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Charge state of hydrogen in crystalline silicon

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An estimate is given for the relative stabilities of neutral and positive bond-center hydrogen interstitials and of negatively charged hydrogen at the antibonding site as a function of Fermi-level position. We predict the hydrogen-related donor level to be below the intrinsic Fermi level, and the existence of a Fermi-energy region around midgap where the neutral charge state is stable.

Hydrogen in crystalline silicon has received much attention lately due to its ability to passivate electrically active defects.[1,2] In this respect, the stable states and diffusion of hydrogen are crucial questions. A number of theoretical calculations have established the bond-center (BC) site as the equilibrium position for neutral atomic hydrogen.[3-8] While positively charged hydrogen has been found also at the BC site,[5,6] negatively charged hydrogen is predicted to be stable at, or close to, the tetrahedral site.[9,10] Although electron-paramagnetic-resonance[11] (EPR) [and indirectly muon-spin-resonance[12] (μSR)] experiments support the existence of *neutral* hydrogen at the BC site in high-resistivity samples, it has been suggested[9,13] that hydrogen might be a *negative-U* system, i.e., its stable charge state is either positive (in p-type Si) or negative (in n-type Si). Drift experiments have indicated that hydrogen can move as a positively charged species under the action of an electric field in the depletion region of a p-type Si diode.[14-16] This implies a hydrogen-related donor level. Theoretical fits to experimental diffusion profiles[17] as well as calculations[9] suggest this level to be above midgap. The model used in Ref. 17 has been criticized, however, and it has been noted[18] that the changes in the nature of the diffusion profile in p-type silicon of various resistivities are not consistent with a level above midgap, but suggest instead that the level is at $E_v+0.3$ eV. Recent experiments in n-type Si reveal the drift of negatively charged hydrogen,[19,20] which is proof of the existence of a hydrogen-related acceptor level.

Based on calculations using the semiempirical cyclic-cluster model,[21] we reported earlier the possibility of hydrogen-related donor and acceptor levels,[5] and the stable states of the three charge states.[5,10] In this paper we attempt to give an estimate for the relative stabilities of the three charge states as a function of Fermi-level position.

To a first approximation, the Fermi energy, at which a given defect converts from one charge state to another, can be given by the one-electron energy level related to the defect in the gap. Previously, we have used this approach to predict donor and acceptor states of hydrogen.[5] This approach implies that, for example, the singly occupied donor level loses its electron whenever the Fermi level sinks below it, assuming that the only energy change involved is the energy difference between the donor level of the equilibrium neutral state and the Fermi level.

To a better approximation, however, the relative stability of a given charge state depends on the adiabatic ionization energy, i.e., on the difference between the total energies (more precisely the free energies) of the different charge states in their respective relaxed equilibriums. The calculated external adiabatic ionization energy can be obtained from the total energies calculated in our 32-atom cyclic-cluster calculations:

$$E(\mathrm{Si_{32}H_{BC}^{+}})-E(\mathrm{Si_{32}H_{BC}^{0}})\equiv I^{e}(\mathrm{Si_{32}H})\,. \tag{1}$$

Similarly, we define the calculated external adiabatic electron affinity as

$$E(\mathrm{Si_{32}H_{AB}^{-}})-E(\mathrm{Si_{32}H_{BC}^{0}})\equiv A^{e}(\mathrm{Si_{32}H})\,, \tag{2}$$

where AB denotes the antibonding site (close to the tetrahedral site), which we find as the equilibrium of the negative charge state.

What we are interested in, instead, is the internal ionization energy or electron affinity, i.e., the energy required to create a charged defect at the expense of the electron reservoir of the crystal. Since in a real silicon crystal (at finite temperature and dopant concentration) electrons can be taken from or put on both the valence- and conduction-band edges, the average energy of electrons in the reservoir is given by the Fermi energy. Therefore, the internal ionization energy and electron affinity can be defined as

$$\begin{aligned} &I^{e}(\mathrm{Si_{32}H})+1E_F\equiv I^{i}(\mathrm{Si_{32}H})\,,\\ &A^{e}(\mathrm{Si_{32}H})-1E_F\equiv A^{i}(\mathrm{Si_{32}H})\,. \end{aligned} \tag{3}$$

The first equation describes the removal of an electron from the defect to the vacuum level and from there into the electron reservoir of the rest of the crystal, while the second describes the removal of an electron from this reservoir to the vacuum level and from there to the defect.

