

## Effective correlation energy of a Si dangling bond calculated with the local-spin-density approximation

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The effective correlation ( $U_{\text{eff}}$ ) for a Si dangling bond has been calculated within the local-spin-density approximation. A positive value of  $U_{\text{eff}}$  equal to  $0.4 \pm 0.2$  eV was obtained. The effect of including spin polarization in the total-energy calculation was to increase  $U_{\text{eff}}$  by 0.24 eV.

Nonbonding  $sp$  orbitals which are localized on threefold-coordinated Si atoms are known as dangling bonds. They give rise to many of the surface states and resonances seen on Si surfaces. They are also thought to be the origin of the prominent gap-state defect levels observed in  $\alpha$ -Si:H and at the Si-SiO<sub>2</sub> interface. For the Si-SiO<sub>2</sub> interface, this identification has been established on the basis of detailed agreement between theory<sup>1,2</sup> and experiment<sup>3</sup> of the hyperfine splitting observed in electron-spin resonance (ESR) measurements. For  $\alpha$ -Si:H the hyperfine splitting of the ESR signal has also been measured<sup>4</sup> and compared with model calculations. On the basis of such comparisons it has been argued that the defect state is a dangling bond<sup>4</sup> on a threefold-coordinated atom. On the other hand, it has also been argued that the hyperfine data are more consistent with an interpretation where the defect state arises from a fivefold-coordinated Si atom.<sup>5</sup> An argument which has been raised against the dangling-bond interpretation is that the dangling bond would be a *negative*  $U$  defect<sup>6,7</sup> and thus not be visible in ESR. The dangling bonds on the threefold atoms can exist in three different charge states denoted  $D^+$ ,  $D^0$ , and  $D^-$  corresponding to zero, one, or two electrons in the dangling-bond orbital. Since neither  $D^+$  nor  $D^-$  is spin active, the identification of a neutral dangling bond with the ESR signal requires that  $U_{\text{eff}}$ , the energy of the reaction  $2D^0 \rightarrow D^+ + D^-$ , is positive. If  $U_{\text{eff}}$  is negative, two  $D^0$  defects would convert to a  $D^+$  and a  $D^-$ ; and  $D^0$  would not be present in the electronic ground state. In that case it would be necessary to invoke a different defect, with positive  $U_{\text{eff}}$ , to account for the spin signal. The purpose of the present work is to calculate  $U_{\text{eff}}$  for a simple structural model corresponding to an isolated dangling bond pointing into a microvoid. The present calculations, which employ the first-principles pseudopotential method and the local-spin-density approximation, indicate that  $U_{\text{eff}}$  is *positive* with a value of  $0.4 \pm 0.2$  eV.

The effective  $U$  for a defect can be written in terms of the bare  $U$  and the relaxation energies of the positively and negatively charged defects,

$$U_{\text{eff}} = U_{\text{bare}} - W^+(0) - W^-(0).$$

$U_{\text{bare}}$  is the energy required to remove an electron from a neutral defect and add it to another neutral defect, without allowing any structural changes. This electron

transfer produces a pair of charged defects which can relax structurally to new equilibrium atomic structures.  $W^+(0)$  and  $W^-(0)$  denote the relaxation energies of the charged defects.<sup>8</sup> If the defect charge arises from the change in occupation of a localized electronic orbital (such as a dangling bond), then an order of magnitude estimate for  $U_{\text{bare}}$  is  $e^2/\epsilon r_d$ . Here  $\epsilon$  is a measure of the screening, and is of the same order of magnitude as the dielectric constant; and  $r_d$  is a measure of the extent of the localized orbital. For  $\epsilon \sim 10$ , and  $r_d \sim 1$  Å,  $U_{\text{bare}} \sim 1$  eV. The relaxation energies can be large if there is a significant amount of orbital rehybridization in the charged states. This is the case for the Si dangling bond. Crudely speaking, the positively charged defect exhibits  $sp^2$  hybridization with an empty  $p_z$  orbital, the neutral defect exhibits  $sp^3$  hybridization with one singly occupied  $sp^3$  hybrid orbital, and the negatively charged defect exhibits  $s^2p^3$  hybridization with a doubly occupied lone pair. Previous calculations<sup>7</sup> indicate that the relaxation energies and  $U_{\text{bare}}$  are each of order 0.5 eV. Thus  $U_{\text{eff}}$  is the difference in two sets of terms which are nearly the same magnitude.

