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DC electrical conductivity of some Cd–Ge–As glasses

A GIRIDHAR and SUDHA MAHADEVAN
Materials Science Division, National Aeronautical Laboratory, Bangalore 560 017, India

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Abstract. Results of measurement of d.c. electrical conductivity σ from 85 to 550 K are reported for eleven glass compositions of the Cd–Ge–As system. Three regions are seen in the σ–T data of all these glasses. In region I (85 to 140 K), σ is essentially constant and independent of temperature. In region II (200 to 430 K), σ is thermally activated with a single activation energy. In region III (>430 K) a sudden increase is seen in σ with temperature. From an analysis of the results, it has been possible to identify the mechanism of hopping conductivity among localised 'defect' states with region I, normal band type conductivity due to carriers excited to the extended states with region II and thermally assisted memory switching with region III.

In the composition dependence of σ and ΔE for the $CdGe_xAs_2$ glasses, special features are seen at the composition $Cd_{28\cdot57}Ge_{14\cdot28}As_{57\cdot15}$, which has equal mol fractions of $CdAs_2$ and $CdGeAs_2$. For the Cd_2Ge–As glasses also, a maximum in ΔE and a minimum in σ are seen at this composition.

Keywords. Cd–Ge–As glasses; d.c. electrical conductivity; mechanisms of d.c. conductivity.

1. Introduction

In the Cd–Ge–As system, glasses can be formed up to the addition of 28 at.% of Ge. There are a few studies on the d.c. electrical conductivity (σ) of some Cd–Ge–As glasses in the temperature range 200 to 500 K (Callearts *et al* 1971; Cervinka *et al* 1970). In this work, the results of measurement of σ on eleven glass compositions of the Cd–Ge–As system from 85 to 500 K are reported. Further, an attempt has been made to analyse the mechanism of conduction in the various temperature ranges.

The glasses studied (table 1) can be classified into the following groups. Compositions 1 to 7 fall along the $CdAs_2$–Ge join and glasses 7 to 11 fall along the Cd_2Ge–As join. The composition $Cd_{28\cdot57}Ge_{14\cdot28}As_{57\cdot15}$ belongs to both these groups and can be referred to as the reference composition. In the composition dependence of T_g, T_c and density of $CdAs_2$–Ge glasses, special features (like a kink, change in slope) are seen at this reference composition, which has equal mole fractions (0·5) each of $CdAs_2$ and $CdGeAs_2$ (A Giridhar and Sudha Mahadevan, unpublished data). For the Cd_2Ge–As glasses also, features like a minimum in density and change in slope in the composition dependence of T_g and T_c are seen at this reference composition (A Giridhar and Sudha Mahadevan, unpublished data).

2. Experimental

Appropriate quantities (total of 8 g per batch) of high purity (99·999%, from the Atomergic Chemmetals Corpn., USA) Cd, Ge and As were weighed into quartz ampoules (12 mm dia). The inner walls of the ampoule were graphitised prior to introducing the elements. The contents of the ampoule were sealed under a vacuum of 10^{-5} torr. The contents were then melted and homogenised by heating to 800°C

Table 1. Data on T_g^*, T_c^* and C, $\triangle E$ and temperature range of region II for Cd–Ge–As glasses.

Cd:Ge:As	$T_g^*(K)$	$T_c^*(K)$	Temp. range	$\log C$ ($ohm^{-1} cm^{-1}$)	$\triangle E$ (eV)
33·33:0:66·67	559	602	194–407	2·40	0·44
32:4:64	577	638	196–429	3·20	0·50
30:10:60	602	680	200–429	3·31	0·51
27·78:16·67:55·56	630	717	200–429	2·84	0·51
27:19:54	640	716	200–435	2·98	0·54
25:25:50	662	718	200–444	2·47	0·48
28·57:14·28:57·15	622	714	204–435	3·46	0·56
32:16:52	632	679	194–378	2·64	0·47
30:15:55	625	702	202–444	2·54	0·48
26:13:61	617	706	196–429	1·97	0·48
23:11·5:65·5	616	718	196–429	2·40	0·47

