CHAPTER - III

RESULTS
CHAPTER - III

RESULTS

A : STUDY OF Al-CdS-Al STRUCTURES

Samples of aluminium-cadmium sulphide-aluminium sandwich structures have been prepared by depositing thin films in the above sequence on a clean microscope glass slide. The cadmium sulphide film (≈ 1.5 μ thick) is deposited on the substrate at room temperature in a vacuum of the order of $10^{-3} - 10^{-4}$ torr with the source at about 900°C. The current-voltage characteristics of these structures at room temperature show two stages. The first is a pre-breakdown stage in which the structure shows a higher resistance and the second is the post-breakdown stage where the resistance is about 1/4 to 1/5 of that in the pre-breakdown stage. When the voltage in the first stage is increased beyond a critical value $V_x$, the structure transforms irreversibly into the second stage in which a dual negative resistance is observed. In both the pre-breakdown and post-breakdown stages, a non-linear dependence of current on voltage is obtained. In what follows, we describe these two stages in detail.

(1) Pre-breakdown stage

Figure 15 shows the room temperature current-voltage characteristic in the pre-breakdown stage for Al-CdS-Al sandwich structure. Triangular pulses of frequency $0.25$ c/sec have been used (Fig. 14). Most of the samples are found to
Fig : 14 : Applied pulse characteristic with repetition frequency 0.25 c/s.

X - 5 small divisions per second. Y - 4 small divisions = 1 volt.
Fig. 15
Aging effect on I-V characteristic of Al-CdS-Al diode in the pre-breakdown stage:
(1) Initial curve
X-4 small divisions = 1 volt
Y-4 small divisions = 5 μΩ.

Fig. 16: Effect of frequency on I-V characteristic of Al-CdS-Al diode in the pre-breakdown stage.
(1) Repetition frequency
0.025 c/s
X-4 small divisions = 1 volt
(2) Repetition frequency
0.25 c/s
Y-4 small divisions
show higher resistance and hysteresis when the top electrode is made positive (upper right hand quadrant in Figure 15). During the other half of the cycle in which the top electrode is negative, the resistance is smaller and the hysteresis is nearly absent. From Fig. 15 we can also see that the current varies non-linearly with voltage. Figure 15 also shows some aging effect. The curve marked (2) is taken after subjecting the sample for 5 minutes to a voltage cycling between ±2.5 volts. The curve marked (1) is the initial curve. We can clearly see that the current density decreases on repeated cycling. The original curve (1) is not restored even after keeping the field off for several hours.

Figure 16 shows the effect of frequency (0.25 and 1826 c/sec.) of the applied voltage on the I-V characteristic. The increase in the frequency decreases the current density in both the directions. If the field is kept on at 0.25 c/sec., the current density keeps on reducing continuously to lower values. Furthermore, it takes several hours to come to its original conductivity state after the field is switched off. If the duration of the applied field is long then the original conductivity stage is not restored. In most of the samples the current on low resistance side falls more rapidly than that on the other side and after some time the rectification observed in Figure 15 vanishes completely.

The above mentioned behaviour is maintained as long as the applied voltage does not exceed a certain critical voltage $V_x$, the value of which depends upon the nature, thickness and
Fig. 17: I-V characteristic of Al-CdS-Al in the post-breakdown stage.
X = 4 small divisions = 1 volt. Y = 4 small divisions = 5 ma

Fig. 18: Steps and current saturation in the I-V characteristic of Al-CdS-Al diode in the post-breakdown stage.
X = 4 small divisions = 1 volt. Y = 4 small divisions = 5 ma
temperature of the cadmium sulphide film. If the applied voltage is increased beyond this point ($V_x$) an irreversible breakdown takes place. In most of the samples this is observed first on the high resistance side and then on the other side. After this breakdown is complete, the structure transforms into the second (or post-breakdown) stage characterised by a dual negative resistance.

