



Frequency Dependant Conduction In Thermally Evaporated Cds Thin Films

S.Tewari

Department of Physics, Karimganj College, Karimganj, Assam, India

A.Bhattacharjee

Department of Physics, National Institute of technology, Silchar, Assam, India

Abstract:

Thin films of Cadmium Sulphide (CdS) and the sandwich structures of CdS in Ag electrodes (Ag/CdS/Ag) are prepared by thermal evaporation technique at different substrate temperatures. Investigations on the frequency dependant di-electric properties of the film as a function of the substrate temperature of deposition are carried out. The investigation reveals that there is hopping type of conduction in the CdS film. The nature of variation of a.c. conductivity agrees well with correlated barrier-hopping (CBH) model. The dielectric and impedance spectra indicate multi-relaxation behavior in the sample.

Keywords: *cadmium sulfide, thin films, thermal evaporation, electrical properties, a.c. conductivity.*

Introduction

One of the most intensively studied II–VI semiconductor is Cadmium sulphide (CdS), because of its multiple advantages such as intermediate energy band gap, reasonable conversion efficiency, stability, low cost and of also due to its wide range of prominent applications [1-10].

The performance and efficiency of the thin film based devices are strongly determined the structural, electrical and di-electric properties of the component thin films. Hence, the study of these properties is of utmost importance for using the material in thin film devices. Thus studies on these physical properties of the thin films are very important. CdS is an extensively studied material [1-16], still there exists is a lacuna on the frequency dependent studies. The a.c. conductivity is very important parameter for exploring information relating to the dynamic properties in the interior of the films. Studies on a.c. conductivity and impedance analysis of thin films are immensely important which have been extensively used to understand the transport mechanism in these semiconductor materials [17–21] and to investigate the electrical, dielectric properties.

This paper reports the investigations carried out on CdS thin films deposited by thermal evaporation at different substrate temperature.

Experimental

Bulk CdS material was prepared by pyrosynthesis of the high purity constituent elements cadmium and sulfur obtained from Johnson Matthey (U.K.). Details of preparation technique have been described elsewhere [22]. CdS films of thickness varying from 500 to 2000 Å were deposited on glass by the thermal evaporation technique at different substrate temperatures in a vacuum $\sim 2 \times 10^{-5}$ mbar using HINDHIVAC 12'' Vacuum Coating Unit (Model: 12A4DM) with molybdenum boat. The substrate temperatures were fixed at 25, 100, 200 and 300 °C for different depositions. Deposition rate and film thickness were measured and controlled in situ by using HINDHIVAC digital thickness monitor (Model: DTM 101). The deposition rate was kept at ~ 3 Å/s. The dimensions of the films were 2 cm x 1.2 cm x t cm, where t is the thickness of the film. Silver electrodes of thickness 2000 Å are deposited from a tungsten spiral at vacuum of $\sim 2 \times 10^{-5}$ mbar at the rate of 3 Å /s. Silver electrodes are used as they provide ohmic contacts on CdS with work functions of Ag 4.44 eV [23] and that of CdS > 4.8 eV [22], Using masks Ag/CdS/Ag sandwich

structures of area $4.16 \times 10^{-6} \text{ m}^2$ were obtained for all the films deposited at different substrate temperatures.

X-ray diffraction (XRD) scans of the films were performed using a PANalytical X'pert Pro X-ray diffractometer applying the step scanning mode in the scanning angle range $20\text{--}80^\circ$ with a step of 0.01° (2θ) and a counting time of 0.3 s for each step using $\text{Cu-K}\alpha$ radiation with wavelength $\lambda = 1.54060 \text{ \AA}$. The X-ray source settings were 30 mA and 40 kV.

The a.c. measurements of impedance, capacitance, Loss factor and phase angle carried out as function of frequency (10 Hz to 100 kHz) and temperature in the range $25\text{--}200^\circ\text{C}$ using HIOKI- LCR (Model:3522–50 Hioki, Japan) hi-ester, maintaining a vacuum of 10^{-2} mbar in an indigenously built unit for electrical characterisation (Fig.1).

