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Capacitance Variations in Cd_3As_2 Thin Film Sandwich Structures

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Cadmium arsenide (Cd_3As_2) is a high conductivity II-V semiconductor. Following a recent dc investigation, capacitance has been measured as a function of film thickness, temperature (163 - 453 K), and frequency (100 Hz - 20 kHz) in Ag-Cd_3As_2-Al structures. There was a decrease with frequency and an increase with temperature, as reported in various other materials. After annealing at 473 K the decrease in capacitance with frequency was enhanced due to concomitant changes in the equivalent circuit parameters, whereas unannealed Ag-Cd_3As_2-(Au or Ag) structures showed reduced capacitance, ascribed to changes in the contact impedance.

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1. Introduction

Cadmium arsenide (Cd_3As_2) is a high conductivity semiconductor having several interesting features which have stimulated research in this material. Turner *et al* [1] showed that pulled crystals of the material have a very high mobility of up to 1.5 $m^2\ V^{-1}\ s^{-1}$ and optical absorption measurements indicate a narrow energy band gap of 0.13 eV at 300 K. _danowicz [2] has shown that the resistivity and Hall mobility of n-type Cd_3As_2 thin films are strongly dependent on the substrate temperature and deposition rate.

Other reports concerning the transport properties of this material [3,4] have also shown that the conduction mechanisms observed may depend, among other factors, on the deposition rate. Films deposited at a low rate are generally of lower mobility, having an excess of arsenic over cadmium. When deposited at a higher rate the films are normally of higher mobility with a high electron concentration, and have an excess of cadmium over arsenic. In the former case the low temperature conductivity is by means of localised states situated below the conduction band edge, whereas in the latter the conductivity appears not to be thermally activated.

Films are normally amorphous when deposited at substrate temperatures below about 400 K, while those deposited at higher temperatures are crystalline [2,5,6]. In amorphous films Shubnikov-de Haas oscillations have been observed in the magnetoresistance and Hall voltage at 4.2 K and 20 K [7]. Films prepared by the pulsed laser evaporation (PLE) technique showed a very weak temperature dependence of the carrier mobility [5] which indicated differences in stoichiometry from the bulk material; such differences were absent in films prepared by simple vacuum evaporation. More recently the present workers have made detailed measurements of dc electrical conduction properties in evaporated Cd_3As_2 films [8]. Experiments were performed for a wide range of deposition rates (0.5 - 6.0 nm s^{-1}) and thicknesses of 0.3 - 1.1 μm and substrate temperatures of 293 - 393 K. Below field levels of typically 5×10^7 V m^{-1} all samples showed a high-field conduction process with $\log J \propto V^{1/2}$, where J is the current density and V the applied voltage.

This type of conductivity indicates carrier excitation over a potential barrier, whose effective barrier height has been lowered by the effects of the high electric field. In the case of thinner films (typically 0.1 μm) this was identified with field-lowering at the injecting electrode (Schottky effect), while for thicker films (typically 1 μm and above) field-lowering of the potential barrier at donor-like centres (Poole-Frenkel effect) was identified. Since these effects are more usually associated with high resistivity than with high mobility materials, the present work was directed at ascertaining whether or not the ac capacitance behaviour is also similar to that previously observed in high resistivity cadmium compound films such as CdTe [9].

2. Experimental

The initial Cd_3As_2 evaporant material was of purity 99.99% and was obtained from Aldrich. Films were deposited using conventional vacuum evaporation at a background pressure of 10^{-4} Pa on to Corning 7059 glass substrates maintained at room temperature. These were thoroughly cleaned using a detergent before inserting into the deposition chamber, and also submitted to ionic bombardment cleaning for a period of 5 min prior to deposition. Deposition of metal-Cd_3As_2-metal sandwich structures proceeded sequentially without breaking vacuum, using a mask-changing system described previously [10].

