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Ab initio survey of the electronic structure of tetrahedrally bonded phases of silicon

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We present an *ab initio* study of the electronic structure of a number of high-pressure metastable phases of silicon with tetrahedral bonding. The phases studied include all experimentally determined phases that result from decompression from the metallic β-Sn phase, namely, the BC8 (Si III), hexagonal diamond (Si IV), and R8 (Si XII) phases. In addition to these we have also studied the hypothetical ST12 structure that is found upon decompression from β-Sn in germanium. We find that the local-density approximation incorrectly predicts the R8 phase to be semimetallic and that the quasiparticle spectrum exhibits a band gap. The effective masses found in R8 suggest that R8 may be useful for high-mobility applications. In addition, the ST12 phase is found to have a large density of electronic states at the band edge which could lead to interesting superconducting behavior.

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I. INTRODUCTION

Crystalline silicon in the cubic diamond (cd) phase has been the subject of a large number of theoretical and experimental studies because of its importance in electronic and photovoltaic devices. Less studied have been the other members of silicon's rich phase diagram. This includes a large number of metastable silicon polytypes which are found upon decompression from the metallic β-Sn phase. Some of these phases have only been known for a little more than a decade. These phases, the BC8, hexagonal diamond, R8, and yet unobserved ST12 phase, are in many ways similar to their cubic counterpart. They are all characterized by fourfold coordination, distorted tetrahedral bonding, and are of semiconducting (or semimetallic) nature. These similarities lead to the hope that the electronic features of the cubic phase found useful in applications might also be found in these phases, perhaps resulting in one of these phases being better suited for a particular application than its cubic counterpart. In particular, we will be looking at the features in the electronic structure which would be relevant for application in high-mobility semiconductor devices and comparing these to those found in the cubic diamond phase.

The majority of previous theoretical work on the high-pressure phases of silicon have concentrated on their structural properties and characteristics of the phase transitions between them with results generally in good agreement with experiment.[1–7] These calculations were done using density-functional theory (DFT) within the local-density approximation (LDA), which is known to give band gaps in disagreement with experiment.[8] This has been shown to arise from the discontinuity in the exchange-correlation potential upon the addition of an electron.[9,10] Strictly speaking the Kohn-Sham eigenvalues have no justification as the quasiparticle energies in a solid.[11] The true quasiparticle energies can be calculated from a Green's function approach, allowing the full nonlocal energy-dependent electron self-energy to be calculated. A successful approximation within this framework is the so-called *GW* approximation (GWA). In this work we present our findings from calculations of the quasiparticle spectrum within the GWA for materials whose electronic nature is in question with regards to LDA.

To evaluate the suitability of these materials for high-mobility applications we examine the carrier effective masses which allow for an estimate of the relative magnitude of the low-field mobility at room temperature. The mobility μ of the carriers in a semiconductor depend strongly on their effective masses, as can be seen by simple scaling arguments for the scattering amplitudes which give[12]

$$\mu \propto T^{-3/2} m_{\mathrm{DOS}}^{*-3/2} m_t^{*-1}, \tag{1}$$

where m_{DOS}^{*} is the density-of-states effective mass and m_t^{*} is the transport effective mass. Missing in the above simple expression is a detailed account of the scattering matrix elements. However, in this work the phases under study have similar bonding characteristics and atomic densities and so we assume that the electron-phonon-scattering matrix elements are comparable. In order to get an estimate of the mobility of the carriers relative to those in cd silicon we compare a thermally averaged density-of-states effective mass, given by

$$\left(\frac{m^*}{m_0}\right)_{\mathrm{DOS}}^{3/2} = \frac{\int f(E)N(E)dE}{\int f(E)N_0(E)dE}, \tag{2}$$

where $f(E)$ is the Boltzmann distribution given by $f(E) = \exp[-E/(k_b T)]$ and $N(E)$ and $N_0(E)$ are the calculated density of states and the free-electron density of states, respectively. The effective masses are determined to a very high precision by using a Wannier interpolation scheme which approximates $100 \times 100 \times 100$ grids in the Brillouin zone (BZ).

