Photoconductive relaxation studies of SnSe thin films

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Abstract. The compound tin selenide was prepared from the constituent elements (Sn and Se) using the standard fusing technique and from X-ray diffraction studies it was identified as tin selenide. Thin films of SnSe were obtained on thoroughly cleaned glass substrates by vacuum sublimation on substrates maintained at 301 K. The photoconductive relaxation of these films was studied with oxidation. The results have been explained with the help of grain boundary potential barrier model.

Keywords. Thin films; tin selenide; photoconductive relaxation; grain boundary potential barrier.

1. Introduction

Tin selenide whose room temperature indirect gap is about 0·9 eV, possesses some essential solar materials qualities (Loferski 1956, 1963; Rodot 1975, 1977). Photoelectric and optical studies of tin selenide polycrystalline films have been reported to some extent in literature (Bennouna *et al* 1983; Dang Tran Quan 1984; Subba Rao and Chaudhuri 1985; Engelken *et al* 1986). Charge carrier photorelaxation time is a basic parameter to characterize the photoelectronic properties of semiconductor. The present investigation was undertaken to study the photoconductance relaxation phenomenon in tin selenide polycrystalline thin films with oxidation as well as microstructural effects. The results have been explained with the help of grain boundary potential barrier. The photorelaxation time of charge carriers is found to lie between 50 and 150 sec for as grown SnSe films deposited on glass substrates keeping the substrates at 301 K during deposition.

2. Experimental

To obtain thin films, the compound already prepared in a polycrystalline powder form was used. The polycrystalline powder was obtained after direct synthesis in an evacuated quartz ampoule (10^{-4} Pa), the initial components (Sn and Se) having a 5N degree of purity (Sn and Se) (Nuclear Fuel Complex, Hyderabad, India). The synthesis temperature was about 1133 K. After 30 h of constant heating, it was quenched in water. The final compound was analysed with X-ray diffraction and showed that the structure was orthorhombic with lattice constants $a = 11·4$ Å, $b = 4·16$ Å and $c = 4·42$ Å. On comparing with available data in literature (Agnihotri *et al* 1979), the compound was identified as tin selenide.

Evaporation was performed by ohmic heating. The deposition rate was about 30 nm/min, the thoroughly cleaned glass substrates being at 20 cm from the molybdenum boat. During deposition, pressure went up to 10^{-5} to 10^{-4} Pa. Thickness of the samples were determined both by weighing and by interference methods.

Electrical conductivity and photoconductivity measurements were carried out in a conventional apparatus suitable for making measurements continuously from high

temperatures to low temperatures (301 to 110 K) (Subba Rao 1988). The amount of light falling on the sample during photoconductivity measurement was determined with the help of Eppley's calibrated thermopile. The source of light was a tungsten halogen lamp fed by a constant voltage supply. The light intensity of the order of 200 mW/cm^2 with tungsten halogen lamp (600 W, 230 V) in all cases was maintained at a constant level.