The bottom electrode of Ag and the Cd_3As_2 films were evaporated from molybdenum boats, normally followed by

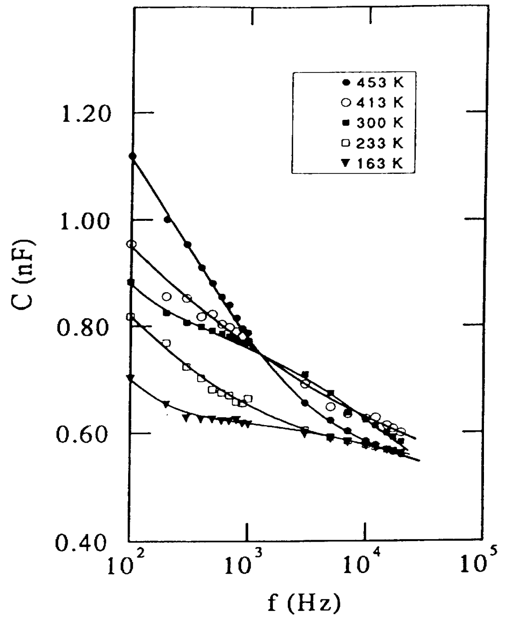

Figure 1. Dependence of capacitance on frequency for a Ag-Cd_3As_2-Al sample of thickness 0.64 μm at various temperatures. Capacitance decreases with increasing frequency at all temperatures tending to a constant value at low temperature and high frequency.

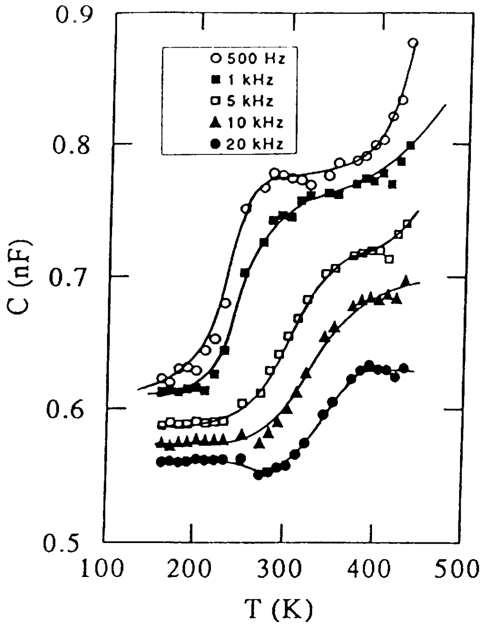

Figure 2. Dependence of capacitance on temperature at various frequencies for the Ag-Cd_3As_2-Al sample of Fig. 1. Capacitance is insensitive to frequency at low temperatures, but increases rapidly with temperature above 220 K.

an Al electrode which utilised a tungsten spiral. In some samples the top Al electrode was replaced by either Ag or Au using a molybdenum boat for evaporation. Deposition rates were monitored and controlled using a conventional quartz crystal system, and were 0.5 nm s^{-1} for the Cd_3As_2 and typically 1 nm s^{-1} for the metal electrodes. The Cd_3As_2 film thicknesses were in the range 0.15 - 1.31 μm and the electrode thicknesses were typically 100 nm. Each of the Corning substrates supported six sandwich samples, each of active area 1.2×10^{-5} m^2. All film thicknesses were determined accurately after deposition using a Planer Surfometer SF200 stylus instrument.

Capacitance measurements were performed in a subsidiary vacuum system at a pressure of typically 10^{-3} Pa using a Hewlett-Packard 4276A LCZ meter over a frequency range of 100 Hz - 20 kHz. Measurement temperatures were controlled in the range 163 - 453 K using liquid nitrogen cooling and a heating system.

3. Results and discussion

3.1 Basic capacitance characteristics

Fig. 1 shows the dependence of capacitance C on frequency f at various temperatures for a Ag-Cd_3As_2-Al sample with thickness d = 0.64 μm. The capacitance decreases with increasing frequency, and is particularly frequency dependent at higher temperatures and lower frequencies.

A wide dispersion in the capacitance values is observed at lower frequencies; however, at the lowest temperature of 163 K the capacitance decreases only very slightly with frequency. At higher frequencies the curves for all temperatures tend to approach a common capacitance value. A decrease in capacitance with increasing frequency has been observed in several other thin film materials, including the cadmium compounds CdTe [9] and CdSe [11] in this laboratory.

These results are also shown in Fig. 2, where the capacitance is shown as a function of temperature at various frequencies. This figure also illustrates that at lower temperatures the capacitance is insensitive to the frequency, but increases monotonically with temperature above approximately 220 K. At higher temperatures the curves characteristic of the individual frequencies are well separated. Similar behaviour has also been observed in CdTe [9] and CdSe [11] films.

