*Available online at* www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Physics Research, 2015, 6 (3):12-20
*(http://scholarsresearchlibrary.com/archive.html)*

ISSN : 0976-0970
CODEN (USA): APRRC7

# Substrate temperature dependent structural, optical and electrical properties of spray pyrolysis deposited MgSe thin film

**Y. S. Sakhare[1], N. R. Thakare[1] and A. U. Ubale[*2]**

*[1]Department of Engg. Physics, P. R. Pote (Patil) College of Engineering and Management, Amravati*
*[2]Nanostructured Thin Film Materials Laboratory, Department of Physics, Government Vidarbha Institute of Science and Humanities, VMV Road, Amravati, Maharashtra, India*

---

## ABSTRACT

*MgSe thin films were prepared by spray pyrolysis method by varying substrate temperature. The effects of the varying substrate temperature on structural, electrical, morphological and optical properties of MgSe thin films were discussed. X-ray diffraction studies confirm the formation of cubic structure with (111) & (200) as the preferred orientation. The optical studies revealed that the deposited MgSe has direct band gap and it varies from 2.60 to 2.45 eV depending on substrate temperature. The electrical resistivity of MgSe decreases with temperature indicating its semiconducting nature. The electrical resistivity, activation energy and optical band gap energy is found to depend upon substrate temperature. Thermo-emf measurement showed that the electrical conductivity in spray deposited MgSe is of p-type.*

---

## INTRODUCTION

There has been an increasing interest on the growth of nanostructured semiconducting chalcogenides thin films due to their wide range of applications in various fields of science and technology. The magnesium chalcogenides (MgX, X = O, S, Se, Te) are wide band gap semiconductors and can be potentially utilized in many optoelectronic devices. However, MgSe is so far not well understood due to its hygroscopic and its unstable structure. Among the various metal selenides, MgSe is one of the most important members of the family of wide band gap semiconductors which was prepared by many sophisticated physical methods. Literature survey reveles that many reports are available on theoretical calculation of fundamental properties of MgSe [1]. In the rocksalt structure, magnesium chalcogenide are indirect band gap type semiconductors, which limit their applications in elect-optical devices [2–4]. These compounds are optically inactive and hence, one of the challenging tasks in this regard is to modify them into active materials through band gap engineering. Jiang et al [5] have successfully deposited MgSe thin films on GaAs substrates by metal organic chemical vapour deposition (MOCVD) method. Prete et al [6] have reported growth and characterization of ZnMgSe and MgSe on (100) GaAs by low pressure MOVPE. Wang et al [7] have investigated structural properties of MgSe films deposited on ZnTe substrates by molecular beam epitaxy method. Spray pyrolysis technique has been used for several decades in glass industry and in solar cell production to deposit electrically conducting electrodes. Thin film formation using this technique involves spraying a metal salt solution onto a heated substrate. The sprayed droplet on reaching the hot substrate surface undergoes pyrolytic decomposition and forms the desired product. The other volatile by-products escape in the vapour phase. The quality and properties of the films deposited depend largely on the substrate temperature, precursor solution concentration, atomization type and substrate nature etc. In the present investigation MgSe thin films were deposited by using an aqueous solution of magnesium chloride ($MgCl_2$), selenium dioxide ($SeO_2$) and triethanolamine (NH $(CH_2\text{-}CH_2)_3$).

To investigate the influence of substrate temperature on physical properties of MgSe it was varied between 473 to 673 K.

## RESULTS AND DISCUSSION

### 2.1 Deposition of MgSe thin films

The $SeO_2$ was prepared by mixing 1 g of selenium metal powder (99% purity, Merck) with 10 ml of nitric acid ($HNO_3$) in a glass beaker and boiled for 5 to 10 min to get white powder. Then this powder was dissolved in 500 ml of double distilled water to prepare $SeO_2$ of 0.13 M. The aqueous solution of $MgCl_2$, $SeO_2$ and NH $(CH_2\text{-}CH_2)_3$ were prepared using double distilled water. The glass substrates used for the deposition were ultrasonically cleaned and purged with acetone prior to the deposition. For the deposition of magnesium selenide thin films the spray solution was prepared by mixing 10 ml of 0.12 M $MgCl_2$, 10 ml of 0.1 M TEA and 10 ml of 0.13 M $SeO_2$ in a 100 ml beaker. From it 10 ml of spray solution was sprayed onto preheated substrates at 4 ml/min spray rate. Five different sets of MgSe films were prepared by varying the substrate temperature from 473 to 673 K in step of 50 K. The optimized deposition parameters are listed in Table 1.

