Chapter VII

Resistivity Analysis
7.1 Introduction

Thin films of CdTe used in electronic devices often have problems with electrical contacts. This is due to the non-availability of a contacting material with a large work function for proper matching with p-CdTe. Because of the rather high work function of CdTe and the difficulty of achieving high doping levels in p-type CdTe, a low-resistance ohmic contact cannot be formed by a simple metallization. ZnTe, which has a small valence band discontinuity with CdTe and can be doped degenerately with Cu, has been used as an intermediate layer between the high-resistivity CdTe and the metal contact.

The resistivity of the semiconductor film is very sensitive to deposition conditions and nature of the material. It is also related to film thickness and free path of the charge carriers.

The II-VI compound semiconductors are known for large band gaps and are widely used in optoelectronic devices of the visible spectrum including solar cells and LEDs [1]. However, the problem with these materials is that they are highly prone to self-compensation [2,3] and in the majority of them the type of conductivity is hard to control. ZnTe is a prominent member of the II-VI group and exists as a p-type semiconductor only. Only scant data are available in the literature regarding the electron transport in ZnTe films. Burgelman [4] has made an attempt to understand the conduction mechanism in high-resistivity evaporated ZnTe films. Senokosov et al [5] have prepared single-crystal ZnTe films and investigated their current transport characteristics. Low frequency current oscillation in ZnTe films has been reported by Matveeva et al [6]. A few other reports [7-9] are available about amorphous ZnTe films prepared in ultrahigh vacuum with reproducible properties. The variation of electrical resistivity and photosensitivity in ZnTe films grown on glass substrates by vacuum evaporation has been explained by Patel [10] on the basis of stoichiometric composition and crystallite size. The low resistivity of copper doped ZnTe films was fabricated [11] and abnormal conductivity behavior with
The electrical resistivity of pure ZnTe films lies in the range $10^5$-$10^6$ $\Omega$cm [13], whereas all the doped ZnTe films show comparatively lower resistivity. Due to the high resistivity of pure ZnTe films, no four probe, Hall or thermoelectric measurements could be performed to probe into the mechanism of electronic phenomena in these films properly [14].

According to the modern quantum electronic theory, electrical conduction in metals is due to electrons, while electrical resistivity results from the scattering of the electrons by the lattice. Resistivity being, therefore, a measure of the extent to which a metal lattice departs from perfect regularity.

ZnTe is highly prone to self-compensation. This may result in light variation in the electrical resistivity of such materials when doped lightly because most of the dopant atoms are not finding appropriate lattice sites and thus remain ineffective [13].

This chapter deals with the resistivity studies on copper layered ZnTe thin films by four probe method. The type of conduction in pure and copper layered ZnTe films were identified by using hot-probe method.

### 7.2 Electrical conductivity

If an electric current $I$ flows through a conductor with resistance $R$, then the potential difference across the ends of the conductor $V$ is given by Ohm’s law:

$$ V = IR \quad \text{or} \quad R = \frac{V}{I} \quad \text{----- (7.1)} $$

The resistance of a material is directly proportional to its length (l) and inversely proportional to the cross-sectional area ($A$). The proportionality constant is called the resistivity or the specific resistance ($\rho$), and

$$ R = \rho \frac{l}{A} \quad \text{----- (7.2)} $$

$\rho$ is an important material-dependent property that is usually a function of temperature. The value of $\rho$ at room temperature is indicative of whether the material is a metal ($\rho$ is of the order of $10^{-6}$ $\Omega$m or less) or an insulator ($\rho$ is of the order of $10^{6}$ $\Omega$m or more). Materials that are somewhere in-between are called...
Fig. 7.1 Four probe technique for measuring electrical resistivity.

In the collision processes, the transition probability for electron collision is directly related to the density of collision centers, and the collision rate is inversely proportional to the collision time constant. For example, in the case of electron-phonon scattering, the number of scattering centers is equal to the phonon population in thermal equilibrium. At high temperatures the average phonon density is proportional to temperature. Consequently, at high temperatures, the collision time varies inversely with temperature, and hence the electrical conductivity varies inversely with temperature $T$. This prediction is consistent with the observed temperature dependence of electrical conductivity in a metal. In general, the electron density in a semiconductor is a strong function of temperature, and the relaxation time may depend on both the energy and temperature.

