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Electronic-structure investigations of siloxenic clusters and films

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Calculations on two forms of siloxenic clusters and periodic films have been performed to address the unusual luminescence in porous silicon and to further investigate how the optical gap varies as a function of hydroxyl- or hydrogen-passivator concentration. Within conventional approximations to the density functional theory, our optimized cluster calculations confirm that low-dimensional siloxenic complexes, of stoichiometry [Si]:[O]:[H] = 2:1:2, are most stable when the oxygen atoms form bridging bonds with pairs of silicon atoms. To aid in experimental characterization of siloxenic films, we present equilibrium geometries, electronic structures, chemically induced core-level shifts, and joint densities of states for two forms of siloxenic clusters.

I. INTRODUCTION

Recent reports of a strong visible photoluminescence in porous silicon[1,2] have prompted many theoretical and experimental studies aimed at explaining this phenomenon. Nevertheless, the origins of the luminescence remain controversial. By comparing the observed luminescence and vibrational properties of anodically oxidized porous silicon to that of chemically synthesized siloxene [$Si_6O_3H_6$], Brandt *et al.*[3] have suggested that the luminescence is primarily caused by siloxenic derivatives within the porous silicon. More recently, Deak *et al.*[4] have performed semiempirical electronic-structure calculations that support these assertions. However, Tischler and Collins[6] have presented data suggesting that oxygen-related vibrations in freshly prepared porous silicon are absent. Buda *et al.*[7] and Read *et al.*[8] have performed calculations on hydrogenated silicon wires as a function of size. For wires with appropriate thicknesses, they obtain energy gaps that are not inconsistent with the luminescence observed in porous silicon. Another suggestion is that the photoluminescence is an intrinsic property of porous silicon itself and is due to the columnar voids in the material. Within this hypothesis, the blueshift is accounted for by the quantum size effects in the wirelike structures. Banerjee *et al.*[5] have performed experiments that support the view that the luminescence is due to complex formation and not to quantum size effects.

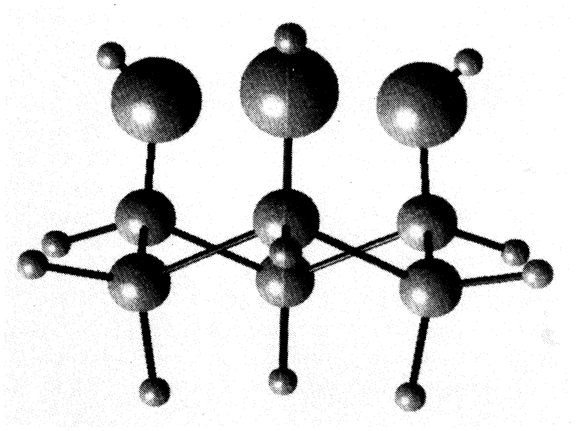
The energy gap of any collection of fourfold-coordinated silicon atoms decreases more or less monotonically with the number of bulklike silicon atoms, from several eV to about 1 eV. This fact underscores the difficulty in determining unambiguously what system of atoms is responsible for the luminescence in porous silicon. In this work, we present results from density-functional-based calculations on low dimensional complexes of stoichiometry Si_2OH_2. We refer to these complexes as siloxenic systems. While our total-energy results clearly predict that such complexes will be observed with Si-O-Si chains, rather than Si-Si-Si, we find that the optical characteristics of both species are quite similar. Since the optical characteristics are similar for these two materials, and because it is always possible to find a (probably nonunique) silicon-based complex with almost any band gap between 1 and several eV, we have also studied the influence of passivator electronegativity and concentration on the energy gaps. Here, we find that the presence of subsurface Si-O-Si bonds can cause quantitatively and possibly qualitatively different results for the two types of structures. Such studies supply experimentalists with an additional way of probing their samples and should be helpful in more clearly identifying whether a particular complex is responsible for luminescence in porous silicon.

