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Fabrication and electrical characterization of Al/p-$ZnIn_2Se_4$ thin film Schottky diode structure

D.K. Dhruv *, B.H. Patel

Department of Electronics, Sardar Patel University, Vallabh Vidyanagar 388120, Gujarat, India

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ABSTRACT

Polycrystalline thin films of ternary $ZnIn_2Se_4$ compound with p-type conductivity were deposited on a pre-deposited aluminium (*Al*) film by a flash evaporation technique. A Schottky diode comprising of Al/p-$ZnIn_2Se_4$ structure was fabricated and characterized in the temperature range 303–323 K in dark condition. The Schottky diode was subjected to current (*I*)-voltage (*V*) and capacitance (*C*)-voltage (*V*) characterization. The Al/p-$ZnIn_2Se_4$ Schottky diode showed behaviour typical of a *p-n* junction diode. The devices showed very good diode behaviour with the rectification ratio of about 10^5 at 1.0 V in dark. The Schottky diode ideality factor, barrier height, carrier concentration, *etc.* were derived from *I-V* and *C-V* measurements. At lower applied voltages ($V \leq 0.5$ V), the electrical conduction was found to take place by thermionic emission (*TE*) whereas at higher voltages ($V > 0.5$ V), a space charge limited conduction mechanism (*SCLC*) was observed. An energy band diagram was constructed for fabricated Al/p-$ZnIn_2Se_4$ Schottky diode.

1. Introduction

Typical Schottky barrier diodes (*SBDs*) have a simple structure of metal-semiconductor (*MS*) contact. In spite of their simple structure, they have been playing an important role in large number of compound semiconductor electronic devices [1]. There are various applications for Schottky barriers in the area of integrated circuits including high-frequency units, photodiodes and power Schottky diodes [2]. The interface quality between metal and semiconductor affects the performance and reliability of a Schottky diode. The electrical properties of Schottky contacts depend markedly on the quality of Metal-Semiconductor (*MS*) interface. The capacitance method [3] is one of the most important method of characterization of the interface states in real Schottky diodes. Therefore, the understanding of the electrical properties of the interface between metal and semiconductor is important for device applications. There are many factors that can have a significant effect on the properties of the junction, including formation of barrier height, ideality factor, *etc.*

The ternary semiconducting compounds with the composition *II-III$_2$-VI$_4$* (where *II*=zinc, cadmium or mercury; *III*=aluminium, gallium or indium; *VI*=sulphur, selenium or tellurium) have been widely investigated because of their potential applications as photoconductors, non-linear harmonic generators [4], *IR* detectors, temperature sensors [5], narrow-band optical filters, *etc.* [6]. Among the *II-III$_2$-VI$_4$* chalcopyrites, $ZnIn_2Se_4$ has drawn special interest because it has relatively high photoelectronic sensitivity in the spectrum range from visible to near infrared and also, it is expected as a promising material for optoelectronic applications. Many studies have been made on the crystal structure [7], photosensitive properties [8], photoelectrical memory effect [9], and solar cell [10] of $ZnIn_2Se_4$. We recently reported the growth [11] and electrical properties [12] of $ZnIn_2Se_4$ thin films by flash evaporation technique and its applications as a memory switching device [13] and heterojunction diode [14].

A variety of thin film deposition techniques including chemical bath deposition, spray pyrolysis, electrodeposition, sputtering, three-source co-evaporation *etc.* have been employed by various authors for the deposition of $ZnIn_2Se_4$ thin films [15–17]. Flash evaporation technique is used for the deposition of thin films of compound semiconductor whose constituents have different vapour pressures. For a compound which dissociates on evaporation, a given evaporant charge will lose its most volatile component first, so that the deposited film will have a layered structure with high and low vapour pressure ingredients at its bottom and top surfaces, respectively. This generally causes a heavy disturbance of the stoichiometric composition of the grown thin film. To optimize this issue, the evaporant charge is reduced in size to a point, where, on complete evaporation it produces a condensed layer at the substrate effectively one compound molecule thick, this monolayer should possess ideal stoichiometry. If a series of such monolayers is built up by sequential and complete evaporation of

* Corresponding author.
E-mail address: dhananjaydhruv@rediffmail.com (D.K. Dhruv).