### 7.2.1 Sheet resistance

Rectangular section of thin films has resistance, given by

$$ R = \frac{\rho}{b} \left( \frac{l}{t} \right) $$

where $b$ and $t$ are breadth and thickness of the film section respectively.
If \( l = b \)

\[
R = \frac{\rho}{t} = R_s
\]

\[\text{(7.5)}\]

In the Sheet Resistance \( 'R_s' \) of one square of film is independent of the size of the square and is expressed in ohms per square. It depends only on resistivity and thickness. If the thickness is known, the resistivity is readily obtained from,

\[
\rho = t \times R_s
\]

\[\text{(7.6)}\]

The most direct method of measuring \( R_s \) is to prepare a rectangular sample of film, and measure its resistance, and divide by the number of squares of film material that lie between the end terminals may be a problem, a four terminal method is necessary. The number of squares now being counted between the two voltage terminals and \( R_s \times \left(\frac{V}{I}\right) \).

Further more, it may be necessary to measure the variation of sheet resistance in a film from one part of the substrate to another, and measurement of a large number of tiny rectangles become highly impractical. Accordingly, widespread use is made of four point probe methods. Then the resistivity is given by

\[
\rho = \frac{V}{I} \left( \frac{1}{S_1} \right) \times 2 \times \pi \times S
\]

When

\[
S_1 = S_2 = S_3 = S, \text{ this reduces to}
\]

\[
\rho = \left(\frac{V}{I}\right) \times 2 \times \pi \times S
\]

\[\text{(7.7)}\]

where \( S \) is the distance between two probes.

If the material on which the probes are placed is an infinitely thin slice resting on an insulating support, then the above equation(7.7) becomes,
\[ \rho = \left( \frac{V}{I} \right) \frac{d\pi}{\ln^2} \]

or

\[ \left( \frac{\rho}{t} \right) = R_s = 4.532 \left( \frac{V}{I} \right) \]

----- (7.8)

and

\[ \rho = R \times t \]

----- (7.9)

### 7.2.2 Band gap energy

The electrical conductivity of the intrinsic semiconductor will be the sum of the contributions of both electrons and holes

\[ \sigma = (n_e \mu_e + n_h \mu_h) \]

----- (7.10)

where \( e \) is the charge of an electron, \( \mu_e \) and \( \mu_h \) are the average velocities acquired by the electrons and holes in unit electric field and known as mobilities of electrons and holes respectively.

In case of intrinsic crystals, the number of electrons is equal to the number of holes, because the thermal excitation of an electron leaves behind a hole in the valance band.

\[ i.e. n_i = p_i = 2 \left[ \frac{kT}{2\pi \hbar^2} \right]^{3/2} (m_e m_h)^{3/4} \exp\left(\frac{-E_g}{2kT}\right) \]

----- (7.11)

Thus, we see that the concentration of intrinsic carrier depend exponentially on \( E_g / 2kT \).

Equation (7.10) can be written as

\[ \sigma = e n_i (\mu_e + \mu_h) \exp\left(\frac{-E_g}{2kT}\right) \]

----- (7.12)

where \( k \) is a constant which is equal to

\[ \left[ \frac{2k}{2\pi \hbar^2} \right]^{3/2} (m_e m_h)^{3/4} \]
The factor $T^{3/2}$ and mobility change relatively slow with temperature compared with the exponential term, and hence the logarithm of resistivity $\rho$ varies linearly with $1/T$. The width of the energy gap may be determined from the slope of the curve.

Thus we have,

$$\log_e \rho = \frac{E_g}{2kT} - \log_e k$$

The band gap energy of the material is given by

$$E_g = (2k) \times \left( \frac{\log_\rho}{I/T} \right)$$

----- (7.13)

7.3 Hot probe method

A simple method, which is widely used to determine the conductivity type of a specimen is hot probe method. The typical experimental setup of hot probe method is given in the Fig. 7.2. Two fine metal probes preferably made of stainless steel or nickel is placed on the semiconductor sample and a zero centered galvanometer is connected between them. One of the probes is kept at room temperature and the other is heated to about 80°C. The hot probe heats the semiconductor beneath it so that the kinetic energy of free carriers in this region is increased. Therefore the carriers diffuse out of the hot region at a faster rate rather than they diffuse into this region from the adjacent low temperature regions. If the semiconductor is n-type, electrons will move away from the hot probe leaving behind the charge carriers of donors and the hot probe becomes positive with respect to cold probe. The current then will flow away from the hot probe to the cold probe. In a p-type semiconductor, the direction of the current flow is reversed. Thus the polarity of the hot probe indicates whether the semiconductor is n or p-type. Form the hot probe method; it is observed that the current flows from hot probe to the cold probe. It is inferred that the pure and copper layered ZnTe films are p-type in nature.
7.4 Results and discussion

The variation of current with voltage for typical copper layered ZnTe thin film of thickness 650 Å is shown in Fig. 7.3. It is observed from the figure that the voltage increases with increase in current while it decreases with increase in temperature. At lower temperature and for low values of current the voltage varies linearly with current in the d.c. field.