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The division of the internal ionization process into two steps in Eqs. (3) establishes the connection between the finite defect environment treated explicitly in the cyclic-cluster model and the real, infinite crystal with a Fermi level depending on doping and temperature. However, this division is also a source of error. Namely, the first term is the energy required to decrease or increase the number of electrons in a finite system (the number of electrons is 129 ± 1), while the second is the energy required to increase or decrease it in an infinite one (the number of electrons is $\sim10^{23}\pm1$). The incompatibility involved here has important consequences for calculating the (external) electron affinity and ionization energy, as we will demonstrate it on the example of the perfect Si_{32} cyclic cluster.

In the framework of a one-electron theory the energy change following the removal or addition of an electron to the system can be divided into three terms. Term (i) is the loss or gain of the one-electron energy related to the crystalline orbital the occupation of which has been changed. We shall refer to this term as the Koopman ionization energy (the negative of the energy of the orbital from which an electron has been removed) or Koopman's electron affinity (the energy of the orbital to which an electron has been added). Term (ii) is the change in the energy of the other electrons with the nuclei fixed. The sum of (i) and (ii) is observed as the vertical ionization energy (or electron affinity). Term (iii) is connected with the relaxation of the nuclei. The sum of all three terms is what we call the adiabatic ionization energy (or electron affinity).

In a crystal the Bloch wave functions at the bottom of the conduction band or at the top of the valence band are completely delocalized. In a macroscopic crystal they spread out over $N\sim10^{23}$ unit cells and an extra electron or hole will introduce a negligible $\pm1/10^{23}$ charge into each unit cell. Accordingly, the Koopman ionization energy and electron affinity do not differ from the vertical or even the adiabatic values, and the electronic transition from the valence-band edge to the conduction-band edge (i.e., the gap) can be given, in principle, by the sum of the Koopman ionization energy and electron affinity (i.e., the difference of the one-electron energies). In our cyclic cluster calculation, however, the crystal is modeled by 16 unit cells only, i.e., the charge induced by removing or adding an electron is $\pm1/16$. This has the effect that term (ii) in the calculated vertical ionization energy and electron affinity is significant. The relaxation of the nuclei, i.e., term (iii), is already negligible at this size. Accordingly, the adiabatic ionization energy and electron affinity of the perfect Si_{32} cyclic cluster

$$
\begin{aligned}
I^e(\mathrm{Si}_{32}) &\equiv E(\mathrm{Si}_{32}{}^{+})-E(\mathrm{Si}_{32})=5.76\ \mathrm{eV}\,,\\
A^e(\mathrm{Si}_{32}) &\equiv E(\mathrm{Si}_{32}{}^{-})-E(\mathrm{Si}_{32})=-0.33\ \mathrm{eV}\,,
\end{aligned}
\tag{4}
$$

differ from the values of the infinite crystal and they do not add up to the energy of the gap. Within the modified intermediate neglect-of-differential-overlap (MINDO/3) approximation[22] which we use, the calculated ionization energy of the infinite silicon crystal, as obtained from a complete band-structure calculation,[23] is in very close agreement with the value found experimentally[24] as the ionization threshold of bulk electronic states,

$$I^e(\mathrm{Si})=5.35\ \mathrm{eV}\,.$$

Therefore, the deviation is entirely due to the size effect. The energy of the gap in this finite-size approximation is the energy difference between the excited state (one electron promoted from the top of the valence band to the bottom of the conduction band) and the ground state of the 32-atom cluster. Our calculated value, 1.91 eV, should be compared to the experimentally observed energy of the gap for the infinite crystal, 1.12 eV. Using this value (no inverse photoelectron spectroscopy data are available), the "experimental" electron affinity is

$$A^e(\mathrm{Si})=-4.23\ \mathrm{eV}\,.$$

The electron affinity of the 32-atom cyclic cluster differs from that of the infinite crystal by almost 4 eV. The difference between the errors in the ionization energy and in the electron affinity follows from the fact that, for a given finite system, term (ii) is always smaller for the former than for the latter (the number of electron-electron interactions grows by $N-1$ when going from the positive to the neutral system and by N when going from the neutral to the negative one).

