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PHYSICAL PROPERTIES OF DOPED CHALCOGENIDE GLASSY SEMICONDUCTORS WHICH ARE GOVERNED BY THE INTERACTION OF NEGATIVE-U DEFECTS AND IMPURITY STATES.

K. D. Tsendin

A. F. Ioffe Physico-Technical Institute, 194021 St.Petersburg, Russia

It is shown that negative-U centres in doped chalcogenide glasses control the electrical properties of the materials. Possible superconductivity is discussed theoretically.

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1. Introduction

Previous investigations have been revealed that electrical and optical properties of doped chalcogenide glassy semiconductors (CGS) may be interpreted in the frame of model which considers a doped CGS as a medium consists of small clusters which are constructed from atoms with a first coordination mean number z more than this one (z_0) in the low-coordinated CGS [1-3]. In As_2Se_3 films doped with Bi and prepared by thermal sputtering technique the clusters have been observed in optical microscope. They have Bi_2Se_3 composition and size L which is equal or less than 100 nm [3]. In As_2Se_3 films prepared and doped with Ni by modification technique the clusters have not been observed by direct methods but all electrical and optical data evidenced that its L is equal or less than 5 nm. The real composition of clusters in this case is unknown. The clusters of the same size $L \approx 5$ nm in synthesized samples of Ge-(S, Se) systems doped with Bi have been observed in electronic microscope [4].

According to the paper [1] the appearance of clusters with $z > z_0$ very important for effective doping process. It is known that CGS have soft, labile atomic structure with a great number lone-pair (LP) electrons of chalcogenide atoms, which do not take part in a net of CGS covalent bonds. These facts together with a disorder provide a fulfillment of famous 8-N rule and inefficiency of CGS doping. More rigid atomic structure of clusters prevents a fulfillment of 8-N rule and allows to exist donor- and acceptor-like electronic impurity states inside the clusters. Then "official" doping elements (Bi and Ni in our cases) together with CGS atoms (As and Se) play role of the main constituent atoms of clusters. Therefore the real chemical nature of donor- or acceptor-like electronic impurity states must be determined in each individual case and may not coincides with the "official" doping elements.

This approach allows us to consider these doped CGS as nanostructured chalcogenides in which an efficiency of doping process depends on appearance of nano-clusters.

The second result of doping treatment is creation of intrinsic defects of CGS (negative-U centers). Experimental facts have evidenced, that concentrations of intrinsic defects D and electronic impurity states N are very close to each other [2,3,5]. This phenomenon may be considered as self-compensation process. Then one can see that a strong interaction of negative-U centers and impurity centers takes place. This interaction has both statistical (or thermodynamically) and direct quantum-mechanical character. The main result of the statistical interaction is so-called self-compensation processes, which happen in time of doping treatment. Due to self-compensation processes a concentration of negative-U centers D is approximately equal to concentration of electrically active impurity centers N . The direct quantum-mechanical interaction has a result in a correlation between energies of negative-U centers and impurity states.

The first part of the present paper is devoted to consideration of physical properties of doped chalcogenide glassy semiconductors which are governed by different relationship between D and N ($D \geq N$ or $N \geq D$).

First of all it will be discussed how relationship between D and N manifests in theoretical temperature dependence of direct current conductivity. Then we will discuss the experimental temperature dependence of direct current conductivity in CGS doped with transitional metals and temperature dependence of drift mobility in CGS doped with halogens.

The last part of the paper concerns with the case when concentration of negative-U centers is enough to create band-like states. Possible superconductivity of this system is considered theoretically. The experimental data on mixture of doped selenium with micro-crystalline particles of high temperature superconductors is discussed.

2. The self-compensation processes

2.1 Direct current measurement data

In the our paper [5] a compensation coefficient $k = D/N$ has been estimated for As_2Se_3 doped with Ni using direct current measurement data. We were surprised by values of k which were very close to unity: $1-k=10^{-5}-10^{-3}$. The similar results may be obtained for As_2Se_3 doped with Bi from data [3]: $1-k=10^{-2}-10^{-1}$. From our point of view this means that there is a strong correlation between localization of impurity and defect states.

