Photoconduction in Pb-Ge-Se semiconducting glasses exhibiting carrier type reversal

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Photoconductivity properties of Pb$_x$Ge$_{1-x}$Se$_y$ ($0 \leq x \leq 20$) and Pb$_y$Ge$_{1-y}$Se$_x$ ($17 \leq y \leq 24$) semiconducting chalcogenide glasses have been studied and reported. Both these systems are known to exhibit carrier type reversal from $p$-type to $n$-type at certain critical compositions. It is shown that carrier type reversal gets reflected clearly in photoconductivity measurements. Temperature dependence of photoconductivity properties has also been investigated. The results are analyzed on the basis of existing models.

1 Introduction

Chalcogenide glasses in the bulk form obtained by fast quenching the melt, are generally $p$-type semiconductors. They are, in general, insensitive to the addition of impurities in small amounts (doping). This property is attributed to the valence saturation of the dopant atoms. Fermi level is considered to be pinned due to equilibrium between negatively and positively charged dangling bonds called valence alternation pairs (VAPs). In late seventies and eighties, however, it has been found that the addition of heavy elemental metallic impurities like Bi or Pb to bulk Ge based chalcogenide glasses can cause a change in the carrier type from $p$ to $n$. This discovery has led to extensive studies on these materials. This phenomenon has initiated work in the direction of fabricating a new class of $p$-$n$ junctions based entirely on semiconducting glasses, which has got several manufacturing advantages over conventional $p$-$n$ junctions.

The Pb-Ge-Se system forms homogenous glasses in the following two series.

- Pb$_x$Ge$_{1-x}$Se$_y$ ($x = 0-20$, series I)
- Pb$_y$Ge$_{1-y}$Se$_x$ ($y = 17-24$, series II)

In both these series, carrier type reversal (CTR) is found to occur at specific compositions of the materials. In series I, CTR is reported to occur at $x = 8$, while in series II CTR occurs at $y = 21$. The thermoelectric power and conductivity activation energy measurements by Tohge et al., gives clear evidence for CTR exhibited by these two series of glasses. In this paper, photoconductivity measurements around the $p$ to $n$ transition composition in both these series of glasses have been carried out. Photoconductivity as well as photodetectivity, which is the ratio of photoconductivity to the corresponding dark conductivity, have been measured as a function of composition, and it is seen that the $p \rightarrow n$ transition gets reflected in these properties. Temperature dependence of these quantities have also been studied and reported. The results are analyzed in terms of the existing photoconductivity models.

2 Experimental Details

Two series of glass samples with formulae Pb$_x$Ge$_{1-x}$Se$_y$ ($0 \leq x \leq 20$) and Pb$_y$Ge$_{1-y}$Se$_x$ ($17 \leq y \leq 24$) have been prepared in the bulk form by the well established melt quenching technique. Appropriate amounts of high purity constituents are weighed and taken in evacuated quartz ampoules and sealed. The ampoules are then kept in a high temperature furnace at 1000 °C for 24 hrs with intermittent rotation of the ampoules for uniform mixing of the constituents. The ampoules are then quenched in ice water at a cooling rate of $\approx 200$ K sec$^{-1}$. The amorphous nature of the samples have been confirmed by XRD technique.

The samples are then cut and polished to appropriate sizes for measurements. Samples with surface area $= 3 \times 3$ mm$^2$ and thickness $= 0.5$ mm
have been used for the present measurements. The sample is sandwiched between two SnO2 coated conducting transparent glass plates acting as electrodes. The sample holder is kept in an enclosed chamber, which can be evacuated and heated. The temperature of the sample is measured and controlled within ±0.1 K using a temperature controller. A 120 mW He-Cd laser (λ = 442 nm) is used as the source of light to initiate photoconduction. The current is measured using a picammeter in a two probe setup. Steady state (dc) photoconductivity is obtained as the difference between the total conductivity under illumination and the corresponding dark conductivity.

3 Results and Discussion

The composition dependence of photoconductivity and photodetectivity for the Pb, Ge~1' Se~x system of glasses are shown in Fig. 1. At x=8, which corresponds to the p→n transition composition, both photoconductivity and photodetectivity show sharp increases. Fig. 2. shows the composition dependence of photoconductivity and photodetectivity for the Pb, Ge,Se~x system. In this case, at the critical composition y=21, photoconductivity shows a minimum, while photodetectivity shows a sharp dip.

The temperature dependence of photoconductivity and photodetectivity have been investigated for selected compositions on either side of the critical compositions in both the series. These results are shown in Figs 3 and 4. It may be noted that in all compositions in both the series, photoconductivity increases with temperature, whereas photodetectivity decreases with temperature.

The results show that the p→n transitions exhibited by the two Pb-Ge-Se systems are clearly reflected in photoconductivity measurements. In series I, there is a sharp increase in photoconductivity around the transition composition, while in series II, photoconductivity decreases up to the transition composition and then increases, exhibiting a threshold minimum at the transition composition.

