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Effect of indium impurities on the electrical properties of amorphous $Ga_{30}Se_{70}$

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Abstract. Temperature dependences of the dark conductivity and the photoconductivity for amorphous thin films of $Ga_{30}Se_{70-x}In_x$ in the temperature range 298–328 K have been reported. The dark conductivity and the photoconductivity increase at all temperatures as the concentration of In ($x = 0$, 5, 10, 15 and 20) increases. The results are interpreted in terms of the shift of Fermi level in impurity-incorporated amorphous $Ga_{30}Se_{70}$ binary alloy.

1. Introduction

Chalcogenide glasses have attracted much attention because of their potential applications in solid state devices. Impurity effects in chalcogenide glasses may have importance in fabricating glassy semiconductors. Mott [1] suggested that the impurity atom can satisfy its valence requirements by adjusting its nearest-neighbour environment; thus doping produces little effect on the electrical properties. Several workers [2–4] reported an impurity effect in chalcogenide glasses and found that large concentrations are required to shift the Fermi level. Photoconductivity measurements are an important tool in studying the recombination process, which gives information regarding the defect states.

In the present work, we have studied the electrical transport of selenium as it is widely used in photographic drums, but it does have a disadvantage in the pure state because of its short lifetime and low sensitivity. Certain additives (e.g. Te, Bi, Ge, Sb and Ga) are used to overcome these problems. We have chosen gallium as an additive material because it appears to be a quick hardener when added to pure selenium. Also, it is a typical metal having a low melting point (28 °C) and a very high boiling point (2403 °C). Recently, gallium was used in doping semiconductors and producing solid state devices. Moreover, gallium readily alloys with most metals and has been used as a component of low-melting alloys. It has also become an attractive material as a substrate because of its good lattice matching with solid solutions of III–VI compound semiconductors, which are very useful for the fabrication of solid state devices. Sapre and Mande [5] conducted structural studies of Ga–Se binary alloy in the crystalline state but we have studied the structural [6] as well as the electrical properties in the amorphous state.

The present paper reports the effect of indium impurity on the dark conductivity and photoconductivity (steady state and transient) in vacuum-evaporated thin films of $Ga_{30}Se_{70}$, $Ga_{30}Se_{65}In_5$, $Ga_{30}Se_{60}In_{10}$, $Ga_{30}Se_{55}In_{15}$ and $Ga_{30}Se_{50}In_{20}$ with indium atoms incorporated in the melt.

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2. Experimental details

2.1. Sample preparation

Glassy alloys of $Ga_{30}Se_{70-x}In_x$ (x = 0, 5, 10, 15 and 20) were prepared by the quenching technique. High-purity (99.999%) materials were weighed according to their atomic percentages and sealed in quartz ampoules under a vacuum of about 10^{-5} Torr. The ampoules were heated to 650 °C at 3–4 °C min^{-1}; they were frequently rocked for 12 h to make the melt homogeneous and then quenched into ice–water. The glassy nature was verified by x-ray diffraction.

Thin films of glassy alloys were prepared by the vacuum evaporation technique under a vacuum of about 10^{-6} Torr on degassed glass substrates with pre-deposited indium electrodes. A coplanar structure of amorphous thin films (length, 1.5 cm; electrode gap, 0.06 cm; thickness, about 5000 Å) was used for the photoconductivity measurements. The films were kept in the dark deposition chamber for 18 h before mounting them in the sample holder. This was done to allow room-temperature annealing as suggested by Abkowitz [7]. The homogeneity, atomic percentages and amorphous nature of the films were confirmed by scanning electron microscopy (JSM 840 electron microscope). It has an electron channelling pattern mode. Using this mode, one can easily find whether the films are of a single-crystal nature or not. As we are not able to see the Kikuchi lines, nor any grains up to a size of 40 Å which are characteristic of crystalline material, thus we conclude that these films are amorphous in nature. An EDXA facility was used to verify the composition of the films. These films show the same atomic ratio as reported here for Ga–Se–In. The variation observed was less than 1%.