(2) Post-breakdown stage

After the above mentioned irreversible transformation, the structure shows at room temperature a current-voltage characteristic as shown in Fig.17. Triangular pulses (Fig.14) of frequency $\approx 25$ c/s have been applied. In this stage, when the applied voltage on the top electrode (positive) is increased from zero (point 0), the curve follows the path $0A$. At voltage $V_A$ (point A) the current starts increasing i.e. the sample is transformed into a high conductivity state. During this transition, the voltage across the sample drops down to a value $V_B$ and the current increases from $I_A$ to $I_B$. This transition is slow and irregular but sometimes, clear steps are observed (Fig.18).

After the transformation is complete, on decreasing the applied voltage from $V_B$, the same conductivity state (i.e. high conductivity state) is maintained and the curve $B'BO$ (i.e. different from $OAB$) is traced out. If we decrease the voltage beyond zero (i.e. top electrode negative) a path symmetrical to that of $BO$ is obtained up to the point $C$ (voltage $V_C$). At $C$, the curve drops down to a lower value through an increase in voltage to the point $D$ (voltage $V_D$). Here the transition from high conductivity state to low conductivity state takes place. This transition is smooth and more ra
than the low to high conductivity state transition. However, sometimes discrete steps similar to those in the other transition are also observed (Fig.18). In some samples near the transition point $V_C$, a small current saturation is observed (Fig.18) and in this part of the curve, sometimes random oscillations are also observed. After this low conductivity transformation is complete, further increase in voltage does not change the state (curve DE in Fig.16). When the voltage is decreased from $V_B$, the path EOA is traced out i.e. the sample remains in the low conductivity state.

This process can be described as follows: From voltages $V_0$ to $V_A$, a low conductivity state is maintained, at $V_A$ an increase in the current through a decrease in the voltage to $V_B$ takes place and the structure goes to high conductivity state. This high conductivity state is maintained till a critical voltage $V_C$ is reached at which the current decreases through an increase in voltage and the structure switches back to the low conductivity state. This state is maintained till we reach $V_A$ and the whole pattern is retraced. The part OABO of the curve resembles the current controlled negative resistance region with large hysteresis effects i.e. the path $\overline{OB}$ is not same as $BO$. The path OCDEO resembles a voltage controlled negative resistance region with high hysteresis effects i.e. the path $\overline{OC}$ is not the same as $CO$. So in the same sample both current controlled as well as the voltage controlled negative resistance characteristics are observed and hence the name "Dual Negative Resistance".
In both the states (i.e. the low conductivity as well as the high conductivity state) the current varies non-linearly with voltage. The current controlled negative resistance is observed only when the top electrode is positive and the sample is initially in the low conductivity state and the voltage controlled negative resistance appears only when the top electrode is negative and the sample is in the high conductivity state to start with. These sides correspond to the high resistance and low resistance sides in the pre-breakdown stages. Furthermore, this switching of the conductivity states takes place at the respective critical voltages $V_A$ and $V_C$ only. If, on the other hand, the applied voltage is kept below these critical voltages, the switching over is not observed. For example, if we are in the low conductivity state and the positive voltage on the top electrode is increased from $V_0$ to (Fig.16) voltage say $V_A$ (\( \omega \)) and then start decreasing the voltage, the switching from low to high conductivity state does not take place even if we cross the point $E$ in the curve i.e. the same state is maintained and a path $OA'OEO$ is traced out without any transition or hysteresis. As we go nearer to $V_A$ the distortion starts. Similarly, if we are initially in the high conductivity state and a voltage is applied such that we never cross $V_0$ (say upto $V_C$) the path $OC'O$ is retraced. Even if we go to the other side i.e. if we make the top electrode positive and we come to the point $V_B$, no transition will take place and the curve $OC'OBO$ will be traced out backwards and forwards without hysteresis and any negative resistance characteristic.
Fig. 19: I-V characteristic of Al-CdS-Al diode with incomplete transformation.

