

Some investigations on offstoichiometric zinc telluride films

I. S. ATHWAL, R. K. BEDI

Solid State Research Laboratory, Department of Physics, Guru Nanak Dev University, Amritsar-143 005, India

Stoichiometric and offstoichiometric zinc telluride thin films are prepared by flash evaporation onto glass substrate at 50°C. The films are investigated by transmission electron microscopy, electron diffraction (for selected area diffraction and micro area diffraction) and IR transmittance. The electrical resistivity and its temperature dependence were studied by sandwiching the zinc telluride film between silver electrodes making ohmic contacts. The degradation in structure has been observed on disturbing the stoichiometry of zinc telluride films. Interestingly, the composition dependence of electrical resistivity of the films agrees well with the IR transmission spectra.

1. Introduction

The Group II-VI compounds are known as large bandgap semiconductors and find many applications. Zinc telluride, an important member of the Group II-VI semiconductor family, is highly prone to self compensation, which can be explained with the help of self-generated doubly-ionized metal vacancies [1]. The availability of very high purity materials and sophisticated preparation and analytical techniques have led to a better understanding of the problem of self compensation. Remarkable work in this regard has been done by Dean *et al.* [2].

Zinc telluride always exhibits p-type conductivity. Although Fisher *et al.* [3] have reported the investigations on high resistivity ($10^7 \Omega \text{ cm}$) n-type zinc telluride crystals, no such report is available for films as yet. Senokosov *et al.* [4, 5] have made investigations on single crystal p-ZnTe films and found current oscillations to be present. The space charge limited currents and thermally stimulated currents (TSC) in ZnTe films have been studied by Hino and Yamashita [6]. Burgelman [7] explained the conduction mechanism in ZnTe films using the Poole Frankel effect and Schottky emission. Brodie and co-workers [8-10] prepared amorphous films of ZnTe and investigated their electron transport properties.

In the present communication we report the structure through transmission electron microscopy (TEM) and selected area diffraction (SAD), the electrical resistivity and its temperature dependence and IR transmission spectra of high purity (undoped) zinc telluride films and the zinc telluride films with intentionally disturbed stoichiometry. An attempt has been made to study the role of excess of zinc and tellurium contents in the zinc telluride films.

2. Experimental details

Stoichiometric and offstoichiometric zinc telluride was synthesized from high purity (99.999%) zinc and tellurium obtained from Nuclear Fuel Complex

(India). The desired amounts of zinc and tellurium were taken in evacuated quartz ampoules at a pressure of 3×10^{-4} torr. The sealed ampoules were fired in a furnace at 1000°C for nearly 100 h, to allow the zinc and tellurium to react. After 100 h the ampoules were broken and the product was powdered to 150 mesh size. The powdered material was again sealed in quartz ampoules at a pressure of 3×10^{-4} torr and heated at 1050°C for 50 h to ensure the homogeneity of the product. The ampoules were then dropped into liquid nitrogen to freeze it rapidly and finally powdered to 150 mesh size.

The zinc telluride so obtained was evaporated onto the chemically and ultrasonically cleaned glass substrate (Blue Star PIC-1, Polar Industrial Corporation, Bombay, India) kept at 50°C. The vacuum deposition was done by flash evaporation using a rotating hopper and chute arrangement in Hind High Vacuum (India) coating unit 12A4 at a pressure of 5×10^{-5} torr using a liquid nitrogen trap. Prior to evaporation, zinc telluride and glass substrate were heated to 150°C for 1 h for degassing. The films were annealed at 200°C for 1 h to obtain structural stability. Thickness of the deposit was monitored using a quartz crystal film thickness monitor and later measured using a FECO Interferometer (Optiregion, Delhi, India).

The electrical resistivity of the films was measured by making a sandwich between silver electrodes. The sandwich metal-ZnTe-metal (M-Z-M) was fabricated in a single evacuation using a rotating mask system shown in Fig. 1. The thickness of the films under investigation was kept below $2 \mu\text{m}$. Electrical resistivity was calculated from the I-V characteristics of the sandwich. The contacts were verified to be ohmic from the symmetric straight line I-V characteristics passing through the origin.

