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Observation of Meyer–Neldel rule in CdS thin films

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ABSTRACT

A study of electrical transport in CdS thin films is reported. We have observed, for the first time, that CdS thin film conductivity obeys the Meyer–Neldel rule (MNR). This was deduced from linking the conductivity pre-exponential factor to the activation energy variation. CdS films were deposited by chemical bath deposition at different solution temperatures in order to vary the electrical activation energy of the films. A correlation between the MNR rule and the disorder in the film network is highlighted. The multi-trapping process in the band tail-localized states governs the conductivity in CdS films. This explains the MNR observation in CdS films. The variation of the electrical conductivity pre-exponential factor and activation energy are correlated to the disorder in the film network; this was explained in terms of polaron formation and phonon–electron coupling with disorder.

1. Introduction:

Generally the electrical conductivity of semiconductors is thermally activated and exhibits an exponential behavior, defined by the Arrhenius equation:

$$\sigma = \sigma_0 \exp(-E_a/KT) \qquad (1)$$

The activation energy E_a is dependent upon the doping level of semiconductor, material composition or light exposure. Although the pre-exponential σ_0 and the activation E_a seem, at first glance, to be independent, they are in fact related by an oft-observed exponential relation known as Meyer–Neldel rule (MNR) [1]:

$$\sigma_0 = \sigma_{00} \exp(E_a/KT_m) \qquad (2)$$

T_m is a specific temperature (KT_m is also called the Meyer–Neldel energy).

The most interesting feature of the MNR rule, also called the "compensation effect", is that it has been observed in a variety of materials, e.g. crystalline, polycrystalline, amorphous, liquid semiconductors, organic solids, solid-state ion conductors, and for various properties namely, conductivity, diffusion, thermal crystallization, surface desorption, and adsorption kinetics [2–15]. Understanding the relevance of the MNR to CdS is an interesting and ambitious challenge in condensed matter physics. Several mechanisms have been proposed to understand the MNR origin which is still a controversial subject. Many researchers attribute the MNR to the disorder effect within the material [13,14,16]. However; the origin of MNR is correlated to the transport mechanism in the material. It has been also reported that the MNR is a consequence of the multi-trapping transport process [16].

Most of MNR in electrical conductivity investigations are focused on chalcogenide glass [17–26] .Few studies have been devoted to the MNR in semiconductor thin films. Earlier it has been reported in hydrogenated amorphous silicon thin films a-Si:H [27–31] and recently in Al doped ZnO thin films[2]. CdS thin films have been a subject of interest due to their technological importance and their applications in optoelectronic devices. However, little attention has been paid to their electrical properties

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neither to the presence of the MNR in the electrical conduction.

In chalcogenide glass, MNR is studied through the variation of E_a by changing the composition of glassy alloys [20–22]. Kushwaha et al. [32] have varied E_a through light exposure or by varying the electrical field in dark or under light exposure [23,24]. In ZnO thin film Sagar et al. [2] have modified the Al doping level to change E_a. In a-Si:H films E_a is varied by doping, light exposure or by preparing films under different conditions [29–31].

In previous studies [33,34] we have investigated the influence of solution temperature on the growth mechanism, optical and structural properties of CdS thin films. The aim of the present work is the study the electrical properties and the validation of MNR in CdS thin films. We have prepared a set of films by chemical bath deposition technique with different solution temperatures in order to vary the activation energy of the D.C dark conductivity.