X - 4 small divisions = 1 volt. Y - 4 small divisions = 5 ma

Fig. 20: Effect of frequency on I-V characteristic of Al-CdS-Al diode in post-breakdown stage.

(a) Repetition frequency 0.0025 c/sec.
(b) Repetition frequency 25.00 c/sec.
(c) Repetition frequency 250.00 c/sec.

X - 4 small divisions = 1 volt. Y - 4 small divisions = 5 ma.
It is also observed that the transformation from low to high conductivity state is slow. Furthermore, if we control the voltage such that this transformation is not completed, i.e. the final value \( I_B \) is not reached, then the value of \( V_B \) is higher than that in the samples which are completely transformed (Fig. 19). However, in all the samples \( |V_B| \approx |V_C| \) regardless of the fact that complete transformation from low to high conductivity state has occurred or not. It was not possible to interrupt the voltage during the transition from high conductivity to low conductivity state because this transition is much faster. Furthermore, \( I_B \approx I_C \) in every sample.

At low frequencies (even down to 0.001 c/sec.) no appreciable change in the general behaviour is observed except that the voltage \( V_A \) is a little less and the transformation becomes more irregular (the curve (a) in Fig. 20). At higher frequencies (\( \approx 250 \) c/sec.) the low conductivity to high conductivity transformation is incomplete because of its slowness and the observed behaviour is as shown in Fig. 20, curve (b). The values of voltage \( V_A \) and \( V_D \) increase as the frequency is increased. Furthermore, the voltage \( V_B \) mostly remains equal to \( V_C \) frequencies upto 25 c/sec. They differ slightly at higher frequencies. At very high frequencies of the order of 250 c/sec. the negative resistances vanishes completely and the curve is similar to the low conductivity curve at low frequencies (Fig. 20, curve C).
B : EFFECT OF ELECTRODE

With a view to find out whether this dual negative resistance phenomenon is observed when metals other than aluminium are used as electrodes, Me-CdS-Me sandwiches have been prepared with indium, gold and copper metal electrodes in place of one or both the aluminium electrodes and their I-V characteristics studied.

Aluminium and indium have been observed to give ohmic sulphide contacts to the deposited cadmium films while gold and copper are known to give blocking or rectifying contacts. It is also well-established that the vacuum deposited cadmium sulphide films are always n-type and so the majority carriers are electrons. Furthermore, the ohmic contacts give space charge limited currents while the blocking contacts give either the tunneling or Schottky field emission. The study of the effect of metal electrode on the current voltage characteristic is useful to establish some aspects of conduction mechanism in both the pre-breakdown and post-breakdown stages.

The following three configurations are studied:

1. **Both electrodes are ohmic**
   - (a) Al-CdS-In
   - (b) In-CdS-Al
   - (c) In-CdS-In

2. **One of the two electrodes is ohmic**
   - (a) Al-CdS-Au and Au-CdS-Al
   - (b) Al-CdS-Cu and Cu-CdS-Al
(3) **Both electrodes are blocking**

(a) Au-CdS-Au

(b) Cu-CdS-Cu

**Both electrodes ohmic**

The three sandwiches (a), (b), (c) show the same behaviour as Al-CdS-Al structure discussed earlier. The high resistance and hysteresis are observed when the top electrode (i.e. indium in (a) and (c) and aluminium in (b)] is positive. In the post-breakdown stage the dual negative resistance is observed. The voltages $V_B$ and $V_C$ remain nearly the same as in Al-CdS-Al structure but $V_A$ and $V_B$ are slightly increased. It is also observed that during the CCNR path, patches due to burning are sometimes formed on indium film and if the cycling is continued for a long time, the indium film gets destroyed. Secondly, the transition from high conductivity to low conductivity state (V CNR) is faster than that in the Al-CdS-Al structure.

In general, in all these structures the pre-breakdown stage irreversibly transforms into a second stage where the dual negative resistance is exhibited. The CCNR is observed when the sample is in the low conductivity state and the top electrode is positive irrespective of the electrode metal Al or In.

