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STUDIES OF CHALCOGENIDE VITREOUS SEMICONDUCTORS IN THE IOFFE PHYSICO-TECHNICAL INSTITUTE

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Abstract.

The broad class of semiconductors discovered at the Ioffe Physical-Technical Institute in 1955-56 [1] and termed at present chalcogenide vitreous semiconductors (ChVS) has recently been attracting ever increasing interest of the researchers due to many properties which are unusual for crystalline semiconductors.

During a number of years, our interests have been primarily connected with such basic problems as the transport phenomena, electronic spectrum, the role of impurities, optical and photoelectric phenomena, induced structural transformations etc. [2-6].

Out of many directions pursued at our Institute we have chosen for this paper only a few where, in our opinion, the most interesting and novel results have been obtained.

1. Impurity Effect on the Electrical Properties of ChVS

Already the early experiments revealed the impurities to have only a weak effect on the electrical properties of ChVS which was attributed to a total valence saturation of the impurity atoms [7-9]. Group 1 elements on ChVS conductivity [10], and the Ag impurity was established to lead to a formation of impurity centers which affect markedly the position of the Fermi level [11].

It was shown [12,13] that an efficient doping of some ChVS of complex composition accompanied by a substantial change in electrical parameters can be produced by high-frequency cosputtering of the initial ChVS and the dopant. This doping technique was termed modification. It appeared of importance to check the possibility of modifying in this way vitreous arsenic selenide and sulfide, i.e. the typical materials whose properties were studied most thoroughly.

Our results presented in a separate report at this Conference [14] suggest that the modification process achieved by high-frequency cosputtering and accompanied by a considerable change in the material properties occurs also in films of such typical ChVS as As₂Se₃ and As₂S₃ and is typical for a broad class of ChVS. At the same time, only transition metals with unfilled d-shells rather than any other metal introduced as a dopant can efficiently change the electrical properties. This is illustrated in Fig.1 showing the variation in position of the Fermi level in vitreous As₂Se₃ films with variation of concentration and type of a modifier. The most efficient in this respect are seen to be Ni and Mo characterized by unfilled d-shells.

2. The Role of Impurities in Luminescence

One of the least studied aspects of the ChVS luminescence is the role of impurities which is of interest from both a theoretical and practical standpoints. Indeed, an impurity of a given charge state can manifest itself in different ways in the ChVS network depending on the origin of the luminescence centers.
The available data on the effect of impurities on photoluminescence (PL) are contradictory [12-15] calling for further research along these lines.

We have studied the effect of Group I and IV impurities on the PL of vitreous chalcogenides of arsenic (As$_2$Se$_3$ and As$_2$S$_3$) and germanium (Ge$_2$S$_3$).

The impurities (Cu, Ag, Au, Pb, Sn) were introduced during preparation. All the PL measurements were carried out in the temperature range 4.2 - 770 K, excitation produced at the photon energy corresponding to the peak of the excitation spectrum. A study was made of the PL excitation and emission spectra, as well as of the PL decay kinetics after switching off the excitation.

Fig.1. Modification-induced Fermi level shift in As$_2$Se$_3$ films.

Fig.2. PL excitation emission spectra of vitreous As$_2$S$_3$ and Ge$_2$S$_3$ doped with impurities (T = 4.2 K).

(a) 1 - As$_2$S$_3$; 2 - As$_2$S$_3$ + 0.1 at.% Cu; 3 - Ge$_2$S$_3$ + 0.1 at.% Cu.
(b) 1 - Ge$_2$S$_3$; 2 - Ge$_2$S$_3$ + 0.1 at.% Cu; 3 - Ge$_2$S$_3$ + 0.12 at.% Au.

The PL excitation emission spectra of vitreous As$_2$S$_3$ and Ge$_2$S$_3$ doped with Cu and Ag are presented in Fig.2a. As seen from Fig.2a, introduction 0.1 at.% Cu into As$_2$S$_3$ results in a substantial shift of PL spectra towards low energies (the emission spectrum being shifted by 0.2 eV, and the excitation spectrum, by 0.4 eV). The PL intensity appears to be somewhat reduced compared with an undoped sample.