2. Experimental details

The CdS thin films used in the present study were prepared by chemical bath deposition; details were reported previously [33,34]. The bath solution is composed with $CdSO_4$ (1 M) as source of Cd atoms and thiourea $CS(NH_2)_2$ (1 M) as source of S atoms. Ammonium hydroxide NH_4OH was used as a complexing agent. The bath solution temperature was varied from 50 to 90 °C, in order to modify the film properties and the conductivity activation energy and to verify the MNR behavior of CdS films. Films thicknesses ranged from 200 to 500 nm, increasing with the deposition temperature. The electrical D.C transport characterization was carried using coplanar structures in samples with two evaporated golden strips used as electrodes. The electrodes spacing is 5 mm. The applied voltage is varied from 0 to 20 V, Keithley electrometer 610 is used for current measurements. The optical gap and disorder in films network were calculated from the optical transmission measurements carried in UV–visible range by Shimatzu spectrophotometer. The detailed procedures of calculations are previously reported [33].The structural characterizations of films were carried out by X-ray diffraction (XRD) technique using an X-ray diffractometer (Philips X'Pert) and scanning electron microscopy (SEM) observations using Jeol 5400 SEM microscope.

3. Results and discussion

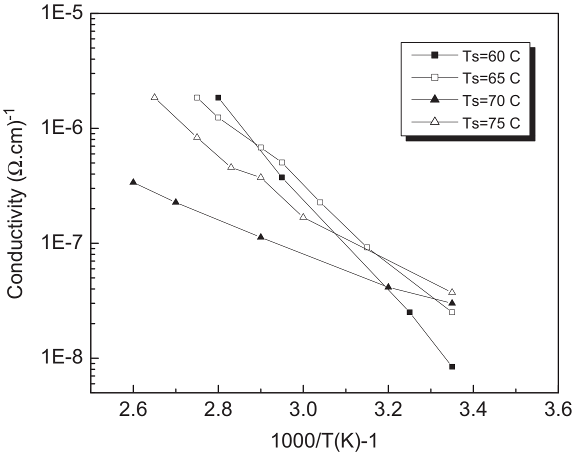

Fig. 1. Variation of the dark conductivity as a function of inverse temperature for different samples.

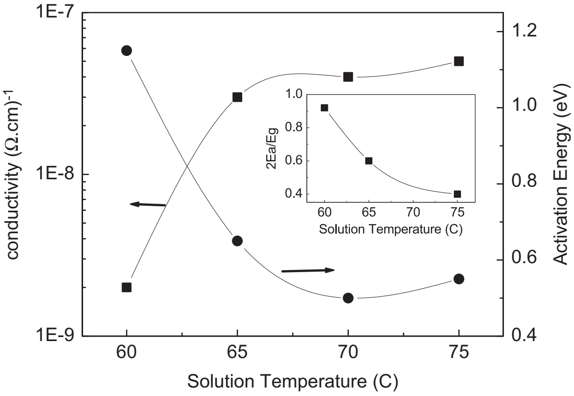

Fig. 2. Dependence of dark conductivity and electrical activation energy on the bath solution temperature. Inset shows the variation of the quantity $2E_a/E_g$.

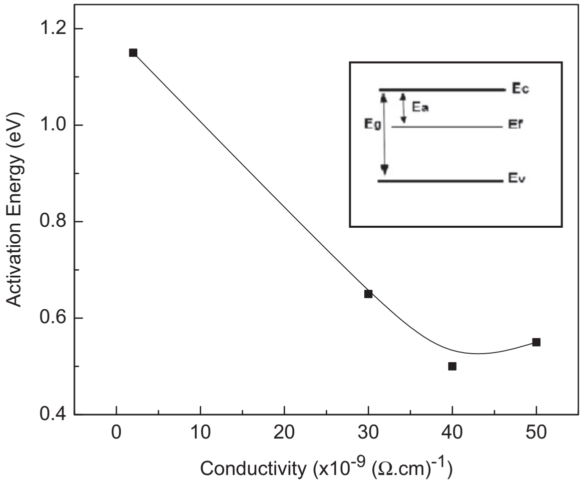

Fig. 3. Correlation between the activation energy and the dark conductivity.