For obtaining the transmission electron micrographs, SAD and micro area diffraction (MAD) patterns, the films were chemically detached from the glass slides and deposited on the grid of the electron

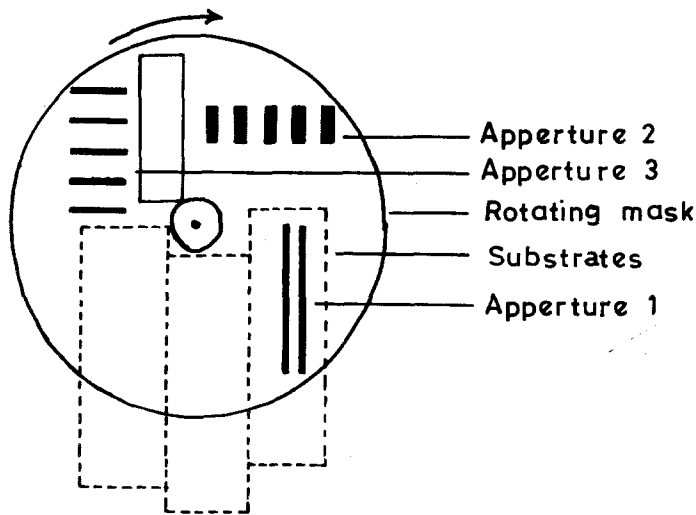


Figure 1 Schematic diagram of the rotating mask for fabrication of a metal-semiconductor-metal sandwich in a single evacuation.

microscope. The TEM and electron diffraction analysis were carried out using a JEOL (Japan) electron microscope JEM 1200 EX keeping the accelerating voltage at 120 kV. The double beam spectrometer Pye Unicam SP3-300 was used to obtain IR transmission spectra of films.

3. Results

3.1. Structure

Figs 2a and b show the TEM and electron diffraction pattern of stoichiometric zinc telluride films. The films obtained are polycrystalline in nature having an average grain size of 130 nm. The SAD pattern reflects the structural perfection within the grains of strain-free films. The TEM and SAD patterns of zinc telluride films with 2 wt % excess of zinc are shown in Figs 3a and b, respectively. The film appears to be highly strained. The same conclusion has been drawn for zinc telluride films with a deficiency of zinc atoms. The grains which are clearly visible in the stoichiometric films lose their shape and get converted into strained partially amorphous grains. The degradation of structures with excess or deficient zinc atoms can be seen from electron diffraction patterns. Due to the loss of crystallinity, the interatomic spacings also appear to be changed. The electron diffraction (SAD and MAD) rings of the same order have different diameters for the same electron wavelength and cameralelength.

3.2. Electrical resistivity

The temperature dependence of electrical resistivity

of stoichiometric and offstoichiometric zinc telluride films is shown in Fig. 4. It has been observed that the stoichiometric zinc telluride films exhibit an exponential behaviour of its resistivity with negative temperature coefficient of resistivity, (t.c.r.) and is closely governed by the equation:

$$\sigma = c\mu p_0 \exp(-E/kT) \quad (1)$$

Where $E = (E_F - E_V)$ is the activation energy of the film material [11].

The electrical resistivity of offstoichiometric zinc telluride films is a complex function of temperature. The resistivity of the films increases rapidly with temperature up to 40° C, then the increase becomes steady followed by a sharp rise. The temperature at which the sharp rise has been observed depends upon the content of excess zinc or tellurium atoms and varies between 70 to 110° C and for higher zinc content, this temperature shifts towards the lower temperature regions. The films deficient in zinc with no compensating element appear to have oscillatory temperature dependence with resistivity. The oscillations however decrease with increase in the deficiency of tellurium.

The composition dependence of electrical resistivity is shown in Fig. 5. The stoichiometric zinc telluride films appear to have a high resistivity and are found to be of the order of 95 kΩ cm at 30° C. It has been observed that a little deviation from stoichiometry lowers the resistivity very rapidly followed by an increase with excess or deficient zinc atoms. The increase in resistivity per unit deviation from

