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Self-compensation and the absence of doping in amorphous GaAs

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Dopants are found to become strongly compensated in most amorphous III-V compound semiconductors because of the relative ease of creating compensating dangling bonds in a random network.

Since Spear and LeComber discovered substitutional doping in hydrogenated amorphous silicon (a-Si:H) this system has been extensively studied.[1] Subsequently, substitutional doping has also been found in a-Ge:H, a-C:H, and in some closely related alloys such as a-SiN$_x$.[1-4] However, to date there has been no reported doping of any of the amorphous III-V compound semiconductors such as a-GaAs which are also tetrahedrally coordinated. We offer here a general reason for this absence of doping, that most amorphous III-V compounds are predicted to be self-compensated. This is found to arise because it costs much less to create compensating defects in a random network than in a crystal.

The possibility of doping of amorphous semiconductors is usually discussed in terms of whether or not impurities will enter substitutional (doping) sites. Here we show that even if they do, in most amorphous III-V compounds, the dopants are likely to be heavily compensated. Consider first the phosphorus doping of a-Si:H where these effects are already evident. The doping mechanism in a-Si:H differs from that in crystalline (c-) Si in two ways. The primary concern has always been that most phosphorus enters neutral, threefold coordinated sites, denoted $P^0_{(3)}$, which are electrically inactive, and only a minority enters substitutional sites, $P_{(4)}$. However, a second, equally important difference is that doping occurs by the formation of dopant-defect pairs, $P^+_{(4)}-D^-$, rather than simple $P^0_{(4)}$ sites.[5] The defect density is thereby increased above that in intrinsic a-Si:H. The Fermi level E_F is now always held below the donor level with the consequence that metallic conductivities are never attained even at the highest doping levels. The resulting equilibrium

$$P^0_{(3)} \rightleftharpoons P^+_{(4)} + D^- \tag{1}$$

can be recognized as a self-compensation process by considering it in two stages; the generation of carriers at the formation of $P^+_{(4)}$ sites

$$P^0_{(3)} \rightleftharpoons P^+_{(4)} + e^- \tag{2}$$

and the compensation of some carriers at dangling-bond defects

$$e^- \rightleftharpoons D^- . \tag{3}$$

Equilibrium (2) is specific to amorphous semiconductors and has been dealt with at length;[5-7] here we concentrate on the second equilibrium which is typical of all compensating systems and is of increasing importance in polar compounds.

Equilibria (2) and (3) are believed to hold during the deposition process. We may therefore apply the law of mass action to (3)

$$K = \frac{[D^-]}{[e^-]} = \frac{D}{n} . \tag{4}$$

The proportion of free carriers can be written in terms of Mandel's[8] compensation ratio $Q = D/n$:

$$\frac{n}{n+D} = \frac{1}{1+Q} = \frac{1}{1+K} . \tag{5}$$

Q is given by

$$Q = Q_0 \exp\left(\frac{\Delta - H}{k_B T}\right) , \tag{6}$$

where Δ is the compensation energy, the energy gained by the donor electron falling down into the defect level (Fig. 1), H is the defect creation enthalpy, Q_0 is a prefactor containing the defect entropy and the density of band states factors, and T is a fictive temperature approximately equal to the deposition temperature in the case of amorphous semiconductors. The overall doping efficiency η is given by

$$\eta = \frac{n}{N} \simeq \left(\frac{1}{1+Q}\right) \frac{N_4}{N} , \tag{7}$$

where N = total dopant concentration and $N_4 = n + D$ = substitutional dopant concentration (and not by $\eta = N_4/N$ as is presently used in the a-Si:H literature). As it is difficult to estimate N_4/N for the new systems, $(1+Q)^{-1}$ is taken as an upper estimate of the possible doping efficiency.

