

Microscopic Mechanism of Hydrogen Passivation of Acceptor Shallow Levels in Silicon

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A microscopic model is proposed which explains recent observations that acceptor shallow levels in crystalline silicon can be inactivated by atomic hydrogen. We are assuming that substitutional-boron-interstitial-hydrogen complex pairs are being formed which passivate the shallow acceptor action of the boron impurity. Rigorous self-consistent calculations show that the acceptor level is removed from the gap and the boron electrical activity is clearly neutralized.

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The interest in the physical properties of hydrogen-related defects in silicon is strongly motivated by their importance for the electronic-device technology based on crystalline, polycrystalline, and amorphous materials. The effects of hydrogen passivation of electrically active defects in semiconductors are well documented.¹⁻¹⁰ Hydrogenization reconstructs the dangling bonds, producing relevant effects on crystalline¹ and amorphous silicon.² Atomic hydrogen reacts with grain-boundary states and improves electrical characteristics in bulk³ and thin-film⁴ polycrystalline silicon. It is also known that hydrogen can passivate point defects in various semiconductors,⁵⁻⁷ and likewise it has been correlated with the electrical inactivity of dislocations,⁸ interfaces,⁹ and swirl defects¹⁰ in silicon.

Recently, the first definitive observation that shallow acceptors in crystalline silicon can be inactivated by atomic hydrogen has been reported.¹¹ It was found that the resistivity of boron-doped silicon single crystals increases when the samples are exposed to a hydrogen plasma. Shortly thereafter it was reported that aluminum, gallium, and indium acceptors in silicon are neutralized by hydrogen.¹² Experiments were made previously which suggested that the deactivation of the boron acceptor in silicon by hydrogen was due to the formation of a B^-H^+ pair.¹³ It has been pointed out that many of the boron sites in amorphous silicon may be inactivated by a mechanism similar to that observed on crystalline silicon.¹¹ In this work we are proposing a model which demonstrates, in a quantitative way, that atomic hydrogen passivates the shallow acceptor activity of the boron impurity.

It is generally accepted that isolated interstitial atomic hydrogen is very mobile in all the common semiconductors, which explains why no direct experimental information about its electrical activity is available.^{13,14} It reacts with other impurities or with defects to form complexes. It is also known from theoretical work that the tetrahedral interstitial lattice site (T) seems to be a stable position in the possible diffusion paths of hydrogen in diamond¹⁵ and silicon.¹⁶ In our model we are assuming first that when hydrogen reaches a T site near a substitutional boron impurity it gets trapped and

a $Si:B_sH_i$ complex pair is formed. Our calculations indicate that hydrogen attempts to bond covalently with boron and moves from the T site towards the boron-impurity site. As a consequence, the boron center is inactivated.

The calculations reported in this Letter were carried out by use of the Watson-sphere-terminated molecular cluster model within the framework of the self-consistent-field multiple-scattering (MS) $X\alpha$ theory. The model is well known and therefore it will not be discussed here.¹⁷ The cluster model adopted in the calculations is schematically shown in Fig. 1.

The results obtained for the $25Si + B_sH_i$ cluster indicate a strong tendency of the hydrogen $1s$ state to bond with boron and with the neighboring silicon atoms. It is worthwhile to point out that this tendency is only observed when boron is present. According to our calculations, performed with use of a $26Si + H_i$ cluster model, T -site hydrogen introduces a hyperdeep $1s$ -atomiclike level below the bottom of the valence band,

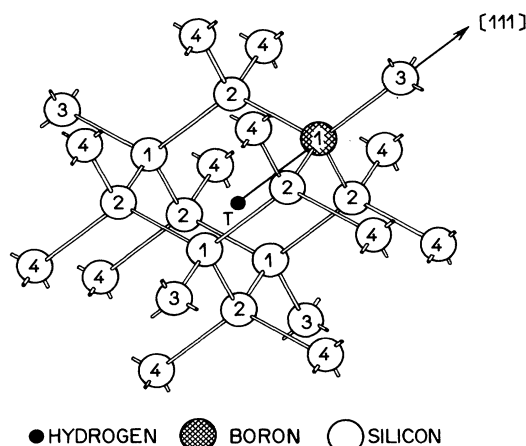


FIG. 1. $25Si + B_sH_i$ cluster model utilized to simulate the complex pair of substitutional boron (B_s) and interstitial hydrogen (H_i). As a T -interstitial-centered cluster it comprises four shells of atoms in C_{3v} symmetry. (The shells are numbered from 1 to 4.)

which suggests a small interaction with its four silicon neighbors.

The results of our search for a stable position for the hydrogen atom along the line joining the T site and the boron atom are shown in Fig. 2. The MS- $X\alpha$ total energy of the $25\text{Si} + \text{B}_s\text{H}_i$ cluster is depicted as a function of the hydrogen position. It is worthwhile to mention that the MS- $X\alpha$ cluster model has been successfully applied to calculate total energies for ionic crystals.¹⁸ According to Fig. 2 a local minimum for the cluster MS- $X\alpha$ total energy is found for hydrogen placed at about 1.80 Å from the boron atom. We have to bear in mind that hydrogen is unable to form a B-H bond of normal strength (1.23 Å for the BH molecule¹⁹), because of competition from other silicon atoms to which boron is bonded, as well as the interaction between hydrogen and the lattice.