*These data are from DSC and are measured at a heating rate of 10 K/min. (A Giridhar and Sudha Mahadevan, unpublished data).

in a rotary furnace for 8 h, and quenched in water to obtain the glasses. The graphitising of the ampoule is necessary because the sample adheres strongly to the wall of an uncoated ampoule. From the bulk glasses prepared as above, experimental specimens in the form of plane parallel discs (of typical thicknesses from 1 to 1·5 mm) were obtained by lapping them by using fine grade silicon carbide powder and cleaning thoroughly. For ensuring good electrical contacts, silver paint (circular, typically 5 mm dia) was applied on the surfaces of the discs and the discs were then held firmly between stainless steel electrodes. Low temperature measurements were performed by introducing the sample into a cryostat using liquid nitrogen under reduced pressure as the refrigerant. The sample was first cooled to 80 K and data was then collected as the sample warmed up to room temperature. With the thermal insulation provided in the set up, this warm up time was typically about 2 h. To prevent condensation of any moisture in the sample chamber (which could form a conducting path over the sample), the sample chamber was evacuated during the measurement. A tubular furnace capable of giving the desired temperature was used for high temperature studies. A chromel–alumel thermocouple situated very close to the sample was used to measure the temperature.

As already described (Sudha Mahadevan *et al* 1977), the σ measurements were made by applying a known voltage (5 V) to the sample and measuring the current using a Hewlett Packard model 425A DC ammeter capable of measuring pico amperes. With proper shielding to avoid stray pickups, the lower limit for conductivity measurement for typical sample dimensions used was 5×10^{-13} $ohm^{-1} cm^{-1}$. For measurements above room temperature, the Hewlett Packard ammeter was replaced by an appropriate ammeter (Universal Motwane avometer) capable of measuring currents up to 10 amperes in convenient ranges.

3. Results and discussion

Figure 1 shows a typical $\log \sigma$ vs. $1/T$ data obtained for one of the compositions ($Cd_{25}Ge_{25}As_{50}$), in which, three regions (as shown in the inset of figure 1) can be

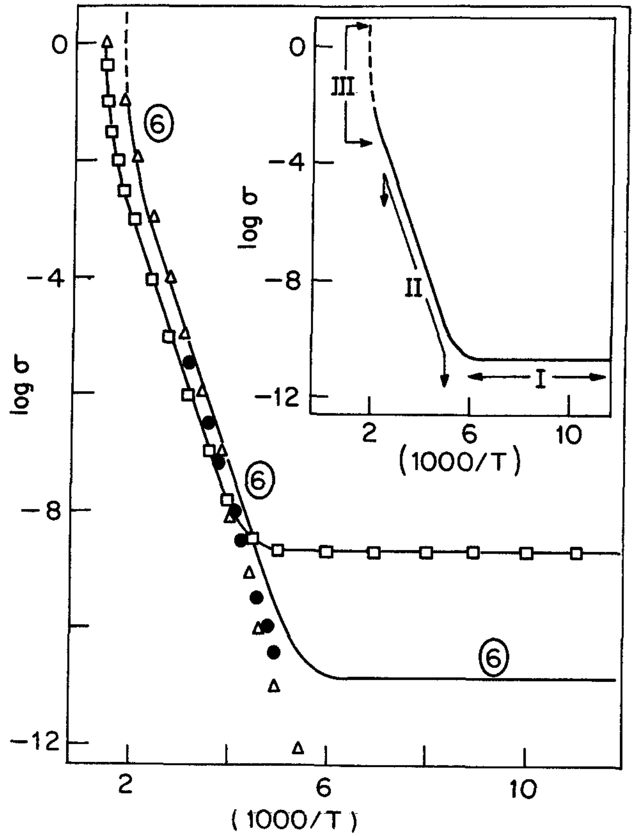

Figure 1. Data of log σ vs $1/T$ for $Cd_{25}Ge_{25}As_{50}$ [continuous line, labelled ⑥] glass. The data △, ● and □ are from literature. [–△– Callearts *et al* 1971, –●– Cervinka *et al* 1970 and –□– Vaipolin *et al* 1966]. The inset shows the typical behaviour at various temperature regions as discussed in the text.

distinguished. In the region marked I, which occurs at low temperatures, σ is seen to be essentially independent of temperature and the associated activation energy is very small. In region II, the linear log σ vs. $1/T$ data can be fitted to a single straight line indicating a single activation energy. The conductivity is given by $\sigma = C \exp(-\Delta E/kT)$. In region III, the increase of σ is faster than that in region II. In the later part of region III, there is an instantaneous increase of σ as indicated by the broken line (figure 1).