In Fig. 1, we have reported the variation of the dark conductivity of different samples as a function of temperature. As can be seen, the dark conductivity follows the Arrhenius behavior with increasing measurement temperature. This indicates that CdS films electrical conductivity is thermally activated. The electrical activation energies were deduced from the slopes of conductivities curves variation in Fig. 1. The obtained results were reported in Fig. 2, we have drawn also the variation of the dark conductivity measured at room temperature as a function of bath temperature. As can be seen, with increasing the bath temperature films conductivity increases about one decade at low temperature from 60 to 70 °C, and tends to saturate with further increasing bath temperature. However its activation energy is reduced with increasing the deposition temperature. In Fig. 3 we have drawn the variation of activation energy as a function of dark conductivity, as can be seen when increased, the conductivity becomes less thermally activated.

In order to determine the conductivity type of the deposited film we have calculated the ratio $2E_a/E_g$, where E_a is the electrical activation energy and E_g is the film optical gap deduced from the UV–visible optical transmittance. It is well known that conductivity activation energy of a semiconductor E_a corresponds to Fermi level E_f position regarding the bottom of conduction band edge E_c ($E_a = E_c - E_f$). Since the band gap energy E_g is equal to the difference $E_c - E_\nu$, then the ratio $2E_a/E_g$ can be an easy tool used for the determination of Fermi level position in the forbidden region(see inset Fig. 3) [35]. If this ratio is close to the unity, this means that the Fermi level is located at the midgap position and the semiconductor is intrinsic. However, reduction of this ratio means that Fermi level moves towards the minimum conduction E_C (or E_ν in p-type semiconductor) band edge and that the material contains donor (or acceptor) impurities.

As can be seen in inset Fig. 2, showing the variation of the ratio $2E_a/E_g$ as a function of deposition temperature, the ratio is always less than the unity, this means that Fermi level is located in the upper region of the forbidden band and then chemical bath deposited CdS film are n type. This is consistent with the common observed feature that CdS thin films are natively n-type [36,37]. Moreover, with increasing the deposition temperature Fermi level is shifted towards the bottom of the conduction band, due to the reduction of $2E_a/E_g$ ratio. This indicates that an increase in the bath temperature acts like an n-type doping effect. It is worth noting that defects such as sulfur vacancy V_S or Cd interstice I_{Cds} are donor defects in CdS thin films. Moreover, CdS thin films are generally S defective material, therefore, CdS thin films are natively n-type semiconductor. Due to sulfur volatility, *S* vacancies concentration is enhanced with increasing the deposition temperature. This induces an increase in the conductivity and the motion of Fermi level towards the bottom of conduction band edge. Pawar et al. [38] have reported that, an effective way to obtain CdS films with low resistivity and high optical transmittance can be achieved by the creation of excess Cd through various heat treatments and/or incorporation of foreign trivalent atoms as donors. In our case, CdS film conductivity is controlled through increasing the solution temperature.

The MNR validation is based on the control of the conductivity activation energy in the studied material. For this purpose, several methods have been adopted to vary the conductivity activation energy e.g.; in a-Si:H (hydrogenated amorphous silicon) thin films E_a was varied by doping, surface absorption, light soaking or by preparing under different conditions [28,39], in chalcogenide glasses E_a was varied by changing the composition [21,40,41] or by varying the electrical field across the sample in dark or by varying the light intensity [42].

The value of pre-exponential σ_o can be used to determine the conduction mechanism. The value of σ_o may distinguish the conduction whether it is in extended states or in localized states. For extended state conduction, the value of σ_o lies in the range 10^3–10^4 $(\Omega\,\text{cm})^{-1}$, whereas for hopping conduction in localized states in band tails, the value of σ_o is smaller than this range [43]. As shown in Fig. 2, the pre-exponential factors of different samples are lower than 10^3 $(\Omega\,\text{cm})^{-1}$. This indicates clearly that the dominant transport in CdS films is in the localized states present in band tails.