**Table 1: Process parameters for the deposition of MgSe thin film**

| Spray Parameters | Optimum Value |
|---|---|
| Nozzle | Glass |
| Nozzle-substrate distance | 25 cm |
| $MgCl_2$ | 0.12 M (10 ml) |
| $SeO_2$ | 0.13 M (10 ml) |
| Triethanolamine | (10 ml) |
| Spray solution | 10 ml |
| Solution flow rate | 4 ml /min |
| Carrier gas | Compress air |
| Substrate temperatures | 473 K to 673 K |

### 2.2 Film formation mechanism

The spray pyrolysis technique is basically a chemical deposition technique in which fine droplets of sprayed solution undergoes pyrolytic decomposition onto the hot substrates. For the deposition of MgSe thin films by spray method Se metal powder is dissolved in concentrated nitric acid to get selenous acid as,

$$3Se + 4HNO_3 + H_2O \rightarrow 3H_2SeO_3 + 4\,NO\uparrow \qquad (2)$$

The dehydration of selenous acid gives $SeO_2$ as,

$$H_2SeO_3 \text{ dehydration} \longrightarrow SeO_2 + H_2O\uparrow \qquad (3)$$

By adding 100 ml distilled water in $SeO_2$ powder 0.13 M $SeO_2$ solution was prepared. The 20 ml 0.12 M $MgCl_2$ was mixed with triethanolamine that forms magnesium-triethanolamine complex, $[Mg(TEA)]^{2-}$ which then decomposes on hot substrate with $SeO_2$ i.e. $H_2SeO_2$ ($SeO_2$ with $H_2O$ gives $H_2SeO_3$ ) to from MgSe film. The substrate temperature was changed from 473 to 673 K. Fig. 1 shows the variation of MgSe film thickness with substrate temperature. It is noted that film thickness increase from 121 to 188 nm with rise in substrate temperature from 473 K to 523 K. However, further rise in substrate temperature shows decrease in film thickness. It is obvious that rise in substrate temperature increases evaporation rate of initial products reducing the quantity of deposit that reaches to the substrate. The film thickness decreases from 188 to 152 nm as the substrate temperature was increased from 523 to 673 K.

### 2.3 Structural studies

The structural identification and changes in crystalinity of MgSe thin films with substrate temperature were studied using XRD technique. Fig. 2 shows the X-ray diffraction patterns of the MgSe thin films deposited at various substrate temperatures. The broad hump observed in XRD pattern is due to amorphous glass substrate. The observed XRD pattern is compared with standard JCPDS data. The prominent peak observed around $2\theta = 32.80^0$ is due (111) & (200) orientation of cubic lattice of MgSe. The intensity of this peak increases as substrate temperature rises from 473 to 523 K and then decreases slightly. At higher substrate temperature above 623 K the (101) and (400) diffraction peaks due to elemental Mg and Se are observed. In addition to that (020) and (410) orientation due to $MgSeO_3$ phase is also observed. A significant change in the features of the XRD pattern is observed for the thin films deposited at various substrate temperatures.