The σ–T data of glasses of other compositions (table 1) were similar to that of $Cd_{25}Ge_{25}As_{50}$. Table 1 lists the values of C, ΔE and the range of temperature covered by region II for the various compositions. It is seen that the region II extends from 200(±5)K to 438(±8)K for most of the compositions. Only for $CdAs_2$ (composition no. 1) and for composition no. 8 which have high Cd contents, the region II extends only up to 405 and 380 K respectively on the high temperature side of region II. The setting in of region III (which corresponds to the high temperature limit of region II) is found to occur well below the corresponding T_g (by about 150 to 250 K depending on the composition, table 1) of these glasses.

A low temperature region where σ is essentially invariant with temperature has been reported for $CdGeAs_2$ (Vaipolin *et al* 1966). These data, along with the σ data of $CdGeAs_2$ available over the temperature ranges 200 to 500 K (Callearts *et al* 1971) and 185 to 300 K (Cervinka *et al* 1970) are also shown in figure 1, along with the present data. The general shape of the log σ vs. $1/T$ data plot obtained presently (solid line, figure 1) agrees well with the earlier one (□, figure 1). However, in the earlier data, the σ in region I has levelled off at a higher value than that obtained presently. In the temperature range of about 220 K and higher, there is general agreement among the various data (figure 1).

3.1 *Mechanisms for d.c. conductivity*

Models for the density of states and mobility as well as mechanisms for d.c. conductivity in amorphous semiconductors have been discussed in detail elsewhere (see for example: Mott and Davis 1971, Fritzsche 1974, Van der Plas and Bube 1977, Emin 1973, Emin *et al* 1972, Seager *et al* 1972). Some of these aspects are summarised here. There are four mechanisms proposed for conduction as given below. Thus conduction could be due to: (a) carriers excited into the extended states beyond the mobility shoulders, also called the band conduction. This is generally operative at high temperatures; (b) carriers excited into the localised states at the band edges, also called thermally assisted tunnelling and observed at intermediate temperatures; (c) carriers hopping between localised states near the Fermi level, E_F, generally operative at low temperatures; (d) small polarons hopping within a 'dominant constituent' with its associated hopping energy, which can be operative over the entire range of temperatures.

All these mechanisms give a variation of σ with temperature of the form $\sigma = C\exp(-\Delta E/kT)$. However, in mechanism (*c*), the carriers are forced to seek centres which are farther away and not necessarily nearest neighbours when temperature is lowered; For this so called 'variable range hopping' process, it has been shown that $\sigma = \sigma_0 \exp(-T_0/T)^{1/4}$ (Mott 1968, 1969). The constants C and ΔE in the expression $\sigma = C\exp(-\Delta E/kT)$ vary for the four mechanisms with $C_a \gg C_b \gg C_c$; $C_d \simeq C_a$ and $\Delta E_a > \Delta E_b > \Delta E_c$. The usual range for C_a is from 10^2 ohm^{-1} cm^{-1} to 10^4 ohm^{-1} cm^{-1}. C_b is generally less than C_a by a factor of 10^3 to 10^4, and C_c is even lower than C_b. If the density of defect states is high, (b) will not dominate in any temperature range and a direct transition from (a) to (c) will result (Mott and Davis 1971). In the region of variable range hopping, a small deviation from the linear log σ vs. $1/T$ data is expected as illustrated (Mott and Davis 1971) in the low temperature end corresponding to (c). The values of C and ΔE in themselves cannot distinguish between processes (a) and (d). Therefore to identify (d), in addition to the σ measurements, thermoelectric power measurements (by which it is possible to identify a characteristic hopping energy that can be associated with a dominant constituent) are necessary. Further, for ascertaining (d), high temperature data are used because distortion-related activation energy is a feature of high temperatures; at low temperatures, it is not possible to isolate this mechanism from hopping between non-polaronic localised states which originate from 'defects'.