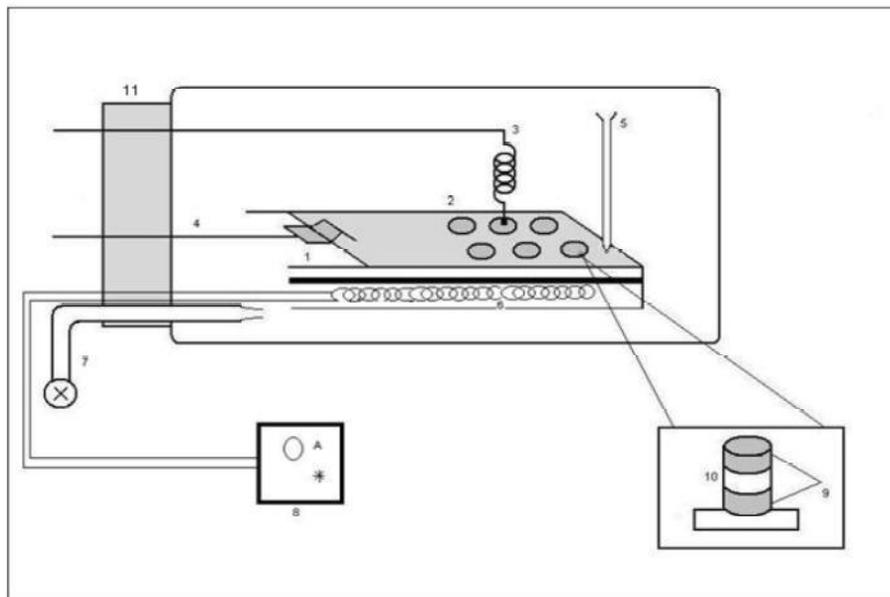


Figure 1: Schematic representation of indigenously built unit for electrical characterisation

1. Substrate 2. Silver electrode 3. Upper Electrode contact 4. Lower Electrode contact
5. Thermocouple 6. Heater 7. Evacuating pump 8. Temperature controller 9. Silver electrodes 10. Sample film 11. Sealed Cap

The a.c. signal applied across the device was maintained at 0.2 V (rms) with zero d.c. bias. The temperature was monitored during entire experiment using a pre-calibrated chromel–alumel thermocouple with the help of a Motwane digital multimeter (Model:

545). The resistivity measurements were conducted at different temperatures in the same temperature range, maintaining a vacuum of 10^{-2} mbar by two probe method using Keithley electrometer (Model: 6514). All the parameters were repeatedly measured using five different Ag/CdS/Ag sandwiches and the data obtained was found to be highly reproducible.

Results And Discussion

Structural studies

The XRD data were analyzed using the X'pert High Score software. Qualitative phase analysis of each diffraction pattern was then carried out using the ICDD diffraction database and the search-match tool. The XRD pattern of the CdS films deposited at different substrate temperatures RT (25°C), 100, 200 and 300°C is shown in Fig.2.

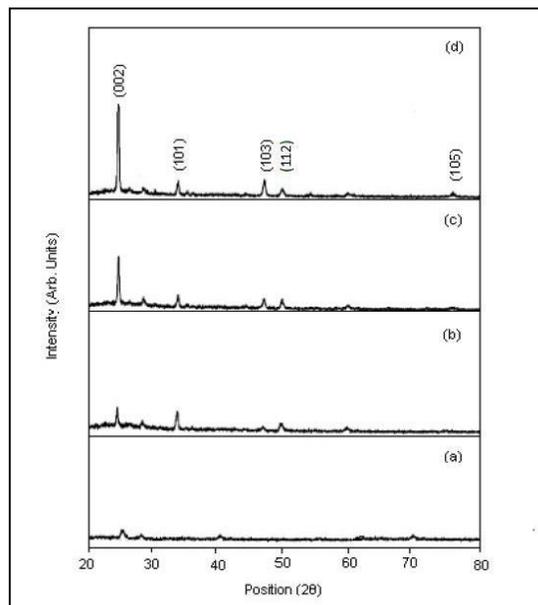


Figure 2: The XRD pattern of the CdS films of thickness 1500 \AA deposited at different substrate temperatures RT (25°C), 100, 200 and 300°C

It shows the formation of polycrystalline CdS films with highest intensity peak along the hexagonal (002) plane, other peaks corresponding to the planes (101), (103),(105),(112) were found to be present with lower intensities. The XRD patterns clearly indicate that in all cases the peak intensity was found to increase with the substrate temperature of deposition. This suggests improvement in crystallinity and increase in thickness with substrate temperature.

