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Bonding or antibonding position of hydrogen in silicon

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We present calculations of hydrogen bonding in a crystalline silicon lattice using covalent two-electron bond theory. It is found that, due to rehybridization of the silicon bonds, the stable position of the hydrogen atom lies outside the silicon vacancy. Our model supports all the relevant experimental data, especially the channeling and infrared measurements on crystalline silicon implanted with protons, as well as experiments on donor and acceptor passivation by hydrogen.

I. INTRODUCTION

Interest in hydrogen in silicon has arisen principally because of its ability to passivate the electrical activity of dangling bonds.[1] This role of hydrogen is essential to current technological advances in the development of amorphous and polycrystalline silicon for solar-cell applications. In spite of this, the understanding of the bonding of hydrogen to a dangling hybrid is not complete. In particular, the ion-channeling experiments of Picraux and Vook[2] have shown that the H atom is at a distance of 1.6 Å from the Si atom, but on the opposite side of the vacancy region. This finding is in disagreement with the calculated position of hydrogen in crystalline silicon.[3] On the basis of the ion-channeling results, the H atom has been assigned to the so-called "antibonding" position. However, it has never been convincingly explained why the H atom does not predominantly saturate the dangling bonds of the Si vacancies, which should be present in large concentrations in proton-implanted samples, but instead occupies the antibonding position.

In contrast to the above conclusion, this article proposes that the so-called antibonding position of hydrogen results from σ-type bonding, with a reconstruction of the environment next to the Si-atom vacancy.

The tight-binding method and the universal tight-binding parameters introduced by Harrison have been able to give approximate but meaningful predictions of the bonding and electronic properties of solids.[4] In recent years important progress has been made in tight-binding calculations of the equilibrium spacing, cohesive energy, and the force constants for rocksalt and zinc-blende structure solids.[5] The tight-binding approach to bond energy made it possible to obtain the nearest-neighbor spacings for tetraheadral semiconductors[6] and for various carbon compounds[7] in very good agreement with experiments. An important simplification of the linear combination of atomic orbitals approach has come from the bond-orbital approximation,[8] which makes a calculation of the total energy rather straightforward. Within this approximation, the coupling between bonding and antibonding states is neglected, so that a broadening of the bond states does not change the energy. As a consequence, one does not have to solve the bond problem in order to calculate total energies. The total energy becomes simply proportional to the sum of bond energies, and the total valence charge density is proportional to the charge density of the bond orbitals.

II. TIGHT-BINDING CALCULATIONS

We shall start with calculations of the Si—H bond in the SiH_4 molecule, which will serve as a test of the accuracy of our predictions. The natural choice of orbitals is sp^3 hybrid orbitals on Si and an s orbital on H. The σ-type covalent-bond energy may be expressed by the following formula:

$$\varepsilon_b = \tfrac{1}{2}(\varepsilon_h^{\mathrm{Si}} + \varepsilon_s^{\mathrm{H}}) - (V_3^2 + V_2^2)^{1/2} + V_2 S \; . \tag{1}$$

The first term is the average of the silicon hybrid energy $\varepsilon_h^{\mathrm{Si}}$ [expressed by the free-atom energies $\varepsilon_s^{\mathrm{Si}}$ and $\varepsilon_p^{\mathrm{Si}}$ (Refs. 9 and 10)] and the hydrogen s-orbital energy $\varepsilon_s^{\mathrm{H}}$. The second term is connected with the σ-type bond-formation energy. For the Si—H bond, the hydrogen s state lies deeper in the energy scale and

$$V_3 = \tfrac{1}{2}(\varepsilon_s^{\mathrm{H}} - \varepsilon_h^{\mathrm{Si}}) \tag{2}$$

is the polar energy. The hybrid covalent energy V_2 is the matrix element between hybrid orbitals pointing at each other

$$V_2 = -\eta_\sigma \hbar^2 / m d^2 \; , \tag{3}$$

where d is the Si-H bond length, $\eta_\sigma = 2.293$ is a dimensionless coefficient resulting from the coupling matrix element, expressed in terms of Harrison universal parameters ($\eta_{ss\sigma} = -1.40$, $\eta_{sp\sigma} = 1.84$, and $\eta_{pp\sigma} = 3.24$ are appropriate for the Herman-Skilmann atomic term values used in Ref. 9). The second term, connected with the covalent energy, is responsible for lowering of the energy of the bonding state. The third term in Eq. (1) is connected with overlap interactions. The hybrid orbitals on adjacent sites are not orthogonal and have a nonzero S overlap. The $V_2S \sim 1/d^4$ term is responsible for the forces which prevent the collapse of matter under the attractive σ-bonding interactions. The overlap energy was taken into account within the Hückel approximation in the same way as in the calculation of bond lengths in other systems.[6] Within this approximation, the following expression has been used:

$$V_2 = k\,|\varepsilon_h|\,S\ , \tag{4}$$

where ε_h is the Si-H average hybrid energy and k is an empirical parameter, equal to 1.455—the value found to be appropriate for the Si row.[6]