**One electrode ohmic**

Under this class, we have studied the sandwiches where aluminium is used as the ohmic metal electrode because indium
Fig: 21: Low voltage I-V characteristic of Al-CdS-Au diode in the post-breakdown stage.

X - 4 small divisions = 1 volt. Y - 4 small divisions = 0.25 ma

Fig: 22: High voltage I-V characteristic of Al-CdS-Au diode in the post-breakdown stage.

X - 4 small divisions = 1 volt. Y - 4 small divisions = 0.5 ma
gives poor reproducibility. For the same reason, gold instead of copper is used as the second electrode. In the following paragraphs the behaviour of the Au-CdS-Al and Al-CdS-Au is described.

In the pre-breakdown stage both these sandwiches have properties similar to those of the sandwiches discussed under (1) above, except that in present case the structure shows high resistance only when the gold electrode is made negative irrespective of whether it is at the top or bottom, whereas in the earlier cases the high resistance was observed when the bottom electrode was made negative. Furthermore, the breakdown voltage \( V_x \) is somewhat higher than that in Al-CdS-Al structure having approximately the same cadmium sulphide thickness.

In the post-breakdown stage a rather interesting behaviour is observed. The current-voltage curve shows two types of characteristics depending on the amplitude of the applied voltage pulse.

(a) Low voltage range

Figure 21 shows the I-V characteristic for Al-CdS-Au diode in the low voltage range in the post-breakdown stage. Although the usual negative resistance is exhibited as before but the nature of the curve is different which can be described as follows. When the aluminium (bottom electrode in Al-CdS-Au diodes and top electrode in Au-CdS-Al diodes) electrode is negative and the sample is in the low conductivity state (curve OA) a transition from low conductivity takes place, say at A (0.5 to 0.7 volts). This transition is similar to that in Al-CdS-Al giving rise to a current controlled negative resistance region. The only
difference is that the value of $V_A$ is much smaller than that in Al-CdS-Al structure. Secondly, the drop in voltage i.e. $V_A - V_B$ is very small. This can be seen from the steep rise of current from point A to B. When the voltage is decreased from $V_B$ this high conductivity state is maintained till the voltage equal to $V_B$, in the opposite direction is reached ($V_C$), where the transition from high conductivity state to low conductivity state takes place through a voltage controlled negative resistance region. Here $V_D$ is higher than $V_A$ which was not so, ($V_A < V_D$) in Al-CdS-Al structure. Furthermore, this nature of the curve as a whole is not affected on increasing the frequency of the applied voltage pulse, which is contrary to what was obtained in the Al-CdS-Al structure. Secondly, the peak current in CCNR side is greater than that in the VCNR side whereas it was just the opposite for Al-CdS-Al sandwich diodes.

(b) High voltage

If the voltage is increased further above $V_B$ (after tracing the path OAB and aluminium negative) the path BF is followed (in agreement with the earlier observations on Al-CdS-Al structure). However, at F the system switches from high to low conductivity state through the path FGH (Fig. 22). This is different from the Al-CdS-Al system where no such behaviour is observed. After decreasing the voltage from H the curve (i) either
retraces the path HGFEOCDE or (ii) follows a new path HGAOC'DEO. It can be seen that in the first case the behaviour is similar to that described earlier for the low voltage case of Al-CdS-Au in the lower right hand quadrant (VCNR side). When the path HGAOC'DEO is followed the loop GFBO is missed out and VCNR peak is much reduced. Furthermore, this peak goes on reducing on repeated cycling till a stage is reached where no negative resistance (neither CCNR nor VCNR) is observed. If the field is made off for sometime the structure regains the initial negative resistance characteristic.

It is generally observed that if the frequency of cycling is small then the behaviour described under (i) is followed, whereas at higher frequencies that under (ii) is observed. Furthermore, in the Au-CdS-Al diodes a direct shorting is observed in many samples and the behaviour described above is rarely observed.