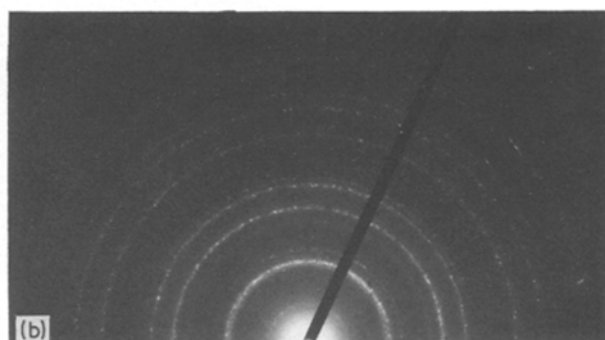
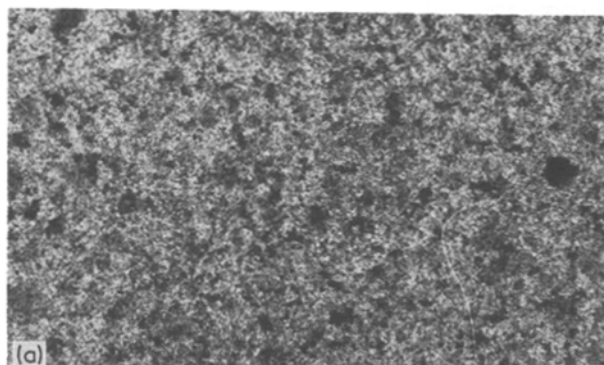


Figure 2 (a) Transmission electron micrograph and (b) SAD pattern of a stoichiometric zinc telluride thin film.

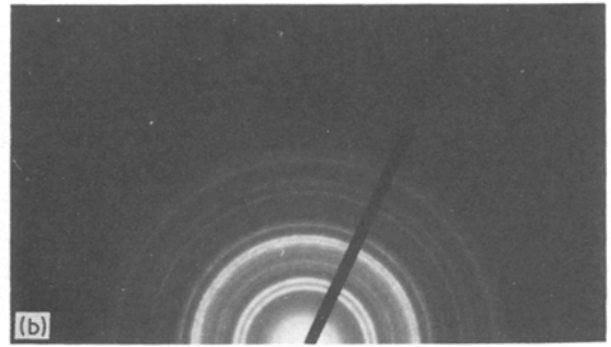
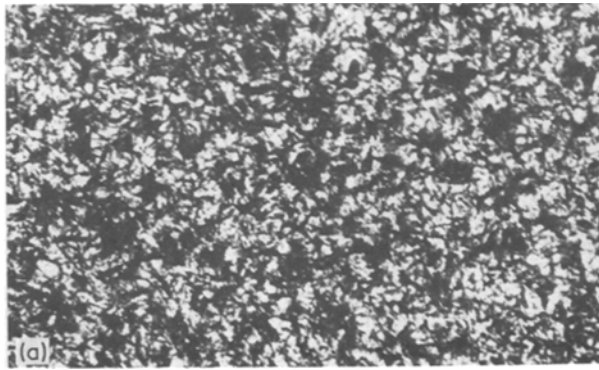


Figure 3 (a) Transmission electron micrograph and (b) electron diffraction (SAD) of an offstoichiometric zinc telluride thin film, having 2 wt % excess of zinc.

stoichiometry is greater towards the zinc-rich side than the zinc-deficient side.

The inverse temperature dependence of \log of conductivity is a straight line thus confirming the general semiconductor behaviour of stoichiometric zinc telluride film. The activation energy obtained from the slope is 1.89 eV.

3.3. Infrared absorption

Optical absorption in polycrystalline thin films arise mainly from (i) non-generative absorption of photons by surface and bulk physical imperfections and (ii) photon scattering by geometrical imperfections [12]. The physical imperfections are the deviation from stoichiometry, change in film composition near the film surface due to air absorption and their apparent doping, screening fields developed along the surface and grain boundaries and the presence or absence of long range order within the grains. The geometrical imperfections means the surface roughness, grain boundaries, inclusion of pores and vacancies etc. Depending upon the energy of the incident photons, it either brings about electron transition or phonon transition in the semiconductor material/film. The energy of IR photons is low enough not to bring about electronic transition and so gets absorbed due to phonon transition. Thus IR absorption/transmittance spectrum can be used as a tool to probe the bonding of wide band gap semiconductors.