While the original motivation of this work was to determine whether siloxenic clusters or films could be responsible for the luminescence in porous silicon, the answer to this question is of secondary importance to a first-principles understanding of siloxenic systems generally. Providing that siloxenic films[9] have optical properties similar to those of porous silicon, the possibility arises of tailoring the gap and luminescence efficiency by hydroxyl/hydrogen (or halogen/hydrogen) substitution. This degree of control would be interesting in its own right and, from a practical point of view, quite important, since the entity responsible for luminescence would be clearly identified.

II. CLUSTER GEOMETRIES

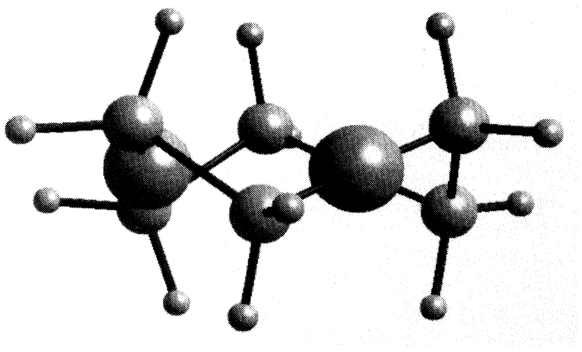
Requisite to a full understanding of the luminescence is knowledge of the ground-state geometry and perhaps low lying polymorphs of $Si_6O_3H_6$ and an understanding of how the optical properties of such materials depend on the geometrical structure and surface passivation. To gain insight into such questions we have performed calculations on two cluster based models of siloxenic polymorphs, pictured in Fig. 1. Both clusters have a composition of $[Si_6O_3H_6]H_6$ and are constructed from fourfold-coordinated silicon atoms, twofold-coordinated oxygen atoms, and singly-bonded hydrogen atoms. The difference between the two structures is that in Fig. 1(a) the oxygen atoms are found in the form of hydroxyl groups that tie off surface dangling bonds, while in Fig. 1(b) oxygen atoms lie between planes of silicon atoms. Both clusters are plausible models for a fragment from a siloxenic film (discussed in Ref. 4) of stoichiometry Si_2OH_2, with six additional hydrogen atoms added to passivate the silicon dangling bonds at the edges of the cluster. We refer to the molecule in Fig. 1(a) as the silicon bilayer structure, since the siloxenic component consists of five layers of atoms with a connectivity of H-Si-Si-OH. We refer to the molecule in Fig. 1(b) as the oxygen-bridged structure since the siloxenic component has a connectivity of H-Si-O-Si-H. The symmetries of the two different models are C_{3v} and D_{3h}, respectively. We have optimized the geometry of both models with the all-electron Gaussian-orbital-based cluster codes that have been developed recently by Pederson and Jackson in the Complex Systems Theory Branch of the Naval Research Laboratory.[10]

(a)



Silicon Bilayer

(b)



Oxygen Bridged

FIG. 1. Equilibrium geometries for two models of siloxenic molecules $[Si_6O_3H_6]H_6$. The silicon bilayer terminated by hydroxyl groups (a) is metastable, with LDA and GGA energies that are 0.2 eV/[Si atom] higher than the oxygen-bridged structure (b) that is terminated by hydrogen atoms.

For both structures we have started with a reasonable geometry based on standard bond lengths, calculated the self-consistent Hellmann-Feynman forces[10] on each atom, and continuously updated the molecular geometry using the conjugate-gradient algorithm. The geometrical optimizations have been terminated when the net force on any given atom was found to be less than 0.07 eV/Å. The resulting bond lengths are presented in Table I. With the exception of the Si-O bond, which exhibits a 0.04 Å increase in the silicon bilayer structure, the bond lengths are not strongly dependent on structure. However, strains away from the ideal tetrahedral environment of Si are evident in both structures, and are quite large in the oxygen-bridged structure.

