Two types of short-range order and impurity behavior in glassy $CdGeAs_2$

V. D. Okunev and Z. A. Samoĭlenko
Physicotechnical Institute, Academy of Sciences of the Ukrainian SSR, Donetsk

(Submitted 18 July 1985; resubmitted 20 September 1985)
Pis'ma Zh. Eksp. Teor. Fiz. **43**, No. 1, 24–27 (10 January 1986)

Glassy $CdGeAs_2$, with states with two types of short-range order and with redistributions between these two states, tends to retain the basic structural elements when doped. The relationship between the electrical activity of the dopant atoms and the structure of films has been determined.

The general interpretation of the physics of amorphous semiconductors is based on the idea, for which there is no rigorous proof, that a single type of short-range order prevails in the arrangement of atoms in these materials and that this order is roughly the same as the short-range order in the corresponding crystalline analogs.[1] In our opinion, simplified structural models are the primary source of the contradictions between experiment and theory. These contradictions can be resolved to some extent by introducing various hypothetical models, e.g., the model of tunneling atomic states,[2] which do not, on the whole, change the interpretation.

In this letter we report a study of amorphous $CdGeAs_2$ films doped with atoms having a low electrical activity (Cu, Ag) or a high electrical activity (Ni, Pt). The results show that glassy $CdGeAs_2$ has two states, with different energies, whose popu-

 © 1986 American Institute of Physics

lations depend on the nature and concentration of the dopant. The films are synthesized by joint sputtering of targets.[3] The structure of the samples is studied by an x-ray method.

The undoped amorphous films have all the characteristics of a glass, and the properties are similar to those of monolithic glasses.[4] On the diffraction pattern we see, in addition to the basic halo of the amorphous state of $CdGeAs_2$, a considerably less intense second halo, which is totally unrelated to the second-order diffraction maximum and which is due to a transition of a fraction of the medium from the ground state I to state II, with a very different short-range order in the arrangement of atoms. The average interatomic distance in glassy $CdGeAs_2$ in state I is $d^{\rm I} = 3.17$ Å, while that in state II is $d^{\rm II} = 2.15$ Å. The relative amount of the medium in state II is no more than 5–7%, and it decreases due to annealing. State II is therefore seen only in the absorption spectra of bulk glasses at $\alpha = 1$–100 cm^{-1}. The optical gap width is $E^{\rm II}_{\rm gopt} = 0.71$ eV (Refs. 5 and 6). In thin films, the value found for $E_{\rm gopt}$ at $\alpha > 10^3$ cm^{-1} corresponds to state I: $E^{\rm I}_{\rm gopt} \cong 1.2$ eV (Ref. 4). At $T > 200$ K, there are two regions in a plot of $\sigma = \sigma_0 \exp(-\Delta E/kT)$, with activation energies $\Delta E^{\rm II} = 0.36 \pm 0.01$ eV and $\Delta E^{\rm I} = 0.6 \pm 0.01$ eV. These two regions correspond to two values of the thermal width of the energy gap: $E^{\rm II}_{gT} = 0.72 \pm 0.02$ eV and $E^{\rm I}_{gT} = 1.2 \pm 0.02$ eV. State II, which persists in part even in the well-annealed samples, is obviously of defect origin and apparently plays a significant role in the mechanism by which the glass is formed and in its thermal stability.

The intensity of the second halo increases rapidly with increasing dopant concentration, in some cases exceeding the intensity of the first halo. The values of $d^{\rm I}$ and $d^{\rm II}$ and the doping of Cu and Ag films to $X < 15\%$ are essentially independent of X (Fig. 1). The value of σ is also conserved (Fig. 2). The optical properties of the samples vary only slightly.[3] The behavior of Cu and Ag, which stimulate a conversion of a progressively greater part of the medium from state I to state II, is similar here to the behavior of isoelectronic substitutional impurities. With increasing X, both of the halos shift toward larger angles. At concentrations above the critical levels, correspond-

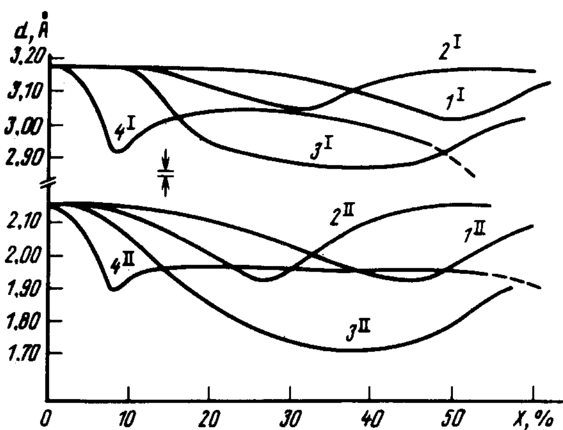

FIG. 1. Average interatomic distances $d^{\rm I}$ and $d^{\rm II}$ in amorphous alloys $(CdGeAs_2)_{100-x}M_x$ versus the dopant concentration. M: 1—Cu; 2—Ag; 3—Ni; 4—Pt.