The paper is organized as follows. In Sec. II we briefly review the structures of the phases discussed in this paper, and in Sec. III we detail the methods used in the calculations. The results of the electronic structure calculations are presented in Sec. IV. Finally, in Sec. V we conclude with a short summary of the results and some final remarks.

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II. STRUCTURES

It is well known that cd silicon (Si I) transforms upon compression at ~11.7 GPa (Ref. 13) to the metallic β-Sn phase (Si II) and that upon release of pressure does not return to the cd phase but instead goes into a series of high-density metastable phases with distorted tetrahedral bonding. Calculation of the energetics of these phases confirms their metastable character and also correctly predicts the ordering of the phases upon decompression.[3,14] Since the structural characteristics of these phases have been studied previously[1,3,5] we will mention below only the features relevant to this study.

The first phase formed under decompression is the R8 phase (Si XII). This structure has a rhombohedral unit cell containing 8 atoms with the space group $R\bar{3}$.[15] The R8 structure has the interesting property of containing five-membered rings, which in addition to affecting the electronic properties[16] have also been used to explain why the BC8 analog has not been seen in III-V semiconductors. If these compound semiconductors were to follow the same transition path as silicon, the existence of odd-membered rings would require the existence of energetically unfavorable same-species bonds.[17]

Upon further decompression the R8 phase transforms into the BC8 phase (Si III) with body-centered-cubic symmetry and 8 atoms in the primitive cell. Its space-group classification is $T_h^7(Ia\bar{3})$. This structure is closely related to that of R8 and in fact can be formed by changing only one pair of bonds.[3] The internal structure is specified by a single parameter x, which experimentally has the value 0.1025.[15] The relations connecting the internal parameter to bond lengths and angles can be found in the work of Crain *et al.*[1]

Upon moderate heating of the BC8 phase the hexagonal diamond structure, also referred to as lonesdaleite, is formed. The four-atom primitive cell of lonedaleite is classified with space group $P6_3/mmc$. Further details of this structure can be found in the literature.[18,19]

Another possible structure examined in this work is the tetragonal ST12 structure, which has a 12-atom unit cell given by space group $P4_32_12(D_8^4)$. The ST12 phase of silicon has been the study of a number of theoretical calculations although has yet to be experimentally observed in silicon. It is, however, seen in germanium upon slow decompression from the germanium β-Sn phase.[20] Work done by Clark *et al.*[4] using an empirical potential model suggest that the reason for this is that in silicon bond bending is more costly than in germanium because of the additional electrons in the Ge core. The ST12 phase has bond angles further from the ideal diamond value than BC8, and it is this fact which results in ST12 being favored in Ge and BC8 in Si. From their model they also suggest that it might be possible to form ST12 silicon by decompressing from β-Sn at high temperature.

III. METHOD

As a starting point, we have performed *ab initio* pseudopotential calculations within density-functional theory using the parametrization by Perdew and Zunger[21] of the Ceperley-Alder[22] exchange-correlation functional in the LDA. The interaction of the valence electrons with the ion cores is described by a norm-conserving pseudopotential generated by the scheme proposed by von Barth and Car.[23] The wave functions are expanded in plane waves[24] up to a cutoff of 40 Ry. Structural relaxation of the lattice parameters and internal degrees of freedom were performed unless otherwise specified using a quasi-Newton method.[25]

As noted in Sec. I, density-functional theory is unable to correctly predict the quasiparticle energies, and hence the band gap, in solids. In this work we employ the *GW* approximation to the self-energy, which results from setting the vertex function to unity in Hedin's equations.[26] The self-energy then becomes a simple product of the Green's function G and the screened interaction W,[8]

$$\Sigma(1,2) = iG(1,2)W(1^+,2), \tag{3}$$

from which the name follows. The Green's function and the screened interaction must in principle be calculated self-consistently, although this is rarely done in practice. We follow the technique of Hybertsen and Louie[8] in which the Green's function is approximated by the wave functions and energies that result from a DFT calculation and the frequency-dependent dielectric matrix needed to compute the screened interaction is obtained by extending the static dielectric matrix to finite frequencies by using a generalized plasmon-pole model. The *GW* calculations are done using the PARATEC plane-wave code, which implements this approach to the GWA.[27] Density-of-states and effective-mass calculations were performed on a $100\times100\times100$ fine mesh of Wannier-interpolated eigenvalues[28] calculated from the WANNIER90 code[29] used in conjunction with the Bloch states obtained from the QUANTUM ESPRESSO package.[30]