The present study models the dangling bond as shown in Fig. 1. This geometry is chosen to simulate a plausible *local* atomic structure (within one or two bond lengths) seen by a threefold-coordinated Si atom with a dangling bond pointing into a microvoid such as might occur in  $\alpha$ -Si:H or at the Si-SiO<sub>2</sub> interface. This model is constructed by placing hydrogen-terminated pyramidal clusters in a  $2 \times 2$  array on a Si(111) surface. Each pyramidal cluster contains four Si atoms, three at the base and one at the apex. The basal atoms are each bonded to a Si atom in the (111) surface plane and to the apical atom. The remaining two bonds of the basal atom are saturated by hydrogen atoms. Thus, each basal atom is bonded to two Si and to two H atoms. The apical atom is bonded to three Si atoms in the base and the remaining bond is saturated by an apical hydrogen atom. A  $2 \times 2$  array of these H-terminated clusters effectively isolates a threefold-coordinated Si atom in the bottom of a deep hole in each unit cell. The threefold Si atom is back bonded to three Si atoms (bond length  $\sim 2.35$  Å). The six nearest basal H atoms are approximately 3.9 Å away from the threefold-coordinated Si atom. The calculations were performed within the repeated supercell approach with a cen-

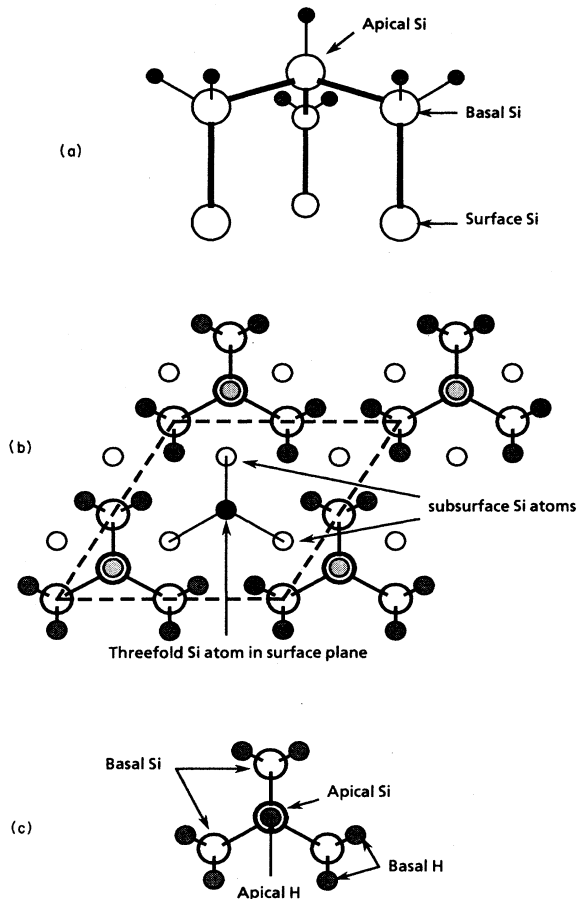


FIG. 1. (a) Schematic view of a hydrogen-terminated pyramidal cluster bonded to three Si surface atoms. (b) Top view of  $2 \times 2$  unit cell containing a threefold-coordinated Si atom surrounded by pyramidal clusters. The dashed line indicates the boundaries of the  $2 \times 2$  unit cell. This geometry is employed to simulate an isolated dangling bond pointing into a microvoid. (c) Top view of individual pyramidal cluster.

trosymmetric supercell containing 40 Si atoms and 14 H atoms. There are two dangling bonds and two pyramidal clusters in each unit cell. The cell volume is  $\sim 8100 a_B^3$ .

Local-spin-density-functional total-energy calculations were carried out using the first-principles pseudopotential method.<sup>9,10</sup> The momentum space formalism was employed to solve the Kohn-Sham equations<sup>11</sup> with a plane-wave cutoff of 8 Ry. Forces were calculated and employed in obtaining the equilibrium structures for each charge state.<sup>12</sup> The neutral defect  $D^0$  has spin  $\frac{1}{2}$  corresponding to the singly occupied  $sp$  orbital localized on the threefold-coordinated atom. Within the density-functional approach, this situation corresponds to a nonzero spin density ( $\rho_{\uparrow} - \rho_{\downarrow}$ ) and necessitates the use of the local-spin-density formalism.<sup>13</sup> The spin-dependent exchange-correlation potentials were obtained from the Perdew-Zunger<sup>14</sup> parametrization of the Ceperley-Alder electron-gas data. This type of an approach has been applied previously to determine the ground-state

configuration and calculate the bond length and vibrational frequencies for the  $\text{Si}_2$  and  $\text{Ge}_2$  molecules,<sup>15</sup> which exhibit spin polarization in their ground states. It has also been used to study hypothetical spin-density waves on an ideal Si(111) surface.<sup>16</sup>