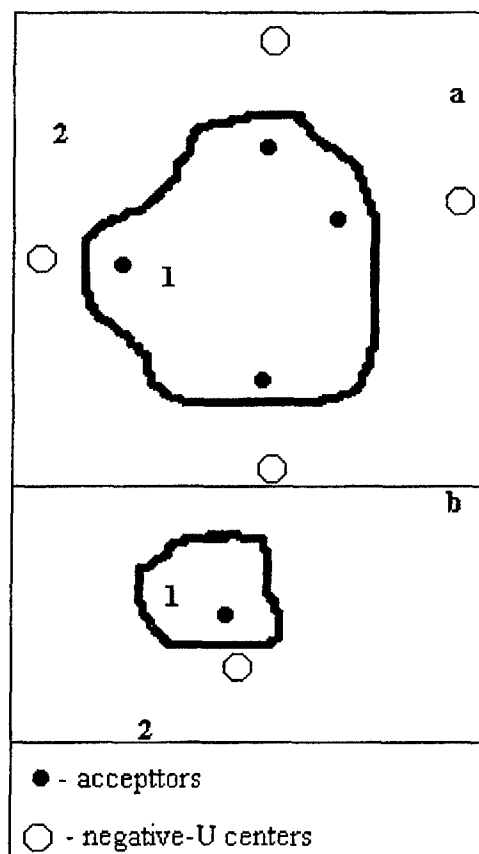


Fig. 1. Schematically representation of doped As_2Se_3 with Bi (a) and Ni (b) in the microheterogeneity doping model [1]. Area 1 – Bi_2Se_3 on figure (a) and area enriched with Ni on figure (b). Area 2 – As_2Se_3 with a little amount of doped impurities.

For example one can imagine the correlated situation which is depicted in the Fig 1. The cases 1a and 1b schematically present the $As_2Se_3(Bi)$ and $As_2Se_3(Ni)$ correspondingly. In the first case

L is great enough to allow appearance several acceptors inside the clusters. According to [3] energy level of acceptor E_a , which exists in Bi_2Se_3 clusters is approximately equal 0.25 eV. Then radius of electronic state "a" equals $\sim 5\text{-}10 \text{ \AA}$ for effective mass $m^*=(1\text{-}0.25)m$. We do not know the real microscopic reason of simultaneously appearance of impurity and defect states but one can suppose that vacancy of Se or extra Se atom in Bi_2Se_3 clusters may be introduced from CGS matrix. The process of atoms exchanging may be more effective in the nearest vicinity of nano-cluster boundary. In the $\text{As}_2\text{Se}_3(\text{Bi})$ case, if we suppose, that "a" equals $\sim 5\text{-}10 \text{ \AA}$ also, then approximately only one electronic impurity state may be put into the cluster.

Data for $\text{As}_2\text{Se}_3(\text{Bi})$ have evidenced that fresh films correspond to case $N \approx D$. For this case according the paper [6] direct current conductivity may be written as

$$\sigma = \sigma_0 \exp(-(\varepsilon_1 + \varepsilon_2 + E_a)/3kT) \quad (1)$$

where ε_1 and ε_2 are ionization energies of first and second holes from negative-U center. The formulae (1) means that Fermi energy (E_F) lies at the $(\varepsilon_1 + \varepsilon_2 + E_a)/3$ distance from valence band edge E_v . This value is a mean energy of thermal ionization of each of three holes involved in the processes, which have determined the E_F position. After thermal annealing of $\text{As}_2\text{Se}_3(\text{Bi})$ films temperature dependence of conductivity became

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (2)$$

which takes place for $N > D$ case.

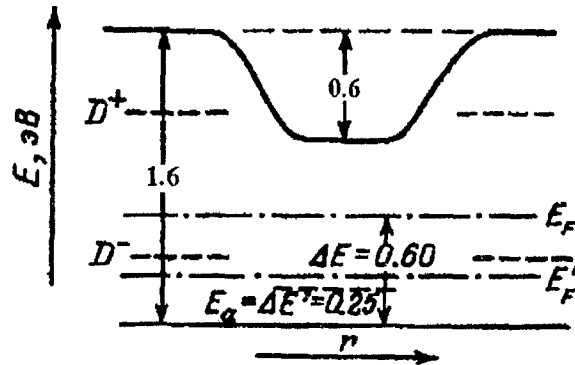


Fig. 2. Energy band diagram of $\text{As}_2\text{Se}_3\text{Bi}_{0.1}$ near Bi_2Se_3 cluster. All energies in eV. E_F and E_F' are Fermi energies before and after annealing.

