

ELECTRICAL MEASUREMENTS OF CADMIUM ARSENIDE THIN FILMS COMPOUND SEMICONDUCTORS

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ABSTRACT

Cadmium arsenide is a II-V semiconductor which exhibits n-type intrinsic conductivity with high mobility and narrow energy band gap. The films were prepared by vacuum evaporation with deposition rates of 0.5 nm s^{-1} and substrate temperatures maintained at constant values of 293 K- 393 K. Sandwich-type samples were deposited with film thicknesses of 0.1-1.1 μm using evaporated electrodes of Ag and occasionally Au or Al. Various electrical measurements have been performed in this work. Van der Pauw measurements on film resistivity values in the range of $10^{-2} - 10^{-6} \Omega\text{m}$ were determined, which were strongly dependent on the deposition conditions and the film thickness. The resistivity decreased with increasing film thickness in the approximate range $10^{-2} - 10^{-5} \Omega\text{m}$ for films of thickness up to about 0.5 μm , retaining the lower value at higher thicknesses. AC capacitance studies were performed on Ag-Cd₃As₂-Al sandwich structures as functions of frequency and temperature over the ranges 100 Hz - 20 kHz and 163 - 453 K. It was observed that the capacitance decreased with increasing frequency and increased with increasing temperature, tending to constant values at high frequencies and low temperatures. A linear $\log J \propto V^{1/2}$ dependence in sandwich structures it is clear that lowering of a potential barrier occurs at high fields in Cd₃As₂ thin films. The measured values of the field-lowering coefficient β for films having two Ag electrodes suggests that dominant Schottky field lowering in the thinner films (typically 0.1 μm) gives way to Poole-Frenkel field lowering for thicker films (typically 1 μm and above).

INTRODUCTION

Cadmium arsenide (Cd₃As₂) is an n-type narrow band-gap semiconductor. Semiconductors are materials having electrical conductivity values in the region between those of good conductors ($\sim 10^8 \Omega\text{m}^{-1}$) and of insulators ($\sim 10^{-5} \Omega\text{m}^{-1}$). These materials have many actual and potential uses in the electronics industry. Among the most common semiconductor materials are silicon (Si) and germanium (Ge), which both belong to group IV of the periodic table, and the compound semiconductors such as gallium arsenide (GaAs) (group III-V), which are widely used as fast electronic components and in solar energy conversion devices. The most obvious progress in high technology over the past few decades has taken place in the electronics industry, in which semiconductor materials are very important and widely used, especially in the

form of thin films. In fact thin film technology has been used for more than 100 years for optical purposes, such as in mirrors coated with a silver layer and in coatings for lenses in cameras and telescopes. More recently, the development of thin film technology has progressed very significantly, in particular in high technology applications, such as in magneto-optic disks and in integrated circuits (ICs) in the microelectronics industry. Associated with their wide use, their various deposition technologies have become very interesting and important areas for research and in commerce. At present the ready availability of various types of commercial deposition methods, such as molecular beam epitaxy (MBE), electron beam coating, pulsed laser evaporation (PLE), sputtering, vacuum deposition and the Langmuir-Blodgett technique, allow the detailed study of the electrical and other properties of thin films, in order to meet the requirements of current developments for highly-reliable electronic devices, such as those required for operation in space.

During the past five decades, the elemental semiconductor Si has been widely investigated, following earlier work on the scarcer Ge. However Si has remained the major electronic material, which is used extensively in electronic devices. This material has a simple cubic crystalline structure, is abundantly available and the main difficulties connected with its technology are relatively easy to overcome. Consequently, many semiconductor laboratories have worked on Si and heavy investment has been made. There are many different types of silicon, such as single crystal, amorphous, polycrystalline and porous varieties, all of which have been used for different applications.