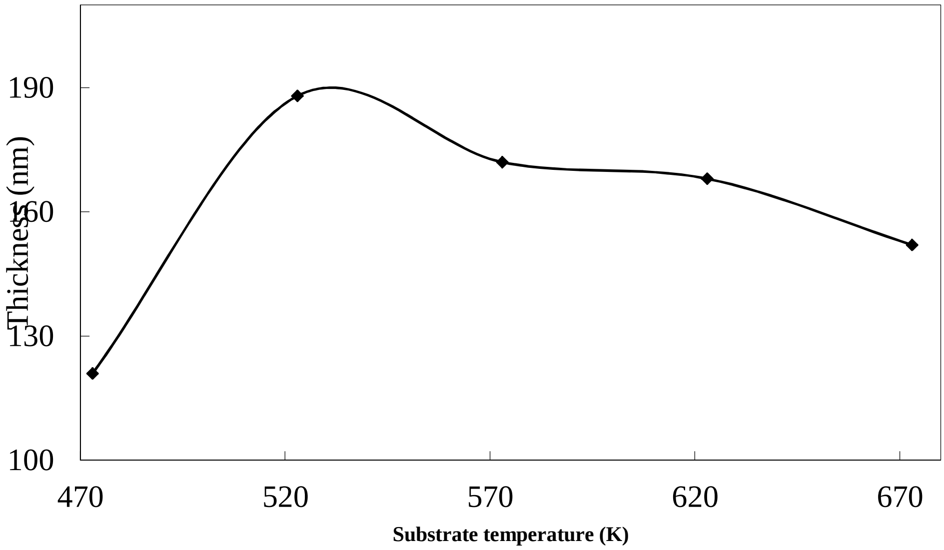


**Fig.1. Variation of MgSe film thickness (nm) with substrate temperature (K)**

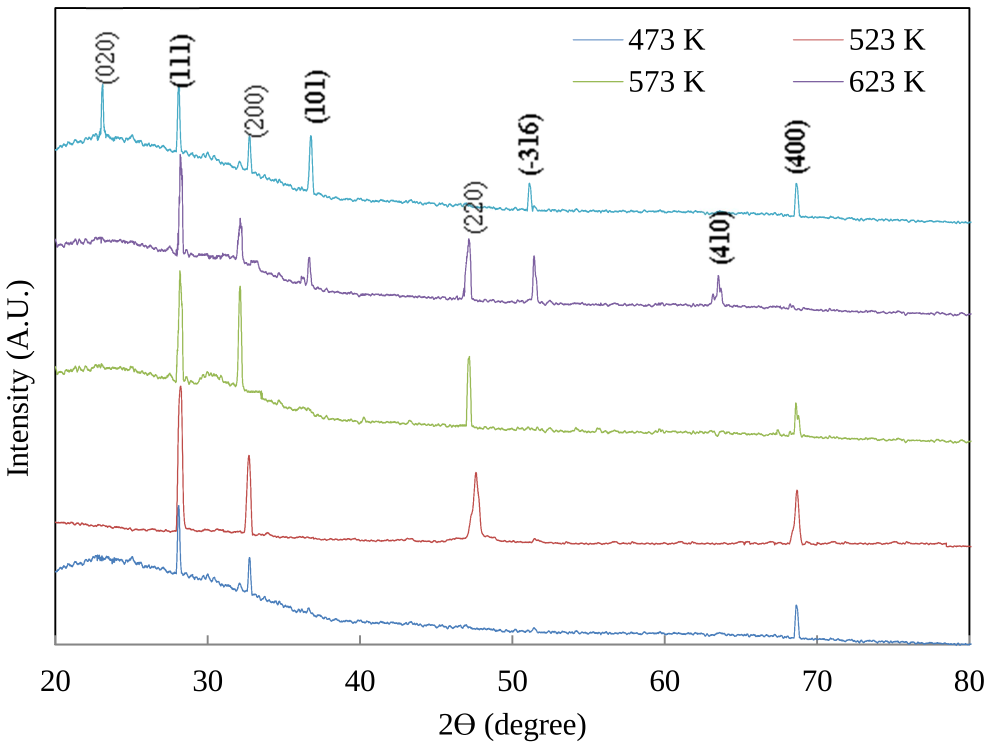


**Fig.2. X-ray diffraction patterns of MgSe thin films deposited at various substrate temperatures**

The crystalline nature strongly depends on substrate temperature. Therefore these result shows that it is necessary to optimize deposition temperature to get nanocrystalline cubic phase of MgSe. In present investigation it was observed that films deposited at 523 K temperature are more polycrystalline with cubic lattice. However previous result on MgSe films deposited by MBE and MOVCD shows rocksalt, wurtizite and zinc blende structures [5,6] The average crystallite size of the deposited material was determined by using Debye-Scherer's formula,

$$d = \frac{0.9\,\lambda}{\beta \mathrm{Cos}\,\theta} \qquad (4)$$

Where β is full width at half maximum of the peak in radians, λ is the wavelength of CuKα radiation (λ=1.5418 $A^0$), θ is the Bragg's diffraction angle at peak position in degrees. The average crystallite size was found to very between 14 to 24 nm depending on deposition temperature. (Table 2). The crystallite size of the film deposited at 523 K temperature is more as compare to other temperatures, which is in support with SEM results.