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these small unit charges, a stoichiometric thin film should result. The flash evaporation technique neither requires provisions to monitor the vapour density nor the control of the source temperature unlike multisource thermal evaporation. The objective of thin film composition/stoichiometry is accomplished by evaporating to completion small quantities of the constituents in the desired ratio. The flash evaporation technique has been selected for the deposition of $ZnIn_2Se_4$ thin films in this paper because the vapour pressure of indium (*In*) is greatly different from that of zinc (*Zn*) and selenium (*Se*) at the same temperature. Flash evaporation technique provides ability to have better control of material falling rate from chute towards the boat. Flash evaporation requires simple and inexpensive apparatus and gives thin films with acceptable quality at a reduced cost. These advantages of flash evaporation technique are highly desirable for fabrication of semiconducting thin-film electronic devices.

The authors believe that the present investigation on the, hitherto unfabricated, unstudied and unreported, Al/p-$ZnIn_2Se_4$ thin film Schottky diode structure should not only be an addition to the list of the existing Schottky diodes but also lead to a further understanding of the Schottky diodes towards novel electronic device applications.

Various physical parameters of Al/p-$ZnIn_2Se_4$ Schottky diode, such as, rectification ratio (R_R), diode ideality factor (n), Schottky barrier height, carrier concentration *etc.* are studied at different temperatures (T) (303–323 K). Band diagram for Al/p-$ZnIn_2Se_4$ Schottky diode device is presented in this paper.

2. Experimental details

Stoichiometric amounts of the elements of 99.999% pure zinc (*Zn*), indium (*In*) and selenium (*Se*) (make: Sigma-Aldrich Chemie GmbH, Germany) were used to prepare the initial ingot of $ZnIn_2Se_4$. The mixture was sealed under $\approx 10^{-4}$ Pa vacuum in a thoroughly cleaned quartz ampoule. The evacuated sealed ampoule was introduced in the programmable furnace in such a way that the ampoule remains in the constant temperature zone of the furnace. In order to avoid explosions due to the selenium vapour pressure, the quartz ampoule was heated gradually ($\approx$325 K/h). The charge was heated to a temperature of 1350 K above the melting point of $ZnIn_2Se_4$. A complete homogenization could be obtained by keeping the melt at 1350 K for about 15 h before slowly cooling ($\approx$285 K/h) to room temperature (303 K). Nucleation was found to occur at the ends of the quartz ampoule due to gradients in the furnace. The source material thus obtained was subjected to X-ray powder diffraction (*XRD*) and energy-dispersive analysis of X-ray (*EDAX*) for confirmation of the compound formation. The source material was a single-phase $ZnIn_2Se_4$ with a grain size of 100–150 μm and a tungsten (*W*) boat was used to deposit the thin films of $ZnIn_2Se_4$ as reported earlier. The depositions were carried out inside a 12 in. vacuum chamber (model: 12A4D; make: Hind High Vacuum Co. Pvt. Ltd., Bangalore, India) with a residual pressure of about 7.5×10^{-4} Pa, and a rate of deposition of about 10 nm/s. The thin film thickness and the rate of deposition were determined and/or controlled by the built in digital quartz crystal thickness monitor (model: DTM-101; make: Hind High Vacuum Co. Pvt. Ltd., Bangalore, India).