Within the framework of the Perdew-Zunger parametrization of the Ceperley-Alder local-spin-density (LSD) approximation,[11] we find that the oxygen-bridged structure (H-Si-O-Si-H) is more stable than the silicon bilayer structure (H-Si-Si-OH) by 1.20 eV, or approximately 0.20 eV per silicon atom. Since the LSD approximation is known to overestimate binding energies, we have also calculated the total energies of each of the optimized geometries with the generalized gradient approximation (GGA).[12] This method has recently been tested for obtaining atomization energies and has proven to yield dramatic improvements over the LSD approximation. For example, the LSD-GGA atomization energies of hydrocarbon molecules reproduce experiment to better than 0.1 eV per atom.[12,13] Within the GGA, we also find that the oxygen-bridged structure is more stable than the silicon bilayer structure by 0.22 eV per silicon atom. While LSD is known to yield accurate molecular geometries, the close agreement between the GGA and LSD stabilities is not necessarily expected since the types of bonds are different in each system and LSD does not always overestimate bond strengths uniformly.

For comparison, we note that Deak *et al.*[4] have used two different semiempirical frameworks to perform geometrical optimization on structures that are the periodic equivalents of those in Fig. 1. In accord with the re-

TABLE I. Nearest-neighbor separations (in Å) obtained for two different cluster models of siloxenic polymorphs. The hydroxyl-terminated silicon bilayer is less stable by 0.2 eV per silicon atom than the oxygen-bridged structure.

Bond	Silicon bilayer	Oxygen bridged
Si-Si	2.367	2.369
Si-O	1.711	1.673
Si-H	1.51–1.53	1.527,1.531
O-H	0.993	

sults of this work, they predict that the oxygen-bridged structure is more stable than the silicon bilayer structure by 0.31–0.47 eV per silicon atom. With respect to geometries, our equilibrium bond-lengths are 1–2 % shorter than those of Deak *et al.*

III. ELECTRONIC STRUCTURE OF CLUSTERS

The results from our geometrical optimizations suggest that if siloxenic derivatives exist within porous silicon, they will be found primarily in the oxygen-bridged structure. In an effort to aid experimentalists in positively deducing the presence of siloxenic derivatives we present the electronic structure and optical properties of these clusters in this section. Within the quantitative limitations of the LDA we expect the optical properties presented here to reflect the observed excitation spectra of small siloxenic molecules and to reproduce qualitatively the excitations associated with larger siloxenic systems.

To simulate the qualitative features of the optical absorption spectrum of our siloxenic molecules we have calculated the joint density of states:

$$J(E) = \sum_{i,j,\beta} \frac{\gamma\langle\psi_i|r_\beta|\psi_j\rangle^2}{(\epsilon_i - \epsilon_j - E)^2 + \gamma^2}\ , \tag{1}$$

where ψ_i and ψ_j are, respectively, occupied and unoccupied orbitals with eigenvalues ϵ_i and ϵ_j, $r_\beta = x, y, z$ for $\beta = 1, 2, 3$, and γ is an empirically determined broadening factor. It is evident from Fig. 2 that the low energy optical absorption spectra are similar for both clusters. Coincidentally, both spectra reveal peaks at approximately 4.2–4.3 eV and at 4.7–4.8 eV.[14] While the absorption peaks are similar in shape, the absorption intensity is approximately five times smaller for the oxygen-bridged structure than for the silicon bilayer structure. This information and a closer look at the locations of the excitation peaks suggests an experiment that might confirm the presence of such molecules. At low temperatures, the siloxenic species will exist primarily in the oxygen-bridged structure. At higher temperatures, both the oxygen-bridged and bilayer structure will exist. In general, an increase in temperature should lead to a decrease in the relative population of the oxygen-bridged structure, and to a commensurate increase in the absorption peaks near 4.25 and 4.77 eV, as well as a shift of these peak centers (upward) by approximately 0.1 eV. An increase in the absorption near 6.0 eV is also expected at higher temperatures.