Both the electrodes are gold (or copper)

In Au-CdS-Au structures initially (i.e. corresponding to the pre-breakdown stage of the earlier samples) we get a symmetrical I-V characteristic and no rectification is observed. When the applied voltage is increased the transformation to the low resistance structure (corresponding to the post-breakdown stage of the earlier cases) is never obtained, even if one has reached the destructive breakdown point of the sample. In some samples direct shorting between two gold
electrodes is observed even with thicker CdS films.

The above study of the effect of the electrode material on the I-V characteristic of metal cadmium sulphide sandwiches leads us to the conclusions that (i) the dual negative resistance is observed only when at least one of the electrodes is aluminium or indium and (ii) for any sample showing dual negative resistance $|V_B| \ll |V_C|$ but the exact value of $V_B$ or $V_C$ varies from sample to sample depending on the material of the electrodes.
Fig 23: I-V characteristic of Al-CdS-Al diode at liquid air temperature in the pre-breakdown stage.

X - 4 small divisions = 2 volt. Y - 4 small divisions = 5 μA.

Fig 24: I-V characteristic of Al-CdS-Al diode at -170°C in the post-breakdown stage.

X - 4 small divisions = 1 volt. Y = 4 small divisions = 5 ma.
The current-voltage characteristics of Al-CdS-Al structure have also been studied at different temperatures. Al-CdS-Al sandwich structures have been prepared as usual and the I-V characteristics measured at various temperatures from 77°K to 350°K as described earlier on page 47. Both the pre-breakdown stage as well as the post-breakdown stage with dual negative resistance are observed.

**Pre-breakdown stage**

In this stage the current at any given voltage, in general, decreases on decreasing the temperature. Fig.23 shows that I-V curve for the sample at liquid air temperature. Secondly, \( V_x \), the voltage required for transformation from pre-breakdown to post-breakdown stage increases on decreasing temperature whereas the hysteresis effect decreases. However, the rectification is not affected.

**Post-breakdown stage**

Figures 17 and 24 show the I-V curve of Al-CdS-Al at room temperature and at -170°C respectively. It can be seen that the shape of the I-V curve remains unchanged with temperature. However, the values of the critical voltages \( V_A, V_B, V_C \) and \( V_D \) are, to some extent, affected although no systematic change has been observed. Sometimes the value of \( V_C \) decreases and a sudden increase in current at \( V_C \) is observed. The current density at any given voltage and the area under the loop, in
general, decreases slowly with decreasing temperature.

Table No.7 gives the values of different critical voltages at various temperatures.

Table No.7

<table>
<thead>
<tr>
<th>Temperature°C</th>
<th>Critical voltages in volts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_A$</td>
</tr>
<tr>
<td>-170</td>
<td>3.35</td>
</tr>
<tr>
<td>-142</td>
<td>3.25</td>
</tr>
<tr>
<td>-97</td>
<td>3.20</td>
</tr>
<tr>
<td>-75</td>
<td>3.15</td>
</tr>
<tr>
<td>-53</td>
<td>3.12</td>
</tr>
<tr>
<td>-32</td>
<td>3.10</td>
</tr>
<tr>
<td>-16</td>
<td>3.05</td>
</tr>
<tr>
<td>+20</td>
<td>3.05</td>
</tr>
<tr>
<td>+37</td>
<td>3.10</td>
</tr>
</tbody>
</table>

EFFECT OF THICKNESS

The thickness of the cadmium sulphide layer in Al-CdS-Al structure has been varied from 1.0 $\mu$m to 2.0 $\mu$m by evaporating to completeness different amounts of cadmium sulphide kept in the filament. Other conditions have been maintained identical during all the depositions. The current-voltage characteristics show the following dependence on thickness where the other features remain similar to what has been discussed earlier.
Fig: 25: Effect of thickness of the I-V characteristic of Al-CdS-Al diode in the pre-breakdown stage.

