First-Principles Investigation of Visible Light Emission from Silicon-Based Materials

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(Received 7 August 1992)

The atomic and electronic structure of various Si-based layered structures is calculated using pseudopotential density-functional theory and a self-energy approach. A silicon-hydrogen compound, consisting of a stacking in the [111] direction of double layers of Si terminated with H, is found to have an almost direct band gap of 2.75 eV. Substituting OH groups for H atoms leads to the compound siloxene, which is found to have a direct band gap of ~1.7 eV. Investigations of the band-edge states and calculations of matrix elements show that these direct transitions are very strong.

PACS numbers: 61.43.Bn, 68.65.+g, 71.25.Tn, 73.20.Dx

Recent work has focused attention on the possibility of obtaining strong visible light emission from silicon-based materials [1, 2]. Two mechanisms have been explored: quantum confinement and chemical modification. In this Letter we investigate systems in which both aspects are operative.

To obtain efficient luminescence, the radiative transition rate should be large compared to the nonradiative rate. Since total suppression of the nonradiative channels is usually not feasible or practical, the radiative transitions should be as strong as possible, with a sufficiently large matrix element coupling the band-edge states. In the case of an indirect-gap semiconductor such as Si zone folding can yield a quasidirect band gap. However, if the folded-back conduction-band minimum still largely retains its original character, with little mixing with zone-center states, the resulting optical matrix elements are very weak, as evidenced in studies of short-period Si/Ge superlattices [3].

Quantum confinement has been invoked as an alternative means of obtaining strong transitions in Si-based materials. While there is little doubt that confinement can lead to a direct band gap corresponding to visible photons, this approach may suffer from the same problem as the zone-folding scheme, namely, the failure to change the fundamental character of the lowest conduction-band minimum. Recent calculations based on tight-binding [4] or envelope-function [5] theory indeed produce very small matrix elements, unless one invokes extremely small structures (< 10 Å). It has been pointed out that geometrical restriction of excitons enhances the oscillator strengths [4, 6], but once again such effects become significant only in the smallest structures.

The structures investigated in the present study actually reflect confinement as well as chemical effects due to a change in the structure at the atomic level. Our basic building blocks are corrugated [111] layers of Si, terminated by H atoms. Such Si slabs confine carriers in one dimension (perpendicular to the slab). When the thickness of such quantum-confined structures is shrunk to two Si atoms, we observe a fundamental change in the band structure which produces strong optical transitions.

Figure 1 illustrates such a H-terminated [111] slab of Si. Within the corrugated Si layer, each Si atom is bonded to three other Si atoms. The fourth bond, perpendicular to the [111] plane, is saturated by H. This structure can be described as two-dimensional planar polysilane, a hypothetical polymer [7]. References to compounds consisting of a stacking of such slabs can be found in the chemistry literature, in the context of layered structures referred to as "lepidoidal (scaly) silicon" [8, 9]. No experimental structural information is available, apart from the fact that these compounds likely consist of a stacking of [111] layers of Si, since they are synthesized starting from $CaSi_2$; the latter contains corrugated layers of Si in the [111] direction, separated by Ca atoms. We find the stable structure of the SiH compound to have an indirect band gap, although the direct gap is only 0.2 eV higher in energy, occurring at 2.95 eV. The zone-center transitions have a large matrix element, $|\langle \Gamma_v \mid \mathbf{p} \mid \Gamma_c \rangle|^2 = 0.28$ a.u.

Building upon the SiH compound, and in light of the suggestion that a compound called "siloxene" is responsible for the strong luminescence in porous Si [2], we have substituted half of the H atoms with OH groups (Fig. 2). A compound with this composition has been synthesized starting from $CaSi_2$, although the detailed atomic positions were not determined [2, 10]. For this compound we

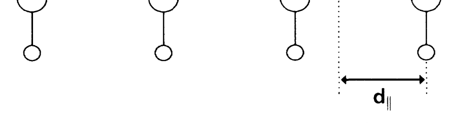

FIG. 1. Schematic representation of the structure of an isolated layer of the SiH compound, projected on a $(1\bar{1}0)$ plane. Large circles represent Si atoms and small circles H atoms. Parameters describing the atomic positions are indicated.