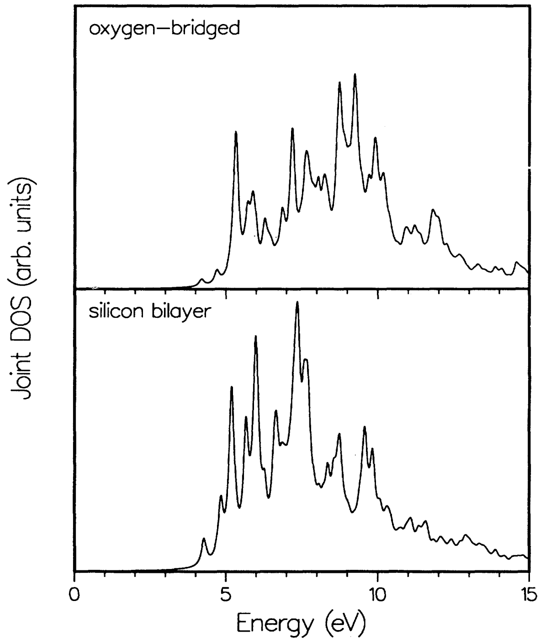


FIG. 2. Joint density of states for the silicon bilayer and oxygen-bridged molecular models of siloxene. While the units here are arbitrary, the relative intensities as a function of structure are accurately illustrated in the figure.

Another way to determine the presence and form of siloxenic molecules is through analysis of 1*s* core ionization thresholds. Such shifts are primarily due to charge transfer between pairs of atoms with different electronegativities and are typically on the order of 1.0–1.5 eV. In this case, the two polymorphs (molecules or films) have qualitatively different signatures. The silicon bilayer should show two silicon 1*s* core peaks, separated by 1.0 eV in the molecule, while the oxygen-bridged structure should show a single silicon 1*s* core peak. For the molecules discussed here, the latter peak occurs at the same energy as the lowest peak of the silicon bilayer. For both structures the oxygen 1*s* core energies have only one peak, with the silicon-bilayer oxygen 1*s* level 0.25 eV lower in energy than that of the oxygen-bridged structures.

There has been some speculation in the literature that the luminescence in porous silicon is due to the presence of complexes such as the clusters discussed here. Our finding of an absorption threshold at approximately 4–5 eV indicates that such complexes would have to be larger than the small molecules considered here.

IV. GAP SUPPRESSION AND ENHANCEMENT DUE TO PASSIVATION

One of the interesting characteristics of siloxenic films, originally reported by Kautsky and Herzberg, is that the energy associated with the luminescence could be tuned by using passivators of varying electronegativity. In Ref. 4, it was shown that the band gap of the oxygen-bridged structure was reduced as the passivating hydrogen atoms were replaced by hydroxyl groups. Since a stable silicon-based film with such tunable behavior could have many technological advantages, we have performed calculations on the siloxenic clusters discussed here to determine whether such behavior is expected to be common, and to investigate how the gap modulation might be further controlled by varying the number of interplanar oxygen bridging atoms.

For the silicon bilayer with connectivity H-Si-Si-OH [Fig. 1(a)], we have calculated changes in the highest-occupied-molecular-orbital / lowest-unoccupied-molecular-orbital (HOMO/LUMO) gap due to hydroxyl/hydrogen passivator substitution. For $x = 0$, 3, and 6, we have optimized geometries of the cluster $[Si_6(OH)_xH_{6-x}]H_6$ [$x = 3$ corresponds to the molecule shown in Fig. 1(a)]. The dependence of the HOMO/LUMO gap as a function of fractional coverages ($\eta = x/6$) of OH surface radicals is presented in Table II. For the completely hydrogenated six membered silicon bilayer ($\eta = 0.0$), the HOMO/LUMO gap was found to be 5.80 eV, which is 1.55 eV larger than the gap obtained for the original model ($\eta = 0.5$). This trend toward smaller gaps with increased hydroxyl-passivator concentration continues in a linear fashion: for the completely hydroxyl-terminated silicon bilayer ($\eta = 1.0$) the HOMO/LUMO gap of 2.7 eV is 1.55 eV *less* than that of the original model.

