

Nature of nonsubstitutional dopant states and the carrier-density statistics in hydrogenated amorphous silicon

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A model for the electronic structure of group-III and -V dopants in tetrahedrally bonded amorphous semiconductors is presented. Based on this model and the charge-neutrality relation appropriate for amorphous solids, the experimental observation of the carrier-density increase with doping level in compensatively doped *a*-Si:H can be explained as a consequence of a significant density of donorlike and/or acceptorlike states near the Fermi level.

The Mott "8-*N*" rule¹ suggests that in covalent amorphous materials each atom takes on its natural coordination determined by the number of valence electrons *N*. Thus the observation of substitutional doping in tetrahedrally bonded amorphous semiconductors, e.g., hydrogenated amorphous silicon (*a*-Si:H),² appears to be an exception to this rule. Recently, Street³ discussed the application of this rule to impurity doping in *a*-Si:H.

In this Rapid Communication, we propose a model of the electronic structure of doped *a*-Si:H, in which the dopant atoms exist in the substitutional sites as well as in the non-substitutional ones. In the latter case, the atoms are coordinated according to the Mott 8-*N* rule. A generalized charge-neutrality equation that includes the contributions from the gap states due to the nonsubstitutional dopants is used to examine the relation between the Fermi level and the dopant concentration. This modified carrier-density statistics is shown to account for the results of recent xerographic discharge measurements⁴ on compensatively doped *a*-Si:H photoreceptors. These experiments suggest that the equilibrium carrier density, as inferred from the charge acceptance, can increase with the dopant concentration, even though the material is compensated.

In amorphous semiconductors, the charge-neutrality condition can be written as

$$n + N_A + N_L^- = p + N_D + N_L^+ \quad (1)$$

where *n* (*p*) is the free-electron (hole) density, *N_A* (*N_D*) is the density of ionized acceptors (donors) in the substitutional sites, and *N_L⁻* (*N_L⁺*) represents the density of negatively (positively) charged gap states other than the substitutional dopant states. The free-carrier densities can be expressed in terms of the Fermi energy *F* as

$$n = n_i \exp(F) \quad (2)$$

$$p = n_i \exp(-F) \quad (3)$$

In crystalline semiconductors, *n_i* is the intrinsic carrier density, and is defined⁵ independent of the density of gap states. One of the objectives of this discussion is to examine how *n_i* is affected by the density of gap states in amorphous semiconductors. Phenomenologically, the Fermi level *F* can be identified as the activation energy of the majority carrier density and, hence, that of dark conductivity. The states of the substitutional dopants, with densities *N_D* and *N_A*, are, in general, so far from the Fermi level that at finite temperatures these dopants are all ionized.

The gap states are, in general, of two types:⁶ the acceptorlike states, with the distribution *N_{AL}*(*E*), are neutral when empty, and negatively charged when occupied. The donorlike states, with the distribution *N_{DL}*(*E*), are neutral when occupied, and positively charged when empty. Thus the densities of positively and negatively charged gap states are, respectively,

$$N_L^+(F) = kT \int_{-\infty}^{\infty} N_{DL}(E) dE / [1 + \exp(F - E)] \quad (4)$$

$$\sim kT \int_F^{\infty} N_{DL}(E) dE \quad (4a)$$

$$N_L^-(F) = kT \int_{-\infty}^{\infty} N_{AL}(E) dE / [1 + \exp(E - F)] \quad (5)$$

$$\sim kT \int_{-\infty}^F N_{AL}(E) dE \quad (5a)$$

where *E* and *F* are measured from the midgap, in units of *kT*. Since the functional forms of gap-state distributions are never exactly known, the zero-temperature approximations, Eqs. (4a) and (5a), are sufficient for this analysis. Then, the positively and negatively charged gap states are given by the donorlike states above the Fermi level and the acceptorlike states below the Fermi level, respectively.

In *a*-Si:H and other tetrahedrally bonded solids, the valence and the conduction bands consist of *sp* orbitals which are of bonding and antibonding nature, respectively.⁷ In undoped materials, the donorlike and the acceptorlike states are formed by the dangling bonds on defect centers.⁸ Since the Fermi level in undoped *a*-Si:H lies at ~ 0.15 eV above the midgap,⁶ it indicates that near the midgap there are more donorlike defect states than acceptorlike ones.

In doped *a*-Si:H, the group-III and -V dopants exist either in a substitutional site or in a nonsubstitutional site. In the latter sites, a lone-pair state is associated with each dopant. These states lie near the center of the band gap, because they originate from nonbonding *sp* hybrids (see Fig. 1).

In the case of group-III dopants, the lone-pair states are neutral when empty, negatively charged when occupied, and hence acceptorlike. Because the valence-state ionization energies of group-III elements are somewhat smaller than that of group-IV elements,⁷ the distribution of these acceptorlike states is likely to be centered in the upper half of the gap.