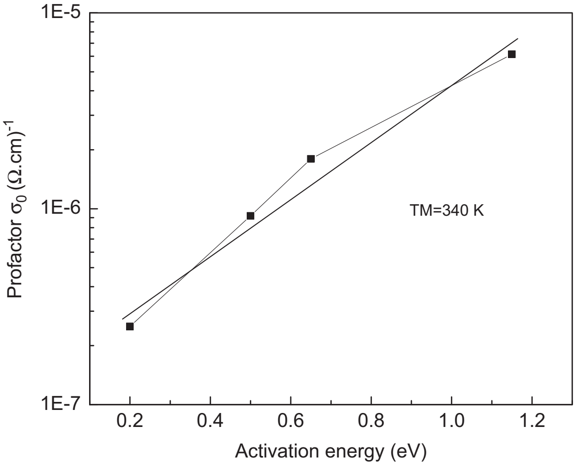

Fig. 4. Variation of the conductivity pre-exponential factor σ_0 as a function of activation energy.

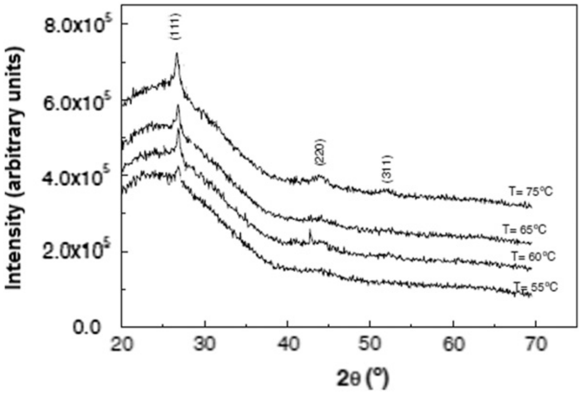

Fig. 5. XRD diffraction patterns of CdS thin films deposited with different solution temperatures.

The variation of pre-exponential factor with respect to activation energy is represented in Fig. 4. The observed linear variation between σ_0 and E_a and its positive slop indicates clearly the presence of the MNR in CdS thin films. The pre-exponential factor is linked to the activation energy by MNR; their relationship can be expressed as

$$\sigma_0 = \sigma_{00}\exp(E_a/KT_M) = \sigma_{00}\exp(E_a/E_{MN}) \qquad (3)$$

where E_{MN} and T_M are Meyer–Neldel rule characteristic energy and temperature respectively. T_{MN} is defined equal to the ratio E_{MN}/K.

In our case, the obtained value of E_{MN} is 29.32 meV, this value is well within the range 25–100 meV generally

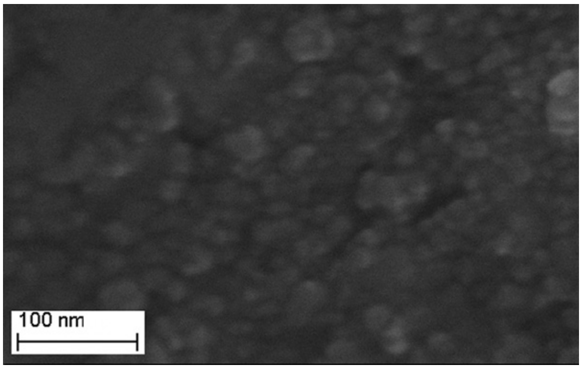

Fig. 6. A typical SEM image of a CdS film prepared with 70 °C substrate temperature.

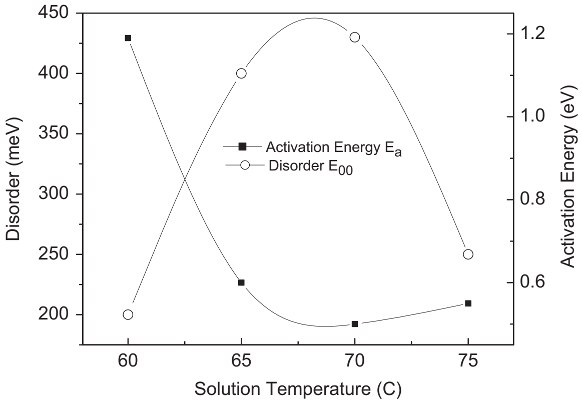

Fig. 7. Correlation between the variation of the disorder and the activation energy as function of the temperature of bath solution.

