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Coulomb effect on doping in amorphous semiconductors

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Traditionally, the low doping efficiency in a-Si:H has been explained by the argument that dopant atoms are incorporated into under- or over-coordinated sites and, therefore, inert in such configurations. However, recent molecular dynamic simulations proved that this view is not generally correct. In the present paper we suggest a purely electronic analytic model explaining the low doping efficiency in amorphous semiconductors. The model shows that, in a random network of localized states, the Coulomb interaction between ionized dopant atoms and the resulting localized charge carriers leads to changes in the electronic density-of-states (DOS) distribution which counter the intended shift of the Fermi-level position.

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Over the years, doping of amorphous semiconductors has been, depending on the material involved, both unsuccessfully pursued and satisfactorily achieved. One basic problem that has to be overcome in each instance is the tendency of the amorphous lattice to allow any extrinsic atom to satisfy its normal bonding requirements, the so-called 8-N rule. For the group of amorphous chalcogenides, considerable changes in the conductivity were achieved through the percents-wise addition of various metals,[1] but only in the cases where around 10 at. % of Bi (or Pb) was added to the germanium glasses was any clear evidence obtained for a change-over from p- to n-type conductivity.[2] However, as the mechanism of the type reversal remains uncertain, it also remains unclear whether the change should be ascribed to doping or to alloying. In general, there is a consensus on relating the difficulty in doping chalcogenide semiconductors to the occurrence of charged coordination defects with negative effective correlation energy (the *negative-U* defects) which pin the Fermi level.[3]

The situation is different for hydrogenated amorphous silicon (a-Si:H) where the report by Spear and LeComber[4] in 1975 that n- and p-type doping with P and B was possible laid the foundation for considerable industrial activity on a worldwide scale. However, throughout the intervening period, and in spite of a considerable research effort, the physical processes involved have remained poorly understood. For instance: While a low doping efficiency can be understood in general terms as a manifestation of the 8-N rule, and chemical mass action relations show that this efficiency should then change as the square root of the dopant concentration, it is not obvious why such square-root relationship should experimentally be better obeyed by the dopant concentration in the gas phase than in the solid. Also unresolved is the discrepancy which exists[5] between the doping efficiency as deduced from investigations of local bonding configurations with extended x-ray fine structure or nuclear magnetic resonance techniques, and the considerably lower value which is suggested by experiments involving the electronic states.

By the use of *ab initio* molecular dynamics simulation, Fedders and Drabold showed that threefold coordinated B in a-Si:H is quite unfavorable energetically and, therefore, the conventional explanation of low doping efficiency in this material was wrong.[6] These authors suggested that the low doping efficiency is primarily due to H passivation of B. However, further structural dynamic simulations[7] proved that H passivation of P is improbable in a-Si:H. Recent numeric calculation of the electronic structure of doped amorphous silicon[8] implied much larger binding energies of band-tail localized states as compared with undoped material. It is our aim in the present contribution to show how the reduced doping efficiency may be understood in terms of a general purely electronic model that ignores specific structural features of sites surrounding a particular dopant atom and emphasizes the effect of Coulomb interaction on the electronic density of states of doped amorphous semiconductors.

When embedded in a random network of localized states, an ionized dopant atom changes the energy of nearby states due to Coulomb interaction of the dopant with charge carriers localized in those states. This observation encompasses the accepted notion of how doping an amorphous semiconductor gives rise to changes in the density-of-states (DOS) distribution of the material, for instance by the creation of charge-compensating dangling bond defects in a-Si:H, but it also applies to the interaction of a dopant atom with carriers localized in band-tail states. The interaction lowers the energy of the localized states surrounding the dopant ion, and thus considerably slows down an upward shift of the Fermi level with increasing dopant concentration.

