MOTT TYPE ELECTRICAL CONDUCTIVITY IN ZnS_xSe_{1-x} THIN FILMS

M. POPA[1], I. TIGINYANU[2], V. URSAKI[2]

[1]*Alecu Russo* State University of Balti, 38 Puskin Str., MD-3100 Balti, Moldova
[2]Institute of Electronic Engineering and Nanotechnology of the Academy of Sciences of Moldova, Academy str. 3/3, MD-2028 Chisinau, Moldova

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Abstract. Thin ZnS_xSe_{1-x} films on glass substrates have been obtained by thermal evaporation. Electrodes from In or other materials have been deposited on thin films, and the temperature dependence of electrical conductivity was investigated during a series of successive cycles of heating and cooling performed at a rate of 6 K/min in a temperature interval from 300 K to 500 K. The measurements demonstrated that the energy of thermal activation at low temperatures (ΔE_2 = 0.13–0.43 eV) is much lower as compared to that measured at high temperatures (ΔE_1 = 0.43–1.89 eV). It was found that in both ranges of low and high temperatures the thermal activation energy increases with increasing the sulfur content in thin films. It was demonstrated that at low temperatures the dominant mechanism of electrical conduction is of Mott-type.

Key words: II-VI semiconductor compounds, solid solutions, thin films, electrical conductivity, thermal activation energy, hopping conduction.

1. INTRODUCTION

II-VI type semiconductor compounds, especially ZnS and ZnSe have attracted considerable interest during the last years in developing different optoelectronic devices both for academic investigations and industrial purposes. ZnS and ZnSe proved to be promising candidates for various technological applications, especially for light emitting diodes, photodetectors and heterojunction devices [1–5].

The preparation of ZnS_xSe_{1-x} solid solutions presents especial interest due to possibilities to obtain compounds with intermediate physical properties between those of ZnS and ZnSe. Materials with bandgap between 2.7 eV and 3.7 eV are obtained as a function of the sulfur content in the solution. These thin layers can be used as buffer layers in solar cells, substituting CdS, which is a toxic material. The enhancement of the solar cell response in the blue spectral region is another advantage, which should allow more light to reach the p-n junction and to contribute to photogeneration.

Electrical conductivity presents a particular interest among the parameters of semiconductor materials. Measuring the electrical conductivity of thin semiconducting layers is a rather difficult problem, since it depends upon a series of factors whose actions can not be separated, namely the form and the dimensions of the sample, the value of the applied voltage, the temperature, the pressure, the nature of the electrode material, the nature and the pressure of the gas in the measuring chamber, etc.

The goal of this paper is to present some experimental results concerning the dependence of electrical conductivity of thin semiconductor ZnS_xSe_{1-x} layers upon temperature. The validity of the Mott model is examined for explanation of the low thermal activation energy of electrical conductivity in these extremely resistive layers.

2. EXPERIMENTAL DETAILS

An automated UVH-70A-1 installation was used for the deposition of thin ZnS_xSe_{1-x} films in vacuum, allowing one to deposit simultaneously layers from four evaporators (three evaporation positions), or to use a single evaporator, in a semiclosed chamber with a volume smaller than the work chamber.

To obtain measuring cells of the surface type, initially ZnS_xSe_{1-x} layers with x value between 0 and 1 have been deposited on Corning glass substrates by thermal evaporation in quasi-closed volume. Electrodes with thickness of 1–2 μm have been deposited over the layers at a distance of 5–7 mm from each other [6]. The evaporator temperature T_{ev} was measured with a Pt/PtRh thermocouple, and it can vary between 700 K and 1500 K. The substrate temperature T_{sub} was measured during the deposition process with a Fe-Constantan thermocouple (or with a NiCr/NiAl thermocouple). The X-ray diffraction (XRD) analysis demonstrated that the ZnS_xSe_{1-x} thin layers have a cubic structure of the zincblende type with a strong (111) crystal plane preferred orientation. The scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy-dispersive X-ray (EDX) analyzes shown that the films are homogeneous, continuous, and stoichiometric [6].