### 2.4 Surface morphology
**Scanning electron microscopy**

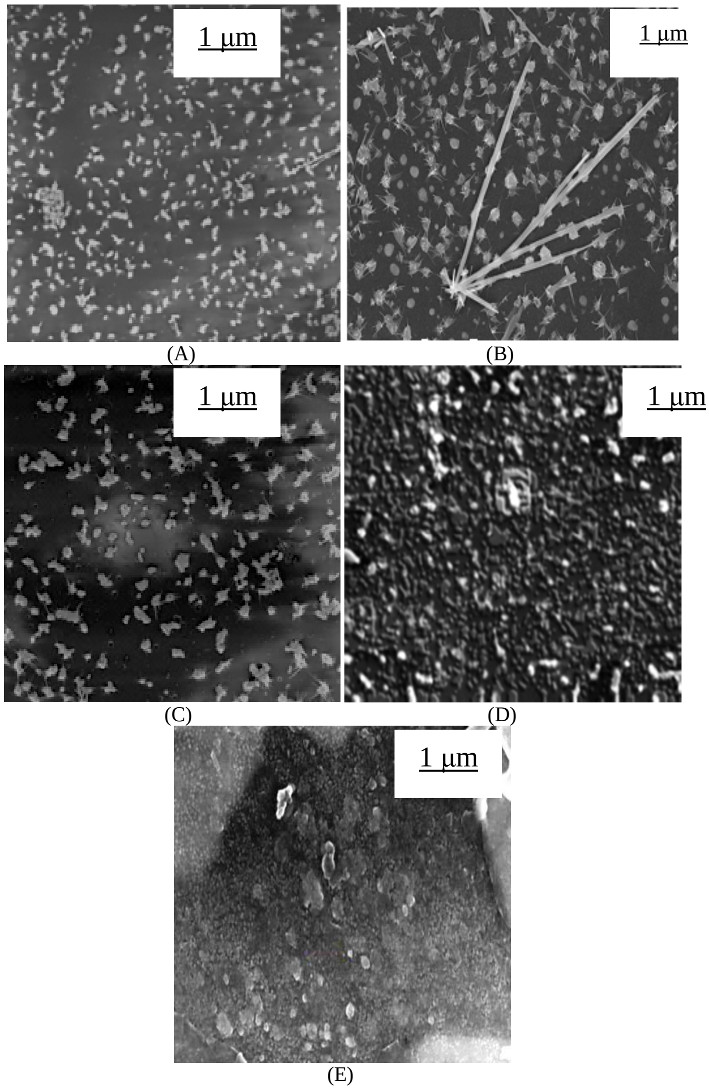


**Fig.3 SEM images of MgSe thin films deposited at various substrate temperatures. Substrate temperature: (A) 473 K (B) 523 K (C) 573 K (D) 623 K and (E) 673 K**

SEM images of the MgSe thin films are shown in figure 3. It can be seen that the films are homogeneous with no visible cracks or holes on the surface. The granular structure of MgSe increases as the substrate temperature rise from 473 to 523 K. The morphology of the film deposited at 523 K is porous and shows growth of nano-rods at some places. The grain size is lesser for the films deposited above and below 523 K temperature confirming that it is optimum value. At higher substrate temperature the deposited spray droplets are almost dry. The precursor vaporizes before it reaches to the substrate and consequently tiny solid particles are formed as powdery and non-adherent deposits. The grain size growth observed from SEM images is in good agreement with XRD results.

**B) Compositional analysis**

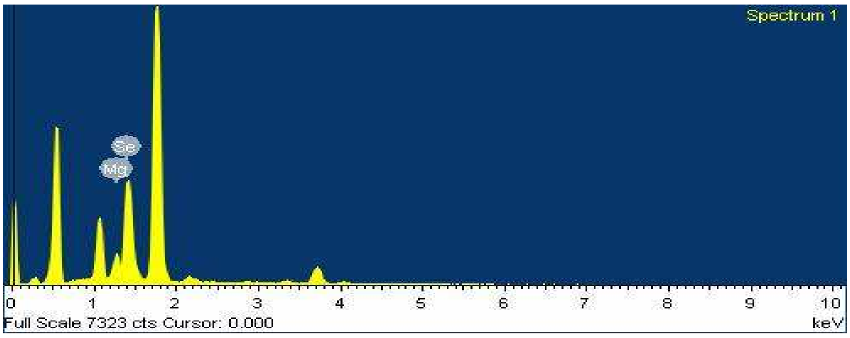


**Fig.4 EDAX spectrum of MgSe thin film deposited at 523 K substrate temperature (K)**

A typical EDAX spectrum of MgSe thin film deposited with the substrate temperature 573 K is shown in Fig.4. The formation of MgSe is confirmed from the elemental analysis. One can also observe other peaks due to glass substrate.

**C) Atomic force microscopy**

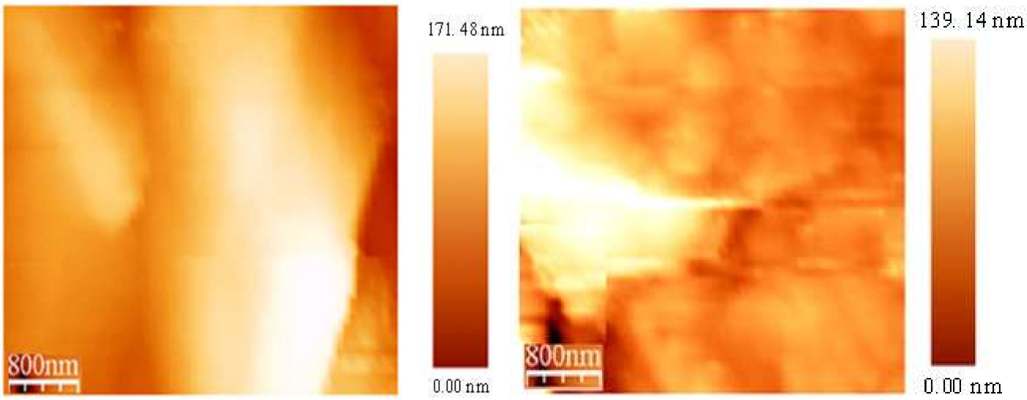


**Fig.5 AFM image of spray deposited MgSe thin films deposited at substrate temperature (K): (A) 523 K (B) 673 K**

The AFM images of the films deposited at 523 and 673 K substrate temperatures are shown in Fig.5 and have uniform and homogenous surface. The grainular structure observed at 523 K temperature confirms its porous nature.