2.2. Dark conductivity

The dark conductivity of the amorphous films was measured in a metallic cryostat under a vacuum of about 10^{-3} Torr. The I–V characteristics of all the films in the dark and in the presence of light show ohmic contacts up to 30 V. The present measurements were made at a DC voltage of 1.5 V, and the DC was measured with a programmable digital electrometer (Keithley model 617). Before measuring the dark current the films were annealed in vacuum at 328 K. The temperature was measured with a calibrated copper–constantan thermocouple.

2.3. Photoconductivity

To measure the transient photoconductivity of the amorphous thin films we exposed them to a 100 W tungsten lamp through the transparent window of the cryostat. Optical filters were used to obtain light of the desired wavelength (420, 546 and 660 nm). The intensity of light was varied by changing the voltage across the lamp. The relative intensity was measured with a luxmeter. The rise and decay of the photocurrent were measured as a function of time with a programmable digital electrometer (Keithley model 617).

3. Results

3.1. Dark conductivity

Figure 1 shows the temperature dependence of the dark conductivity for amorphous $Ga_{30}Se_{70-x}In_x$ (x = 0, 5, 10, 15 and 20). It is clear from the figure that the plot of

ln σ_d against $1000/T$ is linear in nature in the measurement temperature range 298–328 K. This indicates that the electrical conduction is through an activated process with a single activation energy in this temperature range. The dark conductivity σ_d can therefore be expressed by the conventional relation

$$\sigma_d = \sigma_0 \exp(-\Delta E/kT) \tag{1}$$

where ΔE is the activation energy for DC conduction, k is the Boltzmann constant and σ_0 is the pre-exponential factor. The values for the activation energy ΔE are calculated for various samples using the slopes of the curves in figure 1. The values of ΔE, σ_0 and σ_d at 298 K are given in table 1. The values of ΔE and σ_d show that the dark conductivity σ_d increases with increase in the indium concentration and the activation energy decreases with increasing indium concentration up to 10 at.%. However, the values of σ_d and ΔE increase abruptly when the concentration of indium is raised to 15 at.% or higher (figure 2). Table 1 indicates that the value of σ_0 is almost constant up to an indium concentration of 10 at.% while, at an indium concentration of 15 at.% or higher, σ_0 increases abruptly.

Table 1. Electrical parameters in a-$Ga_{30}Se_{70-x}In_x$ at 298 K and electronegativity X_c.

x	σ_d (Ω^{-1} cm^{-1})	ΔE (eV)	σ_0 (Ω^{-1} cm^{-1})	σ_{ph}/σ_d (108 lux)	V (V)	X_c
0	5.34×10^{-10}	0.58	3.37	0.14	0.10	2.12
5	9.73×10^{-10}	0.56	2.82	0.60	0.30	2.08
10	4.82×10^{-9}	0.53	4.35	0.10	0.67	2.05
15	5.08×10^{-7}	0.65	4.89×10^{4}	0.23	0.54	2.01
20	8.31×10^{-7}	0.75	1.12×10^{6}	0.28	0.62	1.98

3.2. Steady-state photoconductivity

Figure 3 shows the temperature dependence of photoconductivity σ_{ph} at a particular intensity (108 lux) and wavelength (660 nm). It is clear from this figure that σ_{ph} increases with increase in temperature in the entire temperature range of the present measurement for an indium concentration of up to 10 at.%. However, the photocurrent σ_{ph} decreases with increase in temperature for indium concentrations of 15 at.% or higher. At a particular temperature, I_{ph} increases with increase in the indium concentration (see figure 3). A similar variation was also observed for the dark conductivity (see figure 2). From the measured values of I_d and I_{ph} we have calculated the photosensitivity σ_{ph}/σ_d at a particular intensity (108 lux) and the results are given in table 1. These results indicate that the photosensitivity is almost constant and is quite low for all the indium concentrations. A low photosensitivity has also been reported by other workers [8, 9].