Following Bar-Yam and Joannopoulos,<sup>7</sup> I employ a low-density positive, or negative, neutralizing background charge density to enable total-energy calculations for charged defects. The density of the background corresponds to  $r_s \sim 10$ . The charged defect experiences an attractive interaction with the neutralizing background and a repulsive interaction with the other defects. These artificial interactions lead to an estimated  $\sim 0.2$  eV uncertainty in the calculation of  $U_{\text{eff}}$ . For a very large supercell, the error is expected to be dominated by the (screened) attractive interaction between the defect charge and the neutralizing background charge. The estimated error in the energy of the charged defects from this attraction is of order  $-e^2/\epsilon r_s$ , where  $\epsilon$  is the dielectric constant of the host material. Thus, for very large cells, the calculated  $U_{\text{eff}}$  will be a lower bound on the true  $U_{\text{eff}}$ .

The principal results of the calculation are the total energies  $E^+$ ,  $E^0$ , an  $E^-$  for the positive, neutral, and negatively charged defects.  $U_{\text{eff}}$  is given in terms of these energies:  $U_{\text{eff}} = E^+ + E^- - 2E^0 = 0.40$  eV.

The transition level  $E(+|0)$  is defined as the value of the electron chemical potential  $\mu$  for which the energies of the neutral and positively charged defects are equal:  $E^+ + \mu = E^0$ . When  $\mu < E(+|0) = E^0 - E^+$ , the defect is positively charged in the ground state. Correspondingly,  $E(0|-)$  is the value of  $\mu$  for which the energies of the neutral and negatively charged defects are equal:  $E^- - \mu = E^0$ . When  $\mu > E(0|-)$  the defect is negatively charged in the ground state. In the present calculations  $E(+|0)$  is found to be  $\approx 0.2$  eV below the bulk-Si valence-band maximum (VBM), and  $E(0|-)$  is found at 0.2 eV above the bulk Si VBM. The defect will be neutral, and spin active, when  $E(+|0) < \mu < E(0|-)$ . A schematic configuration energy diagram for the defect assuming a value of  $\mu$  for which  $E(+|0) < \mu < E(0|-)$  is shown in Fig. 2.

Figure 2 also defines the relaxation energies:  $W^+(0) = 0.16$  eV,  $W^-(0) = 0.36$  eV,  $W^0(-) = 0.18$  eV, and  $W^0(+) = 0.20$  eV. A typical relaxation energy is 0.2 eV. Similar results have been obtained in previous calculations.<sup>7</sup> The relaxation energies of the dangling bond at the Si-SiO<sub>2</sub> interface are expected to be similar to these calculated values. However, one should be cautious in applying these results to  $\alpha$ -Si:H because the structural constraints imposed by a crystalline network on the three back-bond atoms may be rather different than those which actually occur in  $\alpha$ -Si:H.

Calculations for the neutral defect can be performed in the usual local density approximation if the spin-up and spin-down dangling-bond orbitals are each occupied by  $\frac{1}{2}$  of an electron. The present calculations indicate that such an approximation would increase the total energy of the neutral defect,  $E^0$ , by about 0.12 eV and thus would decrease  $U_{\text{eff}}$  by 0.24 eV. Thus, in calculating the effective correlation energy of dangling bonds, it is important to in-

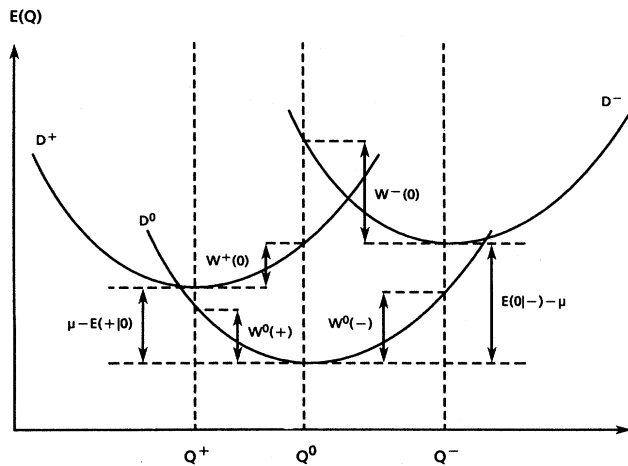


FIG. 2. Configuration coordinate diagram for a positive  $U$  defect. The diagram corresponds to  $E(+|0) < \mu < E(0|-)$ .

clude spin-polarization effects.