3. Results and discussion

The films deposited in vacuum and exposed to atmosphere after deposition are found to be *P*-type as determined by thermoelectric and Hall measurements. X-ray and electron diffraction studies revealed that these films consist of crystallites of different sizes ranging from 25 nm to 35 nm deposited on glass substrates at 301 K (Subba Rao
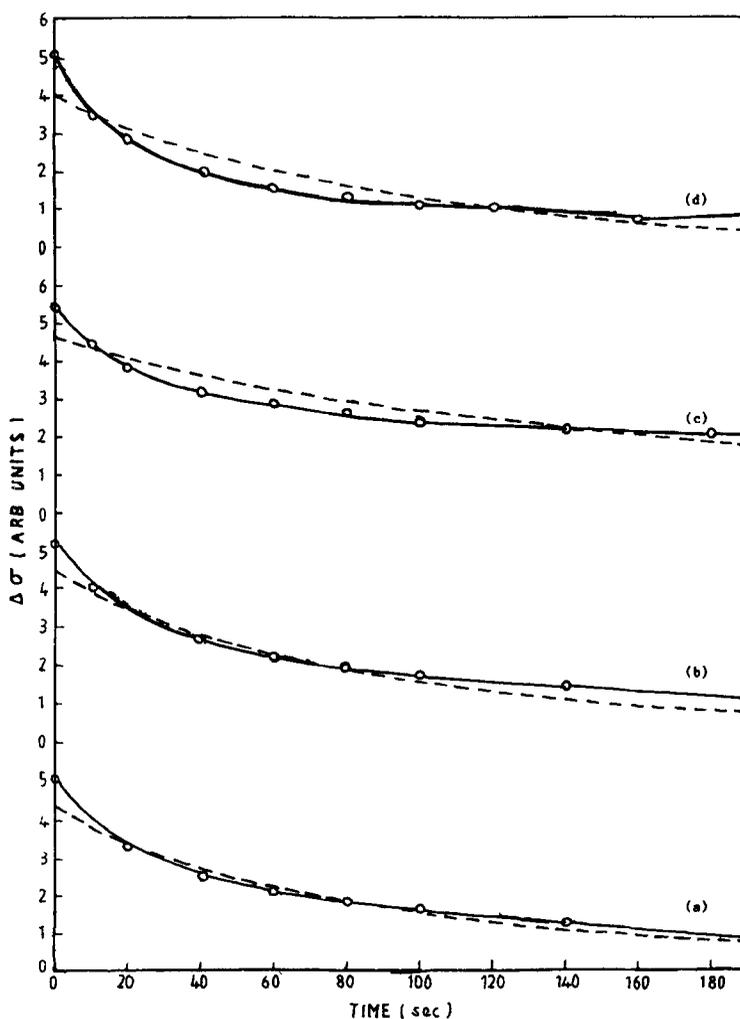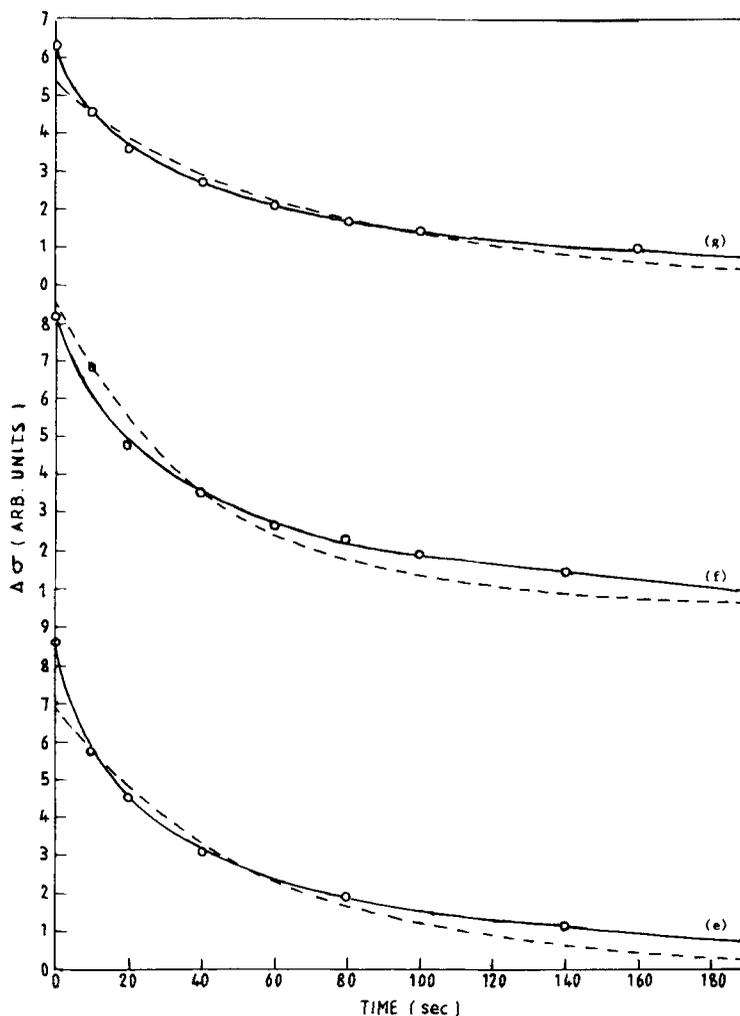
Figure 1.