X - 4 small divisions = 1 volt. Y - 4 small divisions = 5 mA.
Pre-breakdown stage

(i) Decrease in current density as the thickness increases, and

(ii) Increase in $V_X$ as the thickness increases.

In Fig. 25 the curves marked (1), (2) and (3) are respectively for the cadmium sulphide thickness in decreasing order. We can see the current density on both the sides decreases as the thickness increases. Furthermore, the rectification effect as observed in Fig. 15 is reduced in thicker films and the same is also true for the hysteresis effect on the high resistance side. Table No. 8 gives the values of $V_X$ for different samples, from where we can see that the breakdown voltage increases with increasing thickness.

Post-breakdown stage

In the post-breakdown stage the dual negative resistance is observed even in thicker films but there is a small increase in the values of critical voltages $V_A$, $V_B$, $V_C$ and $V_D$ in these films. However, this increase is less than that in $V_X$. The effect on the current density is also not so pronounced. Table No. 8 summarises these observations.

<table>
<thead>
<tr>
<th>No.</th>
<th>Thickness of CdS x $10^{-4}$ cm</th>
<th>Breakdown Voltage $V_X$ in volts</th>
<th>Critical voltages in volts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$V_A$</td>
</tr>
<tr>
<td>1</td>
<td>1.036</td>
<td>3.50</td>
<td>3.05</td>
</tr>
<tr>
<td>2</td>
<td>1.331</td>
<td>4.00</td>
<td>3.05</td>
</tr>
<tr>
<td>3</td>
<td>1.687</td>
<td>4.50</td>
<td>3.10</td>
</tr>
<tr>
<td>4</td>
<td>2.130</td>
<td>4.75</td>
<td>3.15</td>
</tr>
</tbody>
</table>
EFFECT OF SOME OTHER PARAMETERS

In this section we discuss the effect of:

(1) Deposition conditions during cadmium sulphide deposition.

(2) Intermediate exposure to air before or after cadmium sulphide deposition.

(3) Heat treatments of the deposited cadmium sulphide films.

(4) Doping of cadmium sulphide powder before evaporation.

Deposition conditions

It has been observed earlier that the nature of the vacuum deposited cadmium sulphide films vary with the deposition conditions. The resistivity of the film depends largely on the amount of excess Cd in the film. For example, cadmium sulphide deposited on a substrate kept at temperatures above 200°C under a pressure greater than $10^{-5}$ torr is known to give stoichiometric films whereas that deposited at room temperature gives excess cadmium.

The effect of variation in:

(i) Source temperature.

(ii) Vacuum conditions, and

(iii) Substrate temperature on the current voltage characteristics of the Al-CdS-Al has therefore been investigated.
(1) **Source temperature:**

The source (filament) temperature during the cadmium sulphide deposition has been varied between $800^\circ C$ to $1000^\circ C$. Above $1000^\circ C$ there is too much of spurting. The films are transparent and have a high resistivity in all cases. The variation in filament temperature does not show any appreciable change in the current voltage characteristic of the diodes.

(ii) **Vacuum conditions:**

The samples prepared by depositing cadmium sulphide films at vacuum of the order of $10^{-3} - 10^{-4}$ torr give very high order of reproducibility and consistent I-V characteristics, while those prepared at $10^{-6}$ torr or in sulphur atmosphere show a poor reproducibility, although the features remain more or less the same. Furthermore, the value of $V_X$ is larger in samples prepared at $10^{-6}$ torr (6-7 volts) than in those prepared at pressure of the order of $10^{-3} - 10^{-4}$ torr (3-5 volts). Amongst the cadmium sulphide samples deposited at a sulphur pressure of $10^{-6}$ torr, some show initially a pre-breakdown stage as usual which is transformed into an intermediate stage where a dual negative resistance is observed but the polarity for CCNR and VCNR is interchanged i.e. the CCNR region is observed when the top electrode is negative while the VCNR region is observed when the bottom electrode is negative. This intermediate stage is observed till the voltage is below a certain threshold, at which point a second transformation takes place and the structure gives the usual current voltage characteristic as in Fig.17. Further increase in voltage does not change the characteristic. The films deposited at $10^{-6}$ torr.
sometimes show the above mentioned intermediate stage but very rarely.