When selecting the material for electrical contacts one should take into account that the atoms from the electrodes can diffuse into the semiconductor film, behave as impurities, and influence the electrical properties. These processes are especially important when the sample (substrate-film-electrode) is heated to high temperatures. In, In-Ga, and In-Ni electrodes have been used as ohmic contacts to ZnS_xSe_{1-x} thin layers.

Most of experimental data concerning the electrical conductivity of ZnS_xSe_{1-x} thin layers have been measured at continuous current with two probes.

More reliable data are obtained with a four probe method. However, the use of this method is often limited in the case of thin films by the existence of a space charge layer at the surface which strongly influences the accuracy of measurements.

The resistivity of ZnS_xSe_{1-x} thin films was measured with a Keithley 6517 instrument, and the sample temperature was measured with a Cu-Constantan thermocouple. The electrical conductivity was calculated according to the relation [7]:

$$\sigma = \frac{l}{d \cdot l} \frac{1}{R}, \tag{1}$$

where d is the film thickness, L is the film width, and ℓ is the sample length (the distance between the electrodes).

The temperature of the thin film was calculated according to the relation [7]:

$$T_{film} = T = \frac{U_S(\text{mV})}{\alpha_S} + T_{room} + 273 \text{ K}, \tag{2}$$

where α_S = 0.033 mV/^{o}C represents the Seebeck coefficient of the Cu-Constantan thermocouple, U_S is the Seebeck voltage, and T_{room} is the room temperature.

3. EXPERIMENTAL RESULTS

3.1. TEMPERATURE DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY

The temperature dependence of electrical conductivity of ZnS_xSe_{1-x} thin layers was investigated during a series of successive cycles of heating and cooling performed at a rate of 6 K/min in a temperature interval from 300 K to 500 K.

Figure 1 presents the dependence of the type $\ln\sigma = f(10^3/\text{T})$ for two thin ZnS_xSe_{1-x} layers prepared by evaporation in vacuum on non-heated glass substrates (T_{sup} = 300 K) with a deposition rate of r_d = 1.50 nm/s. A rapid increase of electrical conductivity occurs during the first heating. During the first cooling, as well as in consequent heating-cooling cycle, the curves become reversible and they demonstrate two distinct regions: the first regions situated in the range on low temperatures and the second region in the range of high temperature.

The temperature dependence of conductivity measured during the second heating cycle for all the prepared samples is presented in Figure 2. One can observe that with increasing the value of x the conductivity is shifted to lower value and the

slope of curves increases. The values of thermal activation energy of conductivity for both the high temperature range ΔE_1 and low temperature range ΔE_2 have been determined from the slope of $\ln\sigma = f(10^3/T)$ curves, and they are presented in Table 1. Here, d represents the thickness of the thin layer, T_{sub} is the substrate temperature, ΔT_1 is the high temperature range, ΔT_2 is the low temperature range, T_{tr} is the transition temperature from the low temperature range to the high temperature range, σ_{tr} is the transition conductivity.

One can observe that the activation energy in the range of low temperatures (ΔE_2 = 0.13 – 0.43 eV) is significantly lower than the activation energy in the range of high temperatures (ΔE_1 = 0.43 – 1.89 eV). The activation energy increases with increasing the sulfur content in samples in both temperature ranges.

According to the model of band-to-band transitions, the activation energy of conductivity is equal to half the material bandgap ($\Delta E_1 = E_g/2$) in the high temperature range (for $T > T_{tr}$). One can observe that for samples with x = 0.6; 0.8; and 1.0 this rule is fulfilled. The lower values of activation energy for samples with low x value could be due to some contribution from free-to-bound transitions. The energy level of the Zn_i donor is situated below the conduction band bottom at (ΔE_d = 0.90eV) [8, 9], while the energy level of V_{Se} acceptors is localized above the top of valence band at (ΔE_a = 0.01eV) [10, 11]. The shallow impurities (donors and acceptors) are ionized in the temperature range of k_BT = 0.026–0.043eV [10–12], and the Fermi level is situated near the middle of the bandgap.