The normalized IR transmission spectrum of stoichiometric zinc telluride films and films with 5% excess and deficiency of zinc atoms, is shown in Fig. 6. The IR spectra were normalized by considering maximum transmittance (at μm) to be 100% and changing the remaining spectrum proportionally. With such normalization the comparison between height of absorption and transmission peaks become valid. The normalized IR spectra of zinc excess and deficient zinc telluride films show remarkable change in IR transmittance peaks. The peak observed in the case of stoichiometric films around $2.5 \mu\text{m}$ gets broadened and spread from 2 to $2.5 \mu\text{m}$ for zinc deficient films. While the maximum transmittance for zinc excess films is obtained at a wavelength $2.0 \mu\text{m}$. No peak around $3.2 \mu\text{m}$ has been shown with stoichiometric zinc telluride films. The analysis revealed that there is absolutely no transmission beyond $4.75 \mu\text{m}$.

The composition dependence of normalized transmission for the various maxima and minima are plotted in Fig. 7. A sharp maximum in all the cases is observed for stoichiometric zinc telluride films. A slight disturbance in stoichiometry of the films to either side (excess or deficiency of zinc) indicate a rapid decrease in the peak height of the maxima (or depth for the minima). With further deviation from the stoichiometry the transmission peak height (depth for minima) increases. The increments appear to be

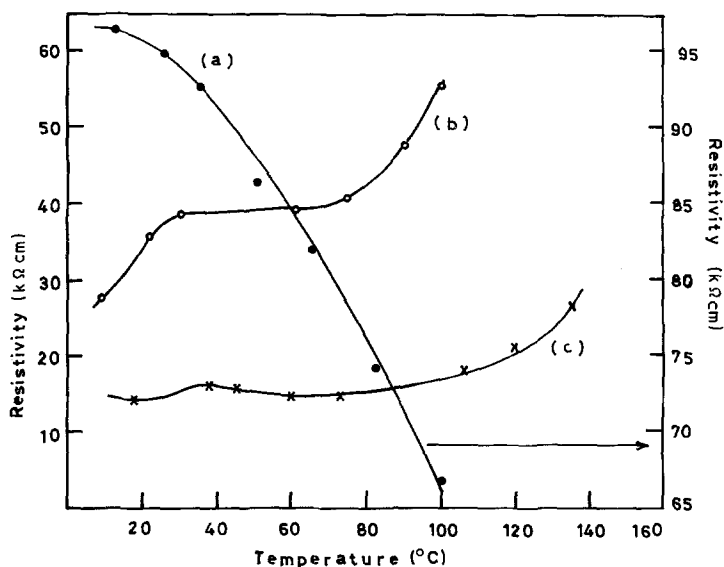


Figure 4 Temperature dependence of the electrical resistivity of zinc telluride films, (a) stoichiometric zinc telluride, (b) Zn Te + 5 wt % Zn, (c) Zn Te - 5 wt % Zn.

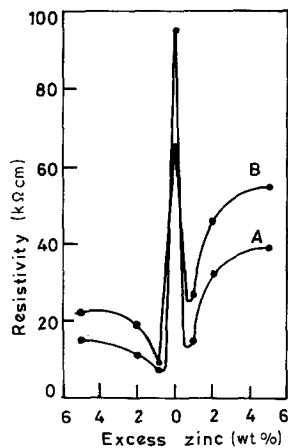


Figure 5 Composition dependence of the electrical resistivity of zinc telluride thin films at (a) 30°C and (b) 100°C.

more pronounced toward the zinc deficiency region than that of the zinc rich region.

4. Discussion

The stoichiometric zinc telluride films have polycrystalline structure with randomly oriented crystallites. The structural ordering appears to have been maintained within the crystallites as indicated by SAD and MAD patterns. On disturbing the stoichiometry, irrespective of excess zinc or tellurium, the crystallinity of the films is destroyed. As the films are prepared at low substrate temperature, the excess component is more or less uniformly distributed throughout the film. Due to a large thermal energy difference between the adatom and substrate, the adatoms thermalize very rapidly without maintaining appropriate crystallinity resulting in partially strained bonds. The strained bonds are generally associated with the change in bond lengths which may be assumed to be responsible for the change in lattice constants as revealed in the electron diffraction patterns. Thus the spreading of the electron diffraction rings may be assigned to the spatial variation in the lattice constants, and hence irregularities in the crystalline planes. The TEMs indicate the random orientation of grains.