For a given localized state, the probability density, $w(r)$, of having a nearest dopant ion at a distance r is determined from the Poisson distribution as

$$w(r)=4\pi r^2 N_d \exp\left(-\frac{4\pi}{3}N_d r^3\right), \tag{1}$$

where N_d is the concentration of ionized dopant atoms. If a carrier is trapped by this localized state, the Coulomb binding energy,

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$$E_c=\frac{e^2}{4\pi\varepsilon_0\varepsilon r}, \tag{2}$$

must be added to the disorder energy, E_d, to get the total energy of the state, E, with e being the elementary charge, ε_0 the dielectric permittivity, and ε the relative dielectric constant. We do consider a relatively weak doping whereby the concentration of dopant ions remains much smaller than the density of localized states, N_t. Under these conditions, the energy of a localized state will be essentially affected by just the one nearest ion. Using Eqs. (1) and (2), one can then find a distribution of the localized states over the Coulomb binding energy, $W(E_c)$. The result reads

$$W(E_c)=w[r(E_c)]\left|\frac{dr}{dE_c}\right|=\frac{4\pi e^6 N_d}{(4\pi\varepsilon_0\varepsilon)^3 E_c^4}\times\exp\left[-\frac{4\pi N_d}{3}\frac{e^6}{(4\pi\varepsilon_0\varepsilon E_c)^3}\right]. \tag{3}$$

As already stated, the total energy of a localized state is the sum of the disorder and Coulomb energies:

$$E=E_d+E_c. \tag{4}$$

Combining Eqs. (3) and (4) leads to the following expression for the distribution function of the localized-state density as a function of E:

$$g(E)=\frac{4\pi e^6 N_d}{(4\pi\varepsilon_0\varepsilon)^3}\int_0^\infty \frac{dE_c}{E_c^4}\exp\left[-\frac{4\pi N_d}{3}\frac{e^6}{(4\pi\varepsilon_0\varepsilon E_c)^3}\right]\times\int_0^\infty dE_d g_0(E_d)\,\delta(E-E_c-E_d), \tag{5}$$

where $g_0(E_d)$ is the distribution of localized states over the disorder energy in the undoped material and δ is the Dirac delta function. Evaluating the integral over E_d in the right-hand side of Eq. (5) yields:

$$g(E)=\frac{4\pi e^6 N_d}{(4\pi\varepsilon_0\varepsilon)^3}\int_0^E \frac{dE_c}{E_c^4}\exp\left[-\frac{4\pi N_d}{3}\frac{e^6}{(4\pi\varepsilon_0\varepsilon E_c)^3}\right]\times g_0(E-E_c). \tag{6}$$

It is worth noting that Eq. (6) is derived on the basis of one-carrier DOS distribution. The model ignores both the Coulomb interaction between charge carriers and contributions of next-nearest dopant ions to the Coulomb energy of localized states. This approximation is quite justifiable if the total density of localized states strongly exceeds the dopant concentration. Under such conditions, every localized state has, on average, only one well defined nearest dopant ion which contributes significantly to the Coulomb energy of the state. This contribution will also be much higher than the energy of Coulomb interaction with other charge carriers. Such approximation is not, of course, valid in very heavily doped amorphous materials in which N_d approaches N_t. Since the value of N_t in amorphous semiconductors is typically around $10^{20}-10^{21}\,\mathrm{cm}^{-3}$ the formulated model gives a reasonably good estimate for the effect of doping on the DOS distribution at dopant concentrations up to $10^{18}-10^{19}\,\mathrm{cm}^{-3}$.