The crystallite size D is calculated using the Debye-Scherrer formula [20]

$$D = \frac{k\lambda}{\beta \cos\theta} \dots\dots\dots (1)$$

Where, k is a constant and in our case k = 0.9, λ is wavelength of the incident x-ray (λ = 1.5418 Å), β is the corrected FWHM (Full width at half maximum) for instrumental broadening of the maximum intensity peak and θ is the angle at which the maximum peak occurs.

The grain size thus calculated for the strongest peak corresponding to the plane (002) is found to be in between 167.6 nm to 282.2 nm, as listed in Table 1.

| Substrate temperature of deposition °C | Crystallite size (nm) |
|--|-----------------------|
| 300 | 167.6 |
| 373 | 182.4 |
| 473 | 258.3 |
| 573 | 282.2 |

Table1: Variation of crystallite size with temperature of deposition

The crystallite size was found to increase with the substrate temperature of deposition which is the same behaviour reported in literature for spray-pyrollysed CdS [24] thin films and also on other materials [25]. This is because increasing the substrate temperature decreases the density of nucleation centres and, under these circumstances, a smaller number of centres start to grow, resulting in larger grains.

Electrical and dielectric properties

Dielectric properties

The relative dielectric constant (ε_r) of the sandwich film is determined from the

relation $\epsilon_r = \frac{Cd}{\epsilon_0 A}$

Where, C= Capacitance, ε₀ = 8.85 x 10⁻¹² Fm⁻¹, A is the area of the sandwich structure = 4.16 x10⁻⁶ m² and d is the film thickness = 1500 Å in our case.

The dielectric constant (ε_r) of the CdS film is found to increase with increasing frequency and temperature as shown in Fig.4.

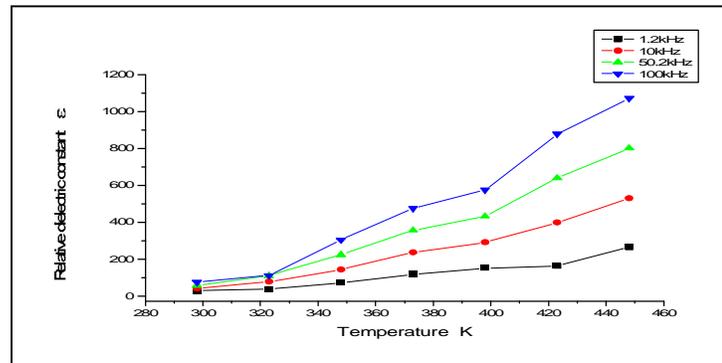


Figure 3: Variation of relative dielectric constant with temperature

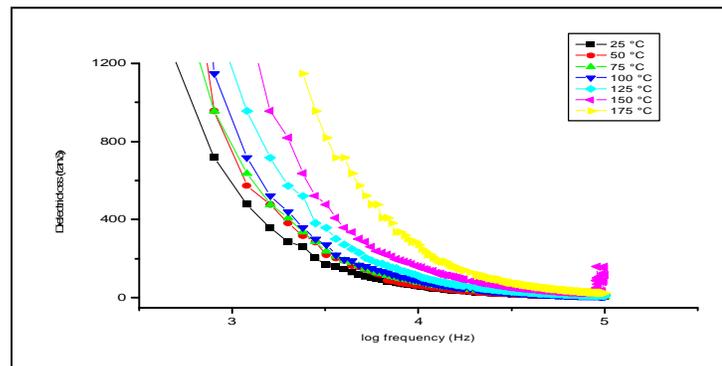


Figure 4: Variation of dielectric loss with frequency at different constant temperatures

This behaviour is attributed to the fact that at lower frequencies the dielectric constant depends on different types polarizations such as atomic, interfacial and electronic polarization but at higher frequencies the electronic polarization becomes dominant. Also, the variation of the dielectric loss $\tan\delta$ with frequency for the CdS thin film in the frequency range and temperature range (25 °C to 200 °C) for CdS films is shown in the Fig.5.

