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The Effect of Halogen Impurities on Electroconductivity of Chalcogenide Glass Semiconductor Se-As System

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Abstract

DC conductivity has been measured as function of dopant concentration for Se-As glass containing 2-10 % As, doped with Cl or Br. It was established that concentration dependences of the conductivity have maxima for concentration of Cl or Br between 10^{-3} and 10^{-2} at %. The effect of halogen impurities on electroconductivity of Se-As glasses has been attributed to the change of relative concentrations of the charged defect centers (C_1^-, C_3^+) and to the occurrence of new Cl^-, Br^- centers associated with chlorine (bromine) atoms and the compensation of the effect of arsenic on the energy spectrum of electron states.

The adding of bromine as an impurity to a Se-As system causes an intense increase a drift mobility of a hole by 2-3 orders of magnitude. This phenomenon and its mechanism, as explained by the effect halogens (bromine) have on local states thus controlling the charge transfer in Se-As, has been discussed in [1-3]. To obtain additional information about local states in the "forbidden band" of Se-As system with halogen (chlorine, bromine) impurities, electroconductivity measurements have been carried out and the results are presented in this paper.

Samples 1 to 10 μm thick were prepared by vacuum evaporation on glass substrates covered with SnO_2 thin films. Aluminium and gold contacts deposited in vacuum were used as the upper electrodes.

The dependence of chalcogenide glass semiconductor (CGS) Se-As system electroconductivity on chlorine and bromine impurity consentrations are shown in Figure 1 and Figure 2, respectively. The temperature dependence of the electroconductivity of all investigated samples obey the relationship $\sigma = C \exp(-\frac{\Delta E}{kT})$.

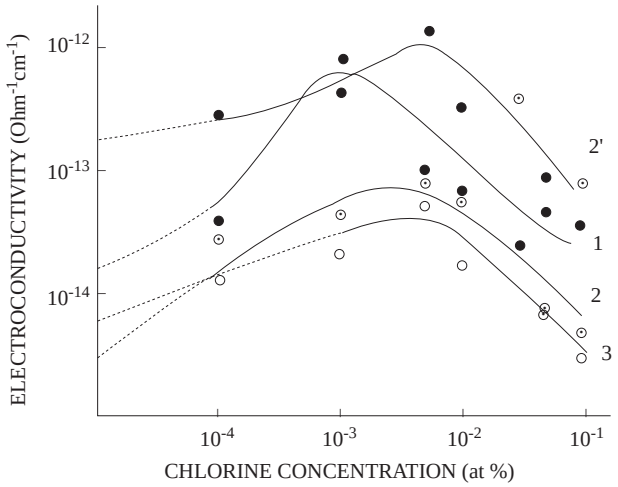

Figure 1. The dependence of the electroconductivity of the $Se_{98}As_2$ (Curve 1), $Se_{95}As_5$ (Curves 2, 2'), $Se_{90}As_{10}$ (Curve 3) compositions on the chlorine impurity concentration. The curves 1, 2 and 3 correspond to room temperature, and the curve 2' corresponds to 333 K.

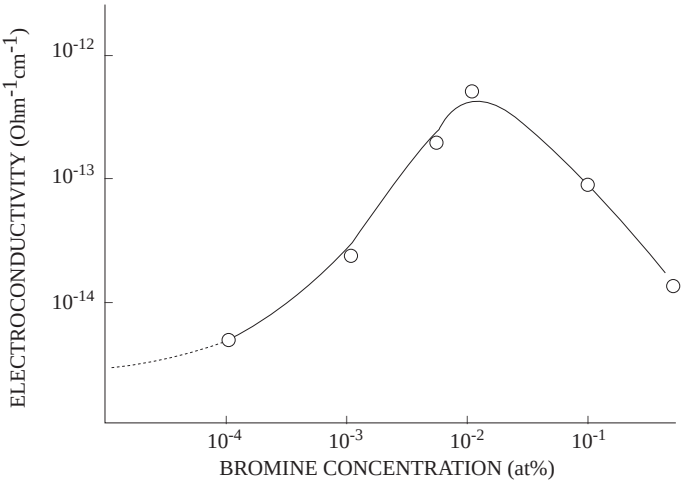

Figure 2. The dependence of electroconductivity in the $Se_{95}As_5$ system on bromine impurity concentration at room temperature.