**2.5 Optical properties**

Fig.6 shows the optical absorption spectrum of MgSe thin films deposited at different substrate temperatures. There is significant change in optical absorption of MgSe thin films with deposition temperature. The variation in film thickness with temperature has noticeable effect on optical absorption of sprayed MgSe thin films. In order to confirm the nature of the optical transition in these samples; the optical data was analyzed using classical relation [8, 9],

$$\alpha h\nu = A(Eg - h\nu)^n \qquad (5)$$

where α is the absorption coefficient, A is a constant, h is Planck's constant, n is the photon frequency, Eg is the optical band-gap energy, and n is 1/2 and 2 for the transition being direct and indirect respectively. Fig.7 shows the variation of $(\alpha h\upsilon)^2$ versus (hυ) for MgSe thin films deposited at various substrate temperatures. The extrapolation of the straight-line portion of the plot to zero absorption coefficient gives the value of band gap energy (Eg). The optical band gap of MgSe shows dependence on substrate temperature (Fig.8). The optical band gap of film deposited at 472 K temperature is 2.60 eV and becomes minimum (2.45 eV) at 523 K. This decrease in direct band gap energy with increase in deposition temperature is attributed to the increase in the film thickness and crystalline nature of MgSe. The value of optical band gap energy of MgSe reported by Rabah et al [1] is very close to our result.

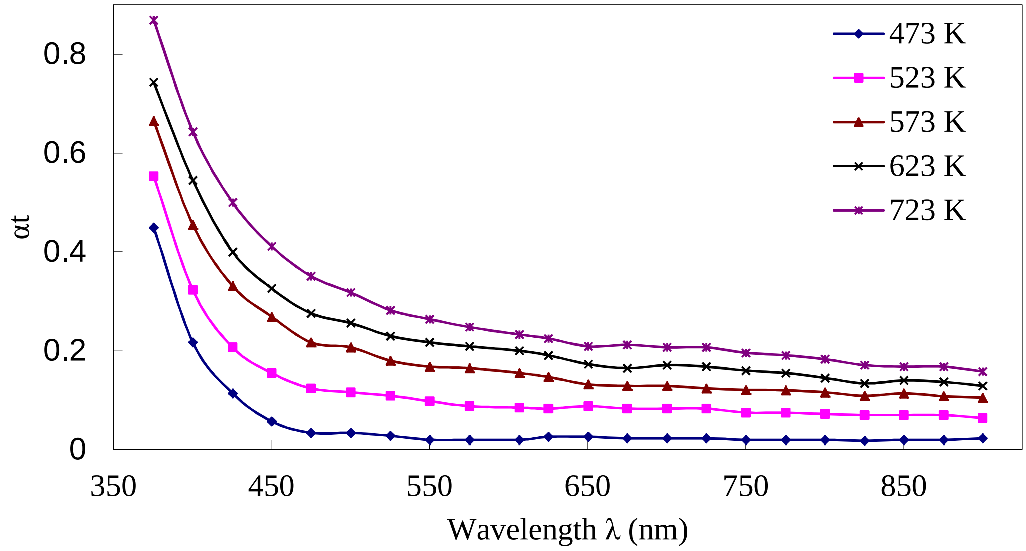


**Fig.6 Plots of optical absorption (αt) versus wavelength λ (nm) of MgSe thin films deposited at various substrate temperatures**

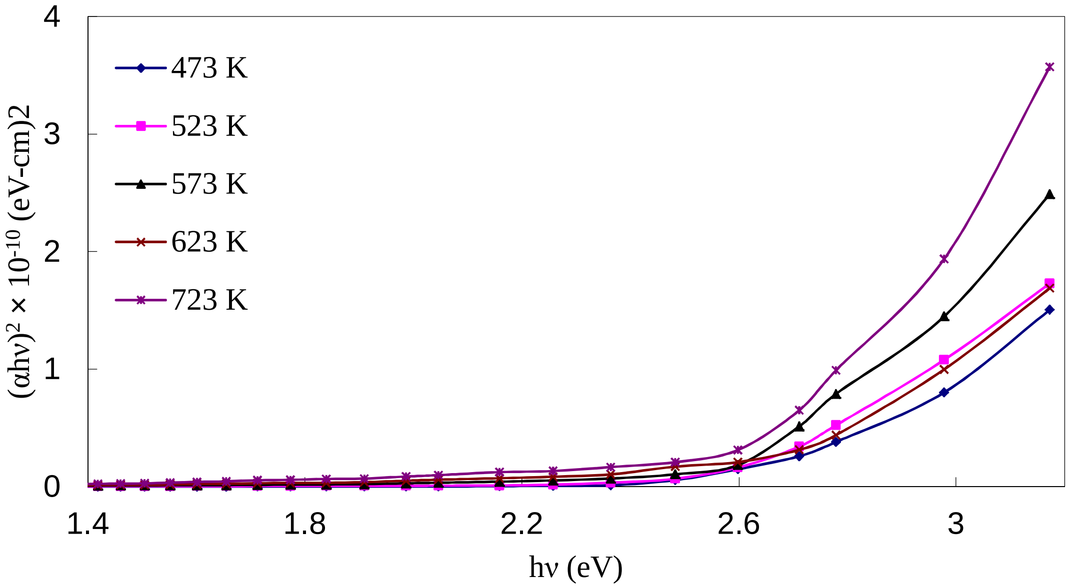


**Fig.7 Plots of $(\alpha h\upsilon)^2$ versus hυ for MgSe thin films deposited at various substrate temperature (K): (A) 473 K (B) 523 K (C) 573 K (D) 623 K and (E) 673 K**