To determine whether this behavior is common in low-dimensional silicon complexes, we have checked for hydroxyl-induced gap suppression in the oxygen-bridged structure as well. We have replaced the six surface hydrogens of the oxygen-bridged structure [Fig. 1(b)] by six hydroxyl groups, optimized the geometry and examined the resulting electronic structure. This result is also presented in Table II. In contrast to the silicon bilayer, we observe no gap suppression. The HOMO/LUMO gaps for the fully hydrogen- and fully hydroxyl-passivated complexes are 4.19 eV and 4.57 eV, respectively. However, we note that for the unrelaxed hydroxyl-terminated structure, some degree of gap suppression was evident. Simply replacing the hydrogen atoms by hydroxyl groups (with appropriate bond lengths) and neglecting geometrical relaxation leads to a gap of 3.78 eV. We have also looked at oxygen-bridged clusters with fractional hydroxyl coverages of $\eta = 0.5$ and a connectivity OH-Si-O-Si-H. For this system, we find a HOMO/LUMO gap of 4.30 eV. This result also suggests that small oxygen-bridged complexes will not exhibit the hydroxyl-induced gap suppresion that is observed in the silicon-bilayer clusters. Since the oxygen-bridged complexes studied here are devoid of Si-Si, bonds, these results suggest that the degree of passivator-induced gap suppression can be modulated if the concentration of subsurface oxygen atoms can be controlled in siloxenic films.

TABLE II. HOMO/LUMO gap as a function of fractional coverage η of OH passivators. The remaining surface sites are passivated by hydrogen atoms. The hydroxyl-induced gap suppression is observed in the siloxenic-bilayer clusters but not in the oxygen-bridged species. The species that have the ideal siloxenic stoichiometry and coincide with the clusters shown in Fig. 1 are designated with an asterisk.

Connectivity	η	HOMO/LUMO (eV)
OH-Si-Si-OH	1.0	2.70
H-Si-Si-OH*	0.5	4.25
H-Si-Si-H	0.0	5.80
OH-Si-O-Si-OH	1.0	4.57
H-Si-O-Si-OH	0.5	4.30
H-Si-O-Si-H*	0.0	4.19

V. SILOXENIC SILICON BILAYERS

We have also used the equilibrium geometries from our clusters to construct unit cells for two-dimensional free standing films. Here we present electronic structures for two-dimensional siloxenic silicon bilayers ($\eta = 0.5$) and compare our results to other LDA calculations on hydrogenated silicon bilayers ($\eta = 0.0$). These all-electron LDA calculations have been performed with the linear-augmented-plane-wave (LAPW) method of Krakauer and co-workers[15] and the linear-combination-of-atomic-orbitals (LCAO) method of Erwin *et al.*[16]

For the case of the silicon bilayer cluster, the tetrahedral environment of each silicon atom is not severely perturbed and it is possible to construct a unit cell with bond lengths that are very close to those found in the cluster. The unit cell consists of five inequivalent atoms (two silicons, two hydrogens, and one oxygen), and real space translation vectors given by $1.913(1,\sqrt{3},0)$ Å and $1.913(-1,\sqrt{3},0)$ Å. This leads to nearest-neighbor distances of $R_{\text{Si-Si}}$=2.386 Å, $R_{\text{Si-O}}$=1.703 Å, $R_{\text{Si-H}}$=1.506 Å, and $R_{\text{O-H}}$=0.987 Å. For computational convenience, the films were also periodically repeated in the z direction; the separation between films, approximately 5 Å, leads to negligible interlayer dispersion. In Fig. 3 we present the electronic density of states for the silicon bilayer. The gap is direct with an energy of 1.2 eV. Since the LDA typically underestimates experimental gaps by about 40%, an experimental band gap for this film would be approximately 1.6–1.7 eV, which is in the experimentally determined luminescence range. Examination of the projected density of states (Fig. 3) shows that both the valence band maximum and conduction band minimum are primarily composed of Si 3p states. Since the LDA underestimates the bulk Si gap by approximately 0.5 eV, this again suggests that the band gap for the bilayer structure would be close to 1.7 eV.