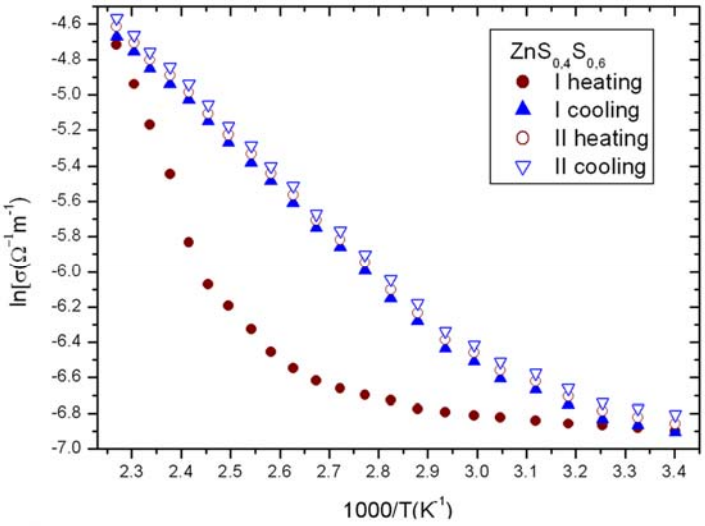

Fig. 1

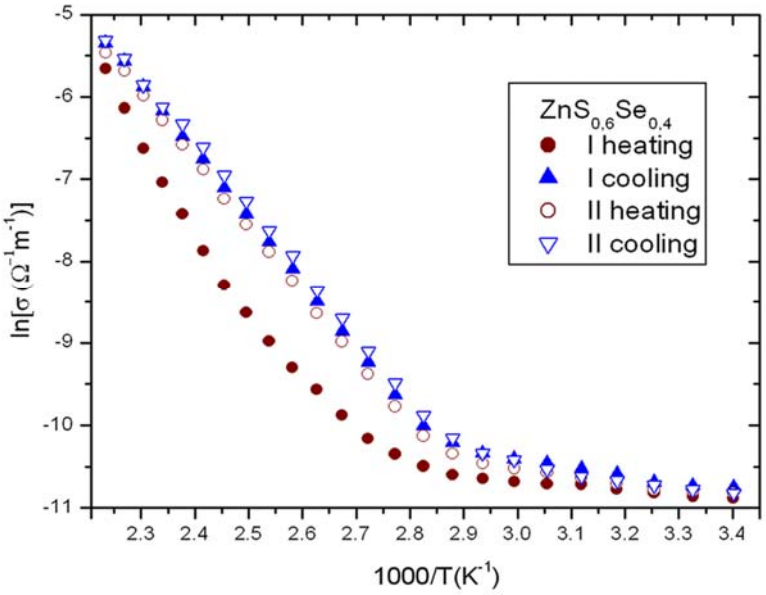

Fig. 1 (continued) – Dependence of the type $\ln\sigma = 10^3/T$ for a $ZnS_{0.4}Se_{0.6}$ (a), and a $ZnS_{0.6}Se_{0.4}$ (b) thin film.