In the case of group-V dopants, the lone-pair states are neutral when occupied, positive when empty, and hence donorlike. Since the valence-state ionization energies of group-V elements are slightly larger than that of group-IV

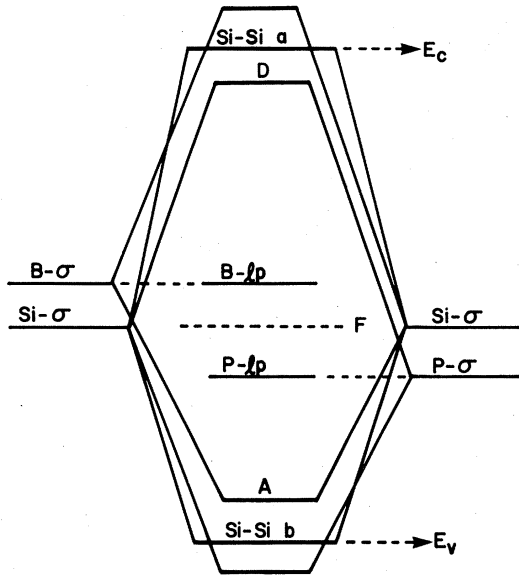


FIG. 1. Schematic diagrams of molecular-orbital energy levels for Si-Si, Si-B, and Si-P complexes. The positions equivalent to the conduction band (E_c), the valence band (E_v), and the Fermi level (F) in solids are indicated.

elements,⁷ most of these donorlike states are expected in the lower half of the gap.

With this model, the roles of nonsubstitutional dopants are similar to that of substitutional dopants. However, while each and every substitutional donor (or acceptor) can be counted in the neutrality equation, and contributes to the determination of Fermi level, only those nonsubstitutional donorlike (or acceptorlike) states which are near and above (or below) the Fermi level can do so. Consequently, the farther the Fermi level is from the midgap, the smaller is the effective portion of nonsubstitutional dopants. This accounts for the decrease of doping efficiency with increasing dopant concentration, observed in *a*-Si:H.^{2,3}

With Eqs. (2), (3), (4a), and (5a), the neutrality equation (1) can be rewritten as

$$n - p = n_i \sinh(F) \quad (6)$$

$$= [N_D - N_A] + kT \left[\int_F^\infty N_{DL}(E) dE - \int_{-\infty}^F N_{AL}(E) dE \right]. \quad (7)$$

The right-hand side of Eq. (7) can be divided into two parts (grouped by the square braces): the first is the contribution from the substitutional dopants and the second from the nonsubstitutional dopants. The first part is independent of the Fermi level, as long as the latter is more than a few kT 's from the donor and the acceptor levels. Then, if the second part is negligible, these equations state that, for given carrier densities, the Fermi level can be uniquely determined only if n_i is known independently. This is the case in crystalline semiconductors, and any changes in the carrier density must be accompanied by a change in the Fermi level.

In contrast, the contribution from nonsubstitutional dopants (the second part) is a sensitive function of the Fermi level, provided $N_{DL}(E)$ and/or $N_{AL}(E)$ have significant values near the Fermi level. Then, for a given gap-state

distribution, the carrier-density difference, $n - p$, uniquely determines the Fermi level F from Eq. (7), and together with F it determines n_i from Eq. (6). In other words, with the existence of significant density of gap states near the Fermi level, n_i is not "intrinsic," but can vary with the carrier densities and the gap-state distributions, which, in turn, can be changed by doping.

To further examine this feature, consider an *a*-Si:H specimen doped simultaneously with a group-III and -V impurities. Suppose the total density of group-V impurities, N_5 , is slightly larger than that of group-III impurities, N_3 . If all the impurities were in the substitutional sites, i.e., $N_D = N_5$ and $N_A = N_3$, then the Fermi energy would increase logarithmically with the off-compensation, $N_5 - N_3$, and hence, with the doping level, even if the fractional off-compensation,

$$C = (N_5 - N_3)/N_5, \quad (8)$$

remains small. On the other hand, if only a fraction S of the impurities is in the substitutional sites, i.e.,

$$N_D = SN_5; \quad N_A = SN_3 = S(1 - C)N_5, \quad (9)$$

and the rest in the nonsubstitutional sites, then it can be seen from Eq. (7) that the upward shift of F decreases the net density of charged nonsubstitutional states, eventually to a negative value. If the Fermi level moves to a position where this negative value cannot be compensated by the net positive charge of the substitutional dopants, $N_D - N_A$, then $n - p$ becomes negative. This cannot be expected of a specimen with more group-V dopants than group-III dopants, $N_5 > N_3$. Thus, because of the existence of a significant density of gap states near the midgap, the shift of the Fermi level due to a given off-compensation is much reduced.