The equilibrium spacing is obtained by taking the derivative of the bond energy with respect to the distance and comparing it to zero. For partly polar bonds this derivative leads to $S = \frac{1}{2}\alpha_c$, where α_c is covalency of the bond.[4] This derivative leads to the following equation for the equilibrium spacing:

$$d = (\hbar^2/m\eta_\sigma)^{1/2}/(\tfrac{1}{4}k^2|\varepsilon_h|^2 - V_3^2)^{1/4}\ . \tag{5}$$

Thus, the equilibrium spacing is expressed directly by the Herman-Skilmann atomic term values and by the η_σ coupling coefficient, and may be obtained without introducing any parameters.

The equilibrium spacing $d = 1.52$ Å, obtained from Eq. (5) for the Si—H bond in SiH_4, is in good agreement with the experimental value of 1.48 Å. Equation (5) has been used previously for calculating the C—H bond length for the C_2H_2, C_2H_4, and C_2H_6 molecules, with the resulting values also found to be in good agreement with experiment.[7] In all these cases the accuracy of the predictions is of the order of a few percent.

Let us now consider the case of decoration of a Si vacancy by four hydrogen atoms. The system contains 4 H(s)—Si(sp^3) bonds and 12 next Si(sp^3)—Si(sp^3) bulklike bonds. The total energy of the system is, in our approximation, given by the sum of the corresponding bond energies. However, the H(s)-Si(sp^3) bond is partially polar and our calculation shows that a net negative charge, equal to 0.33 of the electron charge, is located on each hydrogen atom. Bearing in mind that full hydrogen decoration of the vacancy is connected with placing four negatively charged hydrogen atoms inside the vacancy, we see that there will be a relatively large Coulomb interaction increasing the energy of the system.

Saturation of the four sp^3 dangling orbitals by hydrogen atoms seems to be in agreement with our intuition. This solution does not take into account the relaxation of the four Si atoms nearest to the vacancy. Such a relaxation of all four Si atoms will be connected with rehybridization of the four hybrid orbitals of the relaxed atoms. The symmetry of the problem suggests rehybridization from sp^3 to sp^2 hybrid orbitals. Indeed, it is found that such rehybridization substantially lowers the total energy of the system.

Relaxation of the four Si atoms is totally symmetric and takes place in the $[\bar{1}\bar{1}\bar{1}]$ direction, as shown in Fig. 1, and in equivalent directions. The details of the sp^3-sp^2 covalent-bond formation for one of the Si atoms are shown in Fig. 2. There is a misalignment of the angles between the sp^2 hybrid orbitals of the relaxed atom, which are in the (111) plane, and the sp^3 hybrid orbitals which are directed under the angle of 19.5° to the (111) plane. Our calculation shows that in spite of the sp^2 character of the hybrid orbitals the minimum of the energy does not correspond to a position of the relaxing Si atom on the same (111) plane on which the nearest neighbors are situated. Instead, the lowest energy is found when the relaxing silicon atom moves away by 0.22 Å from the vacant site along the $[\bar{1}\bar{1}\bar{1}]$ direction, as shown in Fig. 2. The relaxation shortens the Si(sp^3)—Si(sp^2) bond to 2.28 Å. This strengthens the bonds of the relaxing atoms with respect to the rest of the crystal by making them more graphitelike. The effect was pointed out by Scheffler in the discussion of the electronic structure of a vacancy in Si.[11] The slight contraction of the first interlayer spacing with respect to the bulk value at an unreconstructed Si(111) surface has been found to have the same nature.[12] The recent self-consistent tight-binding calculations of the Si(111) 1×1 surface yield a contraction of 0.24 Å of the first atomic layer,[13] which is of the same order as our result. Apart from the three sp^2 hybrid orbitals in the (111) plane, there is a fourth p orbital, perpendicular to the plane. The hydrogen atom may be bound to the p orbital, forming a H(s)—Si(p) covalent bond. The calculated length of the H(s)—Si(p) bond is 1.47 Å. The calculated total energy of the system containing one H(s)—Si(p) and three Si(sp^3)—Si(sp^2) back bonds is 0.87 eV lower than the energy of the corresponding unrelaxed system.