IV. RESULTS

A. R8

Experimentally the R8 phase is formed upon decompression from the high-pressure metallic β-Sn phase at ~10 GPa and measurements taken at 8.2 GPa find β-Sn to be only a small fraction of the experimental sample.[17] As the pressure is reduced R8 remains the dominant phase until approximately 2 GPa, when BC8 is formed. The R8 phase persists, albeit as a small minority, at ambient pressure. Upon increase in pressure the R8 phase is found to begin and complete its transition to the β-Sn phase at 10 and 12 GPa, respectively.[15] We have performed *ab initio* calculations over the range of pressures that R8 has been observed experimentally from 0 to 12 GPa.

A central question left unresolved by previous theoretical studies of R8 is whether R8 should be semiconducting or metallic, the uncertainty being a result of the "band-gap" problem of LDA. Our calculations showing the LDA overlap as a function of external pressure are shown in Fig. 1. At ambient pressure we find an indirect overlap of 0.3 eV between the T and L points in agreement with Pfrommer *et al.*[3] This is somewhat lower than the 0.5 eV found by Piltz *et*

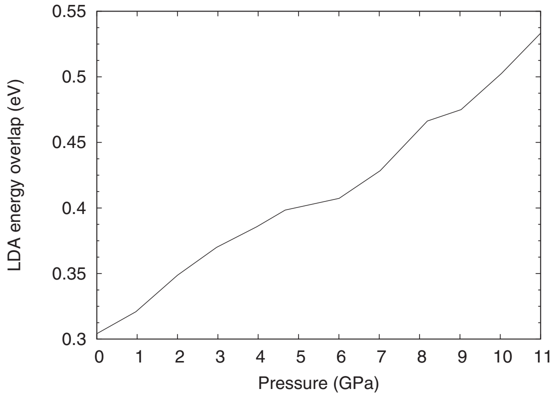

FIG. 1. The LDA energy overlap in R8 as a function of pressure. The overlap occurs between the *T* and the *L* points of the Brillouin zone.

al.[17] This value compares more favorably to our value of 0.47 eV at 8.2 GPa, the pressure of the x-ray diffraction profile. The LDA band structure for R8 at ambient pressure is shown in Fig. 2.

An overlap of 0.3 eV is small enough that it could conceivably be lifted by quasiparticle corrections to the LDA. The *GW* approximation for the electron self-energy generally yields gaps much closer to experiment than what one would get if using the Kohn-Sham DFT eigenvalues. Cubic silicon is a well-known example of this. Here LDA predicts an indirect gap of 0.52 eV while the gap computed using GWA is 1.21 eV, which compares much more favorably to the experimental value of 1.17 eV.[8] With this motivation we have performed calculations of the electron self-energy within the GWA on the R8 structure at ambient pressure. The usual application of the GWA is to ignore the fact that self-consistency is in principle required. This "one-shot GWA," or G^0W^0A, was used in calculating the quasiparticle corrections and we find that it results in an indirect gap of 0.1 eV, resulting in R8 being semiconducting. However, since the screening is qualitatively different in a semiconductor than it is in a metal, a one-shot GWA approach may be insufficient and it may be better to go to self-consistency in *G* and *W*. We approximate the self-consistency requirement by using updated quasiparticle energies from one iteration to construct *G* and *W* for the next iteration. The energies are updated by using a "scissor shift" by which the quasiparticle energy shifts are approximated by a linear relation of the LDA energy.[31] By following this procedure until self-consistency is reached we find the indirect gap increasing to the value of 0.24 eV. If this value of the quasiparticle energy correction changes little with pressure,[32] R8 should exhibit a gap over a substantial range of pressures for which it occurs. Noting the increase in the LDA overlap with increasing pressure, we find that the quasiparticle gap should be eliminated at ~11 GPa. This pressure lies between the onset and completion of the R8 to β-Sn transition upon recompression of the R8 phase. Inadequacies in applying the zero-pressure quasiparticle corrections to finite pressure or in the *GW* approximation itself could result in a lowering of this semiconductor-to-metal transition pressure. It may also be possible to experimentally adjust the gap by applying a strain. Applying a uniaxial strain equivalent to a 1% decrease in the c/a ratio of the equivalent hexagonal lattice[33] we find that the overlap within LDA is reduced by 0.07 eV, a reduction of ~23% of its unstrained value. This would increase the gap from the value found above when including self-energy effects. On the other hand, it may be possible to eliminate the gap by straining in the opposite sense. This could result in a material with a pressure-induced metal-semiconductor transition, which may have applications in fabricating modulators, polarizers, and microwave switches.[34]

