

ON DESCRIPTION OF COULOMB EFFECTS CAUSED BY DOPING IN AMORPHOUS AND DISORDERED ORGANIC SEMICONDUCTORS

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Several attempts were devoted recently to theoretical interpretation of the experimentally established low efficiency of chemical doping in amorphous and organic semiconductors. Some of these attempts are based on calculations of the effect of Coulomb potentials of dopant species on charge carriers in the host material. We estimate the effect of the Coulomb centres introduced by doping on the charge carriers in localized states of the host system and show that there is very strong correlation between spatial positions of dopant ions and extra charge carriers, in particular, in lightly doped materials. Previous calculations carried out in the framework of such an approach neither take the charge neutrality of the system, nor screening effects into account.

(Received July 4, 2005; accepted July 21, 2005)

Keywords: Disordered semiconductors, Coulomb effects, Hopping transport, Localized states

1. Introduction

Applications of semiconductors in electronic devices are usually based on the ability of these materials to be doped by chemically foreign species, which supply the system with extra charge carriers. Disordered semiconductors, such as amorphous materials and conjugated polymers, are not an exception. However, it has been established experimentally that the doping efficiency of disordered materials is much lower than that of crystalline semiconductors. For example, in amorphous inorganic semiconductors, such as hydrogenated amorphous silicon, a-Si:H, the concentration of impurities as deduced from experiments involving electronic states is considerably lower than that determined from the study of local bonding configurations by extended x-ray fine structure or nuclear magnetic resonance [1]. Also in disordered organic materials it has been established that at low doping levels electrochemical doping is much less efficient than the field-effect doping in which the same amount of charge carriers is injected into the system without inducing some chemically foreign impurities [2,3]. Moreover, at low dopant concentrations, chemical doping can even lead to decreasing carrier mobility [4]. At high doping levels the mobility steeply increases with dopant concentration [2-4]. Qualitatively this result was interpreted by assuming that in chemically doped materials charge carriers can be trapped by Coulomb potentials of ionized dopant species at low doping levels [3]. Consequently, the carrier mobility could be much smaller than the field-effect mobility measured without introducing charged dopants into the sample. At high doping levels in the electrochemical process the energy landscape might become more uniform leading to the increase of carrier mobility [3].

Two identical attempts [5], [6] were recently performed by Arkhipov and co-workers in order to put this argument onto a quantitative theoretical basis. We briefly describe these attempts and show that the set of equations suggested in such an approach is irrelevant for the description of the problem under study since neither charge neutrality, nor screening effects were properly taken into account.

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Arkhipov et al. considered an array of localized states of the host system with some high concentrations $N_l \sim 10^{21} \text{ cm}^{-3}$ and an array of dopant atoms with much lower concentration $N_d \sim 10^{18} \text{ cm}^{-3}$. To be specific we will consider the case of donors as dopant species. The case of acceptors can be treated in an analogous way. Donors are supposed to give their electrons into localized states of the host system and to become positively charged. Arkhipov et al. [5, 6] considered a localized state and estimated the Coulomb energy shift of this state due to the presence of the charged donors with concentration N_d . They considered the contribution to the Coulomb potential from only the nearest donor. The probability density, $w(r)$, of having a nearest donor at a distance r to a chosen localized state is determined by the Poisson distribution as

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

The energy of the considered localized state is shifted downward by the Coulomb potential of the nearest donor. Let the energy of this localized state in the absence of donors be ε . Arkhipov et al. argue that in the doped system the energy of this state becomes equal to $E = \varepsilon + E_c$, where

$$E_c = -\frac{e^2}{\kappa r} \quad (2)$$

is the energy shift due to the Coulomb potential of the nearest donor. In Eq.(2) e is the electron charge and κ is the dielectric constant of the host material. Arkhipov et al. considered weak doping when the concentration of dopant ions, N_d , remains much smaller than the total density of intrinsic hopping sites, N_l . They claim that under these conditions, the energy of almost every localized state will be essentially affected only by the nearest dopant ion. In such a case one can easily find the distribution $G(E)$ of site energies, $E = \varepsilon + E_c$, from the given density of states (DOS) for intrinsic energies, $g(\varepsilon)$, using Eqs. (1) and (2) for the distribution of Coulomb energies, E_c . Due to the effect of the positively charged donors, the distribution $G(E)$ appears shifted to lower energies compared to the distribution of intrinsic energies $g(\varepsilon)$. Hence the extra electrons supplied into the system by chemical doping are forced to fill not the intrinsic density of states (thus pushing the Fermi level upwards), but rather they fill the density of states already shifted towards lower energies by Coulomb potentials of the positively charge donors [5, 6]. Therefore the increase of the Fermi level with doping occurs much slower than it would be the case in the intrinsic DOS $g(\varepsilon)$ filled by the same amount of electrons. After having calculated $G(E)$, Arkhipov et al. [6] studied the hopping transport of electrons treating the system as spatially homogeneous with a DOS $G(E)$. In this note we analyse the above statements and point out their deficiency.