Values of the preexponential factor and the activation energy of the electroconductivity are tabulated (Table 1). As seen from Table 1 both the preexponential factor and the activation energy are found to change in Se-As system, i.e. the position of Fermi level changes. The latter is indicative of changes occuring at the allowed band edges, with which the relative concentrations of the charged defects should in turn affect the conduction mechanism.

Table 1.

Substance composition	Preexponential factor, $\Omega^{-1}cm^{-1}$	Activation energy, eV
Se	5 10^5	1.15
$Se_{95}As_5$	0.5 10^2	0.95
$Se_{95}As_5Cl_{0.0001}$	0.5 10^2	0.93
$Se_{95}As_5Cl_{0.001}$	1.5 10^2	0.9
$Se_{95}As_5Cl_{0.01}$	0.15 10^2	0.9
$Se_{95}As_5Cl_{0.05}$	1 10^2	1.0
$Se_{95}As_5Cl_{0.1}$	10^3	1.04

It has been noted in [4] that when alloying arsenic with selenium, the arsenic σ^*-orbitals fall within the "mobility gap", leading to the change of conduction and valence band edges.

When selenium is doped by arsenic the individual components modify by the reaction

$$As^{\circ}(3) + Se^{\circ}(2) \rightarrow As^{-}(2) + Se^{+}(3).$$

The new negatively charged centers associated with arsenic atoms ($As^{-}(2)$) are formed and, simultaneously, the concentration of positively charged centers ($Se^{+}(3)$) increases. According to [5-6], at low As concentrations (2 to 6 at %) these centers are considered to be isolated because the selenium lattice with the distributed arsenic atoms remains as the basic structural element.

Thus, the doping of selenium by arsenic leads to an increase in concentration of the charged free bindings, the inhomogenius distribution of which in material volume results in the formation of potential wells with finite geometrical dimensions and of random potential fluctuations.

Based on the above considerations, decrease of the preexponential factor in the CGS Se-As system with increasing arsenic concentration is attributed to a random potential fluctuation resulting in band edge curvature, leading to a decrease of carrier mobility at the band edges.

The curves showing the electroconductivity dependence in the CGS Se-As system on chlorine and bromine concentration (Figs. 1, 2) pass through the maxima, i.e. they have the same dependence as that of the drift mobility [1]. However, if the hole drift mobility increases by 2 to 3 orders with halogen doping, the electroconductivity, in this case, changes by 1-2 orders of magnitude only.

As seen from Table 1, the charge of halogen impurity concentration is accompanied by a shift of Fermi level, which should affect the electroconductivity values. However, the change of electroconductivity observed experimentally appeared to be larger than that calculated with regard to the shift of the Fermi level.

The discrepancy between the calculated and experimental electroconductivity values is probably due to the fact that chlorine (bromine) in low concentrations shows itself as a chemically active element, the function of which leads not only to a change of relative concentration of the charged intrinsic centers, but also compensates the change of the energy spectrum of electron states caused by arsenic doping, resulting in an increase of carrier mobility at the band edges. At high concentrations, the new negatively charged impurity centers Cl^-, Br^- form, accounting for the decrease of electroconductivity with the subsequent activation energy increase (Table 1).

Thus, the effect of halogen impurities on the electroconductivity of CGS Se-As system is attributed to the change of relative concentrations of the charged defect centers (C_1^-, C_3^+) and to the occurence of new Cl^-, Br^- centers associated with clorine (bromine) atoms and the compensation of the arsenics effect on the energy spectrum of electron states.

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