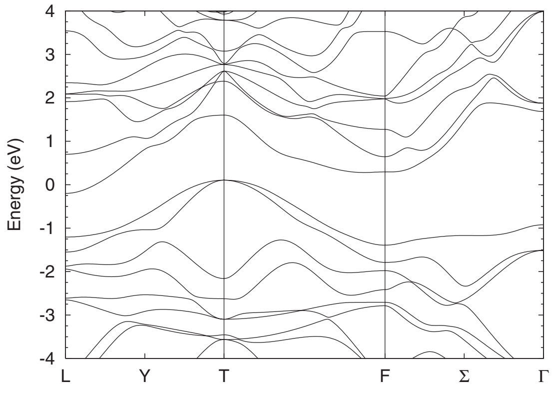

FIG. 2. Band structure of silicon in the R8 phase.

In order to get an estimate of what the relative mobility would be in the R8 phase compared to that in the cubic phase we examine the effective masses. Silicon in the cubic phase is characterized by six equivalent conduction-band minima, which at 300 K give a density-of-states mass of $1.09m_0$.[35] The valence-band maximum at Γ is double degenerate between a "heavy-hole" band and a "light-hole" band in addition to a "split-off" band slightly lower in energy as a result of the spin-orbit interaction. The density-of-states effective mass for this valence band is $1.15m_0$.[35]

In R8 the density-of-states within LDA does not exhibit a gap due to the indirect overlap. We separate out the states associated with the conduction and valence bands before integrating and find a thermally averaged density-of-states effective mass for the conduction band of $0.54m_0$. This is lower than unstrained cd silicon and is comparable to biaxially strained silicon, which lowers two of the six equivalent conduction-band minima and reduces the DOS effective mass by approximately a factor of $3^{2/3}$. We calculate a value of $0.61m_0$ for the valence band at a temperature of 300 K. This value is obtained neglecting spin orbit, which may decrease the effective mass by splitting the degeneracy at *T*.

In R8 the *L* point in the Brillouin zone is threefold degenerate. This degeneracy can be lifted by applying a strain of 1% in the $[0\bar{1}1]$ direction, taken with respect to the equivalent hexagonal lattice.[33] This results in one of the previously equivalent minima being lowered by approximately 90 meV relative to the other two and a decrease in the conduction-band DOS effective mass to the value of $0.27m_0$. For the holes, the valence-band degeneracy at *T* is lifted by the strain. The consequence of this is that the valence-band DOS effective mass is reduced to the value of $0.36m_0$.

B. BC8

Upon further decompression the R8 phase reversibly transforms to the BC8 phase at a pressure of 2 GPa and remains metastable down to ambient pressure.[15] Previous theoretical work done on BC8 has found it to be a semimetal within LDA with a direct overlap of 0.8 eV at the *H* point in the bcc BZ.[3] Experimental measurements on BC8 agree with this classification, although the nature of the overlap was suggested to be indirect with a value of 0.3 eV.[36] Impurity effects can sometimes make it difficult to determine transport properties in experimental measurements accurately and previous theoretical work done with empirical pseudopotentials show BC8 to have a direct gap of 0.43 eV at the *H* point.[37] For these reasons the possibility that BC8 might still be a small band-gap semiconductor has not been precluded. In addition to quasiparticle energy corrections that can be included, it may also be possible to eliminate the overlap by straining the structure.