The intensity dependence of the photoconductivity is also studied in the entire temperature range of the experiment. The results of the intensity dependence on photoconductivity at room temperature are plotted in figure 4. This figure indicates that I_{ph} follows a power law with increasing intensity F:

$$I_{ph} \propto F^{\gamma}. \tag{2}$$

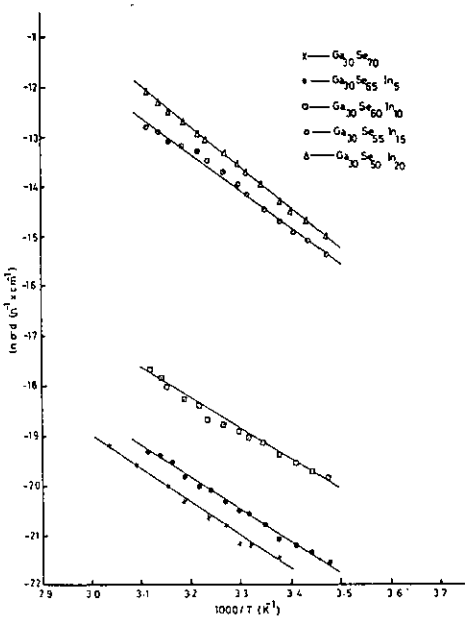

Figure 1. Temperature dependence of the dark conductivity at various In impurity concentrations.

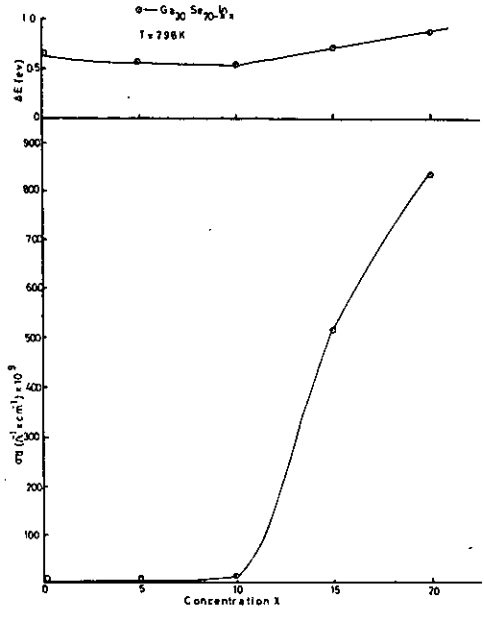

Figure 2. (*a*) Concentration dependence of the activation energy ΔE. (*b*) Concentration dependence of the dark conductivity σ_d at 298 K.

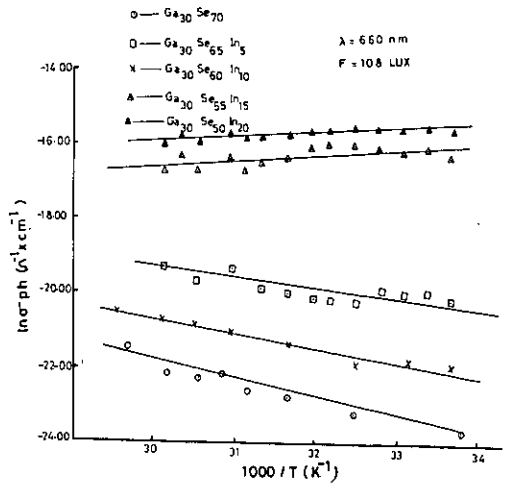

Figure 3. Temperature dependence of the photoconductivity at various indium impurity concentrations at an intensity of 108 lux.

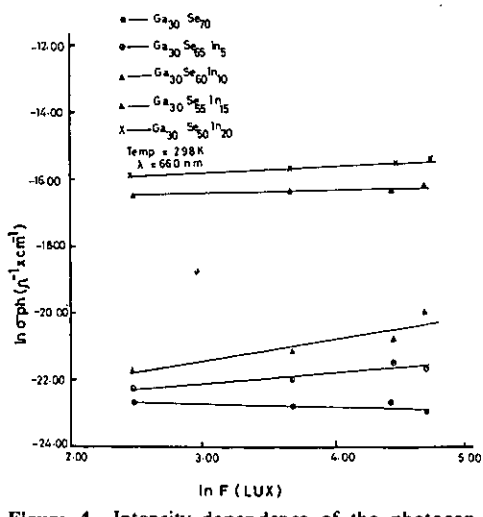

Figure 4. Intensity dependence of the photoconductivity at various indium impurity concentrations; the measurements were made at 298 K.