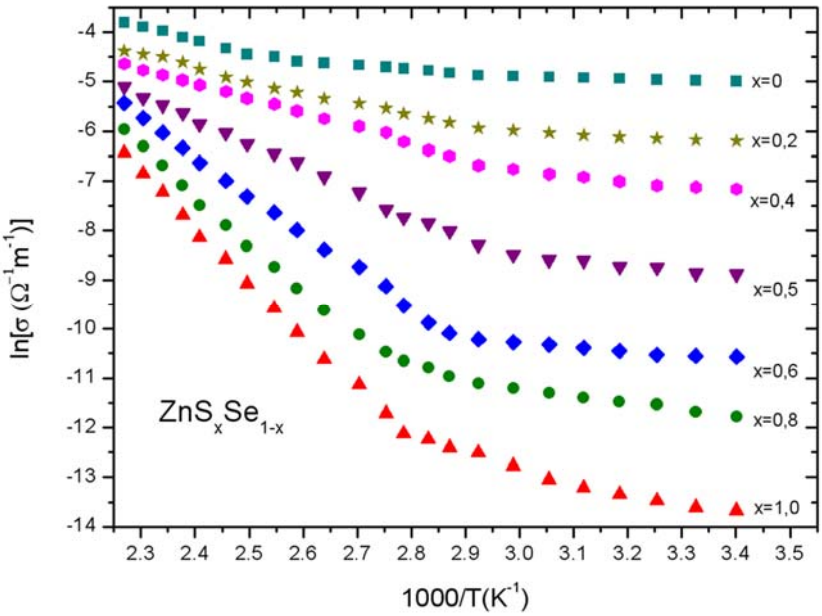

Fig. 2 – Temperature dependence of electrical conductivity (II heating cycle) of ZnS_xSe_{1-x} thin films.

Table 1

The values of thermal activation energy of ZnS_xSe_{1-x} thin films

x	d (μm)	T_{sub} (K)	ΔT_1 (K)	ΔE_1 (eV)	ΔT_2 (K)	ΔE_2 (eV)	T_{tr} (K)	$\ln\sigma_{tr}$	σ_{tr} ($\Omega^{-1}m^{-1}$)
0	0.50	300	327–440	0.43	294–327	0.13	327	–5.00	$6.7*10^{-3}$
0.2	0.67	300	334–440	0.57	294–334	0.18	334	–5.99	$2.5*10^{-3}$
0.4	0.60	300	334–440	0.74	294–334	0.24	334	–6.56	$1.4*10^{-3}$
0.5	0.55	300	347–440	1.05	294–347	0.30	347	–8.79	$1.5*10^{-4}$
0.6	0.60	300	347–440	1.44	294–347	0.34	347	–10.34	$3.2*10^{-5}$
0.8	0.70	300	354–440	1.62	294–354	0.39	354	–10.93	$2.1*10^{-5}$
1.0	0.62	300	354–440	1.89	294–354	0.43	354	–12.24	$4.8*10^{-6}$

The low values of ΔE_2 indicate on the hopping conductivity as most probable mechanism of transport in these layers. Similar results for the thermal activation energy in ZnS_xSe_{1-x} layers have been reported by Ganguly [13] and Subbaiah [14].

We will examine, which of models (Mott [15–17] or Efros-Shklovskii [18, 19]) can be applied to hopping transport in these high resistivity thin layers.

3.2. CONDUCTIVITY IN DISORDERED SYSTEMS

At low temperatures, when the thermal energy k_BT (k_B is the Boltmann constant) is of the order or lower than Coulomb interaction energy between charge carriers, the electronic transport in disordered semiconductors attracts considerable interest both from the theoretical and experimental point of view.

Mott suggested for three-dimensional systems that the density of states (DOS) is constant near the Fermi level, and electronic transport occurs as a result of hopping with variable activation energy and variable-range hopping assisted by phonon emission or absorption [15–17, 20]. This regime can be described by the following relation:

$$\rho = \rho_{Mott} \exp\left(\frac{T_{Mott}}{T}\right)^{1/4}, \tag{3}$$

where ρ_{Mott} is a resistivity parameter, and T_{Mott} is a characteristic temperature.

On the other hand, Efros and Shklovskii (ES) [18–20] shown that at long distances the electron-electron interaction creates a Coulomb gap (CG). In such a case, the density of states in three-dimensional systems is expressed by a relation of $N(E) \sim (E\text{-}E_F)^{1/2}$. Then, the resistivity behaves in the form of:

$$\rho = \rho_{ES} \exp\left(\frac{T_{ES}}{T}\right)^{1/2}, \tag{4}$$

where ρ_{ES} and T_{ES} are constants.

An equation was proposed that combines both the (3) and (4) relations [20]:

$$\rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{p}, \tag{5}$$

where $p = (n + 1)/(n + 4)$. The values of T_0 and ρ_0 depend upon the density of localized states $N(E_F)$ near the Fermi level. Since the value of the energy gap E_g in which the states participating in the hopping transfer are situated continuously decreases with decreasing temperature, the value of p is less that 1. In the case of Efros-Shklovskii hopping $n = 2$ and $p = 0.5$, while $n = 0$ and $p = 0.25$ in the case of Mott hopping.