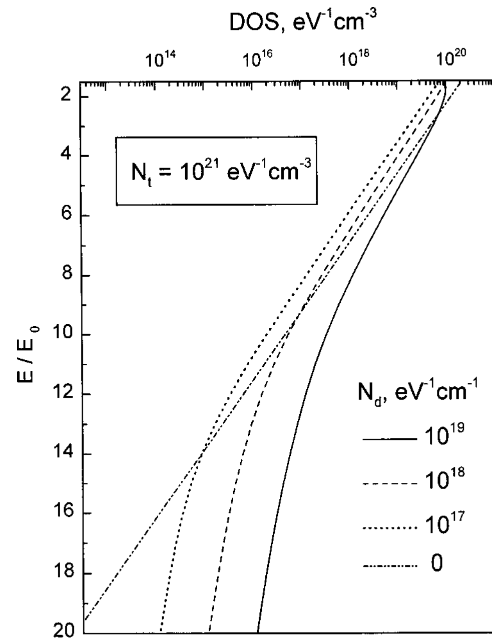

FIG. 1. The effect of Coulomb interaction on the DOS energy distribution in a doped amorphous semiconductor.

The effect on the DOS energy distribution of the Coulomb interaction with dopant ions is shown in Fig. 1, under the assumption of an exponential distribution of localized states in the undoped material, $g_0(E)=(N_t/E_0)\exp(-E/E_0)$, and for several choices of the dopant ion concentration. As may be seen immediately from this figure, an increasing concentration of dopant ions converts increasingly large numbers of shallow states into deep states. This effect can explain experimentally observed increasing width of the Urbach tail with increasing dopant concentration in a-Ge:H.[9] The demarcation energy below which the DOS increases with N_d, and above which it decreases, moves closer to the band edge with increasing N_d.

The result of effective doping of a semiconductor, *in casu* an amorphous semiconductor with sufficiently low density of gap states such as a-Si:H, will be a shift of the material's Fermi level towards either the conduction or the valence band. In order to express the Coulomb-induced changes in the DOS in terms of the energy position of the Fermi level, we will use as definition of the Fermi energy, E_F, the condition that, in equilibrium, the dopants will have filled all localized states up to E_F:

$$\int_{E_F}^\infty dE g(E)=N_d. \tag{7}$$

Use of the DOS distribution described by Eq. (6) in Eq. (7) yields the following transcendental equation for the Fermi energy:

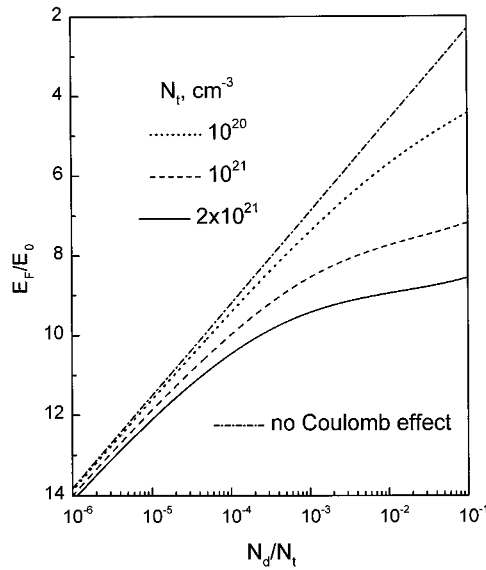

FIG. 2. Dependence of the Fermi energy upon the dopant concentration parametric in the total density of band-tail states.

$$\frac{1}{(4\pi)^2}\left(\frac{e^2}{\varepsilon_0\varepsilon}\right)^3\int_{E_F}^{\infty}dE\int_0^E\frac{dE_c}{E_c^4}$$
$$\times\exp\left[-\frac{4\pi N_d}{3}\frac{e^6}{(4\pi\varepsilon_0\varepsilon E_c)^3}\right]g_0(E-E_c)=1. \tag{8}$$