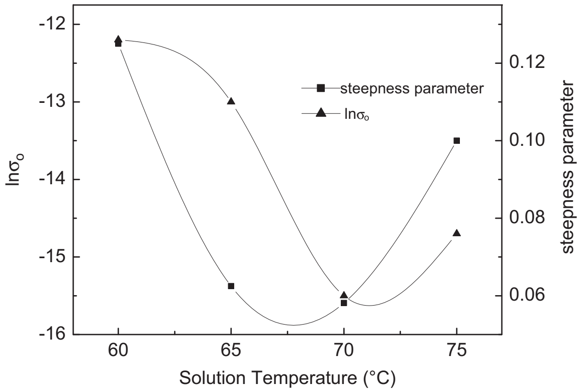

Fig. 8. Correlation between the variation of the steepness parameter and the pre-exponential factor σ_0 as function of the temperature of bath solution.

reported in other semiconductors [44]. This energy corresponds to Meyer–Neldel temperature T_{MN}; it is equal to 340 K, it is within the reported range of temperatures 260–950 K [42].

Several mechanisms to explain the origin of MNR in semiconductors were proposed, Jakson [16] have argued that whenever a multiple trapping transport process is observed as a function of temperature, MNR should be followed. Sagar et al. [45] has studied the applicability of MNR in ZnO thin film. They concluded that MNR is present above room temperature. They explain that the origin of MNR process is due to the pre-exponential energy distribution of defect traps. In a recent calculation Abtew et al. [4] have performed a comparative study of MNR in crystalline Si and non hydrogenated amorphous silicon, they claimed out that MNR is present in amorphous silicon only. They suggested that the existence of localized state and the energy—electron lattice coupling for these states is an essential feature of MNR in silicon amorphous phase. Hence MNR presence is close connected to the presence of band tail states, these states are generally assigned to the disorder in film network.

The XRD patterns of samples deposited at different temperatures are shown in Fig. 5. The diffraction patterns show an intense peak located at $2\theta = 26.6^\circ$, which is associated with the plane (111) of the CdS cubic phase. Two small ones, located at 44.3° and 52.3°, assigned, respectively, to (220) and (311) reflections planes, emerge when the solution temperature is equal to 75 °C. As can be seen all XRD films spectra are composed with a broad peak located at 20–30°. This broad peak is a signature of the presence of an amorphous phase. From XRD analysis we conclude that CdS film are composed with small crystallites embedded in an amorphous tissue. The crystallite sizes, deduced from the XRD pattern using Scherer formula [46], are ranged from 20 to 10 nm. This is consistent with scanning electrons microscopy (SEM) observation as shown in Fig. 6.

The shape of optical absorption coefficient as a function of photon energy can give a good insight on the band tail states width. In disordered semiconductors, subgap absorption coefficient can be expressed as a function of photon energy by the following relation [47]:

$$\alpha = \alpha_0 \exp(h\nu / E_{00}) \tag{4}$$

where E_{00} is the band tail width, it is commonly known as Urbach tail or Urbach energy. The latter can be easily calculated from the slope of $\ln \alpha = f(h\nu)$ curve.

The band tail width E_{00} is correlated to the disorder in film network. The latter is defined as the deviation of bond length from its standard value in the bulk material. The larger the band tail the more disordered is the film network. In Fig. 7 we have reported the variation of the disorder as a function of bath temperature solution. The film disorder variation has a bell shape. This variation is explained in term of growth mechanism and the modification of the deposition mechanism from ion by ion to cluster by cluster deposition as reported elsewhere [33].

As we have mentioned above, according to pre-exponential factor value, the conductivity in the obtained CdS films is governed by the multi-trapping process in band tail localized states, this explains, thereafter, the MNR observation in our CdS films. In disordered semiconductors three conduction mechanisms may occur: (i) hopping from one localized sates to another localized state, (ii) carrier hopping from localized state to an available extended state, and (iii) carrier scattered from one extended state to an empty extended state. The two first conduction mechanisms require phonon assistance. Transition (i) and (ii) plays a role in low and moderate temperature, however the transition (iii) may be significant only in higher temperature.