As noted previously, BC8 is specified by a single internal parameter x. Calculations of the dependence of the LDA band overlap on the parameter x show the band overlap being reduced upon reduction in the parameter from its experimental value of 0.1025. At $x=0.093$, for example, we find a direct gap of 0.23 eV at the bcc *H* point, resulting in an electron density-of-states effective mass of $0.07m_0$. The small value of effective mass can be related to the existence of the small direct gap by standard $\vec{k}\cdot\vec{p}$ arguments. If a strain could be found which effectively changed this internal parameter, it would allow for the tuning of the band gap and effective masses to situations where a small gap high-mobility semiconductor was desirable to cases where a larger gap might be preferred at the expense of the mobility.

Our electronic structure calculations are done by relaxing the structure from the experimental values. We find an x parameter of 0.1016, in good agreement with the experimental value of 0.1025. The calculated zero-pressure volume is 17.78 Å^3 and is in good agreement with the experimental value of 18.26 ± 0.04 $\text{Å}^3/\text{atom}$ (Ref. 38) and in excellent agreement with the calculated value of 17.724 Å^3 per atom by Needs and Mujica.[5] As is typical with LDA calculations the lattice constant and volume are underestimated. The calculations of the electronic structure are in good agreement with the results of Pfrommer *et al.*[3] and we find an overlap of 0.77 eV at the bcc *H* point. This overlap can be seen in the band structure plotted in Fig. 3.

Motivated by the existence of a gap in previous empirical pseudopotential calculations,[37] it is of interest to look at the effect of quasiparticle energy corrections to the direct gap within the GWA. However, this computation is complicated by the fact that within LDA BC8 has a direct overlap. This would require a detailed Brillouin-zone summation to adequately represent the Fermi surface. To avoid this difficulty, we have used another approach to estimate the size of the quasiparticle corrections. Our approach makes use of the fact that the pressure coefficients for the band gap in cd silicon have been found to be similar for both calculations done within the LDA and those done within the GWA.[32] Thus it may be reasonable to expect that the self-energy correction to the band gap does not depend too strongly with strain. Using this approximation, we perform a *GW* calculation on the BC8 structure with an x parameter that has been reduced such that the spectrum exhibits a small band gap. Choosing a value of $x=0.0947$ results in a vanishingly small band gap and taking the shift at the *H* point at this value of x as representative of the shift in the original structure we estimate a reduction in the direct overlap by 0.33 eV due to self-energy corrections. This estimate might also be argued as an upper bound for the quasiparticle energy correction. This follows because even if the *GW* correction does depend strongly on the value of the x parameter, changing the value to one in which we eliminate the gap should decrease the screening and thus enhance the screened interaction and consequently the electron self-energy correction Σ. Therefore we conclude that BC8 is indeed a semimetal judged by the quasiparticle energy spectrum calculated within the GWA.

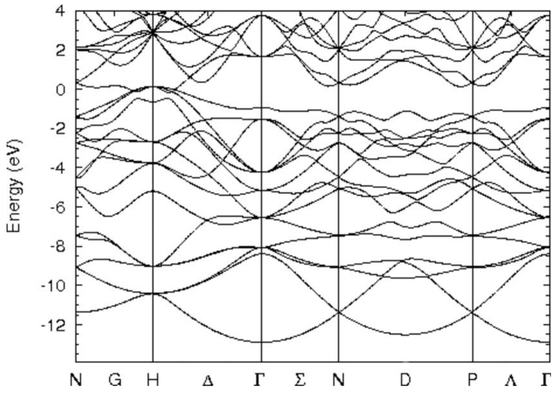

FIG. 3. Band structure of silicon in the BC8 phase.

In searching for a strain that would produce the effects of changing the internal parameter x we have considered a number of strains. This includes simple volume strain, uniaxial strain up to 4%, and the substitutional doping of germanium and carbon atoms. The band overlap was found to be resilient to these changes. Through uniaxial strain and doping we were able to reduce, although not eliminate, the BC8 overlap. In calculating the volume dependence of the x parameter, we find that for realistic volume strains the x parameter does not decrease to a value corresponding to one which would lift the band overlap.