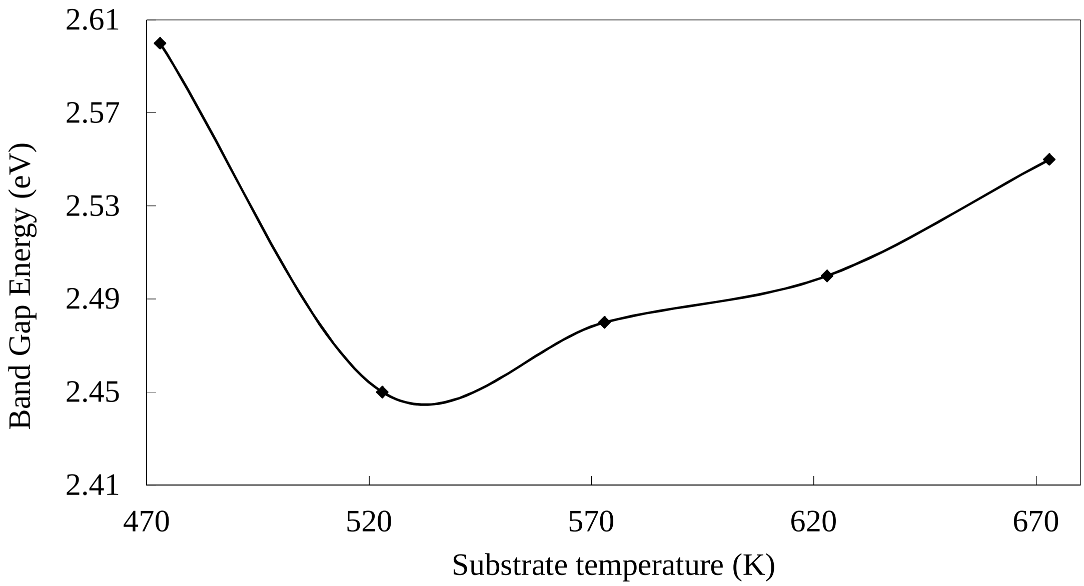


**Fig.8 Variation of optical band gap energy (eV) of MgSe thin film with substrate temperature (K)**

### 2.6 Electrical properties

Fig.9 shows the variation of electrical resistivity with substrate temperature. The electrical resistivity of the film deposited at 523 K is $11 \times 10^2$ Ω-cm and it increases for higher as well as lower temperatures (Table.2).

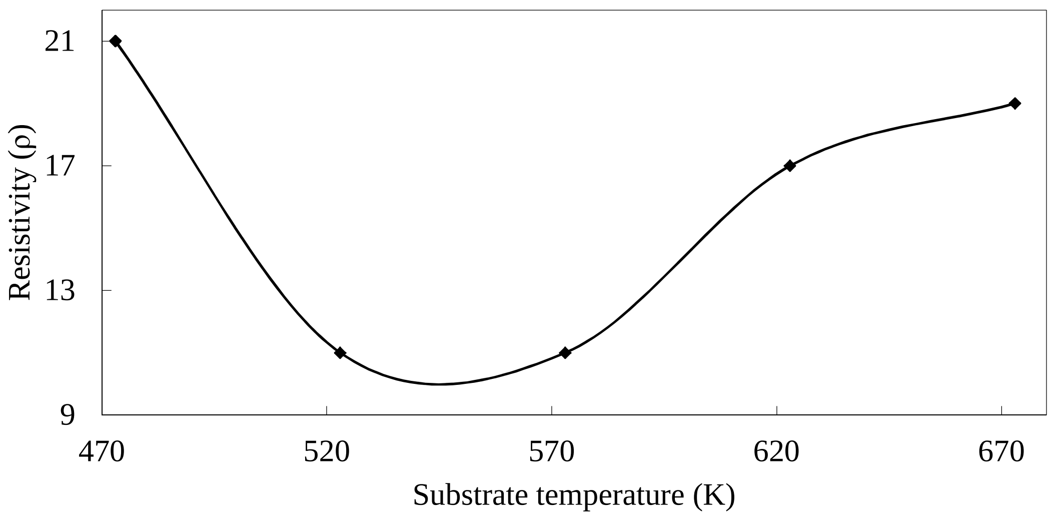


**Fig.9 Variation of electrical resistivity (Ω-cm) of MgSe thin film at 373 K with substrate temperature**

The variation of log ρ with reciprocal of temperature (1000/T) is shown in the Fig.10. The electrical resistivity follows the relation [10],

$$\rho = \rho o \exp\left(\frac{-Eg}{KT}\right) \quad (6)$$

where ρ is resistivity at temperature T, ρo is a constant, K is the Boltzmann constant and Ea is the activation energy required for conduction. The electrical resistivity decreases with temperature indicating its semiconducting nature. The thermal activation energies were calculated and were found to vary from 0.96 to 0.86 eV depending on substrate temperature (Fig.11).