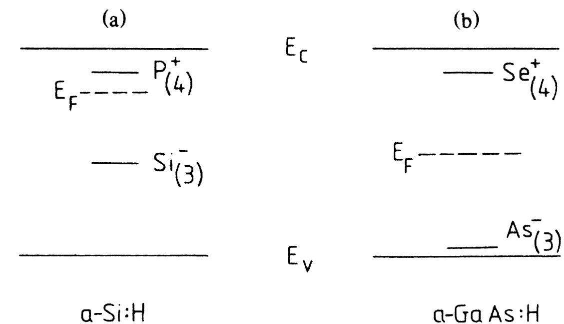

FIG. 1. The energy levels of donors and compensating defects in (a) a-Si:H and (b) a-GaAs:H.

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Let us consider chemical trends in Q for the series Si, GaAs, and ZnSe, first for the crystals. Clearly from (5) and (6) compensation occurs for large Q and is favored if $\Delta \gtrsim H$. Now, the maximum value of Δ is the band-gap energy E_g. The defect compensating donors is the (metal) vacancy. As one less atom is bound for a solid with a vacancy, for a covalently bonded solid:

$$H \simeq E_{\mathrm{coh}} , \tag{8}$$

where E_{coh} is the cohesive energy per atom, and this varies little along the series of compounds. Thus, $\Delta - H$ and Q increase along the series leaving Si and GaAs uncompensated and ZnSe quite strongly compensated[9] (Table I).

The situation in their amorphous phases is different. The simplest defect is now the dangling bond rather than a group of four dangling bonds at a vacancy. A single dangling bond is perfectly able to provide autocompensation, as in a-Si:H. Thus, qualitatively we now have

$$H_a \simeq \tfrac{1}{4} H_c . \tag{9}$$

Meanwhile Δ and E_g are little changed so that the terms $(\Delta - H_a)$ and Q in Eq. (6) are much higher than their corresponding crystalline values. This trend is clear in Table I where we note that even elemental a-Si:H is already partially compensated and a-GaAs is calculated to be strongly compensated. This difference has arisen almost entirely from the relatively low cost of forming defects in a random network because of the network's ability to vary its topology.

We now consider in more detail the numerical estimates of Q_a given in Table I. Δ is the energy difference between a $+/0$ donor level and the $0/-$ defect level. We take $H_a = \frac{1}{4} E_{\mathrm{coh}}$ with E_{coh} as tabulated by Phillips.[10] Thus, we neglect the small energy due to relaxation of the backbonds. For a-Si:H we take $H_a \simeq 1.1$ eV, $T = 600$ K and, from Ref. 7, $\Delta = 0.8$ eV. Experimentally,[7] a-Si:H is quite strongly compensated, with $Q \approx 10$. This corresponds to $Q_0 \approx 3000$, a value which we then use for the other systems. In view of these approximations, Table I only illustrates chemical trends as Q could be in error by factors of 10. In a-GaAs donor states at E_c are compensated by As dangling bonds. Their levels lie at E_v [Fig. 1(b)] rather than at midgap as in a-Si (Ref. 11) so $\Delta = E_g$. As usual, E_g depends on deposition conditions[12] but hydrogenation has less effect than in a-Si (Ref. 13) and appears not to increase E_g beyond its crystalline value, E_g^c. The situation is similar in all amorphous III-V and II-VI compounds, so if no experimental value of E_g^a is available, we take $\Delta = E_g^c$, recognizing that this may underestimate Q_a. Acceptors can be treated in a similar fashion; $Q \simeq 10$ and $\Delta \simeq 0.8$ eV are reasonable values for acceptors in a-Si:H, and also acceptors in the compounds are compensated by metal dangling-bond levels which lie at E_c, so again $\Delta_a \approx E_g$.

TABLE I. Calculated values of the compensation factor Q_a for various hydrogenated amorphous semiconductors. Values for crystals, Q_c, are taken from Mandel (Ref. 8).