Figure 2 shows the shift of the thus-defined Fermi level in an exponential distribution of tail states as a function of the dopant concentration relative to the total density of localized band-tail states, for three values of the latter. At low dopant concentrations, the Coulomb interaction can only slightly increase the density of deep states and, consequently, the Fermi level is only slightly deeper than one could expect when the Coulomb energy is not taken into consideration (dotted line in Fig. 2). However, at higher dopant concentrations, many more states will have an ionized dopant as near neighbor and have their energy shifted downwards by the Coulomb interaction such that the relative increase in deep state density is able to considerably reduce the expected shift of the Fermi energy. The larger the density of band-tail states, N_t, the higher the probability that one such state will be sufficiently close to a dopant ion to be converted by the Coulomb interaction into a deep trap. Therefore, the effect of the Coulomb interaction on the position of the Fermi level becomes stronger with increasing density of tail states. For example, at $N_t=2\times10^{21}\,\mathrm{cm}^{-3}$ and $E_0=45\,\mathrm{meV}$ the Fermi level shifts from 0.45 eV to 0.50 eV with the dopant concentration increasing by three orders of magnitude from 2×10^{17} to $2\times10^{20}\,\mathrm{cm}^{-3}$. Concomitantly, the integrated density of states below the Fermi level increases by three orders of magnitude while the Fermi energy decreases by only one E_0.

In order to express the influence of the Coulomb binding energy on the traditionally used concept of *doping efficiency*, we introduce the notion of an equivalent ionized dopant concentration, $N_d^{(0)}$, that would, in the absence of the Coulomb interaction, result in a shift of the Fermi energy, E_F, to the value obtained with N_d and the appropriate Coulomb interaction. Since N_d stands for the concentration of *ionized* donors, the ratio $N_d^{(0)}/N_d$ does represent the reduced ability of the doping process to move the Fermi level when the Coulomb energy is taken into account. It can, therefore, be used as a relative measure of the doping efficiency. Values for this relative efficiency are shown in Fig. 3 as a function of the dopant density N_d for the earlier used tail-state densities. It may be seen that for doping densities around $10^{18}\,\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}$—not an unusual value for a-Si:H—the actual doping efficiency, as measured by the Fermi-level position, is one order of magnitude below what could be expected on the basis of a rigid DOS distribution and the dopant density.

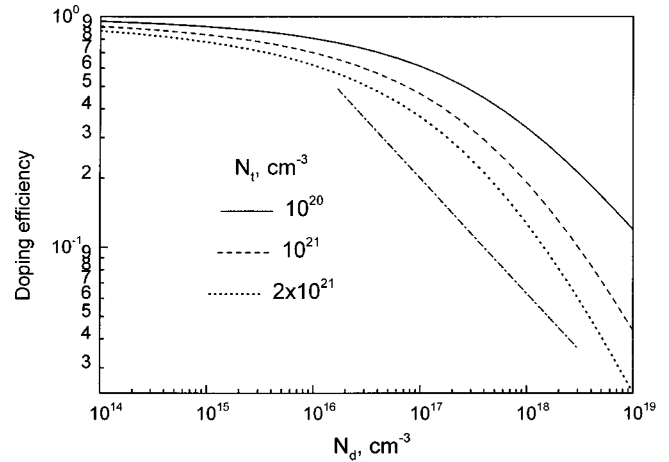

FIG. 3. Doping efficiency as a function of the dopant concentration for different total densities of band-tail states. The straight line indicates the $N_d^{-1/2}$ dependence of the doping efficiency.

It follows from this observation that the perceived discrepancies that were cited in the introduction between structural and electronic determinations of the doping efficiency in a-Si:H, are not contradictory at all but result from the oversight of dopant-induced shifts in the distribution of localized states. It may further be noted that in the same region around $N_d=10^{18}\,\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}$ the doping efficiency changes to first approximation as $N_d^{-1/2}$, which also corresponds to the experimental observations.[10]

In conclusion, a purely electronic model explaining the low doping efficiency in amorphous semiconductors is suggested. The model rests on the notion that the Coulomb interaction of dopant ions with charge carriers localized in band-tail states strongly affects the effective energy distribution of those states making them deeper. It has been shown that the density of deeper states increases almost linearly with increasing dopant concentration implying very low doping efficiencies in amorphous semiconductors, especially at high concentrations of dopant ions. Predictions of the model are consistent with experimentally observed increasing width of the Urbach tail and a low doping efficiency in doped amorphous semiconductors.

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