The equilibrium local atomic structure around the defect is dependent on the charge state. In an ideal geometry corresponding to bulk bond lengths and bond angles, the threefold-coordinated atom is a distance  $z = 0.78 \text{ \AA}$  above the plane of its back-bond neighbors. For the  $D^-$  this atom moves away from its ideal position by  $\delta z = +0.22 \text{ \AA}$ , and for the  $D^0$  and  $D^+$  it moves inwardly by  $\delta z = -0.16 \text{ \AA}$  and  $\delta z = -0.53 \text{ \AA}$ , respectively. The changes in position are associated with the rehybridization of the dangling-bond orbital. As the atom moves along the positive  $z$  direction, the amount of  $3s$  character in the dangling-bond orbital increases. The changes in the local structure of the threefold-coordinated atom which accompany the changes in occupation number of the dangling-bond orbital lead to relaxation energies  $W^+(0) = 0.16 \text{ eV}$  and  $W^-(0) = 0.36 \text{ eV}$ . The corresponding value of  $U_{\text{bare}}$  is  $0.9 \text{ eV}$ . This result is somewhat larger than the values for  $U_{\text{bare}}$  obtained in previous calculations. Bernholc<sup>17</sup> found  $U_{\text{bare}} = 0.5 \text{ eV}$  and Bar-Yam and Joannopoulos<sup>7</sup> found  $U_{\text{bare}} = 0.45 \text{ eV}$ . However, the structural model employed here is different than the one employed previously and spin polarization was not included in the

previous work. In the triply hydrogenated vacancy<sup>17</sup> the dangling-bond atom is within  $\sim 2.6 \text{ \AA}$  of the three hydrogen atoms in the microvoid created by the vacancy. In the model employed here the dangling-bond atom is  $\sim 3.9 \text{ \AA}$  from six hydrogen atoms. Thus, the dangling bond is more isolated in the present geometry. Also, as already mentioned, spin polarization for the neutral defect contributes  $\sim 0.2 \text{ eV}$  to  $U_{\text{bare}}$ .

In comparing theoretical results for idealized models with experiments for  $a\text{-Si:H}$  it should be kept in mind that disorder in  $a\text{-Si:H}$  will lead to a distribution of transition levels and correlation energies.

One method of measuring  $U_{\text{eff}}$  is optical modulation spectroscopy as discussed by Vardeny and Tauc.<sup>18</sup> In this experiment one measures the energies at which photoinduced absorption and photoinduced bleaching occurs. These energies are presumed to correspond to optical transitions from  $D^-$  to the conduction band ( $h\nu_1$ ) and from  $D^0$  to the conduction band ( $h\nu_2$ ). Assuming that the same set of conduction-band electronic states is involved in both transitions, one has

$$h\nu_2 - h\nu_1 = E(0|-) - E(+|0) + W^+(0) - W^0(-).$$

Vardeny and Tauc made the plausible assumption that the relaxation energies  $W^+(0)$  and  $W^0(-)$  were equal. In that case one has  $h\nu_2 - h\nu_1 = U_{\text{eff}}$ . The assumption of equal relaxation energies is in accord with the present results: I find  $W^+(0) = 0.16 \text{ eV}$  and  $W^0(-) = 0.18 \text{ eV}$ . Vardeny and Tauc obtained  $U_{\text{eff}} = 0.5 \text{ eV}$ , but in more recent work involving the same technique, a value of  $U_{\text{eff}}$  equal to  $0.43 \pm 0.09 \text{ eV}$  was reported.<sup>19</sup> Another method of obtaining  $U_{\text{eff}}$  is to measure the intensity of the  $g = 2.0055$  ESR signal as a function of the electron chemical potential. Such measurements are complicated by the fact that the defect concentration is itself a function of chemical potential.<sup>20</sup> Nevertheless, careful analysis of the data leads to an estimate of  $U_{\text{eff}} \sim 0.2 \text{ eV}$ .<sup>21</sup> These experimental values for  $U_{\text{eff}}$ ,  $0.43 \pm 0.09 \text{ eV}$  and  $\sim 0.2 \text{ eV}$ , are in agreement with the calculated value  $0.4 \pm 0.2 \text{ eV}$ . While this agreement is encouraging it does not necessarily prove that the actual defect in  $a\text{-Si:H}$  is a dangling bond. However, if dangling bonds do exist in  $a\text{-Si:H}$ , they could be observable in ESR experiments.

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