# Negative-$U$ States in the Gap in Hydrogenated Amorphous Silicon

R. Fisch and D. C. Licciardello
*Department of Physics, Princeton University, Princeton, New Jersey 08540*
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We propose that Si-H-Si three-center bonds exist in hydrogenated amorphous silicon. These centers give rise to states in the energy gap which have a negative effective electronic correlation energy, $U$. Our model can explain many of the known properties of this material. We make suggestions about how to obtain materials which may prove useful in electronic device applications.

Several years ago Anderson proposed a model[1] for the electronic structure of amorphous semiconductors. The key feature of this model was that the effective correlation energy, $U$, between two electrons in the same state was hypothesized to be negative, so that the ground state of the material was diamagnetic. Subsequently, Mott, Davis, and Street,[2] and Kastner, Adler, and Fritzsche[3] identified specific chemical configurations which occur in lone-pair semiconductors and which are responsible for the existence of negative-$U$ states in the energy gaps of these materials. These authors claimed that tetrahedrally bonded semiconductors (Si, Ge) cannot form such negative-$U$ centers, and thus are fundamentally different from the lone-pair semiconductors. However, Knights, Biegelsen, and Solomon[4] have performed ESR experiments which indicate that negative-$U$ centers do exist in hydrogenated amorphous silicon. In this Letter, we point out that the incorporation of large amounts of hydrogen into amorphous Si (or Ge) will allow the formation of a specific type of negative-$U$ gap state. A previous attempt[5] to explain the properties of this material assumed the existence of a different type of negative-$U$ center. We briefly discuss the implications of our work for the device applications of amorphous silicon-based materials.

The fundamental idea is the following. Because of the random nature of the material, we expect that the Si-Si bonds will have a distribution of energies. Most of the weak bonds will have a larger than normal Si-Si bond length. If there is enough room in the local environment, we will be able to insert two H atoms, break the Si-Si bond, and form two Si-H bonds. If there is somewhat less room available, we will only be able to insert one H atom, and we will form an Si-H-Si three-center bond (TCB). This possibility has been suggested by Mott, Davis, and Street. Appelbaum, Hamann, and Tasso[6] have discussed a chemisorptive bond of this type which may occur on the surface of crystalline Si. If we assume for the moment that the H sits halfway between the two Si's, we can form the following molecular-orbital wave functions from the atomic orbitals $\varphi_{\mathrm{Si}_1}$, $\varphi_{\mathrm{Si}_2}$, and $\varphi_{\mathrm{H}}$:

$$\begin{aligned}\psi_1 &= (2+\alpha^2)^{-1/2}(\varphi_{\mathrm{Si}_1}+\alpha\varphi_{\mathrm{H}}+\varphi_{\mathrm{Si}_2}),\\ \psi_2 &= 2^{-1/2}(\varphi_{\mathrm{Si}_1}-\varphi_{\mathrm{Si}_2}),\\ \psi_3 &= (2+4/\alpha^2)^{-1/2}[\varphi_{\mathrm{Si}_1}-(2/\alpha)\varphi_{\mathrm{H}}+\varphi_{\mathrm{Si}_2}].\end{aligned} \tag{1}$$

The wave functions $\psi_i$ will, of course, change if we vary the position of the proton. For example, if we move the H away from the center position toward one of the Si's, the $\psi_1$ orbital will be well approximated by an Si-H bonding orbital. Under these conditions, the $\psi_2$ orbital is approximately an Si lone-pair orbital and the $\psi_3$ becomes the Si-H antibonding orbital.

$\psi_1$ has an energy which is deep in the valence band, and thus will always be occupied by two electrons. The $\psi_1$ orbital provides the binding energy which keeps the H atom in position between the two Si's. If only the $\psi_1$ orbital is occupied, the H atom should indeed be stable at a position equally distant from the two Si atoms (although *not* necessarily on the line between them) since this minimizes the electronic energy. We shall call TCB's which are occupied by 2, 3, and 4 electrons $T^+$, $T^0$, and $T^-$ states, respectively. Note that the superscript corresponds to the local charge of the bond.