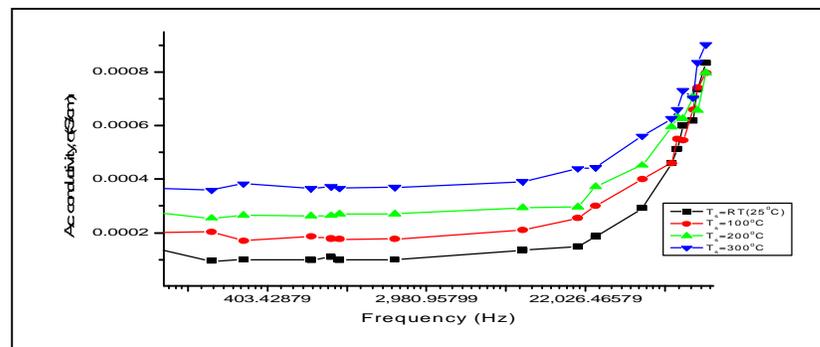


Figure 5: Variation of a.c. conductivity with frequency σ_{ac} at room temperature (25°C) for CdS films deposited at different constant temperatures

The dielectric loss $\tan\delta$ is found to increase with temperature but decrease with frequency. This is related to the fact that at higher temperatures the loss is dominated by thermally activated hopping of electrons whereas the effect dies out at low temperatures, resulting in a decrease or no significant change at low temperatures [25]. This type of behaviour suggests a distribution of relaxation times in the CdS thin film system. The complex microstructure of films involving defects that may be present in the film such as cracks, micro voids, imperfections, defect centres, etc., at sufficiently high concentration give rise to defect states, both shallow and deep states. These states may be of acceptor type (D^0/D^+) or donor type (D^-/D^0), or with three charge states as D^+ , D^- and D^0 [26]. These defects immensely affect the transport properties of the materials by acting as traps and recombination centres for carriers and also, some D^+/D^- centres in close proximity give rise to polar behaviour, which are responsible for the distributed dielectric relaxation. On subjecting the films to an electric field of varying frequency, the electrons hop between localized sites. The charge carriers moving between these sites hop from a donor to an acceptor state.

A.C. conductivity

The a.c. conductivity is determined using the relation $\sigma_{a.c.} = C \omega \tan\delta$ (2)

Where C is the capacitance, ω is the angular frequency and $\tan\delta$ is the loss tangent.

The dependence of $\sigma_{a.c.}$ on temperature is given by the relation

$$\sigma_{a.c.} = \sigma_0 \exp (-E_{ac}/kT) \dots\dots\dots(3)$$

where σ_0 is pre exponential factor, k is Boltzmann’s constant and E_{ac} is the thermal activation energy.

Fig.6(a) shows the variation of a.c. conductivity with frequency at room temperature for CdS films grown at different constant substrate temperatures and Fig.6

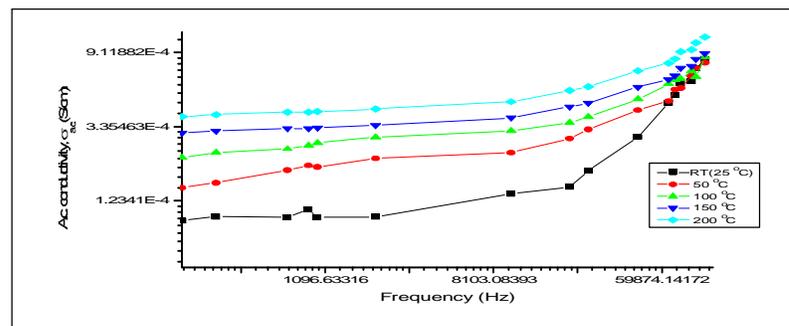


Figure 6: Variation of a.c. conductivity with frequency σ_{ac} versus frequency at different constant temperatures

gives the variation of a.c. conductivity with frequency at different temperatures (in the temperature range 25 °C to 200 °C) for CdS films grown at room temperature. It is evident from the figure that the a.c. conductivity increases with the increase in frequency and temperature. Two distinctly different regions are observed in the variation of a.c. conductivity with frequency. This is a feature of localized conduction where the a.c. conductivity increases with frequency. Contrary to this, in case of free band conduction the a.c. conductivity decreases with frequency [27–31]. This increase in a.c. conductivity with temperature also, evidences in support of thermally activated conduction processes.

This type of variation of a.c. conductivity is ascribed to relaxations caused by the motion of electrons or atoms, which may involve hopping or tunneling between equilibrium sites, where there is an increase of carrier with increased temperature, which may be due to the release of trapped carriers with increase in thermal energy

The a.c. conductivity is found to obey the universal relation

$$\sigma_{ac}(\omega) = A\omega^s \dots\dots\dots(5)$$

where A is a constant independent of frequency but weakly dependent on temperature. The exponent s plays an important role in determining the nature of conduction.