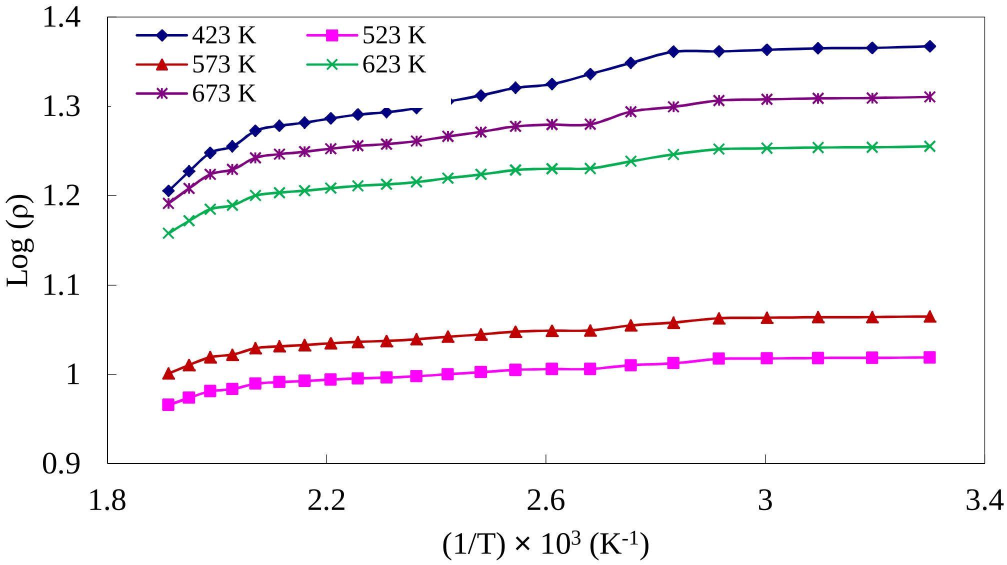


**Fig.10. Variation of log (ρ) vs (1/T) × $10^3$($K^{-1}$) for MgSe films. Substrate temperature (K): (A) 473 K (B) 523 K (C) 573 K (D) 623 K and (E) 673 K**

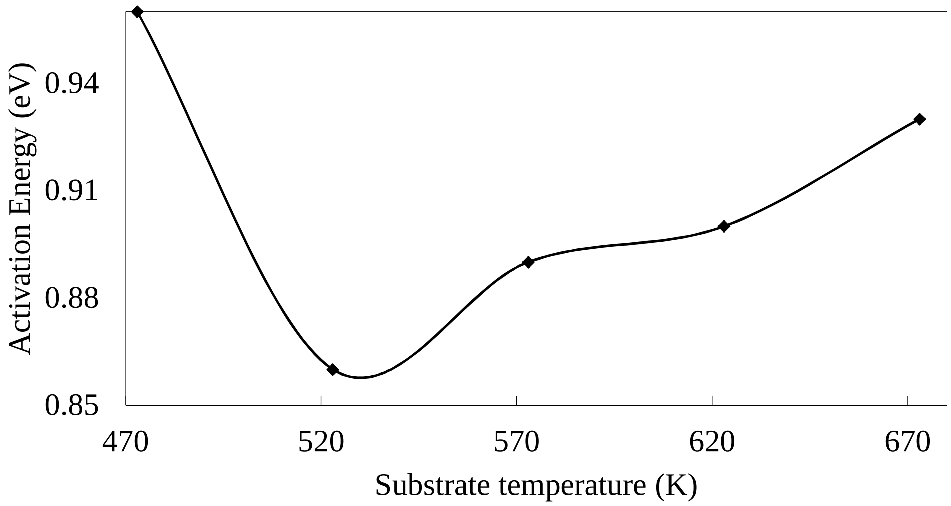


**Fig.11 Variation of activation energy of MgSe thin film with substrate temperature**

### 2.7 Thermo-emf measurement

Thermo-emf measurement gives the information about the type of charge carriers in the given material. The thermo-emf of all the films was measured as a function of temperature difference. From the polarity of the thermally generated voltage at hot end, it is concluded that the films exhibit a p-type electrical conductivity. The variation of thermo-emf with temperature difference for all the samples is shown in Fig.12. The thermo-emf shows dependence on substrate temperature. The thermo-emf generated across the film deposited at 523 K temperature is more which may be because of its improved morphology and crystalline nature.