However, currently there are several alternative semiconducting materials which have become more important, and which have potential applications in devices where the properties of Si are less favourable. The prime example is GaAs, which is a group III-V compound semiconductor. The main advantages of this material are its high electron mobility and its optical band gap of about 1.42 eV; these properties render it particularly useful for applications in high speed devices and in solar cell technology. Furthermore, there are several compound group II-VI semiconductors such as CdS, CdTe, CdSe, HgTe and HgSe which have also been widely investigated and have applications in electronic devices and solar energy conversion. These materials have a broad range of energy gaps (the majority of them being direct gap materials), from a very small value of about 0.02 eV for the semimetal HgTe to a very wide energy gap of about 3.7 eV for ZnS. Among them, the cadmium compounds CdS, CdTe and CdSe are widely used in solar energy applications. The energy band gap of these three cadmium compounds are in the range 0.8-1.4 eV and have very high optical absorption coefficients, which are very important requirements for solar cells capable of absorbing nearly all the usable energy from the solar spectrum. Some of these cadmium compounds, such as CdSe, also have potential uses in gas sensing technology (Ziebert 1972). Thin film gas sensing technology is usually based on oxide films (e.g. tin oxide), but has also been based on suitable organic semiconductors such as the metal phthalocyanines (e.g. CuPc and PbPc) because of the very high sensitivity of their electrical conductivities to the presence of various gases, hence the detection of very low levels (ppb) may be possible. Organic molecules may be easily modified to react with particular gaseous species, thus increasing the selectivity.

EXPERIMENTAL

Cadmium arsenide powder of purity 99.99% (Aldrich) was used to deposit the films by thermal evaporation as described by Zdanowicz [3]. The evaporation was performed from a molybdenum boat onto Corning 7059 substrates, which had been thoroughly cleaned using a detergent and degreasant, and also by ionic bombardment for a period of 5 minutes immediately before deposition. The film thickness d and the deposition rate R were monitored during deposition using a conventional quartz crystal system, and the substrate temperature T_s was also controlled. Temperatures were measured using a chromel-alumel thermocouple junction attached to the substrate. Samples were deposited over a wide range of deposition conditions in the following ranges: $d = 0.1$ - $1.0\ \mu\text{m}$, $R = 0.5\ \text{nm s}^{-1}$ and $T_s = 293\ \text{K}$ - $413\ \text{K}$. Ag and Au electrodes were evaporated from open molybdenum boats whereas Al utilised a coiled tungsten spiral. The substrates supported six sandwich samples, each of active area $1.2 \times 10^{-5}\text{m}^2$. After deposition film thicknesses were measured accurately using a Planer Surfometer SF200 stylus instrument.

Electrical measurements were made at room temperature in a subsidiary vacuum system at a pressure of $1.3 \times 10^{-3}\ \text{Pa}$ or less. Dc currents were measured using a stabilised power supply in conjunction with a Philips 2521 multimeter.

RESULTS AND DISCUSSION

From van der Pauw measurements, film resistivity values in the range of 10^{-2} - $10^{-6}\ \Omega\text{m}$ were determined, which were strongly dependent on the deposition conditions and the film thickness. The resistivity decreased with increasing film thickness in the approximate range 10^{-2} - $10^{-5}\ \Omega\ \text{m}$ for films of thickness up to about $0.5\ \mu\text{m}$, retaining the lower value at higher thicknesses (Figure 1).

This decrease in resistivity was thought to be the result of the lower occurrence of defects and a larger crystallite grain size in the thicker films. Resistivity also decreased significantly with increasing substrate temperature during deposition from about 10^{-4} to about 10^{-5} - $10^{-6}\ \Omega\text{m}$ when the temperature increased from $300\ \text{K}$ to $453\ \text{K}$ (Figure 2). This was attributed to a transition from the amorphous to the crystalline state as reported previously, and also to an increase in the grain size with increasing substrate temperature. The dependence of film resistivity on deposition rate showed a minimum value at approximately $1.3\ \text{nm s}^{-1}$, decreasing from 8×10^{-4} to $7 \times 10^{-6}\ \Omega\ \text{m}$ as the rate increased from $0.2\ \text{nm s}^{-1}$ to about $1.3\ \text{nm s}^{-1}$, but increasing slightly up to about $8.5 \times 10^{-6}\ \Omega\text{m}$ for a rate of $2.4\ \text{nm s}^{-1}$.

The initial decrease in resistivity may be due to an increasing proportion of Cd in the films, while at higher rates the resistivity most probably increases due to an increase in the As content, as suggested by Zdanowicz et al (1981). Further work is clearly required in this area. A slight decrease in resistivity after annealing was observed in Cd_3As_2 films of various thicknesses and may probably be due to the annealing out of structural defects and an increase in the mean grain sizes.