Region I: From the discussions summarised above, and by comparing the σ–T data obtained presently with those illustrated (Mott and Davis 1971), the conductivity in region I can be taken as due to the hopping of carriers in the localised 'defect' states near the Fermi level E_F. Based on this mechanism it is also possible to understand the differences in σ in region I (figure 1, data ⑥ and □). In the Davis–Mott band model for amorphous semiconductors, localised states of sufficiently high density exist near the centre of the gap which pin the Fermi level. The origin of these states is speculative, but they conceivably arise from some specific defects characteristic of the material, for example dangling bonds, interstitials etc.; the number of these defects will depend on the conditions of sample preparation and subsequent annealing treatments (Mott and Davis 1971). The higher density of defect states in one set of samples (□ data points) due to differences in preparation or subsequent annealing conditions could result in a higher conductivity in this region compared to the present data (data ⑥, figure 1).

The other conduction mechanism which has to be considered at low temperatures is the variable range hopping mechanism. The log σ data in region I does not vary as $1/T^{1/4}$, thereby ruling out this mechanism. Linearity of the plot of log σ vs. $1/T^{1/4}$ is generally used to identify the region of variable range hopping. However, various factors besides variable range hopping could lead to a linear log σ vs. $1/T^{1/4}$ (Redfield 1971; Adler *et al* 1973; Maschke *et al* 1974; Fagen 1974). As discussed repeatedly by several authors (Mott 1968, 1969; Morgan and Walley 1971; Brodsky and Gambino 1972; Bluzer and Bahl 1974; Sudha Mahadevan *et al* 1977) and also as pointed by Mott (1972), the linearity of log σ vs. $1/T^{1/4}$ data in itself cannot be taken as evidence for this process. In addition to this validity, the data should yield reasonable values of other parameters like the density of states, pre-exponential factor etc. (Morgan and Walley 1971; Capek *et al* 1975). The present data, when examined, indicate the linearity of log σ vs. $1/T^{1/4}$ from 165 to 300 K for $CdAs_2$; this temperature range increases with increasing Ge content and there is validity from 190 to 350 K for $CdGeAs_2$, as seen from the data given in figure 2. But, based on the unreasonable values of 10^{32} to 10^{60}/cc for the density of states and of about 10^3 ohm^{-1} cm^{-1} for the pre-exponential factor C [evaluated using standard methods already outlined elsewhere (Brodsky and Gambino 1972; Sudha Mahadevan *et al* 1977)], the mechanism of variable range hopping cannot be associated at these temperatures.

Region II: From the results outlined presently (table 1, figure 1), it can be concluded that in region II (200 to 440 K), there is normal band type intrinsic conduction due to carriers excited into the extended states. The features of region II could also be associated with (d) in this temperature region. But an analysis of the present σ data and the data on the thermoelectric power of these glasses (Callearts *et al* 1971), indicated that there is no constant difference between the activation energies obtained from σ and thermoelectric power measurements of these glasses, thereby precluding contribution from (d) in region II.

Figure 3a compares the σ value at room temperature reported for the $CdGe_xAs_2$ glasses (Vaipolin *et al* 1966; Abraham *et al* 1970; Cervinka *et al* 1970; Callearts *et al* 1971; Hruby and Stourac 1971; Gorjunova *et al* 1974). Differences of an order of magnitude are seen in σ value for any given composition. In the present study therefore, σ was measured for three–four samples from two different batch preparations. Figure 3b shows the scatter obtained from such a study; the average of these values for any composition has been shown in figure 3 (solid dots, figure 3a). Inspite of the differences in the σ values, a general trend of σ decreasing with increasing Ge