The important difference between the two situations mentioned above, apart from the energy difference, is that in the case of a relaxed system, the hydrogen atom may saturate the Si(p) dangling hybrid orbital, being *inside* or

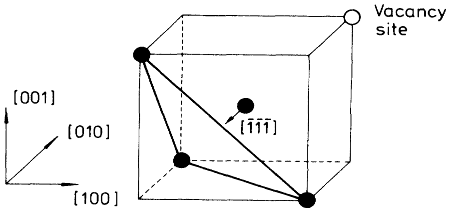

FIG. 1. $[\bar{1}\bar{1}\bar{1}]$ relaxation of a silicon atom next to a vacancy.

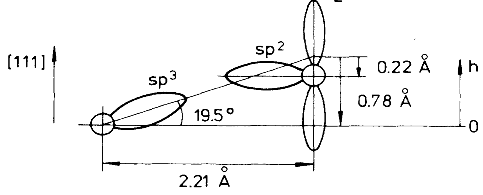

FIG. 2. Schematic visualization of the Si(sp^3)—Si(sp^2) bond formation in the (110) plane. The sp^2 hybrids are in the (111) plane.

outside the vacancy region. The H(s)—Si(p) bond is even more polar than the H(s)—Si(sp^3) one, and the amount of charge transferred from the Si atom onto the hydrogen atom is about 0.46 electron charge. A consideration of the repulsive Coulomb interaction between the hydrogen atoms decorating the vacancy shows that the outside positions of the hydrogen atoms will be energetically favored. Taking into account the fact that the H(s)—Si(p) bond length is 1.47 Å and that the relaxation of the Si atom is 0.22 Å, one finds the position of the hydrogen atom to be 1.69 Å from the site of the Si atom, outside the vacancy. Since the accuracy of our method is of the order of a few percent, this position corresponds very well to the so called antibonding position of the hydrogen atom, found in the channeling experiment of Picraux and Vook.[2]

III. DISCUSSION

We have shown that decoration of a Si vacancy by four hydrogen atoms leads to antibonding positions of hydrogen atoms. The question arises of how one hydrogen atom may decorate the vacancy. This situation is expected to be realized in proton-implanted silicon. The hydrogen atom may be bound inside or outside the vacancy region. Both positions are energetically equivalent within our calculation scheme. However, the electrons from the unsaturated dangling hybrids will form the a_1 and t_2 states and a higher electron density will be present inside the vacancy region than outside, in the interatomic space. Therefore, a repulsive Coulomb interaction between the hydrogen atom and the vacancy charge may force the hydrogen atom into the outside position which was observed in the channeling experiment.

The stretching force constant of the H(s)—Si(p) bond turns out to be equal to 18.9 eV/Å^2; this corresponds to the wave number of 2250 cm^{-1}. When we consider coupled vibrations of the Si$_4$H molecule, we get the energy of the stretching vibrations equal to about 2080 cm^{-1}, which compares well with the experimentally observed[14] Si-H vibrations of about 2000 cm^{-1}. The experimentally established oscillator strength of the stretch mode vibration of about 0.2 (Ref. 15) means that, in the classical model, we are dealing with vibrations of a dipole of 0.45 of the electron charge. This value agrees very well with the calculated transfer of the electron charge from the Si onto the H atom, equal to 0.46 of the electron charge. Another interesting consequence of the presented model (Fig. 3) comes from an analysis of the anisotropic force constants corresponding to a displacement of the relaxed Si(sp^2) atom. The force constant for the Si(sp^2)—Si(sp^3) bond for a displacement perpendicular to the (111) plane is very low: about 2.5 eV/Å^2. The corresponding Si(p)—H(s) in phase vibration [when the Si(p)—H(s) bond length is unchanged] gives a wave number of about 240 cm^{-1}. The characteristic hydrogen low-energy mode of 210 cm^{-1} was reported for amorphous silicon with hydrogen[16] and the nature of this frequency has remained unclear.

