Density of States in the Gap of Tetrahedrally Bonded Amorphous Semiconductors

David Adler
Department of Electrical Engineering and Computer Science and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The lowest-energy defects in tetrahedrally bonded amorphous semiconductors, in particular silane-decomposed films, are analyzed semiquantitatively. The creation energy and effective correlation energy of each defect center are estimated. It is concluded that twofold-coordinated atoms play an important role in these films. The lowest-energy center yielding an EPR signal is not a dangling bond but a positively charged twofold-coordinated atom. The results explain the observed peaks in the density of localized states and the mechanism for the doping of these materials by P and As.

After Anderson[1] proposed that localized states in the gap of amorphous semiconductors are characterized by a negative effective correlation energy, U_{eff}, and Mott, Davis, and Street[2] suggested that this U_{eff} arose from a single defect center in chalcogenide glasses, Kastner, Adler, and Fritzsche[3] made the nature of these defects precise by introducing the concept of a valence-alternation pair (VAP). A VAP is a positively charged overcoordinated atom and a negatively charged undercoordinated atom, and as such can be present in chalcogenide and pnictide glasses, but not in tetrahedrally coordinated amorphous semiconductors. Since the creation energy of VAP's in chalcogenide glasses is approximately U, the additional Coulomb repulsion arising from the presence of an extra electron on a chalcogen atom, which can be estimated to be only about 0.5–1.0 eV, VAP densities of the order of 10^{18}–10^{20} cm^{-3} should characterize chalcogenide glasses. Kastner, Adler, and Fritsche[3] showed that $U_{\text{eff}} = U - 2\Delta$, where Δ is the difference in magnitude between the energy shifts of the bonding and antibonding orbitals. Since Δ is typically 0.5–1.5 eV, U_{eff} is negative in chalcogenides.

Valence alternation is impossible in tetrahedrally bonded amorphous semiconductors (unless d-electron hybridization is used to accomplish fivefold coordination). However, several other types of defect centers are possible. It is the purpose of this Letter to analyze these defect centers, identify those which have the lowest creation energies, and calculate the corresponding effective correlation energies.

Consistent with the notation introduced by Kastner, Adler, and Fitzsche,[3] let us call the ground state of a Group-IV atom T_4^0, where the subscript gives the coordination number and the superscript the charge state. In calculating the energies of defect centers in Group-IV materials, several complications enter that do not arise in chalcogenides. Firstly, the s-p promotion energy, P, is a very important parameter. Throughout this Letter, P will refer to the experimental energy necessary to excite an $s \to p$ transition, which for Group-IV atoms represents the difference between the actual one-electron $s \to p$ transition energy and the Coulomb repulsion between the two electrons in the s orbital in the s^2p^2 configuration. The use of U is reserved for the excess Coulomb repulsion that exists when a fifth outer electron is placed on the atom. A second complication results from the fact that sp^3, sp^2, and p bonding can all occur in the materials under discussion, and these can have very different bond energies. E_p will be used to denote the energy of a Si-Si p bond, while $E_p + B$ will be used for the energy of either sp^3 or sp^2 bonds; this is reasonable because the bond strengths of the last two are essentially equal while p bonds are about 25% weaker.[4]

The zeroth-order energies of the relevant states of a Group-IV atom are indicated in Fig. 1, under the assumption that complete relaxation takes place. Several interesting general relationships between the parameters should be noted. The fact that Group-IV atoms ordinarily bond tetrahedrally rather than with twofold coordination requires $2E_p - (P - 4B)$ to be positive. Furthermore, the fact that the lowest-energy bonding configuration for Group-V atoms is the formation of three p bonds rather than three sp^3 bonds (leaving an sp^3 lone pair) indicates that $P - 4B > 0$.[5] However, in order to analyze the relative energies of the defects, more quantitative estimates for the parameters must be used. Restricting our discussion to silicon, we can estimate the promotion energy directly from the observed atomic spectrum as about 6.0 eV.[6] Since the strength of the sp^3 Si-Si bond is 2.5 eV,[7] we can conclude that E_p is approximately 1.9 eV while B is about 0.6 eV. A rough estimate for U