The values of γ for all the samples have been calculated from the slopes of figure 4 (table 1). The values of γ are less than 0.5 at 298 K and were found to be independent

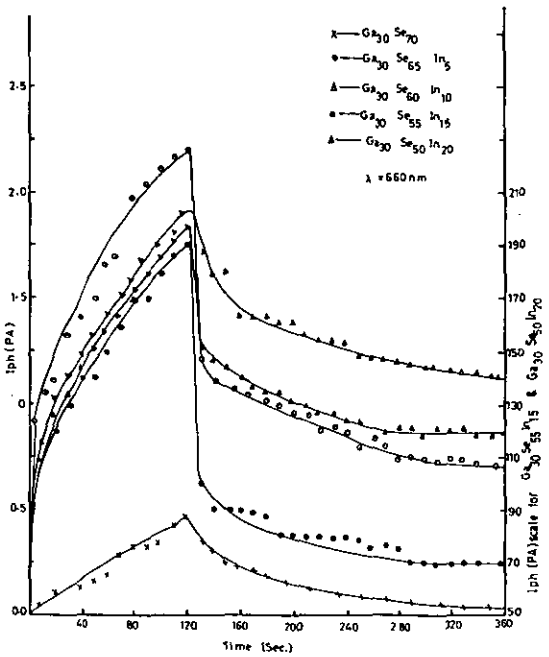

Figure 5. Transient photocurrent at room temperature (298 K) at a particular intensity of 108 lux for amorphous thin films of $Ga_{30}Se_{70-x}In_x$.

of the indium concentration. The values of $I_{ph}(< I_d)$ and $\gamma(< 0.5)$ indicate that quadratic recombination [10] might be taking place.

3.3. Transient photoconductivity

Figure 5 shows the rise and decay of photocurrent in all the samples at a particular wavelength (660 nm). However, a comparative study of the decay (figure 5) shows that the decay of the photocurrent is fast at an indium concentration of 15 at.% or higher. The photocurrent rises monotonically to the steady-state value. A persistent photocurrent is also observed in all the samples. A persistent photocurrent and slow decay is also observed in various other chalcogenide glasses [11–13]. The decay of the photocurrent is exponential. A comparative study of figure 3 indicates that the photocurrent I_{ph} increases as the indium concentration increases.

A strange anomalous behaviour has been observed for $Ga_{30}Se_{70}$ under white light (figure 6). The photocurrent becomes negative when the sample was exposed to light but, after indium impurities were added, the anomalous behaviour under white light ceased and the photocurrent became positive. At wavelengths of 420 and 546 nm, a negative photocurrent was also observed at low temperatures but a positive photocurrent at higher temperatures (figures 7 and 8). The behaviour of the negative photocurrent in the $Ga_{30}Se_{70}$ sample is due to the defect state present at two different levels, which creates holes in the recombination process [14]. The addition of indium impurities has overcome the defect states and the photocurrent rises monotonically. Stockmann [14] has also pointed out that the negative photocurrent appears when photons in semiconductors mainly create minority charge carriers which recombine with thermally generated majority carriers. On the other hand, on the addition of indium to the system the minority charge carrier increases, resulting in an increase in its conductivity so that the photoconductivity becomes positive.