On the other hand, for displacements parallel to the (111) plane, the force constants of the Si(sp^3)—Si(sp^2) bonds are larger than the corresponding force constants of bulk silicon. The stretching force constant of the Si(sp^3)—Si(sp^2) bond is 9.5 eV/Å^2, which can be compared with the calculated (in our model) bulk silicon Si(sp^3)—Si(sp^3) bond stretching force constant of 8.7 eV/Å^2. The increase of the force constant for the Si(sp^3)-Si(sp^2) bond by about 10% has important consequences for bending mode vibrations of deuterium in silicon. It is known that the bending modes of deuterium are in resonance with bulk silicon TO modes.[17,18] In spite of this resonance, deuterium bending modes preserve a localized character and the corresponding optical excitations do not lose their intensities. The oscillator strengths of the bending modes of hydrogen and deuterium are the same within the experimental error,[15] despite the fact that for hydrogen, these vibrations are well above the energy of the optical phonons of silicon (the maximum of the density of the phonon states in silicon is at about 480 cm^{-1}, and the high-energy cutoff is at about 510 cm^{-1}). The reason for the weak coupling between the bending modes of deuterium and the optical modes of bulk Si was stated previously,[17] but no satisfactory explanation of it existed. A displacement of the relaxed Si(sp^2) atom parallel to the (111) plane takes place in the bending mode of the D(s)-Si(p) bond and the hardness of the corresponding local bonds will realize the weak coupling to the silicon lattice vibrations.

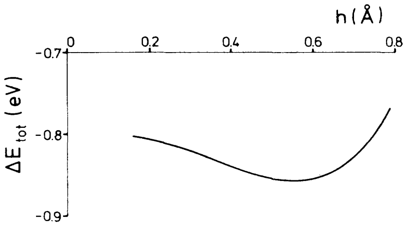

FIG. 3. Change of the total energy of the system containing three Si(sp^3)—Si(sp^2) bonds and one H(s)—Si(p) bond (relative to the energy of the unrelaxed sp^3 bonded system) vs relaxation of the Si atom, where h is defined in Fig. 2.

The main result of our calculation, i.e., that the three sp^3—sp^2 back bonds of the relaxed Si atom and the H(s)—Si(p) bond give the lowest energy state, implies that predominantly monosilanes are formed in proton-implanted silicon. It was recently found by ir absorption measurements that only monosilanes are formed after proton or deuteron implantation of crystalline silicon.[15]

The current interest in the properties of hydrogen in silicon also stems from its ability to passivate shallow levels as well as deep ones. In crystalline silicon, the shallow acceptors are passivated by the reaction with atomic hydrogen.[19] It was recently demonstrated, for the first time, by Johnson *et al.*[20] that hydrogen can also passivate shallow donors, such as phosphorus. Our total energy calculation shows that in the passivation of shallow donors, the H(s)—Si(p) σ-type bond discussed above plays a decisive role. We have considered a P(s^2p^3) atom and a H atom in the vicinity of a Si vacancy. The lowest energy solution is found when three p electrons of the P atom form covalent bonds with the three sp^3 hybrids of the Si atoms. The two s electrons of a P atom do not participate in bond formation, which is of the P(p)—Si(sp^3) type. The fourth Si dangling hybrid is saturated by hydrogen, forming a Si(p)—H(s) bond. Due to small transfer of the negative charge on the phosphorus atom, Coulomb repulsion will force the hydrogen atom to be in the so-called antibonding position. It is worth mentioning that passivation of shallow acceptors may be understood in the same way. An acceptor impurity, such as boron, will saturate the three sp^3 silicon hybrids via formation of three B(sp^2)—Si(sp^3) bonds. The fourth dangling Si hybrid will be saturated by formation of the Si(p)—H(s) bond. Due to the transfer of negative charge onto the B atom from the three neighboring Si atoms, Coulomb repulsion will push the H atom into an "outside" position. It is interesting to note that for Al or Ga impurities, the flow of charge will go the other way, leaving some positive charge on the impurity atom. In this case, hydrogen will be drawn in so as to occupy the inside position. This effect should influence the vibrational properties of hydrogen in Si:B and in Si:Al(Ga) in opposite ways.

IV. CONCLUSIONS

We have shown that rehybridization of the vacancy neighborhood leads to a change of the dangling hybrids character from a sp^3- to a p-like one. Saturation of this orbital by hydrogen makes it possible to bind a hydrogen atom inside or outside the vacancy region.

The presented model explains the position of the hydrogen atom in the lattice and gives a good account of the vibrational properties of hydrogen in silicon. In addition, it gives a clear insight into the mechanism of passivation of donors and acceptors by hydrogen.

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