(iii) substrate temperature:

The non-stoichiometry in cadmium sulphide films due to excess cadmium can be removed by depositing cadmium sulphide on hot substrates. This is due to the fact that above 150°C the vapour pressure of cadmium becomes \( \approx 10^{-5} \) torr, and the condensing probability (on the substrate above 150°C) for cadmium as well as sulphur becomes nearly equal. The substrate temperature has therefore been varied from room temperature to 150°C and its effect on the I-V characteristics of the diode is studied. The samples are prepared as described on page 42.

The samples prepared below 100°C show the usual current-voltage characteristics. The voltage at which the pre-breakdown stage transforms to the second stage (i.e., \( V_X \)) increases slowly as the substrate temperature increases. The samples prepared at the substrate temperature of 150°C the value \( V_X \) is observed to be of the order of 10-15 volts. In thin films sometimes the transformation does not occur because they burn away before that. The samples where this transformation is achieved show the dual negative resistance characteristic. Furthermore, the resistivity increases whereas the hysteresis effects and the current rectification in the pre-breakdown stage decrease as the substrate temperature is increased. This can be seen from the fact that the current at any voltage in the pre-breakdown stage is less for samples deposited on substrates kept at higher temperature. In the post-breakdown stage the values of the critical voltages
$V_A$, $V_B$, $V_C$ and $V_D$ remain nearly unaltered. These observations show that the effect of substrate temperature is pronounced on the pre-breakdown stage but not on the post-breakdown stage. Table No.9 lists the values of the different critical voltages for the samples deposited at various substrate temperatures.

**Table No.9**

<table>
<thead>
<tr>
<th>No.</th>
<th>Substrate temp. °C</th>
<th>Thickness of CdS films $\times 10^{-4}$ cm.</th>
<th>Breakdown voltage volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>2.130</td>
<td>4.75</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>1.600</td>
<td>5.20</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>1.1000</td>
<td>6.00</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>1.010</td>
<td>10.50</td>
</tr>
</tbody>
</table>

**Intermediate exposure to air**

The observed assymetry in the current-voltage characteristic in the post-breakdown stage including the fact that the CCNR occurs only when the bottom electrode is negative and the VCNR when the top electrode is negative, suggests that possibly the two metal-cadmium sulphide contacts may be different in nature. This may be due to the fact that we are exposing the first aluminium film to air before cadmium sulphide is deposited which may give a thin aluminium oxide layer leading to the observed assymetry. Alternatively, it is also possible that a thin
cadmium oxide layer or a layer of adsorbed oxygen or water vapour may be forming on the deposited CdS before the second deposition of Al. The diodes have therefore been prepared after eliminating these intermediate exposures to air and their I-V characteristics have been measured. However, the current voltage characteristics show no appreciable change from the usual behaviour. In the samples prepared without exposing to air before cadmium sulphide deposition, the hysteresis and the rectification are reduced considerably while they are increased in samples in which the exposure is avoided after the deposition of cadmium sulphide. This effect is also increased when the first deposited aluminium is exposed to dry oxygen. In all the samples the post-breakdown behaviour remains unchanged. The field direction required for the CCNR or the VCNR remains unaltered; showing that the asymmetry in the structure is not affected by these changes in the ambient conditions during depositions.

Heat treatments

It is known that heating cadmium sulphide films in vacuum, in inert atmosphere or in sulphur atmosphere removes excess cadmium and makes the compound stoichiometric. The samples prepared during our investigations have been heated in different atmospheres with a view to see its effect on the I-V characteristic of the diodes.
Fig : 26 : I-V characteristic of Al-CdS-Al diode in the pre-breakdown stage. The CdS film is heated in vacuum.