2. Is the Coulomb energy shift of a given localized state determined by only the nearest donor?

In the picture described above, Arkhipov et al. [5,6] assumed that only a single donor, namely, the nearest one, causes the Coulomb shift of the energy of a localized state in the host material. They claim that this assumption is justified by the inequality

$$N_d \ll N_l. \quad (3)$$

Moreover Arkhipov et al. claim that this assumption under condition (3) is obvious [6]. We argue however that this assumption is neither obvious, nor correct. Of course, the contribution of donors to the Coulomb potential on a localized site decreases with the distance from the site to the donors as $1/r$. However, the number of donors in a sphere of radius r around the chosen site increases as r^3 . Therefore the contribution to the Coulomb potential of a chosen hopping site from more distant donors than the nearest one increases proportional to r^2 . In the absence of screening, as considered

by Arkhipov et al. [5], distant donors contribute more to the Coulomb energy shifts on localized states than the nearest ones. The condition expressed via inequality (3) is irrelevant for this conclusion. Furthermore, one should immediately realize that in the picture considered by Arkhipov et al. [5,6] the energy diverges if one considers only donors as charged centres and takes into account the Coulomb contributions to the energy of an intrinsic site from more and more distant donors. This is a trivial result discussed already in several textbooks (see, for example, Refs. [7,8]). In order to avoid the divergence of the Coulomb energy, one should not restrict the consideration to charges of only a given polarity as done by Arkhipov et al. [5,6]. Instead, one should consider both kinds of charges – positive and negative ones keeping the system electrically neutral. Herewith we come to the important though trivial question: are electrons electrically charged?

3. Are electrons electrically charged?

The answer to this question is definitely “yes”. A donor becomes charged positively only because it can get rid of a valence electron. In the picture of Arkhipov et al. described in the Section I, electrons brought into the system by donors were given just a passive role to fill the density of states shifted to lower energies by positively charged donors. One should however take into account that electrons are also charged with opposite polarity to that of the donors. The concentration of the negatively charged extra electrons introduced into the system by donors is equal to that of charged donors, N_d . These electrons are the cause for the effect on the energies of intrinsic sites, which is exactly opposite to that caused by positively charged donors exclusively considered by Arkhipov et al. [5, 6]. Being negatively charged electrons shift the energies of intrinsic hopping sites upward. Arkhipov et al. deliberately took into account only positive charges. If one would do the same with taking into account only negative charges of extra electrons, one would come to the conclusion exactly opposite to that of Arkhipov et al., namely to the conclusion that DOS function would be shifted upward in energy with respect to that in an undoped sample. Of course, none of such deliberate considerations can be correct or even serious. One should consider an electrically neutral system with taking into account both positively charged donors and negatively charged electrons brought by these donors as described in textbooks (see, for example, Refs. [7,8]). The crucial question in such treatments is the question on the spatial distribution of charges.

Donors are assumed to be distributed randomly in space. What about electrons?

4. Where are the electrons?

Following Arkhipov et al. [5, 6] we consider a lightly doped sample when condition (3) is fulfilled. This condition is more than plausible since estimates give $N_d \sim 10^{18} \text{ cm}^{-3}$ and $N_t \sim 10^{21} \text{ cm}^{-3}$ [5,6]. Condition (3) cannot justify that only the nearest donor to a localized state should be taken into account, as described in Section 2, but this strong inequality will help us to answer the question expressed in the title of this Section. A Coulomb energy shift of an intrinsic localized state from the nearest donor is described by Eqs. (1) and (2). It is determined by the typical distance between donors, $r_d \approx N_d^{-1/3}$. Inserting such estimate in Eq. (2), and taking $\kappa = 3$ as known for organic semiconductors, one obtains the typical Coulomb energy of a localized state from the nearest donor of the order $E_c \sim 0.08 \text{ eV}$ for $N_d \sim 10^{18} \text{ cm}^{-3}$ [5,6]. Since the width of the energy distribution of intrinsic hopping sites $g(\varepsilon)$ is of the order of $\sim 0.1 \text{ eV}$, the effect of Coulomb centres on intrinsic localized states seems essential. We claim however that in the above picture one should consider not *a localized state* and the nearest donor of it, but rather *the localized state*, which is the nearest to a donor. While the typical distance between a localized state and the nearest donor is determined by the distance of the order $r_d \approx N_d^{-1/3}$, the distance between a donor and the nearest localized state is determined by the distance $r_t \approx N_t^{-1/3}$, which is much smaller than r_d . Inserting such r_t in Eq. (2) and taking for the concentration of hopping sites the magnitude $N_t \sim 10^{21} \text{ cm}^{-3}$, as