Fig.2b displays data on the effect of Cu and Au impurities on the PL of vitreous Ge$_2$S$_3$ which show that while neither Cu or Au affect noticeably the shape and position of the emission and excitation spectra, they result in an increase of PL intensity. The Au impurity introduced at 0.12 at.% enhances the PL intensity by a factor of 6 compared with an undoped sample. Other Group I impurities likewise enhance PL intensity although to a lesser extent. In contrast, doping Ge$_2$S$_3$ with Group metals (particularly with Pb) decreases PL (see Fig.3).

These experimental data permit certain conclusions to be drawn. None of the metal impurities introduced in the course of preparation into vitreous arsenic and germanium chalcogenides creates an additional emission band, however they effect the PL of undoped glasses. This implies that although an impurity does not produce new emission centers in CHVS it changes either the concentration of the centers already present in the material or the probability of radiative transitions due to the appearance of localised states of another type.

The actual of the impurity action on PL in CHVS depends apparently on the nature of chemical bonds between the atoms of the material. Measurements showed the impurity effect on PL to be stronger in
germanium than in arsenic chalcogenides. This can be attributed to the fact that covalent bonds are more pronounced in germanium chalcogenides, their network being more "rigid" than that in arsenic chalcogenides where Van der Waals forces play an important role. In the latter case, as is well known, local rearrangement of the network can occur, so that the impurity will not cause any change of potential.

3. Electroabsorption

It was believed until recently that electroabsorption (EA) in ChVS, just as absorption, is macroisotropic which would make a distinctive feature of vitreous materials of the type of As$_2$Se$_3$, Se, GeSe$_2$ compared with their crystalline analogs. Our latest studies of EA in polarized light have shown, however, that the amplitude of signal depends substantially on the mutual orientation of the electric field $F$. In the ChVS studied by us, $\Delta \alpha_{\|}(E \parallel F)$ is 1.5 - 3 times larger than $\Delta \alpha_{\perp}(E \perp F)$. For both components $\Delta \alpha \sim F^2$, while the degree of anisotropy $\Delta \alpha_{\perp}/\Delta \alpha_{\|}$ remains constant with varying field, at least up to $10^5$ V cm$^{-1}$. The spectral dependence of $\Delta \alpha_{\perp}/\Delta \alpha_{\|}$ is shown for a number of ChVS in Fig.4 displaying a decrease of the degree of anisotropy with increasing photon energy deficit.

![Fig.3](image1.png)

Fig.3. PL intensity VS impurity concentration in vitreous Ge$_2$S$_3$.
1 - Ag; 2 - Au; 3 - Pb.

![Fig.4](image2.png)

Fig.4. Spectral dependence of EA anisotropy in vitreous As$_2$Se$_3$, AsSe, Ge$_2$S$_3$ and Se at 300°K.

We have proposed a model taking into account local bond anisotropy to explain the optical anisotropy appearing in ChVS under applied electric field. This model is considered in a separate report at this Conference [18].

4. Charge Carrier Transit Time Dispersion

The dispersion exhibited by charge carriers in their transport in ChVS attracts considerable attention.

The stochastic dispersion transport theory yields the following relationships for the hopping distance distribution $\psi(t) = \text{const} t^{-(d+1)}$, variation of current with time, and the dependence of drift mobility on field $F$ and sample thickness $d$:

$J(t) = \begin{cases} t^{-(d+1)}, & (t \leq t_T) \\ t^{-(d+1)}, & (t > t_T) \end{cases}$

$\mu \sim \frac{F^{d-1}}{d-1}$
The parameter $\lambda$ characterizes the degree of dispersion and varies within $0 < \lambda < 1$. The dispersion decreases with increasing $\lambda$. As seen from these expression, the transport characteristics are interrelated via parameter $\lambda$ which, according to the theory, is the same for $t < t_{tr}$ and $t > t_{tr}$.