A comparative study indicates that the dark conductivity and photoconductivity

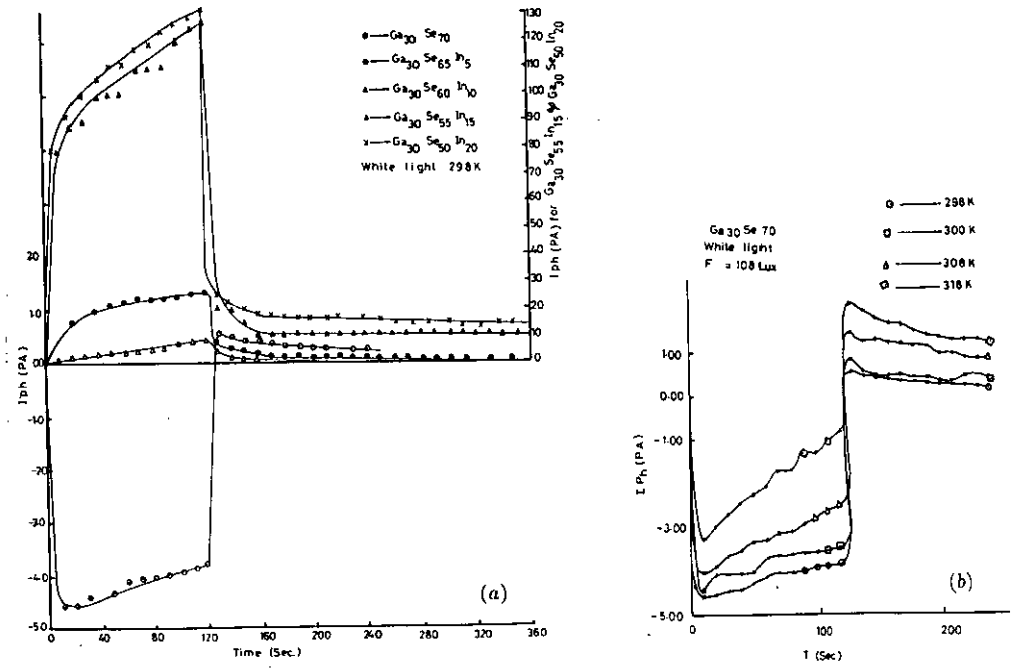

Figure 6. (*a*) Transient photocurrent at room temperature (298 K) at a particular intensity of 108 lux of white light for amorphous thin films of $Ga_{30}Se_{70-x}In_x$. (*b*) Transient photocurrent at various temperatures under white light in amorphous $Ga_{30}Se_{70}$.

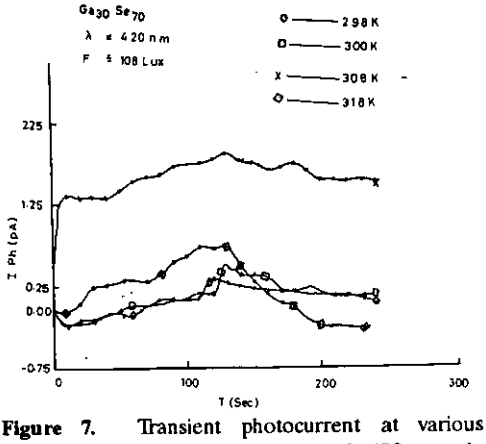

Figure 7. Transient photocurrent at various temperatures for a wavelength of 420 nm in amorphous $Ga_{30}Se_{70}$.

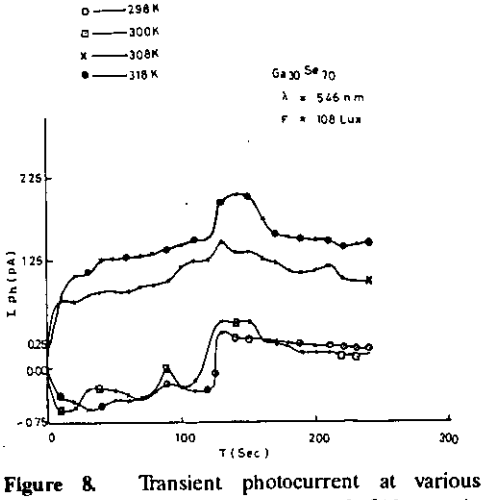

Figure 8. Transient photocurrent at various temperatures for a wavelength of 546 nm in amorphous $Ga_{30}Se_{70}$.

increase after incorporation of indium at all temperatures and intensities. These results are discussed in terms of the shift in Fermi level (figure 9).