To estimate the Fermi-level shift corresponding to a given fractional off-compensation, let the distributions of the intrinsic gap states be exponential, and the nonsubstitutional dopants states be represented by Gaussian distributions:

$$N_{DL}(E) = N_d \exp(-E/d) + (N_p/\sqrt{\pi}wkT) \exp\{-[(E + U)/w]^2\}, \quad (10)$$

$$N_{AL}(E) = N_a \exp(E/a) + (N_b/\sqrt{\pi}wkT) \exp\{-[(E - U)/w]^2\}, \quad (11)$$

where the two Gaussians are centered at $E = -U$ and U , respectively, and have a half-width w . The total densities of nonsubstitutional dopant states, the donorlike N_p , and the acceptorlike N_b are, respectively, from Eq. (8):

$$N_p = (1 - S)N_5; \quad N_b = (1 - S)N_3 = (1 - S)(1 - C)N_5. \quad (12)$$

With these distributions, Eq. (7) reduces to

$$n - p = N_5 \{ SC + 0.5(1 - S) [\operatorname{erfc}((U + F)/w) - (1 - C) \operatorname{erfc}((U - F)/w)] \} + kT [dN_d \exp(-F/d) - aN_a \exp(F/a)]. \quad (13)$$

Figure 2 shows plots of $(n - p)/N_5$ vs F calculated from Eq. (13) for an off-compensation of $C = 0.1$ and various values of S . The parameter values for the gap-state distributions, given in the figure caption, are good representatives for *a*-Si:H, but the conclusions drawn from these examples are independent of these particular values. The

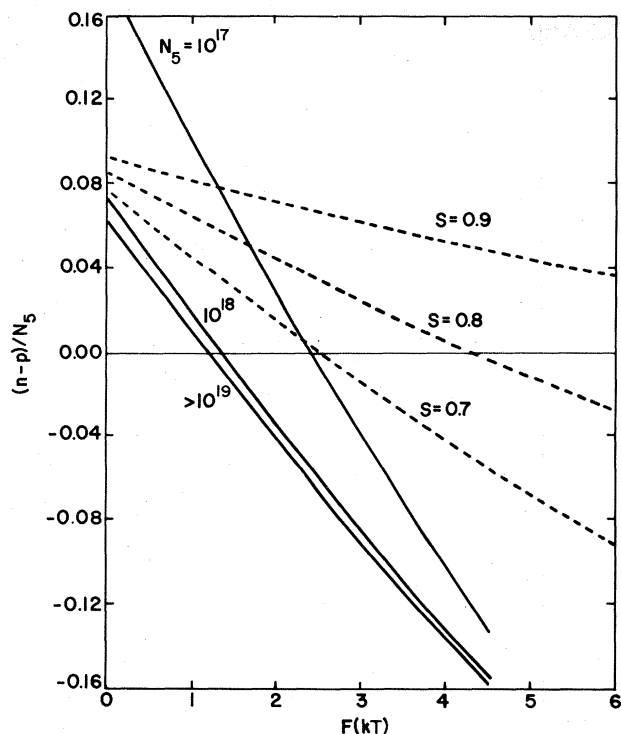


FIG. 2. Carrier densities $(n-p)/N_5$ vs Fermi level, calculated from Eq. (13), where N_5 is the total density of group-V dopants. The fractional off-compensation is $C=0.1$. For solid curves, $S=0.5$ and N_5 varied; for dashed curves, $N_5=10^{19} \text{ cm}^{-3}$ and S varied. The parameter values for the gap-state distributions, Eqs. (10) and (11), are $N_d=10^{17}$, $N_a=7.6 \times 10^{15} \text{ cm}^{-3} \text{ eV}^{-1}$, $d=4.92$, $a=3.58$, $U=4 \text{ (kT)}$, and $w=8 \text{ (kT)}$.

solid curves are for $S=0.5$ and various N_5 . It can be seen that for $S=0.5$ (or smaller) the Fermi level cannot be shifted more than 2 kT above the midgap without $n-p$ to have a contradictory sign (< 0). For a larger value of S , the al-

lowed values of F increase (see the dashed curves). With $S=0.9$, F can be as high as 20 kT. This represents an approach to the crystalline semiconductor limit where all dopants are in the substitutional sites.

As indicated by Eq. (13) and demonstrated by the set of solid curves, at a given value of the Fermi level, the carrier densities, $n-p$, and hence n , p , and n_i , all increase with N_5 , reaching a complete proportionality as the doping level exceeds $N_5 > 10^{19} \text{ cm}^{-3}$. Therefore, as the compensative doping level increases, the conductivity of the specimen also increases, in spite of the fact that the Fermi level remains near the midgap. Experimental evidence of this feature has been observed in *a*-Si:H by xerographic measurements.⁴ It should be noted that in this case both the majority and the minority carrier densities are increased by the same factor. In contrast, in the conventional doping of crystalline semiconductors the density of one type of carriers is increased at the expense of the other.

The same argument can be used to explain the saturation of the Fermi-level shift with phosphorous doping above 10^{19} cm^{-3} , observed in *a*-Si:H.² In this case N_3 is zero. This allows a large Fermi-level shift at low doping. With a constant n_i , one expects F to increase logarithmically with N_5 , as shown by Spear and LeComber.² With n_i increasing with N_5 , the actual shift is always smaller. Finally, as n_i becomes exactly proportional to N_5 (at $\sim 10^{19} \text{ cm}^{-3}$), the Fermi level ceases to shift even with an increase in the carrier density.

In summary, the charge-neutrality equation which includes the contributions from nonsubstitutional dopants has been shown to account for the observed relations among the dopant concentration, the Fermi level, and the carrier density.

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