For the estimations we take the case of $\text{As}_2\text{Se}_3(\text{Bi})_{0.1}$ [3]. Energy of optical gap E_g and energy activation of conductivity ΔE in glassy Bi_2Se_3 films is equal to 1.0 eV and 0.25 eV correspondingly. The latter coincides with energy activation of conductivity for thermal annealed films. This is the reason, why we consider, that E_F in the both cases coincides with $E_a=0.25 \text{ eV}$, put this value in the (2) and reconstruct the band energy diagram depicted on Fig. 2. Before annealing the energy activation of conductivity is equal to 0.6 eV, i.e. initial position of Fermi level (E_F) is situated as it is shown in Fig. 2. Then one can obtain from relation $0.6 = (\varepsilon_1 + \varepsilon_2 + 0.25)/3$ that mean energy ionization of negative-U centers per one hole $\varepsilon = (\varepsilon_1 + \varepsilon_2)/2 = 0.78 \text{ eV}$. This value is very close to half of the energy of optical gap $E_g/2=0.80 \text{ eV}$ measured for $\text{As}_2\text{Se}_3(\text{Bi})_{0.1}$ and so one can conclude that negative-U centers belong to matrix outside the clusters. In the paper [3] it has been shown that at the annealing temperature 130 C the changing of acceptor concentration N occurs in a- Bi_2Se_3 films. So far as at the same annealing temperature the changing from dependence (1) to dependence (2) occurs, we consider that changing of acceptor concentration N is the reason of this. Thus the present estimation corroborates the model depicted on Fig. 1a. One has not any correlation between the position of acceptor level E_a and ionization energies of negative-U centers and it may be concluded that space distance between impurity and negative-U centers is more than several tens of angstrom and overlapping between its wave functions is absent.

Another situation takes place for $\text{As}_2\text{Se}_3(\text{Ni})$ films. Detail analysis, which has been undertaken, in the papers [7,8] shows, that different temperature dependencies of σ , obtained by different groups of scientists, for approximately the same doping level, correspond to $N > D$ (results of papers [9,10]) and to $N < D$ (results of paper [11]) cases. Comparison of these two sets of experimental results has allowed us to determine the position of the acceptor level E_a and ionization energies of negative-U centers. A strong correlation has been revealed, namely $\varepsilon = (\varepsilon_1 + \varepsilon_2)/2 = E_a$ for all doping level. Then it may be concluded that space distance between impurity and negative-U centers is close to sum of its radii, which may be estimated as 15-25 angstrom and there is overlapping between its wave functions, which is the reason for correlation of positions of acceptor level E_a and mean ionization energy of negative-U centers. This conclusion agrees with L value for $\text{As}_2\text{Se}_3(\text{Ni})$ case, because one can not separate acceptor more far from nanocluster boundary than radii of nanocluster.

2.2 Drift mobility data

The method of drift mobility measurement is a very informative for evaluating of defect and impurity states concentrations, because an electron and hole drift mobility (μ_e and μ_h) can be expressed as

$$\mu_{e,h} = (\mu_0)_{e,v} (N_{e,v}/D_{e,h}) \exp(-\Delta E_{e,h}/kT) \quad (3)$$

where $(\mu_0)_{e,v}$ are the free electrons and holes mobility in the conduction and valence bands. $N_{e,v}$ are the effective concentrations of band states at the conduction E_c and valence E_v band edges. $D_{e,h}$ are the concentrations of localized traps which control the electron and hole drift mobility and $\Delta E_{e,h}$ are the absolute values of energy distance between traps energy $E_{e,h}$ and $E_{c,v}$ for electrons and holes correspondingly. It is known that in CGS mobility has been controlled by the charged states D^+ and D^- of negative-U centers, i.e. one can consider that $D_{e,h} = D^+, D^-$. Fig. 3 shows the values of D^+ and D^- which we evaluate using (3) and experimental data on values of the drift mobility are taken from paper [12].