Studies of hole transport in vitreous $\text{As}_2\text{Se}_3$ [19,20] and electron transport in the $S_{1-x}\text{As}_x$ system with $x = 0.05 - 0.17$ [21] carried out in our laboratory showed the transport parameter $\lambda$ in times shorter and longer than the transit time $t_{tr}$ to be different in magnitude which disagrees with the present ideas concerning the dispersion transport. These studies were performed at room temperature and at electric fields $10^4 - 10^5$ V cm$^{-1}$ using the well known drift mobility measurement technique.

Figs. 5 and 6 display current vs. time plots for the drift of holes in $\text{As}_2\text{Se}_3$, and of electrons, in $\text{Se}_{1-x}\text{As}_x$ ($x=0.1$). An analysis showed the slope of the current decay region at $t < t_{tr}$ to be small.

![Fig. 5. Current vs. time profile for hole drift in $\text{As}_2\text{Se}_3$. $d=3.1\mu$m at $V=50$ Volt (1) and $V = 25$ Volt (2).](image1)

![Fig. 6. Current vs. time profile for electron drift in $\text{Se}_{90}\text{As}_{10}$. $d = 1.1\mu$m at $V = 18$ Volt (1), 9 Volt (2) and 5.5 Volt (3).](image2)

Describing it by a function of the form $t^{-4}$, we obtain $n \approx 0.2$, which corresponds to a practically normal transport with $\lambda > 0.8$.

An analysis of the current decay profile at $t > t_{tr}$ yielded characteristics typical for anomalous transport. Indeed, one observed in $\text{As}_2\text{Se}_3$ prolonged current decay corresponding to strong dispersion with $\lambda < 0.2 - 0.3$. A study of the current profile corresponding to electron drift in $\text{Se}_{1-x}\text{As}_x$ at $t > t_{tr}$ showed the current to follow a power law behaviour $t^{-m}$ where $m$ varies from 2.0 to 1.7 with increasing arsenic content and practically does not depend on voltage $\ast$.

$\ast$ For some samples we obtained $m > 2.0$. A consideration of such cases would be beyong the scope of the present paper.
The large extent of the current decay region at $t > t_{tr}$ and the independence of current decay profile on voltage also imply the existence of a relatively strong electron dispersion which does not obey the Gaussian statistics.

Thus the characteristics obtained at $t < t_{tr}$ give evidence for a close-to-normal transport, while at $t > t_{tr}$ dispersion typical for anomalous transport is observed. This can be accounted for by assuming distribution of charge carriers in mobility. In this case, normal transport will take place for charge carriers at $t < t_{tr}$, the current being characterized by a constant mean effective charge carriers having different mobilities. A relationship between the charge carrier distribution function in mobility $P(\mu)$ and the current decay profile was established for this transport mechanism [22]. For a step function

$$P(\mu) = \begin{cases} 
1/\mu_x & \mu \leq \mu_x \\
0 & \mu > \mu_x 
\end{cases}$$

the current was found to be constant up to $t_{tr}$ and to decay by quadratic law after $t_{tr}$.

$$I(t) \sim \begin{cases} 
\frac{1}{2} \frac{e\mu_x F}{d} t & t < \frac{d}{\mu_x F} \\
\frac{1}{2} \frac{e\mu_x F}{d} \left( \frac{\mu_x F t}{d} \right)^2 & t > \frac{d}{\mu_x F}
\end{cases}$$

If the function $P(\mu)$ decreases with $\mu \to 0$, the decrease of current in time after $t_{tr}$ will be stronger pronounced, while if $P(\mu)$ increases with $\mu \to 0$, the current variation will be weaker. For the limiting case $P(\mu) \to \infty$ with $\mu \to 0$ one obtains $\mu(t) \sim t^{-1}$.

A comparison of theory with experimental shows the electron distribution function in Se$_{1-x}$As$_x$ to have a component which varies only weakly with $\mu \to 0$. In the case of holes, however, the distribution apparently has an enhanced number of charge carriers with small $\mu$. Thus the above results imply that one cannot characterize transport in ChVS by one value of mobility only, so that the observed transit time dispersion may be connected with a charge carrier distribution in mobility.