C. Lonesdaleite

The hexagonal diamond, or lonesdaleite, structure is obtained from the heating of BC8 samples above 470 K and is found to be stable up to ~800 K.[36] In addition, it has been formed by applying a shear stress to the cd phase by nonhydrostatic stress in indentation experiments and with ultraviolet laser ablation with a cubic silicon target at lower pressures.[39] Experimental evidence suggests lonesdaleite being semiconducting with a band gap similar to that of the cubic silicon phase.[36] Previous theoretical work using empirical pseudopotentials has predicted an indirect band gap of 0.85 eV between the Γ and *M* points of the Brillouin zone.[37] Our calculations done within the LDA find an indirect gap of 0.33 eV at this point. Again, noting the large effect that self-energy corrections have on the indirect gap in the cd phase,

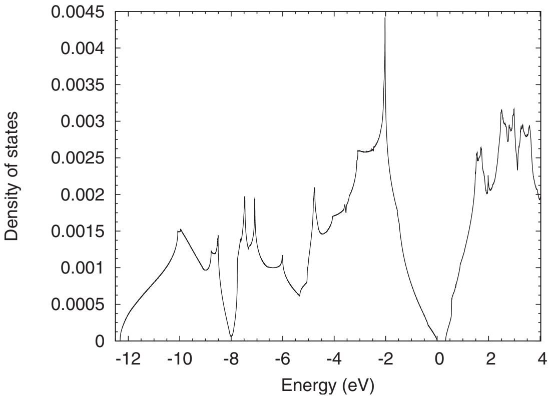

FIG. 4. Density of states per unit volume, per spin, and per eV for silicon in the lonesdaleite phase.

we have also calculated the electronic spectrum within the GWA. This results in an indirect gap of 0.95 eV, similar to both the results derived from empirical methods and experimental observation. Calculations of the electronic density-of-states utilizing the Wannier-interpolated eigenvalues are shown in Fig. 4. These results are in excellent agreement with those found earlier by Joannopoulos and Cohen,[37] including the sharp structure near the Fermi level. Calculations of the thermally averaged DOS effective mass in the absence of the spin-orbit interaction result in the values of $0.94m_0$ for the electrons and $0.58m_0$ for the holes. Similar to the cubic case, we find that applying a biaxial strain results in a reduction in the conduction-band effective mass. A biaxial strain applied in the plane perpendicular to the optical axis causes the three equivalent conduction-band minima located at M in the hexagonal Brillouin zone to be split in energy, resulting in an electron effective mass of $0.63m_0$. The hole effective mass is not significantly affected by this strain.

D. ST12

As was noted in Sec. I, the ST12 phase has been seen upon decompression from β-Sn in germanium but has yet to be found in silicon. Despite this, the ST12 structure has been the subject of numerous theoretical studies[16,40] due to its usefulness in studying the effects of disorder of amorphous materials. Our calculations for silicon in the ST12 structure are done with fully relaxing the cell and the internal degrees of freedom. The band structure of ST12 calculated in LDA is shown in Fig. 5 and is in qualitative agreement with that found by Joannopoulos[37] using empirical pseudopotentials, although we find the indirect gap to be somewhat smaller at 1.1 eV. In ST12 we find that the bands are characterized by a large number of extrema near the gap edges. This results in the large density of states near the band gap as seen in Fig. 6. The observed number of states near the gap edge decreases the mobility of the carriers by providing states with which to scatter into. Computing the DOS effective mass for the electrons we find a value of $0.89m_0$, which while smaller than the value of $1.09m_0$ for unstrained cubic silicon, is still larger than that occurring in the case of the biaxially strained cubic phase. The DOS effective mass of the holes in the unstrained structure takes the large value of $2.69m_0$.

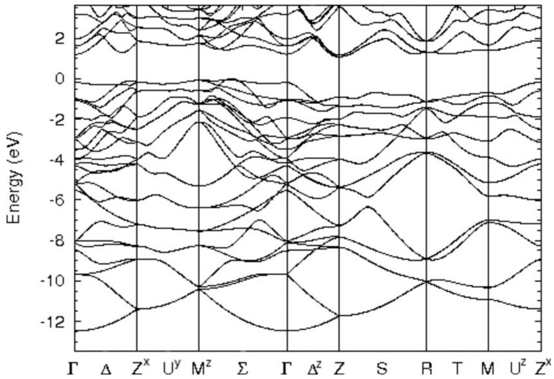

FIG. 5. Band structure of ST12 silicon.