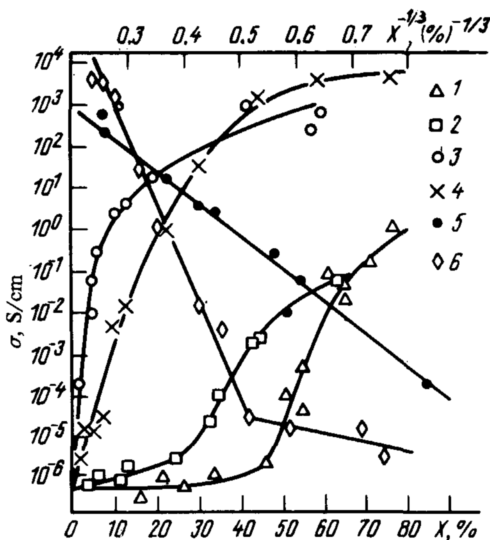

FIG. 2. Electrical conductivity of the films ($T = 300$ K) versus the dopant concentration in the amorphous $(CdGeAs_2)_{100-x}M_x$ alloys. M: 1—Cu; 2—Ag; 3—Ni; 4—Pt. 5,6—Behavior of σ as a function of X in terms of the coordinates $\ln\sigma$, $X^{-1/3}$ for films doped with Ni and Pt, respectively.

ing to the positions of the minima in Fig. 1, lines which are evidence of the initial stage of crystallization appear against the background of the second halo, and both halos gradually return to their original positions. The first halo persists over a broad concentration range after the beginning of the crystallization in the samples. The origin of the minima in Fig. 1 in this case is due primarily to stresses, whose critical value determines the region in which amorphous states I and II exist simultaneously. The appearance of low-resistance crystalline inclusions in the high-resistance host leads to an increase in the value of σ of the films (Fig. 2).

The structure and properties of the films are affected in a different way by Ni and Pt, for which there is no possibility of a complete saturation of their valence bonds. Low concentrations of these dopants change σ by many orders of magnitude (Fig. 2). The conductivity is primarily a hopping conductivity along impurity states created by the Ni and Pt atoms in the basic glassy phase I (Ref. 7). Even at $T = 300$ K the dependence of σ on the impurity concentration N satisfies one of the basic relations for hopping conductivity[8]: $\sigma \sim \exp(-\alpha_0/a_{im} \cdot N^{1/3})$ (Fig. 2), where a_{im} is the apparent radius of the states, since the concentration of electrically active centers in our case is $N_a \ll N$. For the alloys $(CdGeAs_2)_{100-x}Ni_x$ we have $a_{im} = 1.7$ Å. The actual value of the radius a, found from temperature and field measurements of σ, is 9.5 Å, so that N_a is two orders of magnitude lower than N.

At low Ni and Pt concentrations, the system still tends to retain the two states characteristics of the undoped material (Fig. 1), but as X is increased, there are significant changes in d, caused by not only the stresses but also the substantial changes in the short-range order upon the formation of new impurity amorphous phases. At low values of X, these new phases, while having essentially no effect on the values of σ of the films (the distances between individual inclusions exceed the average hopping length), completely alter the optical properties of the samples.[3] At high Ni

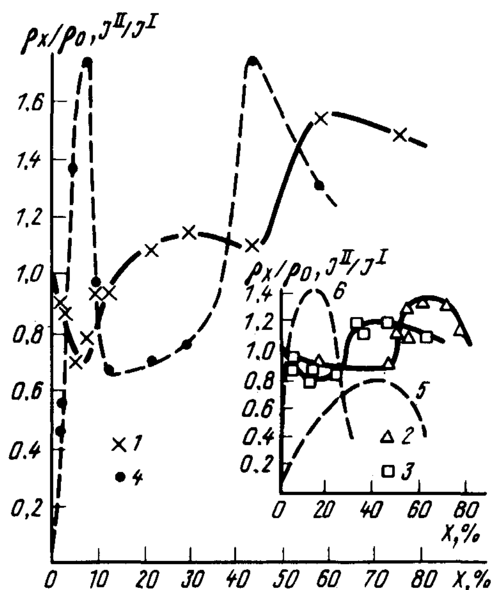

FIG. 3. ρ_x/ρ_0 and $J^{\rm II}/J^{\rm I}$ versus the dopant concentration. Here ρ_x/ρ_0 is the relative density of the films during doping with (1) Pt, (2) Cu, and (3) Ag. Here ρ_0 is the density of the undoped films, and $J^{\rm II}/J^{\rm I}$ is the ratio of the intensities of the first and second halos in the doping of films of (4) Pt, (5) Cu, and (6) Ag.