5. Structural Transformations Induced by External Factors

One of the interesting phenomena revealed in recent years in ChVS and not observed in their crystalline analogs are reversible structural transformations induced by external factors, most notably by light.

Studies showed photoexcitation in ChVS to produce a change not only of optical but of many other properties as well, among them photoelectric, electrical, contact and physicochemical, as shown schematically in Table 1.

Of importance is that these changes are reversible, i.e. they disappear under heating and may recover completely again on illumination.

Photoinduced optical anisotropy was observed in all ChVS exhibiting photoinduced changes of transmittance. As an illustration, Fig. 7 shows spectral characteristics of photoinduced dichroism which appeared in an AsSe film exposed to plane-polarized light from a He-Ne laser (the angle of turn of the plane of light polarization $\gamma$ is
Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Affected parameter</th>
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<tbody>
<tr>
<td>Optical</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td></td>
<td>Refractive index</td>
</tr>
<tr>
<td></td>
<td>Appearance of dichroism and birefringence</td>
</tr>
<tr>
<td>Photoelectrical</td>
<td>Photoconductivity spectrum</td>
</tr>
<tr>
<td></td>
<td>Photoconductivity amplitude</td>
</tr>
<tr>
<td></td>
<td>Photoresponse kinetics</td>
</tr>
<tr>
<td></td>
<td>Lux-ampere characteristic</td>
</tr>
<tr>
<td>Electrical</td>
<td>Dielectric constant</td>
</tr>
<tr>
<td></td>
<td>Charge carrier mobility</td>
</tr>
<tr>
<td>Contact</td>
<td>Magnitude and sign contact photo-emf</td>
</tr>
<tr>
<td></td>
<td>Electret characteristics</td>
</tr>
<tr>
<td>Physicochemical</td>
<td>Microhardness</td>
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<td></td>
<td>Density</td>
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<tr>
<td></td>
<td>Softening temperature</td>
</tr>
<tr>
<td></td>
<td>Solubility in inorganic and organic solvents</td>
</tr>
<tr>
<td>Others</td>
<td>Photoelectron emission spectra</td>
</tr>
<tr>
<td></td>
<td>Mössbauer spectra</td>
</tr>
</tbody>
</table>

proportional to the photoinduced dichroism). Also shown are the initial (T₀) and light-induced spectral characteristics of dichroism and transmittance are correlated; they are due to light interference in the thin film. The appearance of dichroism in ChVS is accompanied by photoinduced birefringence.

Thus the initially optically isotropic ChVS films reveal on illumination with polarized light a photoinduced anisotropy which disappears simultaneously with the disappearance of photoinduced transmittance spectrum shift after the sample anneal. The phenomenon of photoinduced anisotropy is attributed to the presence in ChVS films of optically anisotropic structural elements distributed in a random way in space, in particular, it may be due to an anisotropy of various atomic bonds.

It was shown that structural transformations in ChVS can be induced not only by light but by other external factors as well, in particular, by exposure to X-rays and fast electrons. The discovery of the photobleaching effect on films of the As-Se and As-S system prepared by the conventional evaporation technique but darkened preliminarily attracted considerable attention [24].

As an illustration, we present in Fig. 8 transmission characteristics of As₂Se₂ films as a function of temperature. The line AB shows the photodarkening of the film at room temperature. AC and BEDC display, respectively, the variation with temperature (at a heating rate ~ 3 deg/min) of the transmittance of an exposed and unexposed areas of the film respectively. Interestingly enough, illumination of a preliminarily darkened region at elevated temperatures produces bleaching (sections φ'F' and φ"F"'). Note that the corresponding film transmittance reaches the same level which can be obtained by illumination of unexposed film at the same temperature (sections H'F' and H"F"'). Thus, the line BEF'C shows the steady-state film
transmittance reached under illumination at different temperatures. The photobleaching effect is seen to increase with temperature and most importantly, to have a temperature threshold. The final transmittance level is determined by illumination and temperature and does not depend on the initial state of the film.