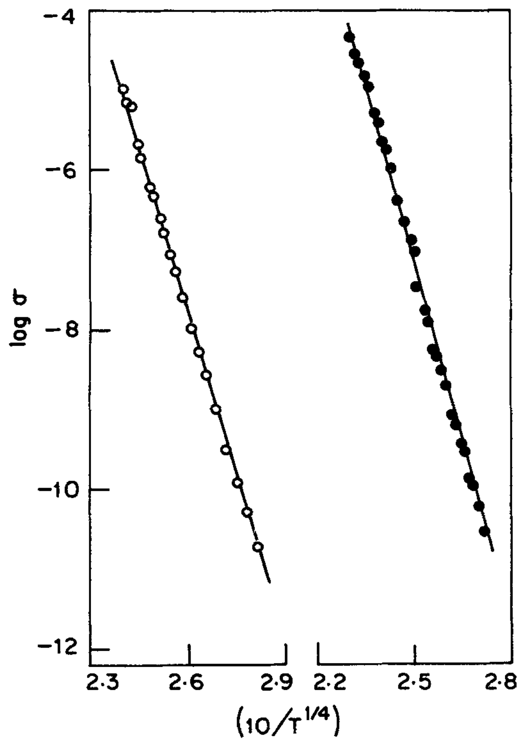

Figure 2. Log σ vs $1/T^{1/4}$ data for $CdAs_2$ (○) and $CdGeAs_2$ (●) glasses.

content up to 15 at.% and levelling at higher Ge contents is seen in all the studies. The results obtained presently (figure 3b) confirm this conclusion. The ΔE values of these glasses are seen to cover a small range (0·44 to 0·56 eV), with a maximum being indicated at the reference composition. For the Cd_2GeAs glasses, a peak in ΔE (table 1) and a corresponding broad minimum in σ are seen at the reference composition.

Region III: The onset of region III is marked by a rapid increase of σ, and in the later part of region III (broken line, figure 1) an instantaneous increase in σ occurs. The associated abnormally large values of the activation energy and the factor C, precludes any of the mechanisms (a) to (d) discussed above as being operative in this region.

In the present σ measurements, as already indicated, a 5 V (5 A rating) d.c. power supply, the sample and the ammeter were all in series without any load resistance included in the circuit. For typical sample dimensions used (for an area of about 5 mm dia, and about 1·8 mm thickness), a current of the order of 150 mA in the samples was found to increase instantaneously to more than 5 A corresponding to the broken line portion of region III. At this stage, the circuit was immediately broken by disconnecting one of the leads of the ammeter. The samples, when examined after cooling to room temperature, were found to retain the conducting state even when disconnected from the measuring circuit. The samples also retained the shine characteristic of the glassy state; further, the temperature corresponding to

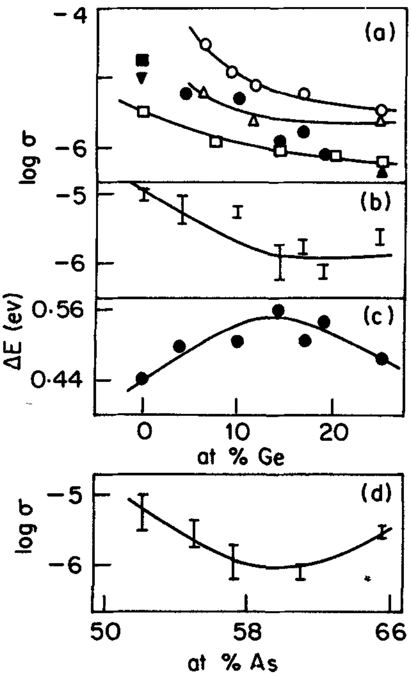

Figure 3. (a) Data on log σ (at 300 K) for $CdGe_xAs_2$ glasses from literature [–○– Callearts *et al* 1971, –△– Cervinka *et al* 1970, –□–Gorjunova *et al* 1974, –■– Abraham *et al* 1970. –▽– Hruby and Stourac 1971, –▲– Vaipolin *et al* 1966]. (b) Log σ obtained from the present study. The average of these values for any composition is denoted by (●) data points in figure 3a. (c) The activation energy for conductivity, ΔE, for the $CdGe_xAs_2$ glasses. (d) Log σ (at 300 K) for Cd_2Ge–As glasses; the ΔE values for these glasses are listed in table 1.