The $T^+$ state is very similar to the TCB's which occur in diborane, $B_2H_6$. Based on the known structure of the diborane, in which the B-H bond length is 0.14 Å bigger in the TCB configuration than in the normal B-H bond, we estimate that the Si-H bond length in this $T^+$ state is about 1.6 Å. (Recall that the normal Si-H bond is 1.48 Å.) The bond energy should be relatively insensitive to the Si-H-Si bond angle, since $\varphi_{\mathrm{H}}$ is an $s$ orbital. This implies that the bond energy may be approximately constant over a range of Si-Si distances.

Now let us consider the case of the TCB occupied by four electrons. If we fill up the $\psi_1$ and $\psi_2$ orbitals, we see that, because of the node in the

$\psi_2$ wave function, the center of the bond is no longer a stable position for the H atom. The H sees a double-bottomed potential well, with a maximum in the center. Thus the H will move close to one of the Si's, into the "hydrogen-bond" configuration. Because of the local charge, the $T^-$ state forms a "strong hydrogen bond,"[7] which lowers its energy relative to the $T^0$ state. Thus the $\psi_2$ orbital has a negative $U$ whose magnitude can be estimated to be 0.6–1.0 eV.[7] The distance over which the H moves on going from the $T^+$ state to the $T^-$ state should be at least 0.15–0.20 Å, and it may be considerably larger, depending on the change in the Si-Si distance. This latter quantity is difficult to estimate, since it depends heavily on the local environment surrounding the bond. We believe that most of the motion of the proton occurs upon addition of the first electron to the $\psi_2$ orbital.

Since $\psi_2$ is essentially a "nonbonding" orbital, we anticipate that it will have an energy which lies in the gap between the valence and conduction bands. [Note that we must not use the wave function of Eq. (1) to calculate the energy of $\psi_2$, since when $\psi_2$ is occupied the H is not in the centered position.] Because of the negative $U$, in the ground state we must put electrons into the $\psi_2$ orbitals in pairs. By charge neutrality, we see that in undoped *a*-Si we can fill half of the available $\psi_2$ orbitals. Since all spins are paired, the ground state of a TCB will be diamagnetic.

The TCB's can be considered to be canonical Anderson-Halperin-Varma[8] tunneling centers. They give linear contributions to the low-temperature specific heat in two ways. First, there is an electronic contribution which results from the movement of pairs of electrons among the available orbitals. Second, there is a "phonon" contribution which results from the hopping of "hydrogen-bond" protons from one side to the other of their double wells. (Because of local-environment effects, the two sides will not be precisely equivalent.) It is not clear that the number of TCB's (not more than $10^{18}/\text{cm}^3$) is large enough to explain the magnitude of the linear specific heat. Their importance in this regard can easily be checked by making measurements on lightly doped samples.

The $T^+$ and $T^-$ states constitute a lower Hubbard (LH) band, with the $T^0$ states making up the upper Hubbard (UH) band. (Recall that $U$ is negative.) From experimental measurements,[9] we can place the LH band at about 0.6 eV below the conduction band. Our estimate of $U$ places the UH band just below the conduction band, since the UH band lies $|\frac{1}{2}U|$ above the LH band. This density of states is shown schematically in Figure 1. It is important to note that one cannot simply obtain the density of gap states as a function of energy, $n(E)$, by varying the density of electrons in the material. This is because the correlation energy $U$ must be accounted for, since the LH band consists of two-particle states rather than single-particle states.

From experiment,[9] we know that the energy gap between the valence- and conduction-band mobility edges $E_g \cong 1.7$ eV. Thus, if we define $W$ to be the energy difference between the valence-band mobility edge and the Fermi energy in the undoped material, $W \cong 1.1$ eV. We can estimate the energies of the various electronic transitions which can occur in terms of these quantities:

$$\text{electron} + \text{hole} \rightleftharpoons h\nu, \quad \Delta E = E_g \cong 1.7 \text{ eV}; \tag{2}$$

$$\text{electron} + T^+ \rightleftharpoons T^0, \quad \Delta E = E_g - W - |U|/2 \cong 0.2 \text{ eV}; \tag{3}$$

$$\text{hole} + T^- \rightleftharpoons T^0, \quad \Delta E = W - |U|/2 \cong 0.7 \text{ eV}; \tag{4}$$

$$\text{electron} + T^0 \rightleftharpoons T^-, \quad \Delta E = E_g - W + |U|/2 \cong 1.0 \text{ eV}; \tag{5}$$

$$\text{hole} + T^0 \rightleftharpoons T^+, \quad \Delta E = W + |U|/2 \cong 1.5 \text{ eV}. \tag{6}$$