Fig. 7.3 Variation of current with voltage for copper layered ZnTe film of thickness 650Å

Fig. 7.4 shows the variation of current with voltage for various thicknesses at 303 K. It is observed from the figure that the voltage decreases with increase in film thickness; this may result in decrease of resistance in the films.
Fig. 7.4 Variation of current with voltage for copper layered ZnTe films at 303 K.

Fig. 7.5 shows the variation of sheet resistance with inverse of temperature for copper layered ZnTe thin films of thickness 650 and 3300 Å. It is seen that the sheet resistance of lower film thickness decreases with increase in temperature, which is characteristic of semiconductors; i.e., an increase in electron number is associated with electrical conductivity in semiconductor materials [15]. But for higher thickness it increases with increase in temperature, which shows that the copper layered ZnTe film looses its semiconducting nature. It may also due to the trapping of free carriers by the deep level defects causes enhancement in resistivity [16]. The decrease in sheet resistance is due to ion exchange of Cu ions with ZnTe film surface [17]. The variation observed in the resistivity-temperature curve of copper layered ZnTe films of different concentrations may also be attributed to the different carrier and dopant densities in them.

The interactions among the copper atoms and the ZnTe atoms may come into the picture, which may cause a change in normal modes of vibration of the lattice. These factors may therefore contribute to an increase of the scattering of free carriers and thus an increase of electrical resistivity with further increase in dopant concentration [13]. The heteroepitaxial layers of highly conducting Zinc Selenide
films are also found to exhibit similar variations of the electrical resistivity by changing the Zinc-Selenium ratio [18]. The segregation of dopant atoms in ZnTe crystals may have a profound effect on their structure and electron transport properties [19]. Although the impurity scattering is significant at low concentration, the copper atoms are fairly far away from each other and thus remain screened by the arrays of ZnTe material atoms.

Furthermore, the concentration of copper atoms at interstitial sites also increases with an increase in dopant concentration, adding to a decrease in the carrier mobility. The rise in temperature increases the atomic vibrations, which may increase scattering of mobile charges [13].
Fig. 7.5 Variation of sheet resistance with temperature for various thickness of copper-layered ZnTe
The activation energy ($E_a$) for copper layered ZnTe films was calculated from the linear plot observed in the log $\rho$ Vs $1/T$ graphs. The calculated values are

Fig. 7.6 variation of Log $\rho$ with $1/T$ for for various thickness of copper layered ZnTe films
From the table it is observed that the activation energy decreases with increase in film thickness. This is due to the influence of copper atom in the ZnTe thin films. This variation of activation energy in thin films can be due to any one or combined effects of the following causes (i) The change in the barrier height due to the size of the grains in polycrystalline films, (ii) a large density of dislocations, (iii) quantum size effect and (iv) change in stoichiometry. In this present observation, $E_g$ decreases with decrease of copper composition due to increase the thickness of ZnTe layers. It is find reasonable to regard the possibility of the effect of the barrier height due to the size of grains in the film. The narrow energy gap in the copper layered films suggests that the films approach metallic nature.

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>Activation Energy (eV)</th>
</tr>
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<tbody>
<tr>
<td>650</td>
<td>0.180</td>
</tr>
<tr>
<td>1000</td>
<td>0.041</td>
</tr>
<tr>
<td>3000</td>
<td>0.040</td>
</tr>
</tbody>
</table>

Table 7.1 Variation of activation energy with thickness for copper layered ZnTe films

7.5 Conclusion

From the hot probe method it is seen that the pure and copper layered ZnTe film exhibits p-type conductivity. Experimentally it is evident that the sheet resistance decreases with decrease in copper composition. The activation energy was calculated and it is found to decrease with decrease in copper composition/increase of thickness of ZnTe layer.
References