account for the formation of the blue-light-emission center because the resulting siloxane bridge will not show any visible PL emission. In this paper, we will hence propose an alternative mechanism of the silanol dehydroxylation reaction that can account for the underlying experimental features related to the blue-PL band

As mentioned above, an efficient blue PL can be generally obtained after annealing the highly hydroxylated silicon or silica surface in the temperature range from ~100 to ~400 °C. It is reasonable to expect that at the surface of highly hydroxylated silicon, some Si atoms are bonded to more than two OH groups. Indeed, it has been well documented[11] that at the surface of nanometer-sized amorphous silica particles, there exist a number of geminal silanols, which consist of two hydroxyl groups attached to one silicon atom. We then consider what happens when the dehydroxylation reaction occurs between the two geminal silanols facing to each other. If we apply the normal silanol condensation reaction to this case, an edge-sharing dimer is expected to be formed (scheme 1 in Fig. 1). However, there is another possibility that a pair of $=\mathrm{Si}(\mathrm{O}_2)$ and $=\mathrm{Si}:$,

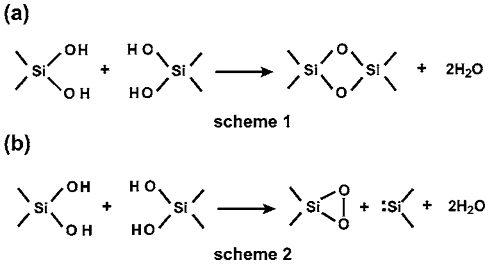

FIG. 1. Models of the dehydroxylation reaction involved in the two adjacent geminal silanol groups: (a) formation of an edge-sharing dimer (scheme 1), (b) formation of a defect pair consisting of $=\mathrm{Si(O_2)}$ and $=\mathrm{Si}$: (scheme 2).

which are called dioxasilirane[12] and silylene, respectively, is generated (scheme 2 in Fig. 1). Since the bonding configurations of the products formed from schemes 1 and 2 are rather different from those in the normal siloxane bridges, these configurations can be viewed as defective oxide structures that might be responsible for the blue PL emission. Hamann,[13] however, has shown from the theoretical calculations based on the density-functional theory (DFT) that the dimer configuration in silica network has an effect to narrow the band gap, E_g, of silicon dioxide ($E_g = \sim 9$ eV) only by $\sim$1 eV and does not create a midgap state, indicating that this type of defect cannot account for the *F* bandlike PL band excited by $\sim 330 - \sim 360$ nm. On the other hand, the dehydroxylation reaction based on scheme 2 has not been previously considered yet but is worth investigating in terms of the structural origin the *F* band PL. For this purpose, we perform a series of DFT calculations using clusters of atoms that model the local structure of the defects proposed in scheme 2. It has already been demonstrated that the DFT cluster calculations are very useful to investigate the structure and energies of defect centers in various silica-based materials.[14] All the DFT calculations in this work have been performed with the[15] GAUSSIAN03 code.

To compare the calculated results with the experimental data, we also measured the blue PL emission from nanometer-sized fumed silica particles (Aerosil 380), obtained from Nippon Aerosil Co., LTD. It had a nominal surface area of 380 ± 30 m^2/g and an average primary particle size of 7 nm (product specification). Steady state PL spectra were measured at room temperature with a Shimadzu RF-5300PC spectrofluorometer (Shimadzu, Kyoto, Japan). Time-resolved PL measurements were performed using a synchroscan streak camera (Hamamatsu, Shizuoka, Japan) and the second harmonic (350 nm) pulse of a mode-lock Ti:sapphire laser (Spectra-Physics, California, USA) with a repetition rate of 1 MHz, an average power of 0.3 mW and typical pulse lengths of <180 fs. As shown in Fig. 2, we confirmed that the fumed silica has a blue PL emission with a decay time on the order of nanoseconds, showing the *F* band characteristics.

Figure 3 depicts the optimized structure of the clusters modeling the surface silanol groups including a pair of geminal silanols (model I) and a pair of $=\mathrm{Si(O_2)}$ and $=\mathrm{Si}$: (model II) obtained by the DFT calculations at the B3LYP/6-31G(d) level.[16,17] We also calculated the optimized structure of an edge-sharing dimer (model III) at the same B3LYP/6-31G(d) level for comparison. As expected from schemes 1 and 2, the present DFT calculations enabled us to obtain the optimized configurations not only for an edge-sharing dimer (model III) but also for a pair of $=\mathrm{Si(O_2)}$ and $=\mathrm{Si}$: (model II). A vibrational analysis was carried out on each optimized structure to ensure that the structure corresponds to a local minimum that has no imaginary frequencies.