Equation (2) represents the intrinsic band-edge recombination process. Equations (3) and (4) represent the trapping of electrons and holes, respectively. We see that $T^-$ centers act as deep hole traps, but $T^+$ centers are shallow electron traps. This is in excellent agreement with the

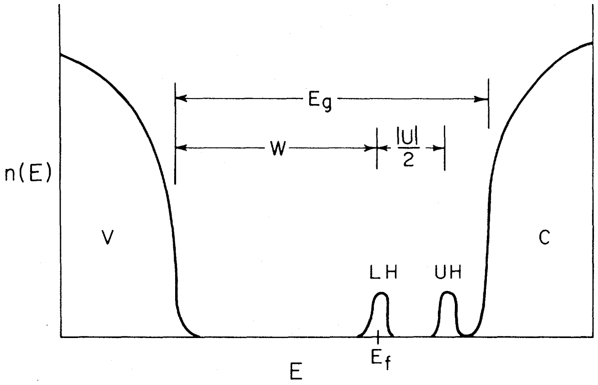

FIG. 1. Schematic density of states of hydrogenated amorphous silicon. (Note that since LH and UH are lower and upper Hubbard bands, their occupation is not independent.)

experimental result[10] that the electron mobility is more than an order of magnitude greater than the hole mobility. Equations (5) and (6) represent the creation of $T^-$ and $T^+$ centers, respectively. All of these processes should give rise to photoluminescence. The creation of $T^+$ centers, Eq. (6), should have an appreciable Stokes shift, because of the associated motion of the H atom. Our model's predictions agree very well with the experimentally observed photoluminescence.[11-14]

Since amorphous silicon is a complex material, it would be unreasonable to expect that all states in the gap arise from the same mechanism. Residual–dangling-bond states and band-tail states undoubtedly do exist, but these types of states should have a positive $U$.

Our model provides a basis for making suggestions of what one might do to obtain technologically useful material. At this point, the major limitation in the use of hydrogenated $a$-Si for solar-cell applications is the poor hole mobility[10] of the $n$-type material. Our model predicts that if we make lightly boron-doped (about 50 ppm) material, we will remove most of the $T^-$ states. Thus, we may obtain material which has a very small number of thermally excited carriers, but also has a relatively high carrier mobility. Whether this type of material will work efficiently in solar cells depends on the rate at which $T^-$ centers are created by recombination processes, Eq. (5), and whether there exist other types of hole traps.

Alternatively, we may attempt to remove the TCB's from the material altogether. This, of course, requires removing all of the hydrogen from the material. As a substitute for hydrogen, we may consider halogenated amorphous silicon. Halogen atoms act to tie up all of the dangling Si bonds, but they connot form TCB's as hydrogen can. We suggest that fluorine is the most likely candidate for obtaining useful material for two reasons. First, the length of the Si-F bond (1.56 Å) is only slightly greater than the length of the Si-H bond (1.48 Å), while Si-Cl (2.03 Å) and Si-Br (2.17 Å) are significantly larger. Second, $SiF_4$, $BF_3$, and $PF_3$ are all gases at room temperature, which may prove convenient for materials preparation.

In summary, we have proposed that hydrogenated amorphous silicon contains significant numbers of Si-H-Si three-center bonds. Since these centers have states which lie in the energy gap and have a negative effective electronic correlation energy $U$, their existence can explain much of the heretofore puzzling experimental information about these materials. Our model allows us to make predictions about how to obtain technologically more useful amorphous silicon-based materials.

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