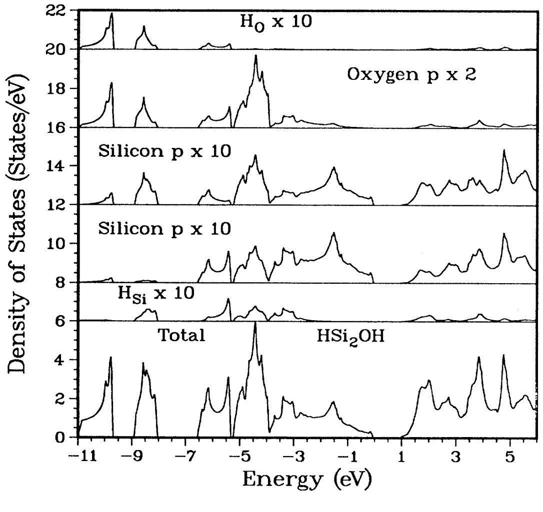


FIG. 3. Density of states of the metastable siloxene film (believed to be the film originally synthesized by Kautsky and Herzberg). The experimental gap for this material is expected to be approximately 0.5 eV larger, which implies a luminescence with energies of approximately 1.7 eV.

While additional calculations may be useful, some information on how the bilayer band gap is expected to vary as a function of passivator stoichiometry $[Si_2H_{2-x}(OH)_x]$ can be estimated in several ways. We first note that an argument similar to that of Ref. 4 suggests that the valence charge in a silicon bilayer will increase as the concentration of the electronegative hydroxyl radicals decreases. The buildup of valence charge within the films causes an increase in the bonding-antibonding splitting which increases the band gap. This argument is in accord with our cluster calculations, where substitution of hydrogen passivators for hydroxyl passivators increased the gap by 1.5 eV. Further support comes from the results of Takeda and Shiraishi[17] for Si_2H_2 films, which predict a LDA band gap of 2.5 eV that is 1.3 eV larger than our hydroxyl terminated film. Combining the LDA results from this paper with those of Takeda and Shiraishi, and including an empirical 0.5 eV adjustment to the theoretical gaps, we suggest that the experimental band gap of $[Si_2H_{2-x}(OH)_x]$ will decrease from about 3.2 eV to 1.7 eV as x varies from 0 to 1 (η varies from 0.0 to 0.5). This behavior is qualitatively similar to what was observed in Ref. 4 for the different oxygen-bridged film. However, the degree of gap suppression is larger in the silicon-based bilayer by a factor of approximately 2. This is in accord with the fact that no suppression is observed in the oxygen-bridged siloxenic clusters which are devoid of Si-Si bonds.

VI. DISCUSSION

In this paper we have reported calculations on two types of siloxenic systems with a stoichiometry of Si_2OH_2. Providing that the luminescence in porous silicon is due to a low-dimensional compound with this stoichiometry, our total-energy results strongly favor the oxygen-bridged geometry as the ground state structure. We have studied the electronic structure of these systems as a function of geometry, bonding, and surface passivation. The optical characteristics are nearly invariant with system structure and do not allow for a direct determination of the atomic geometry of these films. However, our results suggest some experimental tests that might aid in clearly confirming or contradicting the presence of siloxenic complexes in porous silicon.