Figure 1. Photorelaxation curves of an as-grown film ($d = 300$ nm) deposited on glass substrate and after aging for different periods of time. ———, Experimental results and -----, theoretical results. (a) as-grown film, (b) after aging for 8 h, (c) after aging for 2 days, (d) after aging for 24 days, (e) after aging for 40 days, (f) after aging for 31 days and (g) after aging for 36 days.

et al 1985). From the temperature variation of carrier concentration, the values of trap energy (E_t) are estimated. The values of E_t are found to lie between 0·062 eV and 0·025 eV (Subba Rao and Chaudhuri 1985). The value of grain boundary potential barrier estimated from the excess photoconduction as well as from the variation of mobility with temperature was found to be of the order of 0·17 eV (Subba Rao and Chaudhuri 1985). Figure 1 shows the variation of photoconductance relaxation of SnSe as grown films with different aging times. From the experimental data it is apparent that the photorelaxation time constant increases with aging in these films (figure 2).

The effect of photoexcitation of tin selenide films can be described with the increase of carrier concentration in the grain in such films, when the light is put off the change of
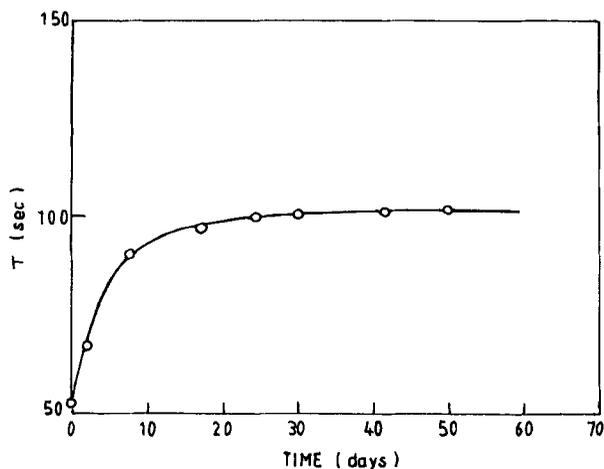
Figure 2. Variation of photoconductive relaxation time constant of as-grown film ($d = 300$ nm) of SnSe with aging time.

Table 1. Aging time along with a photorelaxation time of charge carriers of SnSe thin films.

Aging time (days)	Photorelaxation time (τ) (sec)
As grown	53
2	67
7	91
24	100
30	101
90	143

hole density in the valence band per unit time may be written as

$$\frac{dp}{dt} = -\gamma_p(p + \Delta p)\Delta p_t e^{-\phi 1/KT}, \tag{1}$$

where $\phi 1$ is the barrier height in eV under illumination and Δp_t the density of trapped carrier at the crystallite boundary.

For low level photoexcitation, (1) can be expressed as

$$\frac{dp}{dt} = -\gamma'_p p\Delta p e^{-\phi 1/KT}, \tag{2}$$

where γ'_p is the effective coefficient of capture of holes by traps. Solving this equation, we obtain

$$\Delta p = (\Delta P_0)e^{-t/\tau}, \tag{3}$$

where

$$\tau^{-1} = \gamma'_p p e^{-\phi 1/KT}. \tag{4}$$

From expression (3), it is clear that the increase of τ with time is mainly due to the increase of grain boundary potential barrier with time due to diffusion of oxygen or oxidation at the grain boundary.

The variation of photorelaxation time (τ) with aging time is shown in table 1. The effective coefficient of capture of holes by traps (γ'_p) for as grown SnSe film just after deposition is calculated from the relation (Seto 1975). The value of γ'_p obtained is observed to be of the order of $1\cdot78 \times 10^{-21}\,\text{cm}^3/\text{sec}$.

4. Conclusions

Tin selenide thin films were prepared by vacuum sublimation technique on glass substrates at 301 K. The photoconductive relaxation studies reveal that the excess carrier generation was observed from the grain boundaries and the photorelaxation time increases with aging of the films.

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