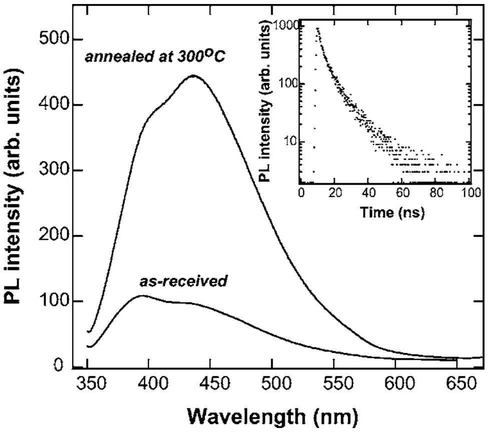

FIG. 2. Steady state photoluminescence (PL) spectra of fumed silica before and after annealing at 300 °C for 2 h. The PL spectra were measured under photoexcitation with a wavelength of 350 nm. The inset shows a PL decay of the 300 °C-annealed sample, for an excitation wavelength of 350 nm and PL detection at 450 nm.

We see from Fig. 3 that the $=\mathrm{Si(O_2)}$ and $=\mathrm{Si}$: centers in model II are specially separated although, in the optimization process, we started from the configuration in which these two defect centers are rather close to each other. It is hence likely that there is no mutual interaction between the two types of defect centers in model II. It has also been found that the total energy of model II is higher than that of model III by 7.1 eV, indicating that the configuration of model II is a metastable state.

We next turn to the singlet-to-singlet excitation energies of the model clusters obtained by the time-dependent DFT (TD-DFT) method[18] with the 6-31++G(d) basis set. The calculated five-lowest excitation energies are shown in Fig. 3. We have found that the calculated excitation energies of model I range from 6.9 eV (180 nm) to 7.2 eV (173 nm), in good agreement with the energy of the absorption band related to the silanol groups[9,10] ($\sim$7.3 eV) mentioned earlier. It is also interesting to note that the excitation energies of model III are almost comparable to those of model I, indicating that the excitation energy of the silanol groups is not affect by the presence of the edge-sharing dimer structure. This result further confirms that the edge-sharing dimer does not contribute to the blue PL, which is normally excited by $\sim 330 - \sim 360$-nm UV light. It should be noted, however, that model II has excitation energies in the near- to mid-UV ($\sim 250 - \sim 350$ nm) region. More interestingly, the calculated excitation energies correspond well with the peak positions of the PL excitation (PLE) spectrum observed for the blue PL of fumed silica particles (see Fig. 4). The PLE spectra of the blue-PL from oxidized porous silicon[19,20] have similar