From the results presented here and in Refs. 4 and 17, there is now considerable evidence that the band gaps of low-dimensional silicon-based complexes can be modulated by selective passivation. While additional calculations as a function of size, stoichiometry, and passivation could quantify these observations further, most trends can be extracted from the existing work. First and foremost, we note that the gap tailoring originally observed by Kautsky and Herzberg appears to be an intrinsic property of Si-Si based complexes and that it is only the details of this phenomenon that depend on size, structure, and surface passivation.

Some insight into how the hydroxyl-induced gap suppression can be modulated by structural changes of the complex itself may be obtained by comparing the effects observed in the silicon bilayers and the oxygen-bridged structures. For the silicon bilayer clusters, the variance in the HOMO/LUMO gap is 3.1 eV in contrast to oxygen-bridged clusters, which did not exhibit any clear degree of gap suppression. The quenching of the gap suppressions in the oxygen-bridged clusters is due to the fact that it requires more energy to remove charge from a Si-O-Si ring than from a Si-Si ring. Consequently, changes in electronegativity of the surface passivators are expected to have smaller effects on the gap. This suggests that the degree of gap suppression in siloxenic complexes can be controlled by vacating some of the oxygen sites between planes. While such an endeavor is expected to fail if OH and H radicals are used to passivate the surface, reoccupation of the empty oxygen sites could be avoided by using halogens (rather than hydroxyl groups) as an electronegative passivating species.

To understand how the passivator-induced gap modulation is influenced by system size, we compare the cluster results to the available periodic calculations. For the silicon bilayer structure, our cluster results predict a 1.55 eV suppression in band gap when a monolayer of hydrogen passivators is replaced by a monolayer of hydroxyl passivators. This is similar to the results obtained from our H-Si-Si-OH film calculations and the H-Si-Si-H film calculations of Ref. 17, which predict a 1.30 eV gap suppression. So, for silicon bilayers we do not expect system size to be an important parameter for determining the degree of gap suppression. Since the results of this work and that of Ref. 4 correspond to different theoretical frameworks, direct comparison between calculations is more difficult. However, in contrast to the case of the silicon bilayer, for systems that are completely devoid of Si-Si bonds, such as the oxygen-bridged cluster discussed here, gap suppression upon passivation by hydroxyl radicals will not occur.

In summary, we find that variable gap systems, constructed from low-dimensional silicon-based bilayers, can be made if the surface-passivator concentration can be controlled. In principle, the degree of gap modulation can be further controlled by vacating some of the bridging oxygen atoms. However, in the presence of an oxygen-enriched environment, low-dimensional silicon-based structures are only expected to be stable when bridging oxygen atoms are present and reoccupation of these vacancies would occur in this situation. From the point of view of identifying the luminescing entity in porous silicon, the implications of our results are not clear. We can rule out the possibility that small siloxenic clusters are responsible for the luminescence, and we can confirm that siloxenic films are expected to be most stable in an oxygen-bridged structure. We can also infer that the luminescing agent must contain some Si-Si bonds. If, as is suggested in Ref. 6, oxygen-related vibrations are clearly absent in freshly prepared porous silicon, the characteristics we have observed for our silicon bilayers would correlate very nicely with the experimentally observed optical properties. However, the similarities between our film results and the results of Ref. 4 suggest that the same (or very similar) optical properties could be present after exposing the samples to oxygen even if, as expected, the chemical composition of the sample is altered. A more complete understanding of passivator-induced gap suppression as a function of system size and bonding might aid in determining whether the luminescing agent has been stabilized by the aquisition of oxygen atoms.

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[1] L. T. Canham, Appl Phys. Lett. **57**, 1046 (1992).

[2] V. Lehmann and U. Goesele, Appl. Phys. Lett. **58**, 856 (1991).

[3] M. S. Brandt, H. D. Fuchs, M. Stutzmann, J. Weber, and M. Cardona, Solid State Commun. **81**, 307 (1992).

[4] P. Deak, M. Rosenbauer, M. Stutzmann, J. Weber, and M. S. Brandt, Phys. Rev. Lett. **69**, 2531 (1992).