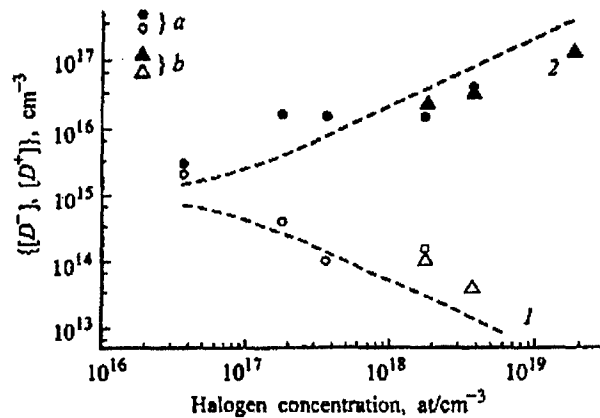


Fig. 3. Dependence of the concentration of negatively (1) and positively (2) charged intrinsic defects in $\text{Se}_{95}\text{As}_5$ doped with Br (a) and Cl (b). Data on values of the drift mobility for concentration of Br and Cl impurities in the range 10^{17} to 10^{19} are taken from [12]. The dashed lines are theoretical dependencies.

In this paper mobility has been measured in $\text{Se}_{95}\text{As}_5$ films, doped with Br and Cl. There are strong dependencies of D^+ and D^- on impurity concentration and therefore one can see the strong pronounced self-compensation process. Electrically active atoms of halogens Br and Cl has negative charge, then according to electro-neutrality equation its promote increasing of the D^+ and suppress the appearance of D^- . We have not any investigations of sample homogeneity and can not conclude would the electrically active impurity centers belong to clusters or not.

3. The possible superconductivity in the negative-U centers system.

The pairs of electrons or holes which are localized at the D^- and D^+ states of negative-U are bosons. If the concentration D of negative-U centers small, all pairs (bosons) are localized.

But in previous sections it has been demonstrated, that due to self-compensation processes doping treatment increases the D and, if the D becomes large enough and disorder is not large one can suppose that band-like non-localized boson states may appear. The Bose condensation of non-localized pairs may provides the superconductivity property of negative-U centers set in principle.

In the paper [13] we applied the theory [14] to the system of negative-U centers in CGS and named model as "negative-U centers model of superconductivity" (NUCS-model). Bose condensation or superconductivity transition temperature T_c may be expressed as

$$T_c = W(1-2\nu)/\ln(\nu^{-1} - 1) \quad (4)$$

Where $\nu = n/2D$ is relative concentration of pairs, n is electron concentration. $W = 2zt^2/U$ is width of pairs band for simple cubic lattice of negative-U centers with $z=6$. Absolute value of effective negative correlation energy of electrons is U ; t is tunneling integral

$$t = t_0 \exp(-2r/a) \quad (5)$$

for electron transferred from one negative-U centers to another, which are separated by distance r . The expression (4) has been obtained for $t \ll U$. In this case we have two narrow bands (Fig. 4, for example we consider a-Se with a large value of D) for electron D^- and hole D^+ pairs, which are separated by large distance U .

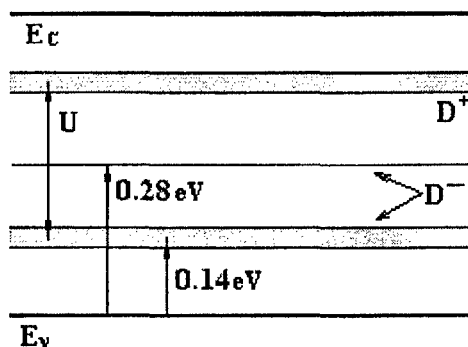


Fig. 4. Band energy diagram of a-Se. The vertical arrows show the thermal and optical transitions of holes to the D^- states of the negative-U center. Dark bands represent the bands of non-localized electron and hole pairs (D^- and D^+ bands), whose Bose condensation is responsible for the superconductivity.