and Pt concentrations, we observe a continuous percolation semiconductor-metal transition.[9] After crystallization of the impurity phase in the alloy $(CdGeAs_2)_{100-x}Ni_x$ at $X > 50\%$, the system can no longer return to its original state (Fig. 1). The alloys containing Pt do not crystallize anywhere in the X range. The $d^{\rm I}$ and $d^{\rm II}$ minima at $X \cong 7\%$ in Fig. 1 and the inflection point on the plot of ln σ versus $X^{-1/3}$ corresponding to this value of X in Fig. 2 (the change in a_{im} with increasing Pt concentration is from 6.8 to 0.6 Å) are directly related to the formation of an impurity phase.

Figure 3 shows the results of measurements of the film density. For the alloys containing Pt, the ρ_x/ρ_0 minimum at $X = 7\%$, corresponds to a maximum of the ratio $J^{\rm II}/J^{\rm I}$. The disordering process gives way to a density increase at $X > 7\%$, at which the actual formation of the impurity phase begins. The next step in the increase in ρ_x/ρ_0 is observed at $X > 45\%$, with the formation of yet another amorphous impurity phase. The corresponding behavior of ρ_x/ρ_0 and $J^{\rm II}/J^{\rm I}$ as a function of the Cu and Ag concentrations turns out to be simpler.

Working from these results, we can offer the following hypothesis regarding the microstructure of the films. Glassy $CdGeAs_2$ is a set of layered structures of mesoscopic scale, formed by two types of atomic packing (in the case $d^{\rm I}$ and $d^{\rm II}$ are the corresponding average interplanar distances). In state I, these layered formations apparently are formed by (111) planes, which are the planes with the closest packing of atoms in crystalline $CdGeAs_2$ (we do not rule out the possibility that this is the total extent of the similarity of the short-range order in crystalline and glassy $CdGeAs_2$). State II is probably determined by a layered structure formed by planes which are not at all characteristic of crystalline $CdGeAs_2$. The density of the atomic packing in such planes is substantially lower than that in (111) planes, and we have $d^{\rm II} \cong 0.7 d^{\rm I}$. The

intercluster zones are characterized by large numbers of ruptured bonds, and they intensify the background on the x-ray diffraction patterns. In view of the facility with which groups of atoms can convert between states I and II (Fig. 3), it is clear that for a transition from one structural state to another just small displacements of atoms from their equilibrium positions are sufficient. As yet we do not have enough information to construct a more definite model of the structure.

These aspects of the behavior of impurities in glassy $CdGeAs_2$ are probably not exceptional cases, and they largely determine the behavior of impurities in other groups of amorphous and glassy semiconductors as well as the generally difficult history of the doping of materials of this class.[1,6]

[1]N. F. Mott and E. A. Davis, Electronic Processes in Noncrystalline Materials, Clarendon, Oxford, (Russ. transl. Mir, Moscow, 1982).

[2]P. W. Anderson, B. I. Halperin, and C. M. Varma, Phil. Mag. **25**, 1 (1972).

[3]V. D. Okunev and A. G. Yurov, Pis'ma Zh. Tekh. Fiz. **5**, 161 (1979) [Sov. Tech. Phys. Lett. **5**, 64 (1979)].

[4]V. D. Okunev, Ya. I. Otman, and A. G. Yurov, Izv. Vyssh. Uchebn. Zaved., Fiz. No. 2 84 (1979).

[5]N. A. Goryunova, Slozhnye almazopodobnye poluprovodniki (Complex Diamond-Like Semiconductors), Sov. Radio, Moscow, 1968.

[6]N. F. Mott and E. A. Davis, Electronic Processes in Noncrystalline Materials, Clarendon, Oxford (Russ. transl. Mir Moscow, 1974).

[7]Y. A. Bratashevskiĭ and V. D. Okunev, Solid State Commun. **52**, 981 (1984).

[8]B. I. Shklovskiĭ and A. L. Efros, Elecktronnye svoĭstva legirovannykh polyprovodnikov (Electronic Properties of Doped Semiconductors) Nauka, Moscow, 1979.

[9]V. A. Alekseev, A. A. Andreev, and M. V. Sadovskiĭ, Usp. Fiz. Nauk **132**, 47 (1980) [Sov. Phys. Usp. **23**, 551 (1980)].

Translated by Dave Parsons