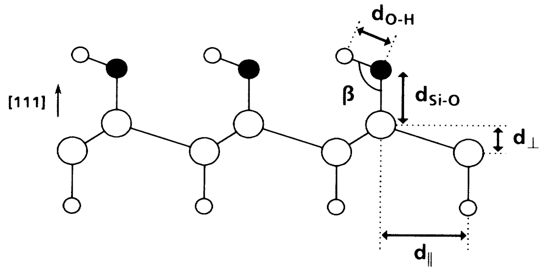

FIG. 2. Schematic representation of the structure of an isolated layer of the siloxene compound, projected on a $(1\bar{1}0)$ plane. Large circles represent Si atoms, small circles H atoms, and black circles O atoms. Parameters describing the atomic positions are indicated.

find the band gap to be direct, with a value of ~1.7 eV. Apart from the difference in value of the direct gap, the nature of the band-edge states is very similar to those in the SiH compound; in particular, strong zone-center optical transitions are possible.

Our calculations of atomic structure are based on density-functional theory in the local-density approximation (LDA) [11] and *ab initio* pseudopotentials [12]. Convergence tests were performed, indicating that a plane-wave cutoff of 12 Ry is sufficient for determining the atomic structure of the SiH compound, and 15 Ry for band-structure calculations. Our calculations of the atomic structure of siloxene were performed with a cutoff of 36 Ry; the band structure was determined at 48 Ry.

The electronic band structure of SiH was calculated using a quasiparticle formalism. The self-energy operator (Σ) is evaluated in the *GW* approximation [13], where Σ is taken to be the first term in a perturbation series involving the screened Coulomb interaction *W* and the electron Green's function *G*. Using this approach quasiparticle energies may be calculated to within an accuracy of about 0.1 eV. The self-energy calculations were performed with the methods developed by Hybertsen and Louie [14]. The frequency dependence of the dielectric matrix is obtained by applying a plasmon pole ansatz to the eigenvalues of the static dielectric matrix [15]. The required static dielectric matrix elements, $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$, were calculated in the random-phase approximation for the reciprocal lattice vectors $\mathbf{G}$ satisfying $|\mathbf{q}+\mathbf{G}| < 3.0$ a.u. In the calculation of the diagonal elements of the self-energy operator the required sum over bands was truncated at the 200th band, and the Brillouin zone (BZ) summation was performed with a weighted sum which included 16 $\mathbf{q}$ points in the irreducible zone.

We now describe our results for the various structures in detail. For the SiH compound, we first study the atomic structure of a single (two-Si-atom thick) slab terminated by H atoms (Fig. 1). These calculations are performed in the usual repeated-slab geometry, but with a very large repeat distance in the [111] direction. The calculated Si-H distance is 1.54 Å. The interplanar distance $d_{\perp}$ is found to be slightly reduced (by 0.06 Å) compared to its value in bulk Si. Concomitantly, an in-plane expansion occurs (increasing $d_{\parallel}$ by 0.03 Å), resulting in conservation of the bulk Si-Si bond length to within 0.01 Å. These relaxations are so small, however, as to have minimal effects (<0.1 eV) on the band structure.

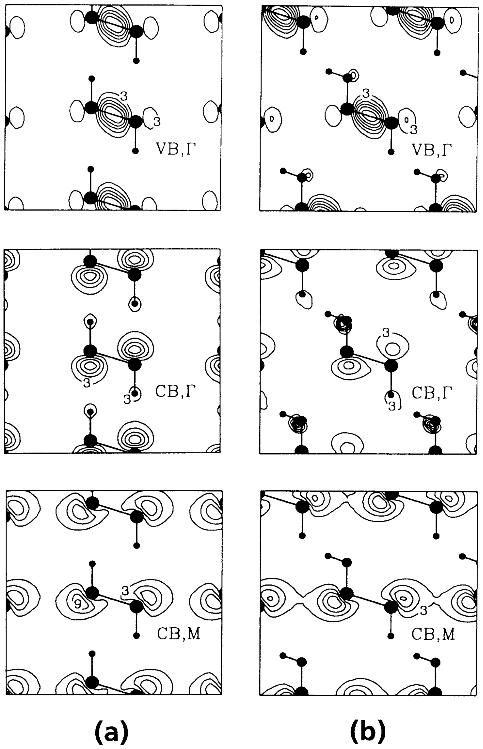

FIG. 3. Contour plots of the charge density corresponding to various band-edge states, in a $(1\bar{1}0)$ plane, (a) in SiH and (b) in siloxene. Large circles indicate Si atoms, intermediate circles O atoms, and small circles H atoms. The contour interval is 3, in units of electrons per unit cell [for a supercell containing 2 Si and 2 H atoms (plus one O atom in siloxene)].