This type of behaviour has previously been accounted for in terms of the equivalent circuit model of Goswami and Goswami [12] which comprises a frequency- and temperature- independent capacitive element C', with a discrete temperature-dependent resistive element R due to the conducting film in parallel with C', both elements in series with a constant low value resistance r due to lead lengths, etc.

According to this model the measured series

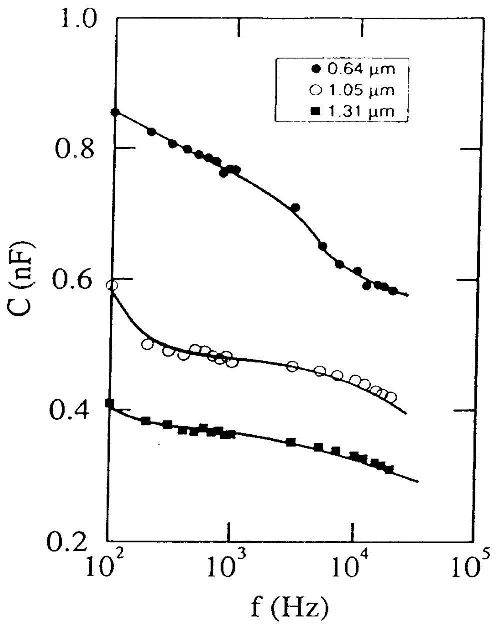

Figure 3. Dependence of capacitance on frequency at room temperature for three Ag-Cd_3As_2-Al samples of different thickness. The rapid decrease in capacitance with increasing thickness is consistent with a normal geometric capacitance variation in the parallel-plate structure.

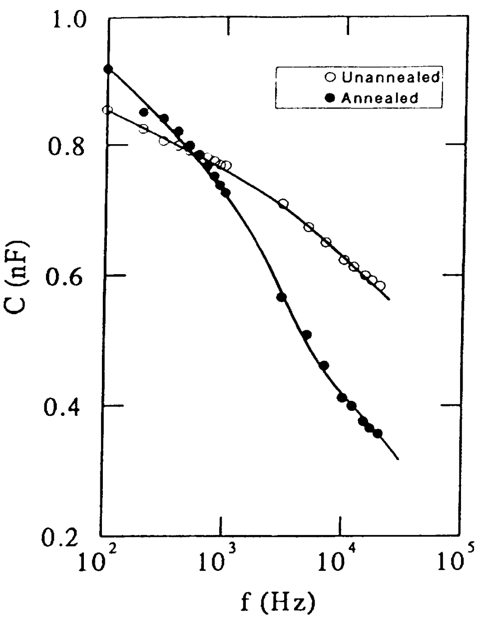

Figure 4. Dependence of capacitance on frequency at room temperature for a Ag-Cd_3As_2-Al sample both before and after annealing at 473 K for 2 hours. The shift in the characteristic was identified with a decrease in R and an increase in C' in Eqn. (1) after annealing.

capacitance is given by

$$C = C' + \frac{1}{w^2 R^2 C'} \qquad \textbf{(1)}$$

The resistive element R is assumed to be thermally activated, with a temperature variation given by

$$R = R_0 \exp\left(\frac{\Delta E}{kT}\right) \qquad \textbf{(2)}$$

where R_0 is a constant and ΔE is the activation energy. Eqn. (1) clearly predicts that the measured capacitance should decrease with increasing frequency, eventually at high frequencies becoming frequency-independent and reaching a constant value C'. Also for any given frequency the capacitance will increase with increasing temperature, since R decreases with increasing temperature from Eqn. (2). All of these effects are qualitatively evident in Figs. 1 and 2 where the value of C tends to a constant value at low temperature.

A geometric dependence of capacitance on temperature is also apparent. Fig. 3 shows the dependence of capacitance on frequency at room temperature for three Ag-Cd_3As_2-Al structures of different thickness. It is clear that the thicker film had a lower capacitance than the thinner samples irrespective of frequency, thus indicating that the major contribution to the capacitance derived from the Cd_3As_2 film and not from Schottky barriers at the interfaces. Indeed our measurements of capacitance at constant frequency as a function of applied voltage (not shown) do not provide any evidence for a depletion region or the existence of Schottky barriers at the contacts, and yield a consistent value of the relative permittivity of 4.7.