For $\nu < 1/2$ and $\nu > 1/2$ the electron and hole pairs superconductivity takes place for $T < T_c$. It has been shown in [13] that, if electron (hole) wave function radius "a" is equal 10 Å, the T_c of order several hundred degrees may be obtained for concentration D of order 10^{19} cm^{-3} . But this estimation is valid for ordered cubic lattice of negative-U centers only. For disorder lattice of negative-U centers the distance r between negative-U centers, which form band-like pairs states, may be more than mean distance (which is of order $D^{-1/3}$) consequently t and T_c may be less.

This model has been applied in [13] to channels, which arise during an switching effect in thin layer of CGS. Typical radii of channel or current filament R equals to ~ 1 micron. It has been supposed that in this channels reversible appearance of large concentration of negative-U centers takes place. The appearance of D^+ (or C_3^+ according to [15]) occurs due to response of active region of channel on pressure which arises during the switching event. The large number of C_3^+ centers with $z = 3$, which exceeds the $z_0 = 2$ for chalcogenide atoms removes stress inside the channel. Ordinarily the concentration D of negative-U centers in CGS is equal 10^{16} - 10^{18} cm^{-3} . We have to suppose the increasing of D up to 10^{19} - $5 \cdot 10^{19} \text{ cm}^{-3}$ in order to explain the temperature of order 300 K and higher. We also suppose that negative-U centers model of superconductivity can explain the states with a resistance which was not greater than instrumental error observed in low-coordinated organic polymers [16].

It is known that classic BCS theory encounters serious difficulties in explanation of high- T_c superconductivity in metal oxides. In our paper [17] it has been shown that negative-U centers model

of superconductivity explains both the high transition temperature T_c and specific – with a maximum – dependence of T_c on chemical composition of samples, observed in many metal oxides. In the contrast to the classic superconductors, high temperature metal oxides superconductors (HTSC) have a very small correlation length $\xi \sim 10\text{-}15$ Å. It means, that superconductivity current may be observed if the distance between micro-crystals of superconductors does not exceed the value of order ξ . In this connection our attention has been attracted by the results of the paper [18]. These results have been discussed in details in the [19] at the present conference and here I would like to emphasize only crucial facts.

The mixture of glassy Se with micro-crystalline pieces of HTSC compound $Y_1Ba_2Cu_3O_7$ with $T_c \approx 90$ K has been investigated in [18]. Micro-crystalline pieces of $Y_1Ba_2Cu_3O_7$ have linear size about several micrometers, occupy approximately 14% of whole volume then all of them have been separated by a-Se. At the high temperature $T > T_c$ the conductivity of samples was of order $10^{-6} \Omega^{-1} \text{cm}^{-1}$. This value strong differs from conductivity $\sim 10^3 \Omega^{-1} \text{cm}^{-1}$ of $Y_1Ba_2Cu_3O_7$ and shows that at the high temperature the conductivity is governed by doped a-Se. It is known that pure a-Se has conductivity of order $10^{-12} \Omega^{-1} \text{cm}^{-1}$, which may be increased by many of orders by doping with oxygen.

The transition temperature T_c of the mixture was the same as for $Y_1Ba_2Cu_3O_7$, i.e. $T_c \approx 90$ K and superconductivity current existences at this temperature through the whole sample. But the mean distance between micro-crystalline pieces of $Y_1Ba_2Cu_3O_7$ was very large. It was equal to several micrometers, i.e. more than 10^3 times exceeded the correlation length ξ . In the [19] we suppose that micro-crystals of HTSC are connected by channels which are similar to those appeared during the switching effect in CGS. A large number of negative-U centers may exist in the channel due to self-compensation processes induced by doping with oxygen. Additional concentration of negative-U centers may be generated during the switching effect in the internal electric field or in the weak external electric field which is used for current observation. The superconductivity in the system of negative-U centers in the channel may be induced by superconductivity phase transition in micro-crystalline pieces of $Y_1Ba_2Cu_3O_7$ which occupy two ends of each channel.

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