We have investigated various possible stacking sequences of these H-terminated Si layers. The stacking sequence having the lowest energy is simple hexagonal (see Fig. 3). For this structure, energy minimization yields a repeat distance along [111] of 4.78 Å, and a binding energy of 0.06 eV per formula unit (consisting of 1 Si and 1 H), as expressed with respect to an isolated layer. The energy of formation, expressed with respect to bulk Si and SiH_4, is found to be −0.05 eV per SiH formula unit (the negative value indicating stability of the compound). The calculations for bulk Si and for the SiH_4 molecule (in a large supercell) were performed consistently within our theoretical framework. Zero-point energies are included here as discussed in Ref. [16]. Using the difference in formation energy between H_2 and SiH_4, the heat of formation of the SiH compound (expressed with respect to bulk Si and H_2) is thus 0.06 eV (i.e., slightly unstable).

We have found that different stacking sequences, corresponding to lateral shifts or rotations of the layers with respect to each other, have rather similar binding energies. We also find that the band structure is not very sensitive (to within 0.2 eV) to the details of the stacking, and is determined mostly by the atomic structure within each layer. Bringing the layers together decreases the band gap by about 0.3 eV. The weak interlayer binding leads to some uncertainty in the equilibrium layer spacing, which translates into an uncertainty of about 0.2 eV for the band gap.

Figure 4 shows the band structure for the SiH compound, as obtained from a quasiparticle calculation. The Z point is located at the edge of the BZ in the direction perpendicular to the layers. The M point lies within the plane of the layers, halfway along one of the reciprocal space translation vectors. The first, fourth, and fifth bands (counting from the bottom) are the bonding states of the Si-Si layers and bear great similarity to the valence bands (VBs) in bulk Si, while the second and third bands are associated with the Si-H bonding states perpendicular to the plane (hence the larger dispersion along the Γ-Z direction). The character of the lowest conduction band (CB) also resembles that in bulk Si (see Fig. 3), although the energy values are of course quite different.

The quasiparticle calculations predict an indirect gap (occurring at a point close to the M point) of 2.75 eV. The minimum energy direct gap occurs at the Γ point and is 2.95 eV. Energy positions of various bands are listed in Table I. The full quasiparticle gap values for the band-edge states are approximately 0.92 eV larger than those obtained in the LDA calculations. The table also lists calculated matrix elements for vertical transitions between VB and CB. $|\langle\Gamma_v\,|\,\mathbf{p}\,|\,\Gamma_c\rangle|^2$ should have a magnitude around 0.25 a.u. for strong allowed transitions; the direct transitions in the SiH compound satisfy this criterion.

TABLE I. Quasiparticle band energies for various states in the SiH compound, referred to the uppermost VB at the zone center. Note that the maximum of the VB occurs at Z. Also listed are the calculated dipole matrix elements, $|\langle\Gamma_v\,|\,\mathbf{p}\,|\,\Gamma_c\rangle|^2$, for vertical transitions.

	Γ	Z	M
VB max	0.0	0.09	−1.54
CB min	2.95	3.57	3.00
$\lvert\langle\Gamma_v\,\lvert\,\mathbf{p}\,\rvert\,\Gamma_c\rangle\rvert^2$	0.28	0.38	0.56

The SiH compound described above can be regarded as a prototype for a variety of compounds with similar structure. Replacing the H atoms on one side of the double layer by OH groups (see Fig. 2), we find one of the modifications of the compound siloxene, which has been proposed to be responsible for the visible luminescence in porous Si [2]. Our calculations indicate that once again the atomic positions within each layer are rather insensitive to the presence of nearby layers, and to the stacking sequence. The Si positions are virtually identical to those in the SiH compound. The Si-O distance is 1.66 Å, and the O-H distance is 1.00 Å (as in H_2O); the Si-O-H angle (β) is ~115° (closer to the H-O-H angle in H_2O than to the Si-O-Si angle in SiO_2). In this case the most favorable stacking involves a lateral translation of the layers, as seen from the atomic positions in Fig. 3. The lattice constant in the [111] direction is 5.32 Å, and the binding energy with respect to a single layer is ~0.2 eV. This binding energy is larger than in the SiH compound; we attribute this to the attractive electrostatic interaction between H atoms bonded to Si on one layer, and H bonded to O on an adjacent layer. The energy of formation of the siloxene compound, with composition Si_2OH_2, when expressed with respect to Si bulk and H_2O, is −0.9 eV, i.e., the compound is stable with respect to disproportionation into bulk Si and water. Siloxene is unstable, however, when compared to SiO_2, in agreement with the results of annealing experiments [10]. Other modifications of siloxene exist, in which O atoms are inserted into Si-Si bonds in the plane [2]. Because the energetically most favorable bond angle of Si-O-Si bonds deviates from 180°, such structures will no longer be planar, and three-dimensional cross-linking will occur.