It is essential that the sensitivity of the photobleaching process exceeds considerably (5-10 times for As-Se films, and 20-30 times for As$_2$S$_3$ films) that of photodarkening.

Fig. 7. Spectral characteristics of light transmittance and photoinduced anisotropy in AsSe film for exposure times 300 s ($T_1$ and $T_4$), 720 s ($T_2$ and $T_3$) and 3000 s ($T_3$ and $T_3$).

An attempt was made to explain the results obtained in the framework of a configurational model involving two stable (ground and metastable) states of atomic units in ChVS between which thermal and optical transitions occur (Fig. 9) [24].

The structure of the film and, accordingly, its properties (optical, physicochemical and others) are determined, just as in solid solution, by the relative number of atomic units residing in the ground and "metastable" states. To an atomic unit in the ground state corresponds an equilibrium configuration coordinate $Q_1$ and energy $E_{10}$, and to the metastable state, $Q_2$ and $E_{20}$, respectively. Optical transitions between the states occur in accordance with the Frank-Condon principle, the atomic configuration remaining unchanged during the transition.

Of particular interest is the case where the elastic properties of a unit in the ground and metastable states differ considerably which may be expressed via different steepness of parabolas characterizing these states (Fig. 9).

An analysis of the direct optical, reverse optical and reverse thermal transitions (the direct thermal transition being neglected) yields an expression for the steady-state population of the metastable state as a function of light intensity $I$ and temperature $T$ [25]. In the expression $\sigma_2$ and $\sigma_1$ are the direct and reverse optical transition cross-sections, $\gamma$ is a frequency of the order of phonon frequency, is the metastable state well depth, the meaning of $E_1(\omega)$ and $E_2(\omega)$ being clear from Fig. 9.

\[
\gamma_\infty = \frac{I}{1 + \frac{\sigma_2}{\sigma_1} \exp\left\{\frac{[E_1(\omega) - E_2(\omega)]}{kT}\right\} + \frac{\gamma}{\sigma_1}} \Rightarrow \frac{e^{-\frac{\Delta}{kT}}}{\sigma_1} \cdot I
\]
The expression thus obtained described well the totality of the experimental results including both the photobleaching at elevated temperatures and the enhanced sensitivity to light of the photobleaching effect, as well as the effect of variation of light intensity and wavelength and a number of features in the kinetics of photostimulated processes.

The configurational model provided a possibility not only to explain the known facts but also to predict new phenomena. Indeed, it was used to predict that compression of samples which is equivalent to heating should reduce photodarkening while the application of tension should lead to an increase of photodarkening. Fig. 10 shows the results of an experimental check on this prediction on As$_2$Se$_3$ films.

![Fig.9. Configurational diagram](image)

![Fig.10. Maximum photodarkening of As$_2$Se$_3$ vs. applied load.](image)

At present, however, one cannot determine with confidence the structure of atomic units in ChVS. One can only suggest, for instance, that the ground state of a unit in As$_2$Se$_3$ or AsSe$_2$ films is occupied by two covalently bonded As atoms, while in the metastable state one of the As atoms is in the interstitial position. We believe that the major effort of researchers in the nearest future should be aimed at elucidating the nature of the ground and metastable states of units in ChVS of different composition.

6. Low Resistance State in Switching

The most interesting and important aspect of the switching effect is, in our opinion, the nature of the low-resistance state appearing after switching. A high current density filament is formed in this case. The processes responsible for the filament formation are at present unclear, and some of its important characteristics are still unknown. Of most interest here is the current filament temperature. It is this temperature that defines such important properties as the reversibility and stability of the switching effect.

Some authors believe the release of Joulean heat to play only a minor role in current filament formation, so that the maximum temperature in the current filament reaches 30–60°C at most [26,27]. An analysis of experimental data carried out in our laboratory showed the current filament temperature to achieve 500–600°C [28].