the onset of region III is well below the crystallization temperature of these glasses for all the compositions studied. A stimulating pulse was required to bring these samples back to the off state. It was therefore concluded that the steep and sudden increase in σ is due to a switching effect wherein a conducting filament is formed between the electrodes. The switching is of the memory type. It could further be conjectured that this filament is probably of cadmium, based on the observation (table 1) that the temperature of the setting in of region III is about 40 to 60 K lower for the glasses 1 and 8 which are rich in Cd.

Threshold and memory switching effects have been observed in bulk $CdGeAs_2$ (Baryshev *et al* 1970). In these studies, the samples were in the form of beads of irregular shape, about 1 to 1·5 mm across. The leads were platinum wires (0·05 to 1·0 mm dia) separated by a distance of 30 to 200 μ. When there was load resistance in the circuit (50 kΩ to 10^6 Ω), threshold switching was seen for voltages of 80 to 500 V, depending on the distance between the electrodes. When the I–V characteristics were recorded using a low load resistance, the transition to the on-state was accompanied with a memory effect in which the device remained in the on-state even when it was disconnected from the circuit. The intensity of this effect was governed by the value of the current and the duration of its flow through the element in the on-state. The passage of current over 2 mA produced strong memory effects. For the sample dimensions used in these studies (Baryshev *et al* 1970), for avoiding heating of the samples, a current of about 3 mA is indicated.

The memory switching observed presently (in region III of the $\sigma-T$ characteristics) differs from that observed in the $CdGeAs_2$ beads (Baryshev *et al* 1970) discussed above, with respect to the magnitude of the currents involved and the field (voltage) at which switching sets in. The larger current handling capability in the present studies is due to the much larger (about 5 mm dia and 1·8 mm thickness) sample dimensions compared to the wire electrodes about 100 μ apart in the experiments with beads. Also, the samples in the present study are at temperatures of about 500 K, compared to the experiments with beads which were at room temperature. Therefore, because of the additional thermal assistance, switching is seen at much lower fields ($\sim$30 V/cm) in the present experiments.

The following observations in the present samples lend further support to the hypothesis that the observed increase in σ (region III) is due to switching. For several samples in region III, there was no continuous or smooth increase of current with temperature. Instead, the current used to fluctuate continuously between low and high values for some time before attaining the final high value of about 150 mA after which the increase to more than 5 A was instantaneous. Some samples, at the end of one cycling to the high current state, were found to have conductivity values in between that of the on-state and the original room temperature value. These samples could be induced to attain the on-state with a further one or two cyclings to the high temperature conducting state. These are all instabilities characterising switching behaviour and are associated with the formation of the conducting filament. The initial portion of region III (continuous line, figure 1) can be associated with the formation of the conducting filament. On completion of the formation of the conducting filament, an instantaneous increase in σ (broken line) results.

4. Summary and conclusions

Results of measurement of the d.c. electrical conductivity σ from 85 to 550 K are reported for eleven glass compositions of the Cd–Ge–As system. Three regions can be distinguished in the σ-T dependence of these glasses. In region I at low temperatures (85 to 145 K), σ is essentially constant and it is possible to associate the mechanism of conduction with carriers hopping in localised defect states in this region. Normal band type conductivity (wherein the carriers are excited to the extended states beyond the mobility edge) seems to account for the conductivity in region II (200 to 440 K), where σ is found to be thermally activated with a single activation energy. In the high temperature region III (above 430 K), there is a steep and instantaneous increase in σ. Further analyses of this data indicate that the observed sudden increase in σ is due to a memory switching effect which, due to the additional thermal assistance, occurs at a fairly low voltage (5 V) in these bulk samples.

The composition dependence of σ at 300 K and ΔE (region II) are also reported for the $CdGe_xAs_2$ and Cd_2GeAs glasses.

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