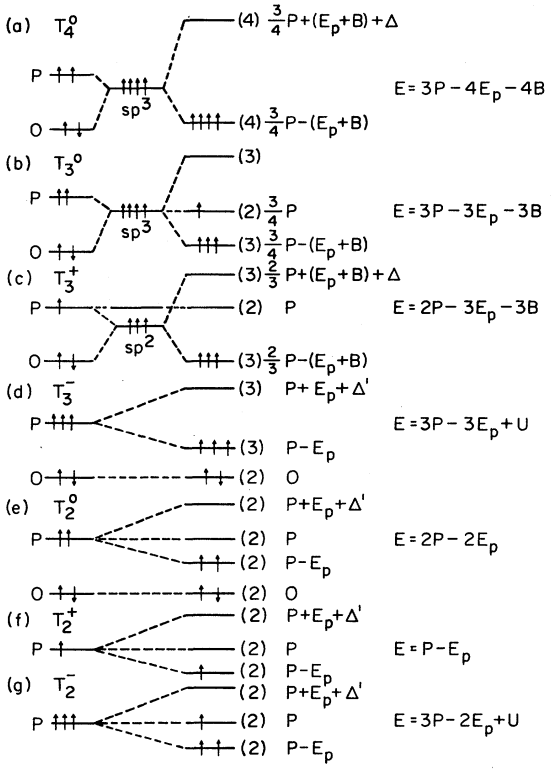

FIG. 1. Energy levels and total energies of silicon atoms in several possible coordinations and charge states. Since only relative energies are important, the differences between silicon-silicon and silicon-hydrogen bond energies are neglected. The notation is discussed in the text. Note that only (b), (f), and (g) contain unpaired spins.

is the difference in the energies of double donors in crystalline Si, about 0.3 eV. Even though these values may be in error by up to 25%, it is clear from Fig. 1 that the lowest-energy defect in amorphous silicon is the twofold-coordinated atom, T_2^0, *not* the dangling bond, T_3^0. T_2^0 is a spinless defect, which tends to place two occupied localized states above the valence-band edge, two unoccupied states towards the middle of the gap, and perhaps two more unoccupied states below the conduction-band edge. This defect also can be seen to have a *positive* effective correlation energy, equal to $E_p + U$. The Fermi level thus behaves normally with variations in occupation number,[8] and unpaired spins are possible. Note that the dangling bond, T_3^0, has a rather large *negative* correlation energy, $U_{\mathrm{eff}} = U - (P - 3B) \simeq -3.7$ eV. Thus, even with incomplete atomic relaxations, it appears unlikely that isolated dangling bonds should result in a significant unpaired-spin density. Furthermore, the creation energy of a dangling bond is large, $E_p + B \simeq 2.5$ eV.

The second-lowest energy defect is a charged pair, $T_2^+ + T_3^-$, the creation energy being $2[2E_p + (P-4B)] + U \simeq 0.7$ eV/pair. It is important to note that the T_2^+ center contains an unpaired spin, and these calculations suggest that this rather than the T_3^0 is the center observed in EPR measurements. The reaction

$$T_2^0 + T_3^0 \rightarrow T_2^+ + T_3^- \tag{1}$$

is exothermic by $P - 3B - E_p - U \simeq 2.0$ eV. The negative correlation energy associated with the dangling bond indicates that the presence of T_3^- centers results in a pinning of the Fermi energy somewhat above the position of the filled localized states resulting from the T_2^0 centers.[8]

It is now possible to analyze the structure of amorphous silicon films on the basis of these calculations. Nominally pure amorphous silicon contains many defects due to the mechanical constraints of tetrahedral bonding. The previous analysis suggests that the resultant strains are relieved primarily by the formation of isolated T_2^0 defects and T_2^+-T_3^- pairs. Only the latter contribute to the unpaired-spin density. As-deposited, evaporated or sputtered, amorphous silicon films contain on the order of 10^{20} cm^{-3} unpaired spins, although these rapidly decrease with annealing.[9] Since this preparation leads to films rather far from equilibrium, there is no reason why dangling-bond states cannot be present in the as-deposited films. However, after annealing, the unpaired-spin density is low while the density of localized states in the gap remains large, with two apparent peaks in the $g(E)$ curves.[10] This is consistent with the existence of a large density of T_2^0 centers. Most of the isolated dangling bonds which are frozen in at low substrate temperatures anneal away via the exothermic reaction

$$2T_3^0 \rightarrow T_3^+ + T_3^-, \tag{2}$$

which gives off about 3.7 eV. This reaction sharply reduces the concentration of unpaired spins. A somewhat smaller number reduce their energy via Reaction (1), thus maintaining some unpaired-spin concentration.