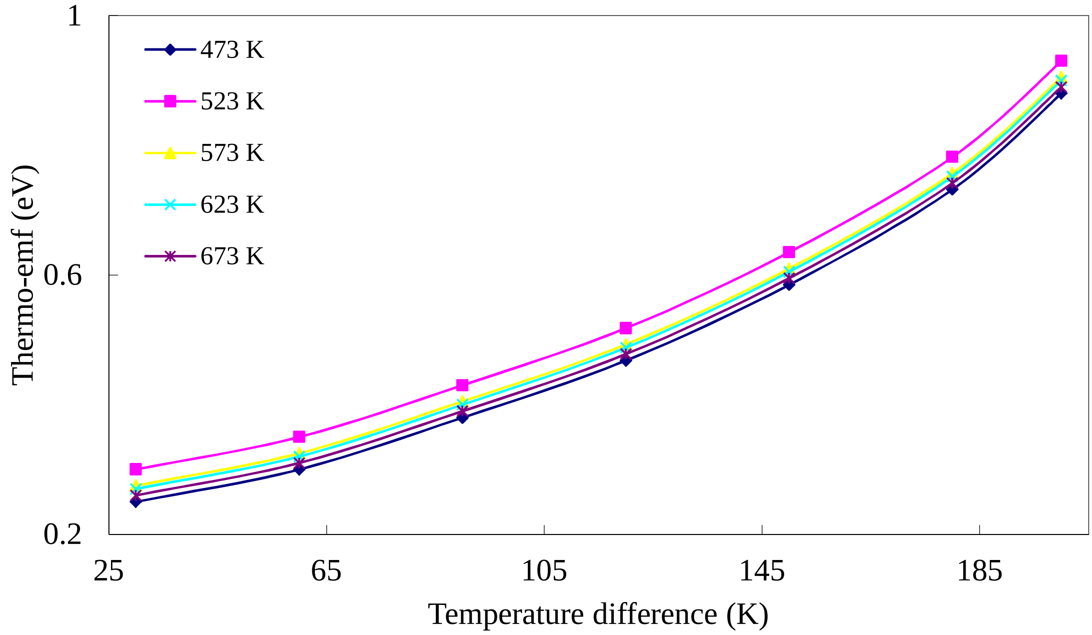


**Fig.12. Plots of thermo- emf versus temperature difference (K) applied across the MgSe thin films**

**Table 2: Grain size, electrical resistivity at 373 K, band-gap energy and activation energy values of MgSe thin film**

| Substrate temperature (K) | Thickness (nm) | Band gap energy (eV) | Activation energy (eV) | Grain size (nm) | $\rho\times 10^2$ ($\Omega$-cm) at 373 K |
|---|---|---|---|---|---|
| 473 | 121 | 2.60 | 0.96 | 14 | 21 |
| 523 | 188 | 2.45 | 0.86 | 24 | 11 |
| 573 | 172 | 2.48 | 0.89 | 22 | 11 |
| 623 | 168 | 2.50 | 0.90 | 19 | 17 |
| 673 | 152 | 2.55 | 0.93 | 16 | 19 |

## CONCLUSION

Magnesium selenide thin films were deposited by using spray pyrolysis technique by varying substrate temperature. The films deposited are nanocrystalline in nature with cubic phase. At higher substrate temperature some peaks due to elemental Mg and Se are observed. The films deposited at 523 K optimized substrate temperature are more crystalline and porous in nature. The electrical resistivity, activation energy and optical band gap energy is found to depend upon substrate temperature. Thermo-emf measurement showed that the electrical conductivity in spray deposited MgSe is of p-type.

## REFERENCES

[1] M. Rabah , B. Abbar, Y. Al-Douri, B. Bouhafs, B. Sahraoui, *Mater. Sci. Eng. B* 100 (**2003**) 163.
[2] G. Gokoglu, M. Durandurdu, O. Gulseren, *Comp. Mat. Sci*. 47 (**2009**) 593.
[3] F. Drief, A. Tadjer, D. Mesri, H. Aourag, *Catal. Today* 89 (**2004**) 343.
[4] S. Duman, S. Bagcı, H.M. Tutuncu, G.P. Srivastava, *Phys. Rev*. B 73 (**2006**) 205201
[5] F.Jiang, Q.Liao,G. Fan, C. Xiong, X. Peng, C. Pan, N. Liu, *J. Cryst. Growth*, 183 (**1998**) 289.
[6] P. Prete, N. Lovergine, L. Tapfer, C.Z. Fregonara, A.M.Mancini, *J.Cryst. Growth*, 214 (**2000**) 119
[7] H.M.Wang, J.H. Chang, T.Hanada, K.Arai, T.Yao, *J.Cryst. Growth* 208 (**2000**) 253.
[8] R.H. Misho, W.A. Murad, *Solar Energy Mater. Solar Cells* 27 (**1992**) 335.
[9] A. U. Ubale, Y. S. Sakhare, M. V. Bhute, M. R. Belkhedkar, A. Singh, *Solid State Sci*. 16 (**2013**) 134.
[10] A.U.Ubale, Y.S.Sakhare, M.R.Belkhedkar, A.Singh, *Mater. Res. Bull*. 48 (**2013**) 863.