Figure 3 summarizes the main features of our calculations. The impurity levels of the $\text{Si}:\text{B}_s\text{H}_i$ complex, referenced to the top of the valence band, are shown. The results correspond to hydrogen located at the T site (a), and at a shorter distance from the boron atom, 1.75 Å (b). We also include in Fig. 3 the results obtained recently for the $\text{Si}:\text{B}_s$ center by application of the Watson-sphere-terminated cluster model to a seventeen-atom cluster with boron as the central atom.²⁰

According to the $16\text{Si} + \text{B}_s$ cluster calculation, the main effect of replacing a silicon atom by boron in the lattice is the appearance of an acceptor level at 0.04 eV above the top of the valence band. This result is in very good agreement with the measured value of the activation energy of the $\text{Si}:\text{B}_s$ ground state, 0.045 eV.²¹ The hole state is rather delocalized with a charge distri-

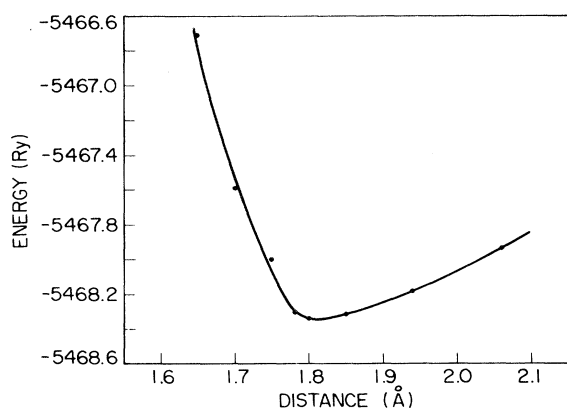


FIG. 2. MS- $X\alpha$ total energy of the $25\text{Si} + \text{B}_s\text{H}_i$ cluster as a function of the hydrogen position in the (111) direction. The origin of the distance is taken at the boron site. The T site is at 2.35 Å. The "frozen"-core energy eigenvalues (Si: 1s, 2s, 2p; B: 1s) are not considered in the total-energy evaluation.

bution corresponding to 14%, 22%, and 38% on the central boron atom and first and second shells of silicon atoms, respectively. The comparison between these results and those obtained for a silicon vacancy¹⁷ leads to the conclusion that the hole state is not exactly a vacancy dangling-bond state. The vacancy-bond t_2 state is more delocalized, having only 3% of the charge in the central sphere. As a consequence the vacancy t_2 gap level lies at the upper half of the band gap.¹⁷ We are bearing this in mind when we assume that the passivation mechanism proposed here is not merely a hydrogen saturation of a silicon dangling bond. The charge in the boron central sphere (radius=1.18 Å) is $5.6e$ which indicates that the ionic limit notation, B_s^- , commonly used for the center is misleading.

The results obtained for the $25\text{Si} + \text{B}_s\text{H}_i$ cluster indicate that when hydrogen is at the T site two fully occupied levels, e and a_1 , are found within the band gap. At this state the boron shallow acceptor action is already neutralized and the complex turns out to be electrically active as a deep donor. As we proceed by moving the hydrogen atom towards the boron site the e and a_1 levels are attracted to the valence band. The results depicted in Fig. 1(b) show that, for hydrogen at 1.75 Å apart from the boron atom, the impurity levels are removed from the gap, which indicates that the center is no longer optically, magnetically, or electrically active.

The charge in the boron impurity sphere does not exceed $5.5e$ and the charge inside the hydrogen sphere, even at the shortest $\text{B}_s\text{-H}_i$ distance, is of the order of $1e$. We conclude that the passivation effect originates from a covalent mechanism which includes, besides hydrogen and boron, also the silicon neighbors. The simple hypothesis that hydrogen provides the fourth electron needed to satisfy the valences of the nearest silicon neighbors¹² is not supported by the

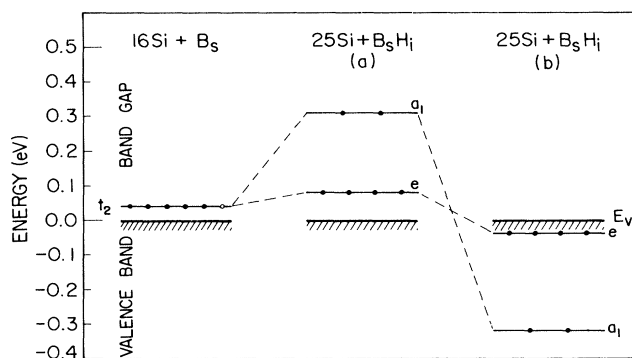


FIG. 3. Impurity levels of the $\text{Si}:\text{B}_s$ and $\text{Si}:\text{B}_s\text{H}_i$ systems near the valence-band edge. The solid (empty) circles indicate electron (hole) occupancies. Hydrogen is placed (a) at the T site, $d = 2.35$ Å from boron; (b) at $d = 1.75$ Å.

calculations, and the notation $B_s^- H_i^+$ for the complex is also misleading.¹³

The microscopic model of hydrogen passivation proposed here is rather different from those discussed previously, where hydrogen is assumed to be directly attached to a silicon dangling bond at a "bonding" position.²²⁻²⁴ We believe that the present model plays a relevant role in explaining the passivation mechanisms of substitutional impurities in semiconductors. In this case the interstitial-site "antibonding" positions considered here for the hydrogens are highly likely.

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