Therefore, since the conduction mechanism in our films involves localized states, the electronic transport is achieved through electrons trapping and detrapping by multi-phonon process with the contribution of many phonons. This conduction model was first suggested by Yelon and Movaghar to explain MNR in thermally activated conduction [48]. In localized states conduction, the activation energy of the transition from localized state I with energy E_i to an empty localized state J with energy E_j is given by [49]

$$E_a = \frac{E_r}{4}\left[1+\frac{(E_j - E_i)}{E_r}\right]^2 \tag{5}$$

where E_r is the reorganization energy of the semiconductor random network for carrier hopping.

It can be expressed as

$$E_r = \frac{(e/2)^2}{4\pi\varepsilon_0}\left[\frac{1}{2\varepsilon_j}+\frac{1}{2\varepsilon_i}-\frac{1}{R}\right]\left[\frac{1}{\varepsilon_{op}}-\frac{1}{\varepsilon_s}\right] \tag{6}$$

where ε_i and ε_j are the localization radii for the two localized state I and J, R is the distance between the two localization centers [50], e is the elementary electric charge, ε_o is the vacuum dielectric constant, ε_{op} and ε_s are, respectively, the optical and static dielectric constants. With increasing the disorder the distance R increases and the film density decreases, consequently the film refractive index and optical dielectric ε_{op} constant are reduced [51,52]. This leads to the increase of the two square brackets in Eq. (6) and then to the increase in the reorganization energy E_r and consequently the reduction of the activation energy E_a.

In Fig. 8 we have drawn the variation of the disorder and the electrical activation energy, as seen the two quantities vary oppositely suggesting that increasing in disorder is followed by the reduction in the electrical activation energy. This is in good concordance with the prediction of Eq. 6.

Using the polaron theory of Kubo–Greewood formula [53], Emin has calculated the hopping rate and the conductivity due to the multi-phonon process. Emin model predicts that the conductivity is extremely sensitive to the polaron binding energy [54]. The phonon supplies the necessary energy to activate an electron from a localized state to another localized state or an available extended state, in the case where n phonons are involved the probability of this process is proportional to g^{2n} [55], g is the electron–phonon coupling constant. For weak electron–phonon coupling the pre-exponential factor σ_0 is proportional to g, however for strong coupling σ_0 is proportional to g^{-1}[56]. Moreover the electron–phonon coupling can be estimated from the steepness parameter σ_p. This parameter which characterize the steepness or width of the straight line near optical absorption edge is close related to the Urbach energy or the disorder E_{oo} through the relation $\sigma_p = KT/E_{oo}$ [57]. The parameter σ_p is inversely proportional to the strength of the coupling between electron–phonons [57]. Both of conductivity prefactor and parameter σ_p are inversely proportional to electron–phonon coupling strength, this explains then the same trends observed in the variation of pre-exponential factor σ_0 and steepness parameter CdS optical absorption as a function of deposition temperature as shown in Fig. 7. With increasing the disorder in our CdS films (e.g. larger E_{oo} and lower σ_p) the network becomes more flexible yielding to a stronger electron–phonon coupling.

4. Conclusions

In the present study we have shown that MNR rule is also present in CdS thin films. The activation energy of the electrical conductivity in films was controlled by varying the deposition temperature. By this way the activation energy was varied in the range from 0.50 to 1.15 eV in the studied temperature ranged from 50 to 90 °C. With increasing the deposition temperature, Fermi level is shifted towards the bottom of the conduction band edge. This is due to the appearance of sulfur vacancy who acts as a donor defects. The transport in CdS film is achieved by hoping through localized states in the band tail. Observation of MNR in the electrical conductivity of CdS films is explained by the presence of disorder in the films network and by the contribution of localized states in the electrical transport. Finally a correlation between disorder and electrical conductivity characteristics namely the pre-exponential and the activation energy is outlined.

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