Taking into account that the electrical conductivity is inversely proportional to resistivity ($\sigma = 1/\rho$), the relation (5) can be written as [21]:

$$\sigma = \sigma_0 \exp\left(-\left(\frac{T_0}{T}\right)^{p}\right) \tag{6}$$

or

$$\ln\sigma = \ln\sigma_0 + K_1 T^{-p}, \tag{7}$$

where K_1 is a constant.

By differentiating this relation one obtains

$$\mathrm{d}(\ln\sigma) = -K_1 p T^{-p-1}\mathrm{d}T \tag{8}$$

or

$$\mathrm{d}(\ln\sigma) = -K_2 T^{-p}\mathrm{d}(\ln T), \tag{9}$$

where $K_2 = K_1 p$.

We now introduce

$$W(T) = \frac{\mathrm{d}(\ln\sigma)}{\mathrm{d}(\ln T)} = -K_2 T^{-p}, \tag{10}$$

from which we have:

$$\ln(W(T)) = \text{const} - p \ln T. \tag{11}$$

The graph of $\ln(W(T) = f(\ln T)$ is a straight line, and the value of p can de determined from the slope of this line.

Such types of dependences have been plotted for ZnS_xSe_{1-x} thin layers, and it was found that these dependences are linear in the temperature range of 294 K–334 K (Fig. 3). The values of p determined form the slopes of graphs vary between 0.242 and 0.282 which indicates that the dominant conduction mechanism in these films is of Mott type.

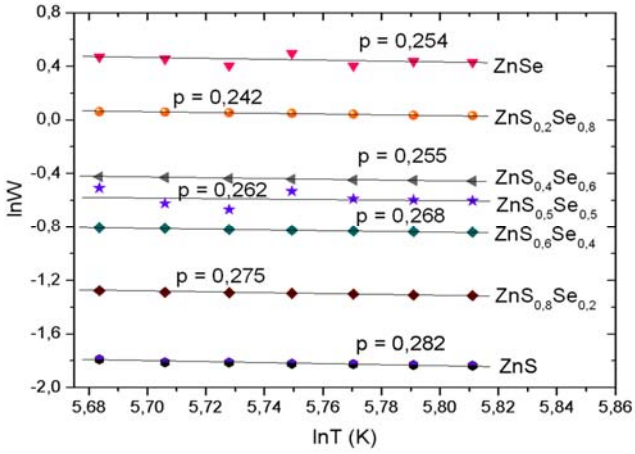

Fig. 3 – Dependence $\ln W = f(\ln T)$ for ZnS_xSe_{1-x} thin films.

3.3. MOTT-TYPE HOPPING CONDUCTION

In the case of hopping with variable distance of the 3D Mott type, the temperature dependence of electrical conductivity is given by the relation [15, 22]:

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_M}{T}\right)^{1/4}\right], \tag{12}$$

or

$$\sigma = \frac{\sigma_{0M}}{T^{1/2}} \exp\left[-\left(\frac{T_M}{T}\right)^{1/4}\right], \tag{13}$$

where σ_{0M} and T_M are characteristic Mott parameters expressed by the following relations [22, 23]:

$$\sigma_{0M} = \frac{3e^2 \nu_{ph}}{2}\left[\frac{N(E_F)}{2\pi\alpha_M k_B T}\right]^{1/2}, \tag{14}$$

$$T_M = \frac{\lambda\alpha_M^3}{k_B N(E_F)}, \tag{15}$$

where T_M is the Mott temperature, which represents a measure of the disordering degree in the layer, e is the electron charge, ν_{ph} is the typical phonon frequency, which depends on the electron-phonon interaction, and according to Mott and Davis [16] is a constant, $N(E_F)$ is the density of states at the Fermi level, α_M is a coefficient of the wave function which expresses the exponential decrease of localized states near the Fermi level, k_B is the Boltzmann constant, and λ is a constant.