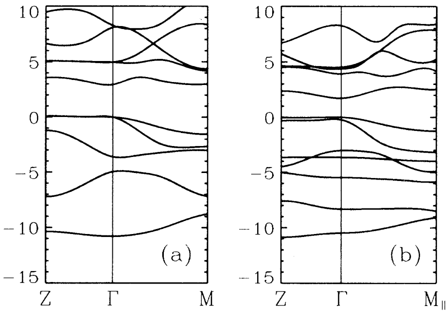

FIG. 4. Quasiparticle band structures (a) for the SiH compound and (b) for the siloxene compound. Self-energy corrections for siloxene have been obtained as described in the text.

The band structure for the siloxene compound (Fig. 4) is qualitatively very similar to that of the SiH compound (the deep-lying band corresponding to the O 2s state is not shown). Since this structure has a real-space translation vector which is not perpendicular to the layers, the reciprocal-space vectors are not parallel to the layers anymore; the band structure is still plotted along an "in-plane" direction, now indicated by Γ-$M_{\|}$. The first, sixth, and seventh bands from the bottom are again similar to the VBs in bulk Si. The three VBs with small dispersion correspond to oxygen-related states, while the remaining VB is related to the Si-H bond. An explicit quasiparticle calculation for siloxene (which would be prohibitively expensive) was not carried out. Instead, because the character and localization of the wave functions at the band

TABLE II. Band energies for various states in the siloxene compound, obtained from LDA calculations and self-energy corrections (see text). The zero of energy is chosen at the VB maximum at Γ.

	Γ	Z	M
VB max	0.0	−0.04	−1.25
CB min	1.73	2.37	2.53

edges are very similar to that in the SiH compound, we apply the same correction to the LDA band gap for siloxene as obtained for SiH.

Figure 3 shows contour plots of the charge density corresponding to various band-edge states, illustrating the similarities between the compounds. For SiH, the self-energy corrections for the lowest-lying CB are nearly uniform throughout the Brillouin zone, and equal to 0.9 eV. Applying this same correction, we find a direct band gap for the siloxene compound of 1.7±0.3 eV (see Table II). The error bar takes the uncertainty in the assumed self-energy correction into account; however, the difference between direct and indirect band gaps is so large (0.8 eV) that this uncertainty cannot affect the conclusion that this is a direct-gap material. Moreover, because of the similarity in wave-function character for the band-edge states, this direct transition will also be strongly allowed. In addition, the band structure of the compound is largely determined by the structure within a single layer, while the stacking sequence and repeat distance produce small perturbations. Excitonic effects are likely to be important in view of the reduced dimensionality of the structure. While a detailed calculation is beyond the scope of this study, inclusion of excitonic effects would produce a lowering in transition energy and an enhancement of matrix elements, strengthening the conclusions of our work. We also note that the large oscillator strength does not necessarily lead to short lifetimes. Indeed, long radiative lifetimes can be due to triplet excitons, or to distant pair recombination. Measurements of the radiative lifetime alone, therefore, do not resolve the issue of the direct or indirect nature of the gap, and additional experimental work is needed to determine the mechanism of the radiative transitions.

Figure 3 also provides insight into why the siloxene compound has a direct gap which is more than 1 eV smaller than in SiH. We note that the wave function at the CB minimum at Γ has some weight on the hydrogen atom in SiH, or alternatively on the oxygen atom in siloxene. The strongly attractive potential of the very electronegative O atom will therefore lower the energy of this state. In contrast, the state corresponding to the indirect CB minimum at the M point has negligible weight on the oxygen site, and is far less affected by the substitution of the OH group. We have observed a similar lowering of the direct gap in calculations of a structure in which a Cl atom takes the place of the OH group. We have also found that substitution of a second H atom by OH, producing a structure with OH groups on both sides of the layers, lowers the direct gap by an additional 1 eV.

In summary, we have carried out first-principles calculations for various structures built out of [111] layers of Si, saturated with H and/or OH. Although the *local character* of the band-edge states remains similar to bulk Si (guaranteeing, for instance, a strong direct transition at Γ), the *energies* of the conduction-band states are significantly affected by the lower dimensionality of the structure. The SiH compound studied here has a large, almost direct gap near the UV. For the oxygen-containing compound, one of the modifications of siloxene, the presence of oxygen lowers the direct gap with respect to the indirect gap, producing a material with strong direct transitions in the visible region.

We acknowledge stimulating interactions with D. Biegelsen, M. Brandt, and R. Street. This work is supported in part by ONR Contract No. N00014-92-C-0009.

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