Some theoretical models have been propounded to explain the conduction mechanism viz. the Quantum mechanical tunneling (QMT) [25,32], small polaron tunneling model (SPTM) [33, 34], large polaron tunneling model (LPTM) [32], correlated barrier hopping (CBH) model [35–37], etc., to explain mechanisms responsible for A.C. conduction.

The QMT model ascribes a.c. conductivity due to a relaxation process arising from electronic or atomic tunnelling between equilibrium sites. It predicts the frequency exponent s to be frequency-dependent but independent of temperature.

The SPTM model explains a.c. conductivity in terms of trapped carriers at structural defects, i.e. small polarons, tunnelling between states lying close to the Fermi level. It predicts that s will increase with increasing temperature and that the tunnelling distance, and hence the a.c. conductivity, will decrease at high frequencies.

The correlated barrier hopping (CBH) model proposed by Pike [31] is concerned with the hopping of electrons over a potential barrier. The CBH model has been extensively applied to some chalcogenide semiconductors to explain the temperature-

dependent properties. This model has been extensively applied to some chalcogenide semiconductors to explain the temperature-dependent properties.

In the CBH model, the electrons in charged defect states hop over the Coulombic barrier whose height, W , is given as

$$W = W_m - (ne^2 / \pi\epsilon\epsilon_0 r) \text{-----(5)}$$

where W_m is the maximum barrier height, ϵ the bulk dielectric constant, ϵ_0 the permittivity of free space, r the distance between hopping sites and n the number of electrons involved in a hop ($n = 1$ and $n = 2$ for the single polaron and bipolaron processes, respectively). In this model the ac conductivity is given by

$$\sigma(\omega) = \frac{\pi^3 \epsilon \epsilon_0 N N_p \omega (R_\omega)^6}{6} \text{-----(6)}$$

where the inter-site separation is given by

$$R_\omega = (e^2 / \pi\epsilon\epsilon_0 W_m) [\ln(1 + kTW_m) \ln(\tau_0 \omega)]^{-1} \text{---- (7)}$$

the frequency index is given by

$$s = 1 - \frac{6kT}{W_m + (kT \ln(\omega\tau_0))} \text{-----(8)}$$

It predicts that s should be less than 1, decreasing with increasing temperature. In the present study it is evident from the s versus T plot (Fig. 7) that s gradually decreases with temperature. The value of s is found to be in the range from 0.33 to 0.76 in the entire frequency range. It is observed that s increases with increasing frequency and decreases with the increase of temperature. This is quite in accordance with the correlated barrier hopping (CBH) model; hence the CBH model is the most suitable model for describing the conduction mechanism in the CdS thin film.

The QMT model ascribes a.c. conductivity due to a relaxation process arising from electronic or atomic tunnelling between equilibrium sites. It predicts the frequency exponent s to be frequency-dependent but independent of temperature.

The SPTM model explains a.c. conductivity in terms of trapped carriers at structural defects, i.e. small polarons, tunnelling between states lying close to the Fermi level. It predicts that s will increase with increasing temperature and that the tunnelling distance, and hence the a.c. conductivity, will decrease at high frequencies.

Impedance studies

The Cole-Cole plots of the real and imaginary parts of Impedance Z' and Z'' for the CdS film are shown in Fig.8 for the films of thickness 1500 Å deposited at different substrate temperatures over the studied frequency range 1Hz to 100 kHz for the temperature ranges (25 °C to 100 °C) and (125°C to 200°C) respectively. The plots for each temperature were found to be single semicircular arcs with their centers lying below the real axis at certain angle. These depressed arcs are typical for material with multi relaxation processes [38]. The curves have non zero intersection with real axis in the high frequency region and also, there is a decrease in the size of the plots with rise of substrate temperature of deposition. The area of the semicircular arcs is found to decrease with the substrate temperature of deposition. This is due to the fact that the films deposited at higher temperatures have less surface defects and better crystalline properties which results in decrease in the film resistances.