X - 4 small divisions = 1 volt. Y - 4 small divisions = 5 μa.
(a) Heating in vacuum

For diodes, where the deposited cadmium sulphide film has been heated in vacuum, the transformation from the pre-breakdown to post-breakdown stage often takes place in two steps. The first step occurs at about 3.75 volts and the second is observed at about 7.5 volts. After this second breakdown the structure shows the usual dual negative resistance characteristic. Before the first breakdown takes place a small peak in current on the high resistance side is sometimes observed (Fig.26), which vanishes on repeated cycling. In the dual negative resistance stage the values of the critical voltages \( V_A, V_B, V_C \) and \( V_D \) are increased to a smaller extent as compared to the samples in which the cadmium sulphide film has not been heated. Furthermore, during the transition from high conductivity state to the low conductivity state (point C) the decrease in current is not so pronounced.

(b) Heating in sulphur atmosphere

Current-voltage characteristics similar to that described above are exhibited. However, these structures the above-mentioned current peak on the high resistance side of the pre-breakdown stage is not observed. Furthermore, in the post-breakdown stage the values of the critical voltages are increased as compared to unheated samples but only slightly.
Doping of the cadmium sulphide

With a view to examine the role of donor or acceptor levels in the observed I-V characteristics, samples containing CdS doped with In$_2$S$_3$ and Ag$_2$S have been prepared and the current voltage characteristics are studied.

In the diodes having cadmium sulphide doped with impurities the transformation voltage $V_X$ at which the pre-breakdown stage goes to the post-breakdown stage slowly decreases with the increase in the concentration of In$_2$S$_3$. No other significant change from the usual pattern is observed. Sometimes, the transition from the low conductivity state to high conductivity state takes place at a slightly lower voltage ($V_A$) and the increase in the current is much steeper as compared to the undoped samples. This effect is more pronounced in samples having high concentrations of In$_2$S$_3$. The other critical voltages remain more or less unaffected.

Similar characteristic features are observed in the diodes containing Ag$_2$S doped cadmium sulphide. The value of $V_X$ is more in these diodes than in those containing In$_2$S$_3$ doped cadmium sulphide. However, in this case the $V_X$ is more or less independent of the Ag$_2$S concentration.
Table No.10

Effect of doping

Thickness of the CdS film $2.5 \times 10^{-4}$ cms.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>$V_X$</th>
<th>$V_A$</th>
<th>$V_B$</th>
<th>$V_C$</th>
<th>$V_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N 1</td>
<td>5.00</td>
<td>3.20</td>
<td>2.40</td>
<td>2.35</td>
<td>3.40</td>
</tr>
<tr>
<td>2</td>
<td>N 2</td>
<td>4.50</td>
<td>3.20</td>
<td>2.40</td>
<td>2.40</td>
<td>3.40</td>
</tr>
<tr>
<td>3</td>
<td>N 3</td>
<td>4.50</td>
<td>3.15</td>
<td>2.45</td>
<td>2.40</td>
<td>3.35</td>
</tr>
<tr>
<td>4</td>
<td>N 4</td>
<td>3.25</td>
<td>3.10</td>
<td>2.35</td>
<td>2.35</td>
<td>3.35</td>
</tr>
<tr>
<td>5</td>
<td>P 1</td>
<td>7.50</td>
<td>3.35</td>
<td>2.45</td>
<td>2.40</td>
<td>3.50</td>
</tr>
<tr>
<td>6</td>
<td>P 2</td>
<td>7.55</td>
<td>3.40</td>
<td>2.40</td>
<td>2.40</td>
<td>3.50</td>
</tr>
<tr>
<td>7</td>
<td>P 3</td>
<td>7.50</td>
<td>3.45</td>
<td>2.35</td>
<td>2.35</td>
<td>3.45</td>
</tr>
<tr>
<td>8</td>
<td>P 4</td>
<td>7.45</td>
<td>3.40</td>
<td>2.35</td>
<td>2.40</td>
<td>3.55</td>
</tr>
</tbody>
</table>