By taking the log of both sides of the equation (13) one obtains

$$\ln(\sigma T^{1/2}) = \ln(\sigma_{0M}) - \left(\frac{T_M}{T}\right)^{1/4}. \tag{16}$$

By plotting the graph $\ln(\sigma T^{1/2})=f(T^{-1/4})$ one obtains a straight line, and the term $(T_M)^{1/4}$ can de determined from the slope of this line. In the case when there is not possible to determine directly the slope of the graph, the Mott temperature is determined from the relation

$$T_M = \frac{\ln(\sigma T^{1/2})_1 - \ln(\sigma T^{1/2})_2}{\left(\frac{1}{T^{1/4}}\right)_2 - \left(\frac{1}{T^{1/4}}\right)_1}. \tag{17}$$

By extrapolating the graphs to $T^{-1/4}\to 0$, it results that

$$\ln(\sigma T^{1/2})_{T^{-1/4}\to 0} = \ln(\sigma_{0M})_{T^{-1/4}\to 0}, \tag{18}$$

from which the value of σ_{0M} is obtained.

Figure 4 presents the graphs of the type $\ln(\sigma T^{1/2}) = f(T^{-1/4})$. The values of the Mott temperature T_M determined according to the graphic method described above are presented in Table 2. The large values of the Mott temperature indicate on a high degree of disorder in the respective films. The obtained value of the T_M and σ_{0M} parameters are in good concordance with those obtained by Ganguly [13] in ZnS_xSe_{1-x} films deposited by high-pressure sputtering.

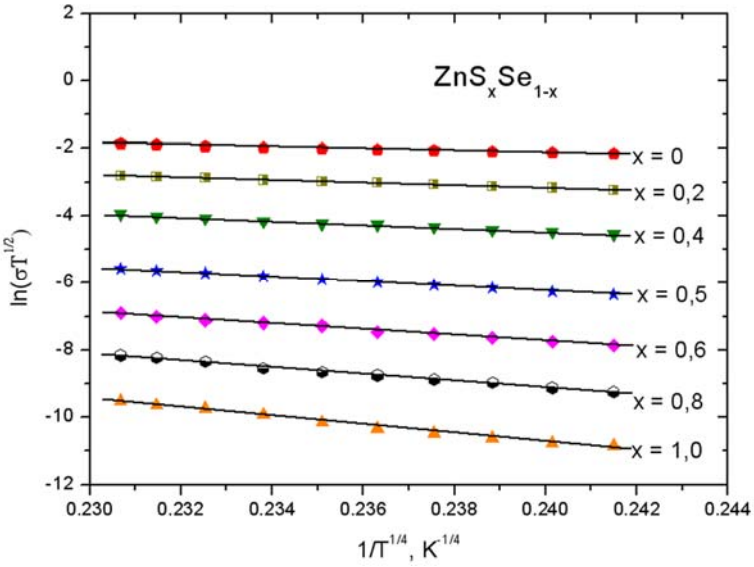

Fig. 4 – Dependence $\ln(\sigma T^{1/2}) = f(T^{-1/4})$ of ZnS_xSe_{1-x} thin films.

Table 2

Mott temperature and Mott conductivity of ZnS_xSe_{1-x} thin films

x	$T_M^{1/4}$ ($K^{1/4}$)	$T_M \times 10^7$ (K)	$\Delta[\ln(\sigma T^{1/2})]$	$\Delta(1/T)^{1/4}$ ($K^{-1/4}$)	$\ln(\sigma_{0M})_{T^{-1/4}\to 0}$	σ_{0M} ($\Omega^{-1}m^{-1}$)
0	58.86	1.2	–1.85 – (–2.15)	0.2415 – 0.2307	10.28	29207
0.2	68.48	2.2	–2.81 – (–3.23)		9.83	18665
0.4	83.24	4.8	–3.94 – (–4.55)		9.11	8974
0.5	95.16	8.2	–5.57 – (–6,31)		8.54	5093
0.6	106.98	13.1	–7.10 – (–8.07)		7.84	2549
0.8	119.80	20.6	–7.85 – (–8.95)		6.92	1016
1	128.54	27.3	–9.51 –(–10.84)		6.06	427