In calculating the external adiabatic ionization energy or electron affinity of a defect, we encounter a similar error and, therefore, the first term on the left-hand side of Eq. (3) is not compatible with the second which *is* relevant to the finite solid (i.e., without error). Considering that the defect wave function, the occupation of which is changed, is more localized than the extended orbitals of the band edges, we can establish an upper limit of the error we are introducing by using Eq. (3) and use them as correction factors:

$$
\begin{aligned}
\Delta_{+} &= I^e(\mathrm{Si})-I^e(\mathrm{Si}_{32})=0.41\ \mathrm{eV}\,,\\
\Delta_{-} &= A^e(\mathrm{Si})-A^e(\mathrm{Si}_{32})=-3.90\ \mathrm{eV}\,.
\end{aligned}
\tag{5}
$$

Now, if we define the formation energy of neutral bond-center hydrogen as

$$\Delta E_f^0=E(\mathrm{Si}_{32}\mathrm{H}_{\mathrm{BC}}^0)-[E(\mathrm{Si}_{32})+E(\mathrm{H}_a)]=-0.28\ \mathrm{eV}\,,\tag{6a}$$

the formation energy of the charged species can be given as

$$\Delta E_f^{+}=\Delta E_f^0+I^i+\Delta_{+}=+4.53+E_F(\mathrm{eV})\,,\tag{6b}$$

$$\Delta E_f^{-}=\Delta E_f^0+A^i+\Delta_{-}=-5.02-E_F(\mathrm{eV})\,.\tag{6c}$$

Equations (6a)–(6c) are displayed in Fig. 1. The crossing points occur at $E_{+/0}=-4.81$ eV and $E_{0/-}=-4.74$ eV, i.e., for Fermi-level positions $E_v+0.54$ eV and $E_c-0.51$ eV, respectively. We can regard these values as upper and lower bounds, respectively, because the correction factors in (5) are the upper limits of error due to size effect. Without applying any correction the $E_{+/0}$ level would be at $E_v+0.13$ eV and $E_{0/-}$ at $E_c+3.39$ eV. Apart from this uncertainty, we have to take into account the expected error of MINDO/3 in predicting adiabatic ioniza-

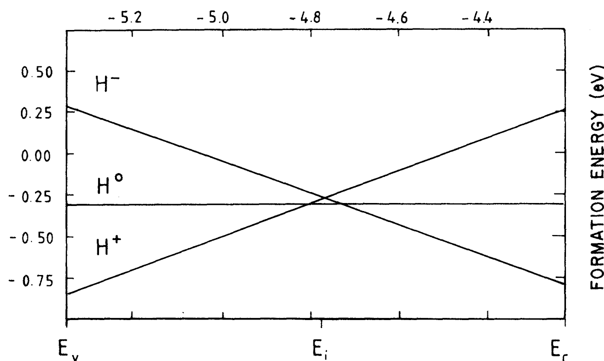

FIG. 1. Formation energy of the three charge states of hydrogen in silicon as a function of Fermi-level position. (E_v and E_c are the edges of the valence and conduction bands, respectively, and E_i is the intrinsic Fermi energy.)

tion energies of (finite) open-shell systems. For a series of radicals the standard deviation of calculated and experimental values was found to be 0.17 eV.[22,25]

Our result puts the donor level of hydrogen below midgap $[E_m=(E_v+E_c)/2]$, i.e., $E_{+/0}<(E_m-0.02)\pm 0.17$ eV. Du, Yan, and Qin have predicted[26] $E_{+/0}=(E_m-0.03)\pm 0.09$ eV, based on the experimentally observed charge states of various radiation defects in the presence of hydrogen.

Between $E_{+/0}$ and $E_{0/-}$ we find a region with a width >0.07 eV around the intrinsic Fermi level, where neutral hydrogen is stable. Regarding the accuracy of MINDO/3 (± 0.17 eV), the reliability of predicting the existence of such a region depends on how close the actual error due to the size effect is to the upper bounds we use. A guess can be made using the experimentally observed localization of the orbital containing the unpaired spin in the neutral charge state. This has been found to be less than 45% within the first two silicon neighbor shells of the hydrogen.[11,12] We may speculate that for such a weakly localized orbital about 55% of the correction is justified (100% corresponding to a completely delocalized orbital). This would put the lower boundary of the region to $E_{+/0}\approx E_v+0.35$ eV in accord with the experimental analysis[18] mentioned earlier. We do not have experimental information about the localization of the orbital containing the electrons in the equilibrium configuration of the negative charge state. Since any amount of localization would raise the $E_{0/-}$ level even stronger than the lowering of the $E_{+/0}$ level (the correction factor is bigger in absolute value), we feel confident that the stability region for the neutral state does in fact exist.

In conclusion, we have given an estimate for the relative stabilities of the three charge states of hydrogen in silicon as a function of Fermi energy. We predict the hydrogen-related donor level to be below the intrinsic Fermi level, and the existence of at least a narrow Fermi-energy region where the neutral charge state is stable.

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