We believe the results of a comparative study into the recovery of the high-resistance states of switches and memory elements (MEE) to be one of the most convincing arguments for a substantial heating of the current filament. These results obtained by the technique of ref. [27] for a switch of Si$_{12}$Ge$_{10}$As$_{30}$Tl$_{48}$ composition and He of composition and MEE of composition Ge$_{15}$As$_4$Tl$_{81}$ are presented in Fig. 11.
One may clearly see a similarity in the recovery processes manifesting itself in the presence of a kink in the resistance $R$ vs. time plots both for the switches and the memory elements. Since in We the material changes its state and the current filament is heated at least up to $T_p$, the similarity between the resistance recovery processes indicates that in switches the current filament is likewise heated to a high temperature. An analysis of experimental data by the electron heat conduction theory showed the filament cooling in switches to occur with a time constant of the order of a microsecond from the maximum current filament temperature $T_m \approx 550^\circ K$. Within this theory, the kink on the $R(t)$ curves is associated with the heating effect of the gating pulse. At times in excess of the time corresponding to the break this effect becomes negligible.

The limitation of the temperature rise by the level of $550^\circ K$ is apparently due to a transition to a metal-type conductivity which is maintained both by temperature and by the electric field. If we assume the presence of such a transition, then from the heat balance $VT_0 = \rho cdA \tau r^2$ obtaining with time of thermal relaxation $t_0 = \frac{\rho cd^2}{4z}$. One can derive an expression for the current density in the filament, $j = \frac{4z}{Vd} (T_{mT_0})$ which gives the value $j \approx 10^8 A m^{-2}$ agreeing with the experimental data [27]. This agreement implies the predominant role of thermal processes in the current filament formation. A number of phenomena of interest for applications are connected with the development of a high temperature in the filament. Among them is the recently described local doping at switching [29] which permits one to obtain within the current filament materials with new properties impossible to achieve by other known techniques.

The operation of the photodoping mechanism in ChVS which had earlier been suggested on the basis of indirect evidence (changes of the optical and electrical properties and of solubility) was demonstrated for the first time by direct diffusion experiments. They yielded the diffusion parameters of Ag and Au both in the dark and under illumination for such model ChVS as $As_2Se_3$ and $As_2Te_3$ [30].

Gubanov and Mott suggested that impurity atoms in ChVS always saturate all their chemical bonds. Mössbauer spectroscopy provided for the first time experimental evidence for this hypothesis [31,32].

Among the theoretical studies carried out in recent years at our Institute one should specially mention works dealing with the effect of electron-electron interaction on the major physical properties of disordered systems with localized states, in particular ChVS. Computer simulation showed the existence of a Coulomb gap in the density of states of excitations determining the static hopping conductivity of the system [33]. The effect of electron-electron interaction on the high-frequency hopping conductivity was also studied. It turned out that this interaction changes substantially the frequency and temperature dependence of conductivity for both the zero-phonon hopping mechanism [34] and the hopping mechanism [34] associated with

![Fig.11. Resistance recovery of switch](image)
electron-phonon interaction [35,36]. These studies stress the inadequacy of one-electron theories in the description of disordered systems with localized electrons.

One should also mention in this context theoretical studies [37], [38] proposing a new model for the localized states in glasses. It is suggested that electrons can become trapped not at defects but rather in specific regions of a perfect covalent glass with an anomalously small local elasticity. This model has not yet progressed to the state where it could be fitted to experimental data, however it may bear fruit in the future.

The present report contains only the most interesting results obtained recently, it being impossible to cover in full the experimental and theoretical studies carried out at the Physicotechnical Institute in the field of ChVS. Indeed, no mention was made of such interesting problems as the effect of a strong field on the electrical and photoelectric properties; the temperature dependence of conductivity and thermo-emf at the transition to the liquid state; the effect of pressure and penetrating radiation; photoinduced ESR and IR absorption; and a number of other phenomena typical only for this new and broad class of semiconductors.

There can be no doubt that a further investigation of ChVS properties will yield in the nearest future a wealth of new information of interest for the solid state physics and relevant applications.

References

18. Gelmont B.L., Kolomiets B.T., Mazets T.F., Pavlov S.K. The paper at this Conference.