[5] S. Banerjee, K. L. Narasimham, P. Ayyub, A. K. Srivastava, and A. Sardesai, Solid State Commun. **84**, 691 (1992).

[6] M. A. Tischler and R. T. Collins, Solid State Commun. **84**, 819 (1992).

[7] F. Buda, J. Kohanoff, and M. Parrinello, Phys. Rev. Lett. **69**, 1272 (1992).

[8] A. J. Read, R. J. Needs, K. J. Nash, L. T. Canham, P. D. J. Calcott, and A. Qteish, Phys. Rev. Lett. **69**, 1232 (1992).

[9] H. Kautsky and G. Herzberg, Z. Anor. Allg. Chem. **139**, 135 (1924).

[10] M. R. Pederson and K. A. Jackson, Phys. Rev. B **41**, 7453 (1990); **43**, 7312 (1991); K. A. Jackson and M. R. Pederson, *ibid.* **42**, 3276 (1990).

[11] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1979).

[12] See J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. Singh, and C. Fiolhais, Phys. Rev. B **45**, 6671 (1992), and references therein.

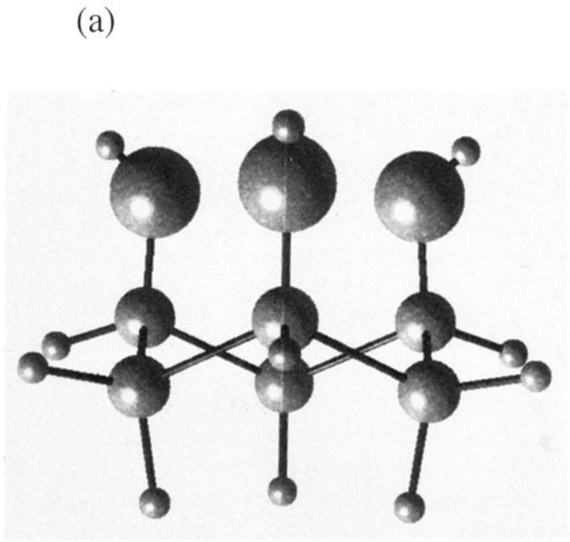
[13] M. R. Pederson, K. A. Jackson, and W. E. Pickett, Phys. Rev. B **44**, 3891 (1991).

[14] For the hydroxyl-terminated structure, the excitation peaks are at 4.28 and 4.84 eV, respectively. For the oxygen-bridged structure the excitation peaks are at 4.19 and 4.70 eV, respectively.

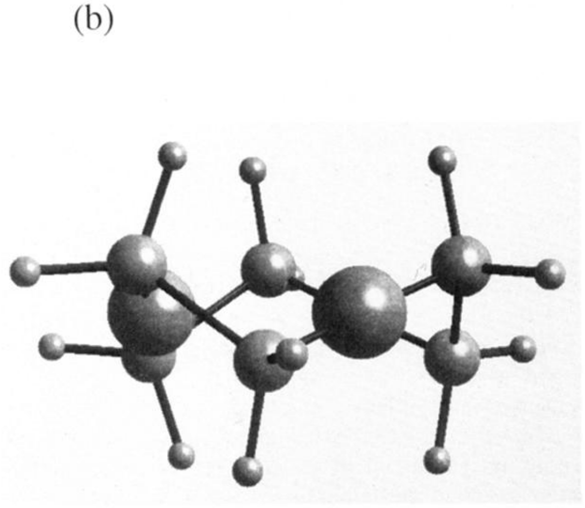
[15] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981); S. H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985).

[16] S. C. Erwin, M. R. Pederson, and W. E. Pickett, Phys. Rev. B **41**, 10 437 (1990).

[17] K. Takeda and K. Shiraishi, Phys. Rev. B **39**, 11 028 (1989).



Silicon Bilayer



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