A schematic arrangement of the Schottky barrier diode device studied in the present investigation is shown in Fig. 1. A high-purity aluminium (*Al*) metal film of about 100 nm thickness was deposited by thermal evaporation on clean glass substrate. $ZnIn_2Se_4$ thin film was then deposited on pre-deposited *Al* film by the flash evaporation method at a substrate temperature of 573 K without breaking the vacuum of deposition chamber. The thickness of $ZnIn_2Se_4$ thin film was varied from 150 to 300 nm. Finally,

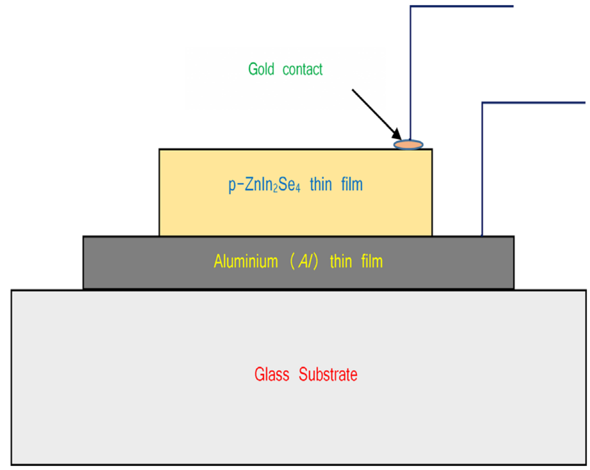

Fig. 1. Cross-sectional schematic diagram of Al/p-$ZnIn_2Se_4$ Schottky diode.

around 100 nm thick gold (*Au*) ohmic contact was made on the top of the $ZnIn_2Se_4$ thin film by thermal evaporation technique. The Al/p-$ZnIn_2Se_4$ Schottky junction was prepared using a proper masking arrangement so as to form a square type device having an active junction area of 0.25 cm^2. The structure was annealed at 423 K for 2 h in vacuum to improve the reproducibility of the contact. It has been observed from our preliminary study of *MS* contact that the *Au* shows good ohmic contacts to the $ZnIn_2Se_4$ film, while the semi-transparent *Al* film shows a good non-ohmic contact to the $ZnIn_2Se_4$ film. The *I-V* and *C-V* characterizations of the device were carried out using a computer-controlled semiconductor characterization system (model: SCS 4200, make: Keithley, USA) in the temperature range 303–323 K in dark condition. All the temperature-related measurements were performed under a vacuum of 1.333 Pa, and a calibrated chromel-alumel (*Cr-Al*) thermocouple was used for the measurement of temperature. A number of Schottky barrier diode device structures were fabricated in a similar manner and the typical results of the *I-V* and *C-V* characterization studies have been presented in detail in this paper.

It is well-known that the physical parameters of the thin films vary with several deposition and post deposition controlling factors. However, during the present investigation of Schottky barrier diode (*SBD*), the deposition rate, deposition temperature, film thickness (300 nm), order of the vacuum, *etc.* have been kept constant for obtaining uniform results. The present results are, therefore, the outcome of a repeated number of experiments and are found to be reproducible with good consistency.

3. Results and discussion

Our studies on flash evaporated $ZnIn_2Se_4$ thin films revealed that the films grown at substrate temperature 573 K onto glass substrate were polycrystalline, single-phase, and stoichiometric and exhibited a tetragonal chalcopyrite structure with a strong preferred (1 1 2) orientation with lattice parameters $a=0.570$ nm and $c=1.144$ nm ($c/a=2.005$). A thermal hot probe analysis as well as Hall effect study indicated the grown $ZnIn_2Se_4$ thin films to be of p-type semiconducting in nature. The electrical resistivity, Hall mobility and carrier density values obtained for $ZnIn_2Se_4$ thin film deposited at 573 K were found to be $2.81\times10^2\ \Omega$ cm, 7.314×10^2 $cm^2\ V^{-1}\ s^{-1}$ and 1.937×10^{13} cm^{-3}, respectively. The acceptor carrier concentration (N_A) obtained from the Hall effect studies is 4.12×10^{13} cm^{-3} [12]. $ZnIn_2Se_4$ is a member of *II-III₂-VI₄* 'defect chalcopyrite' family and the defects in this compound arise from some percentage of vacancies of *Zn* sites. The presence of