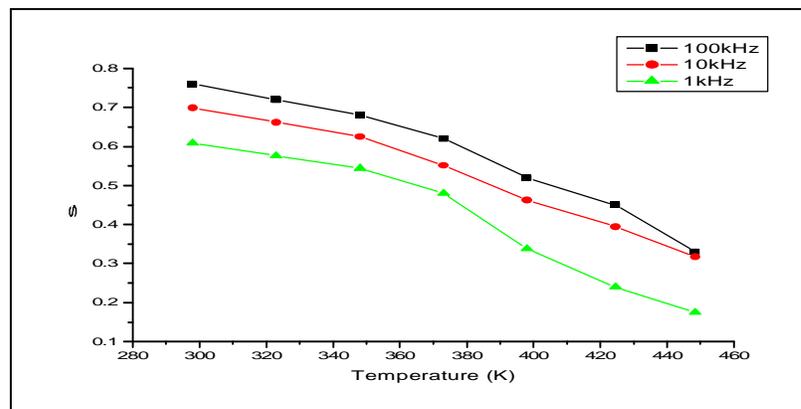


Figure 7: Variation of frequency index s with temperature

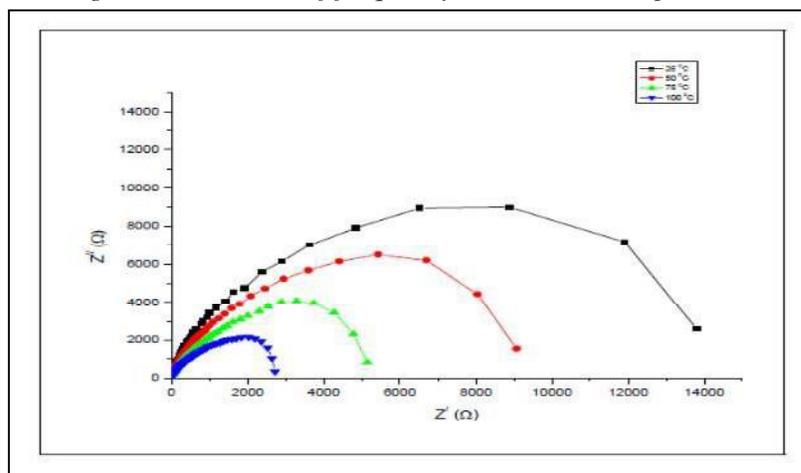


Figure 7(a): Cole –Cole plot for the CdS Films deposited at different substrate temperatures in temperature rangr 125 °C to 200 °C

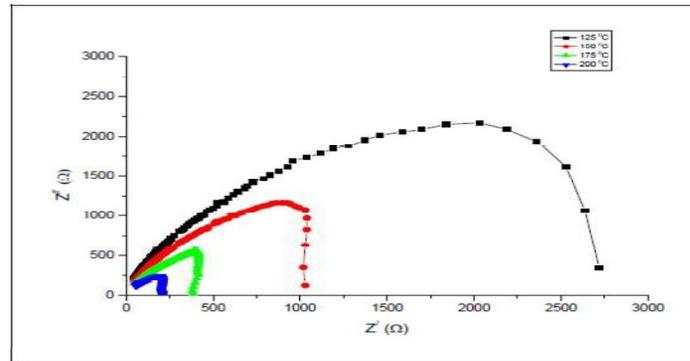


Figure 7(b): Cole –Cole plot for the CdS Films deposited at different substrate temperatures in temperature range 125 °C to 200 °C

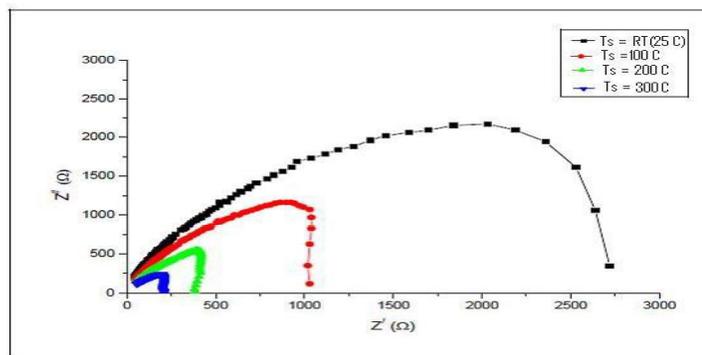


Figure 8: Cole –Cole plot for the CdS Films deposited at different substrate temperature

Conclusion

Structural studies with XRD study revealed that the CdS thin film material is of crystalline nature having most intense peak along (002) plane orientation. The crystallite size was found to be between 167.6 nm to 282.2 nm, which increases with the temperature of deposition. The a.c conductivity of the film increases with temperature and frequency confirming thermally activated conduction from localised states. The dielectric properties such as dielectric constant and dielectric loss are strongly dependent on temperature and frequency and indicate a distributed relaxation. The nature of variation of a.c. conductivity is as per the theoretical prediction of the CBH model. The Cole-Cole plots confirm multi relaxation behavior.

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