	Si	GaAs	ZnSe	GaP	InP	GaSb	InSb
E_{coh}	4.3	3.0	2.4	3.3	2.9	2.6	2.4
H_a	1.1	0.75	0.6	0.8	0.7	0.65	0.6
E_g^a	1.8	1.4	2.3	1.8	1.3	0.7	0.2
Δ	0.8	1.4	2.3	1.8	1.3	0.7	0.2
Q_a	10	10^9	10^{17}	10^{12}	10^8	10^3	1
Q_c	10^{-10}	10^{-3}	10^4				

a-GaAs:H is predicted to be strongly compensated in Table I and we believe that this accounts for the inability to observe doping effects experimentally. Certainly, a-GaAs:H satisfies the other prerequisites: hydrogen passivates its midgap defect states[14,15] to give a density of states (DOS) of $\sim 10^{18}$ cm^{-3} eV^{-1} in the gap which, while not as low as in a-Si:H, is sufficient to allow E_F to move. Compensation works in the following manner. A typical substitutional donor Se (a $\mathrm{Se}_{(4)}^0$ site) will produce a half-filled level just below E_c. A neutral As dangling bond $\mathrm{As}_{(3)}^0$ will produce a partially filled level around E_v. Sufficient $\mathrm{As}_{(3)}$ sites will be induced by doping to cause compensation by the formation of $\mathrm{Se}_{(4)}^+$-$\mathrm{As}_{(3)}^-$ site pairs. Acceptors will behave similarly; a typical acceptor Zn will introduce a shallow level at E_v but it will also induce sufficient extra Ga dangling bonds to become compensated in the form of $\mathrm{Zn}_{(4)}^-$-$\mathrm{Ga}_{(3)}^+$ site pairs. In both cases E_F will remain at midgap. Also, as in a-Si:H, doping is predicted to be accompanied by an increased defect density, but this may not be so readily apparent as the new states lie at the band edges not at midgap.

Self-compensation effects are always smallest in narrow gap semiconductors because of their small values of Δ, and we predict that a-InSb and perhaps a-GaSb may be uncompensated. The possibility of observing doping in these systems now depends entirely on their midgap DOS: in narrow-gap amorphous semiconductors there is the problem that the valence and conduction-band tails may overlap and leave a high gap DOS. This must be tested experimentally.

A second mode of doping is possible in compounds with partial dative bonding like GaAs, the self-doping caused by composition variations. In c-GaAs, an As atom at a Ga site, an $\mathrm{As}_{\mathrm{Ga}}$ antisite, possesses two more electrons than the Ga atom it replaces and these are available to move E_F. They do not, in fact, cause doping in c-GaAs because they occupy a deep midgap level. In a-GaAs however, the possibility is real. The simple As-As "wrong" bond is calculated[11] to have a $0/+$ state near E_c, which is partially occupied when neutral and would cause self-doping of the alloy a-$\mathrm{Ga}_x\mathrm{As}_{1-x}$:H for $x = 0.5 + \delta$. However, just as in the extrinsic case, As dangling bonds would be induced as compensators and no net doping would occur. As shown in detail elsewhere,[16] if As excess is introduced in the proportion of three wrong bonds to two dangling bonds, E_F remains at midgap. The ease with which the a-GaAs network can accommodate composition deviations without a shift in E_F probably accounts for the experimental difficulty of controlling its stoichiometry; molecular-beam-deposited a-$\mathrm{Ga}_x\mathrm{As}_{1-x}$ does not "lock" onto the GaAs composition as c-GaAs does.[17] The corollary of As dangling bonds being acceptors and As-As bonds being donors is that an extrinsic donor could equally well be compensated by an As dangling bond or a Ga-Ga wrong bond in practice. However, the energetics of the latter mechanism are more difficult to quantify so this possibility must be determined by experiment.

In summary, the ability to form single dangling bonds in a random network, rather than complete vacancies, has been

shown to considerably reduce the creation energy of compensating defects in amorphous semiconductors. This greatly increases the possibility of self-compensation to the extent that in the tetrahedral semiconductors *a*-Si:H is already partially compensated and *a*-GaAs is predicted to be heavily compensated. This suggests that the search for dopable wider-gap amorphous semiconductors should concentrate on the more strongly bonded alloys such as a-$Si_{1-x}N_x$ or a-$Si_{1-x}C_x$ rather than on the polar compounds. An analysis of self-compensation effects in these systems is in progress.

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