The relative location of the extrema in the conduction and valence bands can however be altered by applying a strain to the structure. We have applied strains up to 4% on the structure in the [100] and [010] directions. A clear trend could be seen upon increase of strain in both cases. Strain is found to reduce m_{DOS} for the holes because of other states in the zone near the gap are decreased in energy with respect to those at Γ. However, this strain is also seen to result in the lowering of conduction-band states higher in energy which leads to a large increase in m_{DOS} for the electrons and hence decreases their mobility.

Although the large density-of-states near the gap in ST12 makes it unpromising for high-mobility applications, it could have interesting consequences for superconductivity if it were possible to dope into one of the large peaks in the DOS. If we consider rigid-band doping, it would take a unrealistic amount of doping to dope into the largest peak in the valence band. The conduction band, however, can be reached with approximately 4% electron doping. In order to get an estimate of the effect that the observed density of states can have on T_c we use *ab initio* results from a study on superconductivity in doped cubic silicon,[41] in which they calculate a λ of 0.3 for phosphorus n-doped cd silicon and employ the following relation connecting the electron-phonon coupling constant to the density-of-states at the Fermi level,[42]

$$\lambda = \frac{N(0)\langle g^2\rangle}{M\langle\omega^2\rangle}. \qquad (4)$$

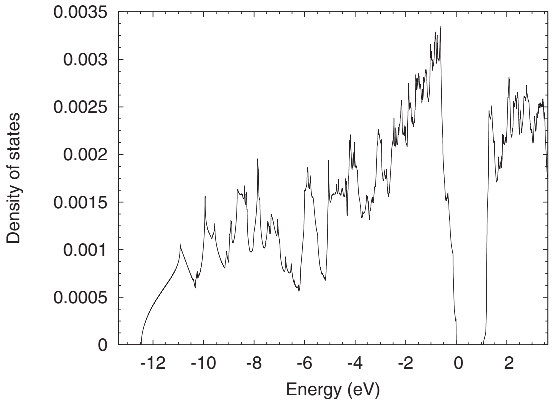

FIG. 6. Density of states per unit volume, per spin, and per eV for silicon in the ST12 phase.

The electron-phonon matrix elements and phonon frequencies, being associated with the Si-Si sp^3 bond, should be similar for the cubic phase and ST12. This approximation allows us to obtain an estimate for T_c by a scaling of $N(0)$, the density-of-states at the Fermi level. Scaling the 4.2% rigid-band doped ST12 to that of phosphorus-doped cubic silicon we obtain a λ of 0.79. Following the work of Bourgeois and Blase[41] we use a modified McMillan expression[43] and values of the Coulomb coupling constant, μ^*, in the range of 0.08–0.12. This results in a T_c between 27 and 39 K. Though this is a rough estimate of the superconducting transition temperature, it does suggest that if silicon in the ST12 phase were experimentally available superconductivity might be an interesting property to study in more detail.

V. CONCLUSION

Ab initio calculations using DFT/LDA were performed on the silicon phases formed under decompression from β-Sn: R8 (Si XII), BC8 (Si III), hexagonal diamond (Si IV), and the unobserved phase ST12. Quasiparticle energy corrections were implemented using the *GW* approximation[8] for phases, in which the electrical nature, metallic, or semiconducting could have been inaccurately determined in previous calculations due to the band-gap problem inherent to DFT calculations.

Our calculations done on the electronic structure of R8 within the *GW* approximation find that LDA incorrectly predicts an indirect overlap in R8 and that the quasiparticle spectrum exhibits a gap. The effective masses found in R8 are smaller than those found in the cubic diamond phase and can be made even smaller by the application of strain. This creates the possibility that R8 might be found useful in applications where high carrier mobility is needed.

In studying the BC8 phase we find a direct overlap in the quasiparticle spectrum, in qualitative agreement with calculations done within LDA. This overlap is found to be resilient to attempts at its elimination by the use of strain and doping. We find that the electron effective mass in the hexagonal diamond phase is reduced, as in the case of cubic silicon, with the application of a biaxial strain. Lastly, the yet unobserved ST12 phase is found to have a large number of electronic states near the band edges, which upon doping might provide a sufficient number of states at the Fermi level to result in a higher T_c than what has previously been found in other silicon polytypes.

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