It follows from Eq. (15) that:

$$N(E_F) = \frac{\lambda \alpha_M^3}{k_B T_M}. \tag{19}$$

By substituting (19) into (14) one obtains:

$$\alpha_M = \frac{2\sqrt{2\pi} k_B}{3e^2 \nu_{ph} \sqrt{\lambda}} \sigma_{0M} \sqrt{T_M}\ . \tag{20}$$

According to literature data, different authors used various but close values for λ, such as 16 [16, 21], or 18 [13, 24, 25]. We used in our calculations the value of λ = 18. The ratio in Eq. 20 is a constant. Therefore, one can use a simpler formula for calculations:

$$\alpha_M = 21.23\sigma_{0M}\sqrt{T_M} \ . \tag{21}$$

Table 3 presents the obtained values for α_M and $N(E_F)$. It was found that the density of energy states at the Fermi level $N(F)$ is inversely proportional to the Mott temperature T_M.

Table 3

Other parameters of Mott conduction in ZnS_xSe_{1-x} thin films

x	$T^{1/2}_M$ ($K^{1/2}$)	$\alpha_M \times 10^9$ (m^{-1})	$\alpha^3_M \times 10^{27}$ (m^{-3})	$N(E_F)$ ($m^{-3}eV^{-1}$)	R_M (nm)	W_M (eV)	$\alpha_M R_M$
0	3464	2.14	9.94	1.71×10^{26}	2.47	0.093	5.29
0.2	4689	1.85	6.44	6.01×10^{25}	3.33	0.108	6.16
0.4	6928	1.33	2.30	1.02×10^{25}	5.63	0.131	7.49
0.5	9055	0.98	0.94	2.42×10^{24}	8,70	0.150	8.56
0.6	11445	0.62	0.24	3.74×10^{23}	15.59	0.168	9.62
0.8	14353	0.31	0.031	2.97×10^{22}	34.93	0.188	10.78
1	16523	0.15	0.0034	2.59×10^{21}	76.95	0.203	11.56

Other Mott parameters such as the hopping distance R_M and the medium hopping energy W are determined from the following relations [22, 26]:

$$R_M = \left[\frac{9}{8\pi\alpha_M k_B T N(E_F)}\right]^{1/4} \tag{22}$$

$$W_M = \frac{3}{4\pi R^3 N(E_F)} \ . \tag{23}$$

For the hopping conduction mechanism with Mott variable distance, the following inequalities are true: $\alpha_M R_M > 1$ and $W_M > kT$. The calculated values of $\alpha_M R_M$ and W_M for ZnS_xSe_{1-x} films are presented in Table 3. These values satisfy the hopping mechanism of conduction. The parameter α_M decreases with increasing the sulfur content in films. This observation is probably due to the decrease of nanocrystallite sizes with increasing the sulfur content, which was also observed in other thin layers [13].

The obtained value of α_M, R_M, and W_M are in good concordance with those obtained by Ganguly [13] in ZnS_xSe_{1-x} layers deposited by high-pressure sputtering.

4. CONCLUSIONS

This study demonstrates the applicability of the Mott model for electronic hopping transport with activation energy of ΔE_2 = 0.13–0.43 eV in the range of low temperature in ZnS_xSe_{1-x} thin films, while the band-to-band transitions model is applied at high temperatures with an activation energy equal to half the bandgap ($\Delta E_1 = E_g/2$). This rule is well fulfilled for high values of x (0.6; 0.8; 1.0), while in samples with lower x values the activation energy is less than half the bandgap. These lower values of the activation energy may be associated with contribution from free-to-bound transitions.