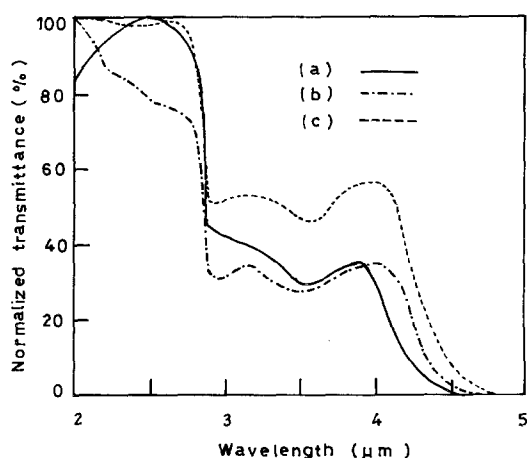


Figure 6 Normalized IR transmission spectra of stoichiometric zinc telluride thin films at room temperature. (a) Stoichiometric, (b) 5 wt % excess of zinc, (c) 5 wt % deficiency of zinc.

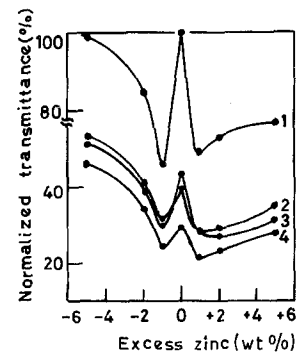


Figure 7 Composition dependence of the minima and maxima in the normalized IR transmittance in zinc telluride thin films (1) first maxima (2) second maxima, (3) first minima, (4) second minima.

A further deviation in the stoichiometry of the films results in the diffractogram becoming blurred and spread.

The electrical conductivity of the offstoichiometric films lies in the range where they may be called semiconductors but their temperature dependence of resistivity and t.c.r. are complicated. Only the stoichiometric films show semiconductor-like behaviour. The composition dependence of electrical resistivity exhibits a very sharp decrease in resistivity with a slight increase or decrease in the number of zinc atoms. This may be attributed to the self-doping of the films. In addition, the structure degradation of the film occurs. The self-doping appears to be dominant for very small deviations from stoichiometry but later the degradation in structure may be dominant for excess zinc and tellurium. Each of the segregated excess atoms is associated with a disturbance in the periodic potential of the structurally perfect crystallites, thus they act as a scattering centre. With a greater deviation from stoichiometry the excess of scattering centres may be responsible for the increase in the electrical resistivity. The composition dependence of the intensity of the IR transmission (the maxima and minima) of zinc telluride films is more or less similar to that of the electrical resistivity.

5. Conclusions

1. Only stoichiometric zinc telluride films exhibit real semiconductor-like behaviour.
2. Any deviation from stoichiometric zinc telluride, irrespective of excess or deficiency of one of the components, causes structural degradation which influences its electrical and optical properties.

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References

1. G. MANDEL, *Phys. Rev. A* **134** (1964) 1073.

2. P. J. DEAN, H. VENHGAUS, J. C. PFISTER, B. SCHANB and J. MARINE, *J. Lumin.* **16** (1978) 363.
3. A. G. FISHER, J. N. CARIDES and J. DRESNER, *Solid State Commun.* **2** (1964) 157.
4. E. A. SENKOSOV, N. M. PAVLENKO and A. N. USATYL, *Sov. Phys. Semicond.* **10** (1976) 1413.
5. T. L. MATVEEVA, N. M. PAVLENKO, E. A. SENKOSIV and A. N. USATYL, *Fiz. Tekh. Poeprovodn.* **11** (1977) 982.
6. T. HINO and K. YAMASHITA, *Jpn J. Appl. Phys.* **13** (1974) 1015.
7. M. BURGELMAN, *Solid State Electronics* **20** (1977) 523.
8. J. B. WEBB and D. E. BRODIE, *Can. J. Phys.* **53** (1975) 2481.
9. C. J. MOORE, B. S. BHARAJ and D. E. BRODIE, *ibid.* **59** (1981) 924.
10. C. J. L. MOORE and D. E. BRODIE, *ibid.* **60** (1982) 540.
11. I. S. ATHWAL, M. THAMAN and R. K. BEDI, *J. Mater. Sci.* **21** (1986) 3243.
12. J. M. PAWLIKOWSKI, Proceedings of the 3rd International Workshop on the Physics of Semiconducting Devices, World Sci. Pub., Singapore (1985) p. 138.

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