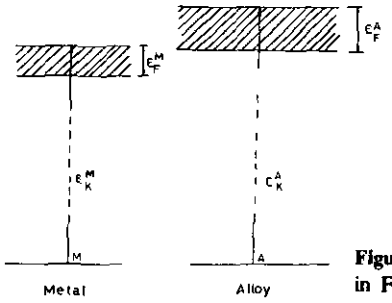

Figure 9. Energy level diagram indicating the shift in Fermi level.

4. Discussion

We can interpret the results in two ways: firstly, by using the concept of the shift in Fermi level and, secondly, by taking into consideration the hopping of charge carriers in the defect states. However, the conductivity of the samples increases and the photosensitivity becomes almost constant on increase in the indium concentration. On the addition of impurities, defect states are increased in the mobility gap and the lifetime of the charge carrier decreases [15]. When this is taken into account, the conductivity as well as photosensitivity should decrease owing to the increase in defect states, but in our case the results are in contradiction to the hopping process. An increase in the dark conductivity and a corresponding decrease in activation energy are found to be associated with a shift in the Fermi level [2, 3, 16, 17] in impurity-doped chalcogenide glasses (figure 9). The increase in σ_d up to 10 at.% In without any appreciable change in σ_0 shows the alloying effect in Ga–Se alloys. It also shows that the Fermi level changes after incorporation of indium. Following Mott and Davis [18], a value of σ_0 in the range 10^3–$10^4\ \Omega^{-1}\ cm^{-1}$ in chalcogenide glasses indicates that the conduction is mostly in extended states. A smaller value of σ_0 indicates a wide range of localized states. The maximum change in σ_0 is observed when 20 at.% In is incorporated (σ_0 changes from 3.37 to $1.12 \times 10^6\ \Omega^{-1}\ cm^{-1}$). The results are explained using the shift in Fermi level on addition of indium impurities. Several workers [19–23] have pointed out that, when a metal undergoes chemical combination, it forms a compound where the distribution of charge takes place in the outer level to the most likely level or surface which can be affected by the redistribution of electrons in the Fermi level or surface. That is, when a metal undergoes chemical combination and forms a compound its Fermi level should change. This can also be explained on the basis of a change in electronegativity. According to Sanderson [24], when an element combines with other elements, they come together at an intermediate value of electronegativity which is the geometric mean of the combining atoms. In the present case we have calculated the electronegativity of different systems using Sanderson's [24] equalization principle. From table 1 we observed that the electronegativity of the system decreases as the In concentration increases. So, one can infer that the increases in DC conductivity decreases the electronegativity of the system.

5. Conclusion

Steady-state and transient photoconductivity measurement have been made on the amorphous thin films of $Ga_{30}Se_{70-x}In_x$ alloys for a wavelength of 660 nm in the temperature range 298–328 K. The DC conductivity increases as the In concentration

increases, while the activation energy decreases on increase in the In concentration up to 10 at.% and increases at 15 at.% or higher. The increase in conductivity, with a corresponding decrease in activation energy for DC conduction up to 10 at.% In without any appreciable effect on σ_0, suggests that the alloying effects in $Ga_{30}Se_{70}$ binary alloy may be due to the shift in the Fermi level in impurity-incorporated samples. The photocurrent increases by three orders of magnitude when a higher In concentration (15 or 20 at.%) is added to the system. The value of γ is less than 0.5 in all the samples, which shows the occurrence of quadratic recombination.

The transient photoconductivity at room temperature in white light and wavelengths of 420 and 546 nm gives a negative photocurrent in the $Ga_{30}Se_{70}$ sample. On adding In impurities under white light and at higher temperatures for wavelengths of 420 and 546 nm the photocurrent becomes positive and rises monotonically.

The increase in transient photoconductivity at a wavelength of 660 nm in the temperature range 298–328 K shows that the incorporation of In shifts the Fermi level.

The values of electronegativity calculated for the system decreases on adding In impurities. On the basis of the electronegativity of the systems, it can also be concluded that the DC conductivity increases with decrease in electronegativity on adding In impurities to the system.

Acknowledgment

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