After deposition it was observed that the resistivity generally decreased with increasing temperature, particularly at temperature above about 330 K. However at lower temperatures the resistivity decreased only slightly with increasing temperature, becoming almost independent of temperature below about 200 K. Activation energies at higher temperatures were normally in the range of 0.10 - 0.16 eV, which are comparable to the value of 0.14 eV reported by Moss (1950) and by Zdanowicz (1964). For lower temperatures the very low activation energy values obtained may be considered as evidence of a hopping mechanism as the dominant mode of conduction. The higher value of activation energy in the high temperature region is evidence of conduction at these temperatures due to a free-band conduction process, with the value of the activation energy determined by intercrystalline potential barriers.

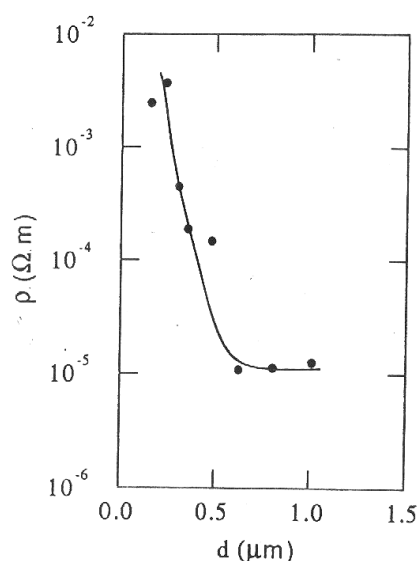


Figure1: The dependence of resistivity of Cd₃As₂ thin film with film thickness.

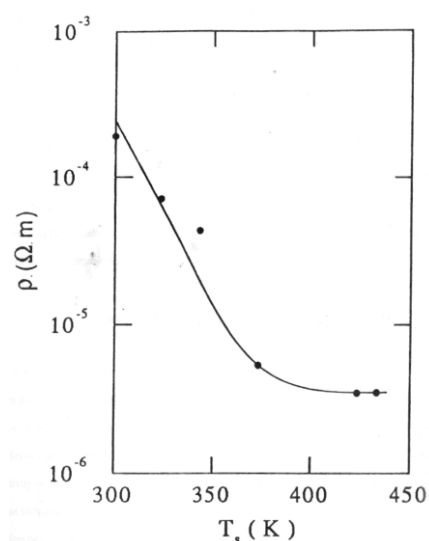


Figure 2: The dependence of resistivity of Cd₃As₂ thin films on substrate temperature during deposition.

AC capacitance studies were performed on Ag-Cd₃As₂-Al sandwich structures as functions of frequency and temperature over the ranges 100 Hz - 20 kHz and 163 - 453 K. It was observed that the capacitance decreased with increasing frequency and increased with increasing temperature, tending to constant values at high frequencies and low temperatures (Figure 3). This behaviour is consistent with the predictions of the equivalent circuit model of Goswami and Goswami (1973). After annealing at 473 K the capacitance reduced much more rapidly at higher frequencies in comparison with fresh samples, but at lower frequencies of up to 800 Hz the capacitance of an annealed sample was slightly higher than for a fresh sample. It was suggested that there was a change in the equivalent circuit resistance and capacitance values after annealing and that a decrease in the former and an increase in the latter would be consistent with the observed overall capacitance variations. It was

also observed that in samples with two Au or Ag electrodes the measured capacitance was lower. It was proposed that in samples with an Al electrode the overall capacitance might be dominated by the contact region, where an oxide layer may be present as reported by Gould (2002).

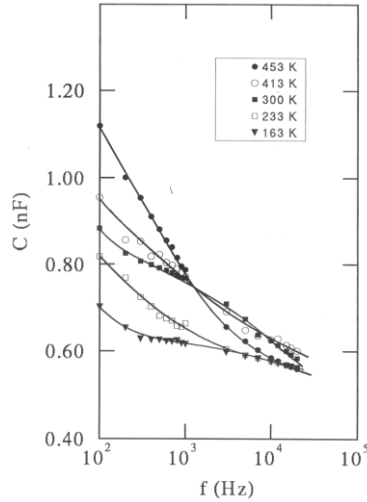


Figure 3: The variations of capacitance on frequency at different substrate temperatures for Ag- Cd_3As_2 -Al sandwich structure $0.64 \mu\text{m}$.