3.2 Effects of annealing and electrode material

Some Ag-Cd_3As_2-Al samples of thickness 0.64 µm were annealed at a temperature of 473 K for 2 hours under vacuum. Fig. 4 shows a typical set of results for the dependence of capacitance on frequency at room temperature, both for a fresh sample and also for the same sample after annealing.

The capacitance of the annealed sample reduced much more rapidly at higher frequencies in comparison with the behaviour of the fresh sample. However at lower frequencies of up to 800 Hz the capacitance value of the annealed sample was slightly higher than in the fresh sample. It would appear in these samples where the capacitance is reduced at frequencies above 800 Hz after annealing that there is a change in the values of both R and C' after annealing. For low frequencies (< 800 Hz) a decrease in R after annealing would result in an increase in the capacitance value. This is consistent with an increase in the current density under dc conditions after annealing which we have also observed. However at higher frequencies an increased value of C' would result in

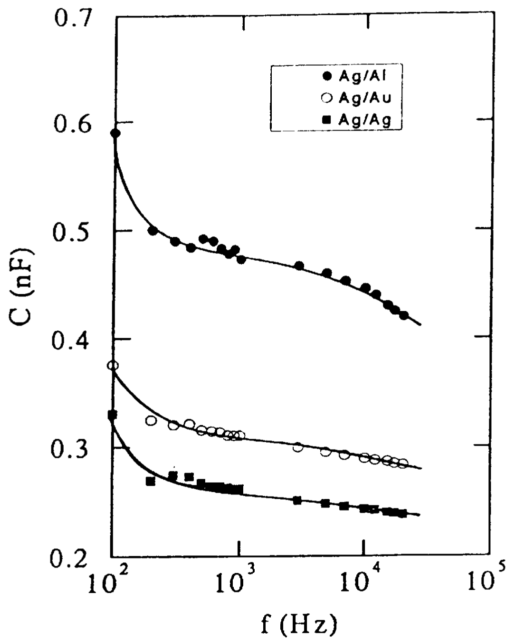

Figure 5. Dependence of capacitance on frequency at room temperature for Ag-Cd_3As_2-Al, Ag-Cd_3As_2-Au and Ag-Cd_3As_2-Ag samples of thickness 1.05 μm. The bottom and top electrodes are indicated on the figure. The lower capacitance values exhibited for the samples with Au and Ag top electrodes suggest that the electrode contact impedance may influence the measured capacitance.

a lower overall capacitance, since the second term on the right-hand side of Eqn. (1) dominates the expression owing to the low Cd_3As_2 resistivity (i.e. low *R*). It is therefore proposed that annealing also results in an increase in C' as the film quality improves.

Finally, Fig. 5 shows the room temperature dependence of capacitance on frequency for three different sample configurations, each with Cd_3As_2 film thickness of 1.05 μm. The three sample configurations were Ag-Cd_3As_2-Al (labelled Ag/Al), Ag-Cd_3As_2-Au (Ag/Au) and Ag-Cd_3As_2-Ag (Ag/Ag). As can be seen the capacitance values for the two latter samples are low in comparison with that of the Ag-Cd_3As_2-Al sample. This suggests that in samples containing an Al electrode the overall capacitance may be influenced by the contact impedance, where the existence of an oxide or other narrow region is possible.

4. Summary and conclusions

The dependence of capacitance in evaporated Cd_3As_2 thin film sandwich structures has been observed as a function of frequency, temperature and film thickness. The effects of annealing and type of electrodes have also been investigated. In general the dependence of capacitance on frequency and temperature in Ag-Cd_3As_2-Al samples could be accounted for using the equivalent circuit model of Goswami and Goswami [12], notwithstanding the fact that Cd_3As_2 is highly conductive with a small energy band gap. Significantly, dc high field conduction processes normally associated with wider band gap materials have also recently been observed in this material [8]. After annealing 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 annealed samples exceeded that of fresh samples. 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 when the top Al electrode was replaced by Au or Ag the measured capacitance was lower. It was suggested that this might be as a result of a change in the contact impedance.

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