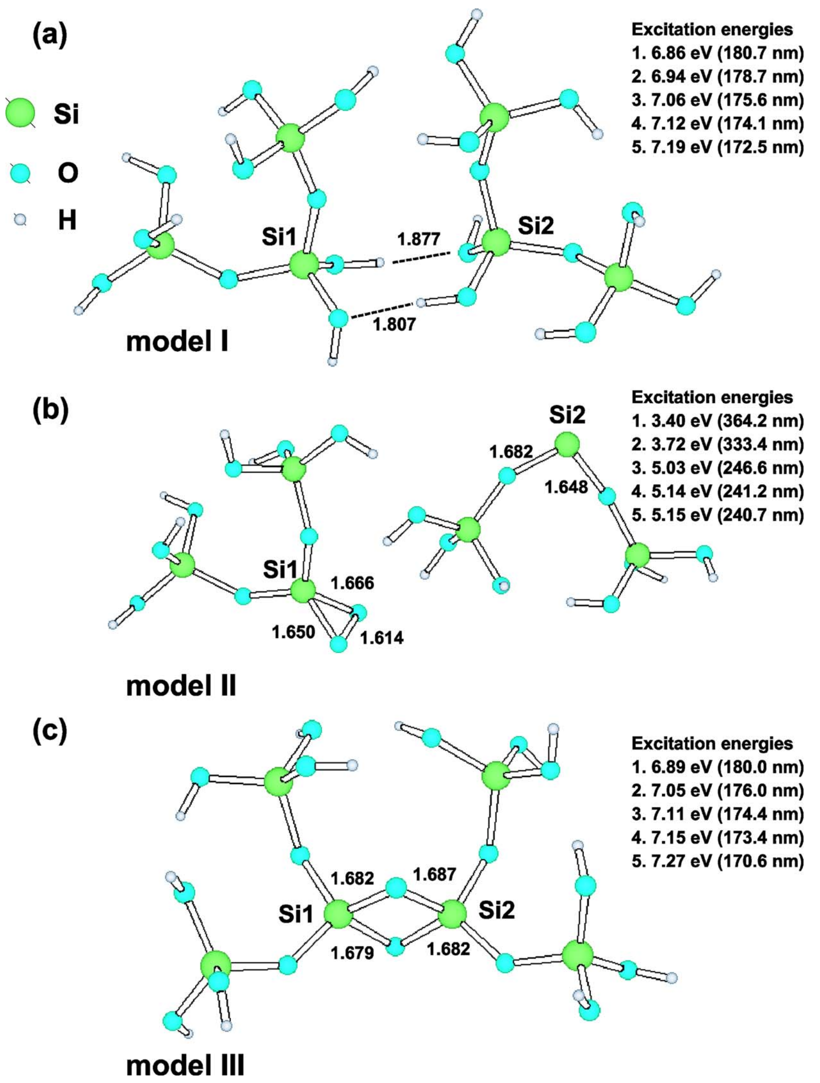

FIG. 3. (Color online) Optimized structures of the model clusters obtained at the B3LYP/6-31G(d) level: (a) a two-adjacent geminal-silanol model (model I), (b) a pair of $=\mathrm{Si}(\mathrm{O}_2)$ and $=\mathrm{Si}:$ model (model II), and (c) an edge-sharing dimer model (model III). Principal bond distances in the defect structures (in Å) and the five-lowest excitation energies calculated at the B3LYP/6-31G(d) and TD-B3LYP/6-31++G(d) levels, respectively, are also shown.

bands peaking at ~260, ~300, and ~360 nm, in agreement with the excitation energies calculated for model II as well. From the good correspondence between the calculated and observed excitation energies, we strongly suggest that the blue-PL band of silicon and silica-based nanostructured materials results from the defect pair shown in scheme 2. In model II, we found that the electronic excitations related to $=\mathrm{Si}(\mathrm{O}_2)$ are mainly responsible for the two-lowest transitions at 3.4 and 3.7 eV. Thus, we can conclude that the main PLE peak at ~350 nm (~3.5 eV) of the blue PL results from the electronic excitation associated with the $=\mathrm{Si}(\mathrm{O}_2)$ center. Previously, the excitation energies of an isolated $=\mathrm{Si}(\mathrm{O}_2)$ center were estimated to occur at ~3–~5 eV using experimental[21] and theoretical techniques,[22] and a possible relationship between $=\mathrm{Si}(\mathrm{O}_2)$ and visible PL emissions was suggested.[23] However, it has not been recognized that this type of center can be generated from the dehydroxylation reaction of geminal silanols and is related to the *F* band-type PL emission.

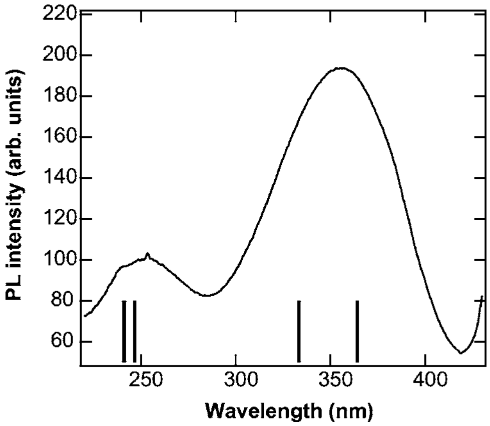

FIG. 4. Photoluminescence excitation spectrum of the 300 °C-annealed fumed silica sample monitored at 440 nm. The vertical lines correspond to the five-lowest excitation energies calculated for model II.

Finally, we comment the annealing-temperature dependence of the PL intensities. We found that the PL intensities from fumed silica reach their maximum values when annealed at ~300 °C. When annealed at temperatures more than ~800 °C, however, the samples do not show any PL emission over the entire spectral range observed. The observed temperature dependence of the PL intensity is basically comparable to the one reported previously for oxidized porous silicon.[7] The initial growth of the PL intensity with annealing temperature can be interpreted in terms of the progression of a metastable defect pair predicted in scheme 2. The thermal quenching of the PL intensity at higher annealing temperatures implies the defect transformation to other more stable structures, including edge-sharing dimers and/or normal corner-sharing siloxane bonds.

In summary, we have proposed an unprecedented structural model of the blue-light-emitting center in oxidized porous silicon and the nanostructured SiO_2 materials. It has been shown that the dehydroxylation reaction of a pair of geminal silanol groups lead to the formation of a metastable defect pair consisting of $=Si(O_2)$ and $=Si:$. The allowed singlet-to-singlet transitions of the defect pair are found to be in good agreement with the peak positions of the PLE from the blue-light-emitting materials.

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