Recently, a great deal of attention has been given to the amorphous silicon-hydrogen alloys produced by the glow-discharge decomposition of silane (SiH_4) gas.[11] The resulting films contain 10–35% hydrogen, depending on the substrate temperature. At low substrate temperatures, larger concentrations of hydrogen are present and large regions of polysilane, $(SiH_2)_n$, exist; at higher substrate temperatures, the hydrogen that is incorporated is generally bound to different silicon atoms.[12] The silicon-hydrogen bond energy is about 3.4 eV, significantly larger than the silicon-silicon bond energy, and this is reflected in a depletion of states near the top of the valence band in photoemission measurements.[13] But also, since hydrogen can be only singly coordinated, it tends to relieve the mechanical strains of pure tetrahedral bonding by loosening up the overall structure. This drastically decreases the density of defect centers which form upon deposition, and thus serves to drastically remove localized states from the gap. Nevertheless, there are $10^{17}-10^{19}$ cm^{-3} localized states remaining in the gap,[10,14] far more than the observed unpaired-spin density of about 5×10^{15} cm^{-3}.[14] This is evidence that T_2^0 states are still present in silane-decomposed films, as would be expected from the small creation energy of this defect.

When the silane-decomposed films are annealed, hydrogen gas is given off, first from Si-H_2 sites, later from Si-H sites.[11] Effusion from an Si-H_2 site immediately produces a T_2^0 center. However, when hydrogen effuses from Si-H sites, T_3^0 centers are left. If there are sufficient T_2^0 centers present, the T_3^0 defects probably equilibrate via Reaction (1) and thus yield unpaired spins. Indeed, the unpaired-spin density sharply increases with annealing.[11]

Under optical excitation, spins can be created via the trapping of both electrons on T_2^0 centers and holes on T_2^0 or T_3^- centers. This explains the observation of strong optically induced EPR signals.[14] Field-effect measurements probe the structure in the density of states resulting from the predominant defects. Upon excess electron injection, the Fermi level should rise freely until the nonbonding states on T_2^0 sites begin to fill. The upper peak in $g(E)$ can be attributed to this effect. On the other hand, excess holes are taken up both by emptying the bonding states on T_2^0 sites and by converting T_3^- to T_3^+ centers. The latter, being characterized by a negative U_{eff}, should yield a larger peak in $g(E)$, in accord with experimental observations.[15]

It has always been difficult to explain the doping of amorphous silicon-hydrogen alloys by the mixing of silane with either phosphine (PH_3) or diborane (B_2H_6) prior to decomposition,[16] since the mechanism for tetrahedral incorporation of atoms from Groups III and V in the absence of crystalline constraints is unclear. Ovshinsky and I proposed[17] that some of the three-center bonds present in diborane molecules are preserved in the boron-doped films, the empty nonbonding orbitals of which then produce the low-lying acceptor levels necessary for *p*-type doping. The new EPR signal recently observed by Stuke[18] in heavily boron-doped films can then be associated with a single electron in these nonbonding orbitals. However, phsophorus has not been shown to exhibit significant three-center bonding in any of its known molecules, so that another mechanism is necessary to explain the doping. The absence of an accurate value for the energy of the P-Si bond makes it difficult to estimate the lowest-energy centers for phosphorus-doped films, but if we assume that the Si-P bond is weaker than the Si-N bond by the same ratio as the C-P bond is weaker than the C-N single bond, we obtain 3.2 eV as a very rough approximation for the Si-P bond energy. With this value, similar calculations to those discussed previously indicate that the lowest-energy defect in a phosphorus-doped film is a P_4^+-T_2^0 pair, while the second-lowest-energy defect is a P_4^+-T_2^- pair (see Ref. 3 for notation). Thus, only after the T_2^0 and T_2^+ centers are all converted to T_2^- does phosphorus tend to enter the material in its ordinary threefold coordination. This results in the interesting conclusion that the most ideal (i.e., defect-free) amorphous films tend to alloy rather than dope upon phosphorus (or arsenic) incorporation. The existence of deep T_2^- hole traps in phosphorus-doped films explains the low hole mobility in such materials relative to that in undoped samples.[19]

Except for the previous discussion of boron-doped films, multicenter bonding has not been considered in this work. Ovshinsky[17,20] was the first to propose that three-center bonds play an important role in amorphous films. Recently, Fisch and Licciardello[21] proposed that three-center Si-H-Si bonds exist in silane-decomposed films and suggested that they have a negative U_{eff}. However, no explicit energy calculations were carried out, so that neither the stability of these defects nor the sign of U_{eff} is clear at present. In addition, no explanation was given for the finite unpaired-spin density that is observed in these materials. Furthermore, as discussed previously, spinless defects such as T_2^0 with a *positive* U_{eff} can account for the bulk of the experimental properties of amorphous silicon-hydrogen alloys. In this regard, it should also be noted that the observation of variable-range hopping in as-deposited amorphous silicon films is, in fact, evidence against defects with a negative U_{eff} in the vicinity of the Fermi energy.

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