Presence of charged defect pairs of the type C;~ and C; is characteristic of chalcogenide glasses. Their formation can be represented by a reaction of the form, 2C;~ → C;~ + C;+, where C represents a chalcogen. The superscript is the formal charge on the chalcogen and the subscript denotes the number of covalent bonds by which the chalcogen atom is connected to other atoms. Charge transport in chalcogenide glasses occurs through the participation of charged defects. The motion of C; centers in chalcogenide glasses is more facile than that of C; centers so that chalcogenide glasses are generally p type conductors.

When Pb is introduced into the Ge-Se network, C; centers are created and their concentration is equal to that of Pb itself. Vaidyanathan et al. have calculated the values for the ratios of different types of defects in Pb,Ge,Se~x glasses. It is seen that as the Pb atom concentration increases from 5 to 20, the value of [C;]/[C;], increases by a factor of 10, while the value of [C;]/[C;] decreases by a factor of 10. This means that the ratio, [C;]/[C;] vary by nearly two orders of magnitude. For low values of x, C; centers are the major charge carriers and the glasses are p type. As x increases, C; centers become the dominant charge carriers and the system switches to an n-type semiconductor. At the same time, the activation energy decreases with x, which means that the concentration of [C;] increases with x, and so the transition is gradual in this case. For Pb,Ge,Se~x, system activation energy also increases. Therefore, concentration of C; decreases and C; increases, so that p→n transition in this system is rather sharp.

Vaidyanathan et al. have proposed a band structure model to account for the transition exhibited by the Pb-Ge-Se system. Here it is assumed that Ge is always tetrahedrally coordinated and Pb is octahedrally coordinated. In this structure, the top of the lone pair band is constituted of C; states. Electronic transport between C; states takes place through an empty sp3d2 state. When the Pb concentration is increased, sp3d2 band as well as the C; states increase rapidly, and hence the electronic contribution to conductivity also increases. Thus the p→n transition in Pb,Ge,Se~x system occurs due to
the spreading of the sp'd' band, which causes a decrease in the sp'd' lone pair band gap. In Pb$_x$Ge$_{12-x}$Se$_{38}$ system, for small values of $x$, sp'd' band is well above the lone pair band. As the value of $x$ increases, the lone pair band spreads upwards in energy because of the perturbation of lone pair levels caused by the presence of larger number of tetrahedrally bonded centres. As a result, the sp'd' band and the lone pair band become closer, and the electronic contribution to the conductivity increases. Thus the CTR in Pb$_x$Ge$_{12-x}$Se$_{38}$ system occurs due to the upward movement of the lone pair levels, closing in the sp'd' lone pair band gap.

For Pb$_x$Ge$_{12-x}$Se$_{38}$ system, the composition dependence of photoconductivity shows that photoconductivity increases with $x$, with a sharp increase at $x=8$. For this series, activation energy decreases with $x$, with a clear slope change at the critical composition. Also, in this case a spreading of the sp'd' band occurs resulting in CTR. For the Pb$_x$Ge$_{12-x}$Se$_{38}$ system, photoconductivity shows a minimum at $x=21$. For this series activation energy shows a maximum at that composition and CTR occurs due to an upward shift of the lone pair levels. Thus, it can be seen that the composition dependence of photoconductivity in both the series is consistent with the variation of conductivity activation energy with composition.

\[ \Delta \sigma = e (\Delta n \mu_n + \Delta p \mu_p) \]
The photoconducting behaviour of these samples is close to that of a Type II photoconductor as per the ABFH model. According to this model, the photoconductivity behaviour of chalcogenide glasses have been classified into Type I and Type II. For Type I photoconductors, photoconductivity has a maximum at a specific temperature \( T_m \). For \( T < T_m \), photoconductivity magnitude is generally larger than the dark conductivity, while for \( T > T_m \) it is smaller than dark conductivity. For Type II photoconductors, the photoconductivity maximum is absent. Photoconductivity increases monotonically with increasing temperature and, in general, photoconductivity is much smaller than dark conductivity. On the basis of the energy level diagram suggested by the ABFH model, transitions from localized to localized states are dominant in a Type II photoconductor, over the whole measurable range. The temperature dependence of photoconductivity of Pb-Ge-Se systems shows that, photoconductivity increases monotonically with temperature in the temperature range in which measurements are carried out. Moreover, the magnitude of photoconductivity is less than that of dark conductivity. This means that the photoconductivity behaviour of these samples is close to that of a Type II photoconductor.

4 Conclusions

Photoconductivity measurements in two series of Pb-Ge-Se system of glasses have been carried out. Both the series exhibit a \( p \rightarrow n \) transition and this transition is clearly reflected in the present measurements. It is found that the composition dependence of photoconductivity and photodetectivity are consistent with the corresponding variations in conductivity activation energy. Temperature dependence of photoconductivity and photodetectivity have been reported and the results are analysed in terms of the existing models.

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References