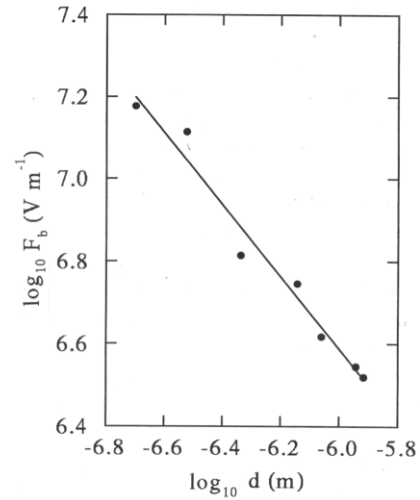


Figure. 4: A linear relationship between $\log_{10} F_d$ with $\log_{10} d$ of Cd_3As_2 films at different temperatures.

Figure 5 shows linear relationship of $\log J \propto V^{1/2}$ in sandwich structures of Ag- Cd_3As_2 – Ag, it is clear that lowering of a potential barrier occurs at high fields in Cd_3As_2 thin films. Two samples of annealed and unannealed exhibit a similar behaviour. The measured values of the field-lowering coefficient β for films having two Ag electrodes suggests that dominant Schottky field lowering in the thinner films (typically $0.1 \mu\text{m}$) gives way to Poole-Frenkel field lowering for thicker films (typically $1 \mu\text{m}$ and above) as mentioned by Din and Gould (1999).

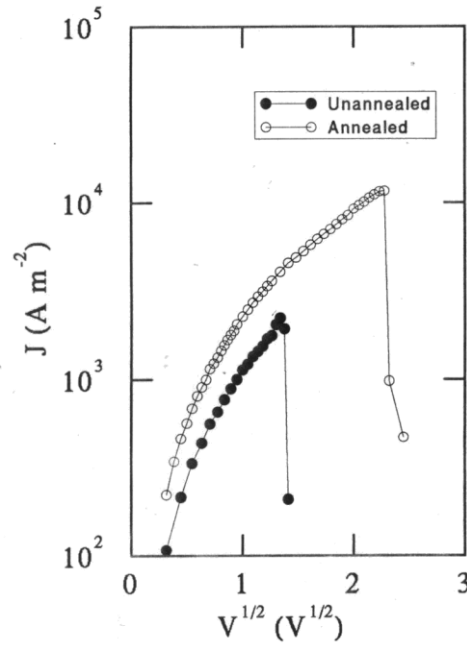


Figure 5: The dependence of $\log J$ versus $V^{1/2}$ of Cd_3As_2 thin films

Values of β in excess of the theoretical Poole-Frenkel value for thicker films imply that a non-linear field distribution occurs.

The field enhancement increased with increasing deposition rate and with the substrate temperature during deposition, probably resulting from differing resistivity values and structural features. Additional evidence for Schottky emission in the thinner films was provided by J-V data obtained on films having different electrode combinations, which suggest a varying potential barrier height at the electrode depending on the type of electrode metal used. Values of barrier height in the range 0.42-0.47 eV were identified, but there was no particular correlation with electrode work function differences. It was proposed that the value of the barrier height is related to the electronic structure at the Cd_3As_2 surface, and that differences between samples having different types of electrodes may reflect the existence or otherwise of an oxide layer.

Most samples showed evidence of dielectric breakdown or electroforming at higher voltage levels. Electroforming was indicated by the appearance of a current maximum and negative resistance, observed under both increasing and decreasing voltages. A linear relationship between $\log F_b$ and $\log d^{-\beta}$ was identified, where F_b is the breakdown or electroforming field strength, d is the film thickness, and β is a constant. Although the value of $\beta = 0.87$ which was obtained is larger than the maximum predicted by Forlani and Minnaja (1964) it was suggested that this may be as a result of the relatively thick Cd_3As_2 films used and also that it may indicate that dielectric breakdown and electroforming occur simultaneously.

CONCLUSION

Various electrical measurements have been performed in this work. Van der Pauw measurements on film resistivity values in the range of 10^{-2} - 10^{-6} Ω m were determined, which were strongly dependent on the deposition conditions and the film thickness. The resistivity decreased with increasing film thickness in the approximate range 10^{-2} – 10^{-5} Ω m for films of thickness up to about 0.5 μ m, retaining the lower value at higher thicknesses. AC capacitance studies were performed on Ag-Cd₃As₂-Al sandwich structures as functions of frequency and temperature over the ranges 100 Hz - 20 kHz and 163 - 453 K. It was observed that the capacitance decreased with increasing frequency and increased with increasing temperature, tending to constant values at high frequencies and low temperatures.

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