suggested by Arkhipov et al. [5,6], we find that the Coulomb energy shift of the localized state nearest to a donor, E_c , is about 0.8 eV. This value is by an order of magnitude larger than the shift $E_c \sim 0.08$ eV of an average localized state from the donor nearest to it. Electrons would prefer to occupy deeper energy levels and therefore they will be situated on the intrinsic sites, which are closest to dopant ions (donors). Therefore one should conclude that all charges brought into the system by donors are gathered in dipoles formed by positively charged donors and the negatively charged intrinsic centres nearest to them. One could suppose that Arkhipov et al. [5,6] considered the effect with typical scale of about 0.1 eV having overseen the effect with typical scale of about 1 eV. The situation is however much worse. We have just shown that due to the effect of the typical scale of ~ 1 eV, the effect of the scale ~ 0.1 eV considered by Arkhipov et al. [5,6] does not exist, since not the point charges, but rather very short dipoles affect localized states in the intrinsic material, which are used by electrons in hopping transport. The extra electrons brought by donors are trapped into states with very deep energies (~ 1 eV at $N_t \approx 10^{21} \text{ cm}^{-3}$) which are the nearest to donors. Therefore no effect of increasing mobility has been observed experimentally at low dopant concentrations when condition (3) is fulfilled. The effect of heavy doping when the strong inequality (3) breaks down, needs a special treatment, which is out of our scope in this brief note. In the next section we instead estimate the effect of Coulomb potentials on a given intrinsic localized state in a lightly doped material.

5. The typical scale of Coulomb potentials on an intrinsic hopping site

Let us estimate the Coulomb contribution to the energy of an intrinsic localized state in the host material due to the presence of the described dipoles created due to doping. Following Arkhipov et al. [5,6] we consider a given localized site in the intrinsic material. The distance, $r_d \approx N_d^{-1/3}$, to the nearest dipole from this localized site is determined by the concentration of dipoles, which is equal to the concentration of donors, N_d . The length of the dipole is determined by the concentration of localized states, $r_t \approx N_t^{-1/3}$. The contribution of such a dipole to the energy of a given localized state is of the order

$$E_c = -\frac{e^2}{\kappa r_d} \frac{r_t}{r_d}. \quad (4)$$

This equation replaces the wrong estimate given by Eqs. (1), (2). The result of Eq. (4) for the energy shift E_c on “a localized state” is by an order of magnitude smaller than that estimated by Arkhipov et al. [5,6], since in Eq. (4) the Coulomb contribution of a point charge at a distance r_d is multiplied by a small parameter, r_t/r_d , which is equal to 0.1 for the ratio $N_d/N_t = 10^{-3}$ chosen by Arkhipov et al [5,6]. This contribution is less than 0.001 eV and it can be well neglected.

6. Conclusions

We have analysed the spatial distribution of charges in a lightly n-doped disordered semiconductor with concentration of donors, N_d , much smaller than the concentration, N_t , of intrinsic localized states which can be occupied by electrons supplied by donors. It is shown that electrons under such conditions occupy the localized states nearest to the donors and hence all charges are gathered into dipoles. The energy of an electron in the nearest localized state is shifted downward by a huge Coulomb potential (~ 1 eV) of the donor. Such a configuration provides a very deep trap for the electron and hence the spatial correlations in the charge distribution drastically suppresses the doping efficiency at low dopant concentrations. It is also shown that the theoretical approach suggested recently by Arkhipov et al. [5,6] in order to interpret the low efficiency of chemical doping in amorphous and organic semiconductors at low doping levels is erroneous and it

cannot be considered for comparison with experimental data. The calculation of transport properties affected by charge distribution at high doping levels is a subject of future studies.

Acknowledgements

Financial support of the Deutsche Forschungsgemeinschaft, of the Fonds der Chemischen Industrie, of the Optodynamic Centre at the Philipps University Marburg and that of the European Graduate College "Electron-Electron Interactions in Solids" Marburg-Budapest is gratefully acknowledged.

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