REFERENCES

1. H. Hartmann, R. Mach, B. Selle, in: E. Kaldis (Ed.), Wide Gap II–VI *Compounds as Electronic Materials, Current Topics in Materials Science*, vol. 9, North-Holland Publishing Company, 1982.
2. J. M. Pawlikowski, Thin Solid Films **127**, 9-28 (1985).
3. H. K. Sadekar, A. V. Ghule, R. Sharma, Composites Part B: Engineer. **41**, 553-557 (2013).
4. M. A. Jafarov, E. F. Nasirov, S. A. Jahangirova, R. Jafarli, *Nanosystems*: Phys. Chem. Mathem. **6**, 644-649 (2015).
5. B. Noikaew, P. Chinvetkitvanich, I. Sripichai, Ch. Chityuttakan, J. Met. Mater. Miner. **18**, 49-52 (2008).
6. M. Popa, M., *Structural and physical properties of ZnS_xSe_{1-x} thin films*, in I. Tiginyanu, P. Topala, V. Ursaki (Eds), Nanostructures and Thin Films for Multifunctional Applications: Technology, Properties and Devices, 2016, pp. 115-142.
7. M. Popa, *Cercetari privind structura si morfologia suprafetei, proprietatile electrice, optice si luminiscente ale straturilor subtiri semiconductoare de ZnSe* (in Romanian), PIM-Iasi, 2014, p. 186.
8. M. Aven and J. S. Prener (Eds.), *Physics and Chemistry of II-VI Compounds*, North Holland Publishing Company, 1967.
9. F. C. Rong, W. A. Barry, J. F. Donegan, G. D. Watkins: Phys. Rev. B **54**, 7779-7788 (1996).
10. D. D. Nedeoglo, A. V. Simaskevici, *Electrical and luminescence properties of zinc selenide* (in Russian). Chisinau, Ştiinţa, 1984.
11. R. Bhargava (Ed.), *Properties of Wide Bandgap II-VI*, Semiconductors, Inspection, London, 1997.
12. M. Jain (Ed.), *II-VI Semiconductor Compounds*, World Scientific, Singapore, 1993.
13. A. Ganguly, S. Chaudhuri, A. K. Pal, J. Phys. D: Appl. Phys. **34,** 506-513 (2001).
14. Y. P. Venkata Subbaiah, P. Prathap, K. T. R. Reddy, D. Mangalaraj, K. Kim, Y. Junsin, J. Phys. D: Appl. Phys. **40**, 3683-3688 (2007).
15. N. F. Mott, N.F, J. Non-Cryst. Sol. **1**, 1-17 (1968).
16. N. F. Mott, E. A. Davis, *Electronic Processes in Non-crystalline Materials*, Oxford: Clarendon, 1979, p. 221.
17. N. F. Mott, *Metal-Insulator Transitions*, Taylor and Francis, London 1974, p. 278.
18. B. I. Shklovsii, A. L. Efros, *Electronic Properties of Doped Semiconductors*, Springer, Berlin, 1984, 195 p.
19. A. L. Efros, B. I. Shklovskii, J. Phys. C: Sol. St. Phys. **8**, L49-L51 (1975).
20. M. Errai, A. El Kaaouachi, A. Narjis, C. T. Liang, L. Limouny, S. Dlimi, A. Sybous, Chinese J. Phys. **52**, 251-260 (2014).
21. T. G. Castner, *Hopping Transport in Solids*, Elsevier, Amsterdam, 1990.

22. M. Z. Ansari, N. Khare, J. Appl. Phys. **117**, 025706 (2015).
23. G. Paasch, T. Lindner, S. Scheinert, Sinthetic Met. **132**, 97-104 (2002).
24. S. Yadav, R. K. Pal, S. K. Sharma, R. K. Shukla, A. Kumar, Digest J. Nanomater. Biostr. **5**, 675-681 (2010).
25. Cr. M. Matarneh, R. Danac, L. Leontie, F. Tudorache, Iu. Petrila, F. Iacomi, A. Carlescu, G. Nedelcu, I. Mangalagiu, Environ. Eng. Manag. J. **14**, 421-431 (2015).
26. R. Kumar, N. Khare, Thin. Sol. Films **516**, 1302-1307 (2008).