PREPARATION AND CHARACTERIZATION ON ZIRCONIUM NANOMATERIAL THIN FILMS

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Abstract

When compared to other deposition techniques, the chemical bath deposition process has various benefits. Numerous researchers have emphasized how easy, affordable, and practical this deposition method is for large-area deposition at low temperatures. In this report, Zirconium Sulphide (ZrS_2) doped with Antimony thin films were deposited using chemical Bath deposition method. The prepared films were characterized by X-ray Diffraction analysis (XRD), Optical, FTIR, Photoluminescence and Electrical studies were carried out and the results were reported.

Keywords: Thinfilms, Zirconium Sulphide, Xrd, Optical, FTIR, PL

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Introduction

Several studies have reported on the preparation and characterization of metal chalcogenide thin films [1-3] due to the extremely distinct physio-chemical, optical properties and electronics [4-5]. Nowadays, thin films made of Zirconium have become an attractive material due to their many applications in areas such as optics, magnetism, thermodynamics, and toughening. Due to its exceptional hardness, high optical transparency, high refractive index, outstanding photochemical stability, and strong thermal mechanical resistance, this material deserves consideration in the field of photonics. There are numerous photonics and commercial uses for it. There are several a varieties of deposition methods, such as chemical and physical Deposition methods were employed to create thin films. Each deposition process has benefits and imitations, as the researcher has noted [6, 7]. The production cost, the availability of resources, and the particular application all had a significant role in the deposition process selection [8]. Sulfur, selenium, and tellurium are the three chalcogen anion cations that are present in chalcogenide compounds [9], together with at least one additional electropositive element. such as indium tin oxide coated glass, soda lime glass, microscope glass slides, titanium, mica, stainless steel, and fluorine doped tin oxide coated glass. Under various circumstances, including pH, bath temperature, solution concentration, complexing agent, and deposition duration, the properties of the films that are produced can be adjusted. Due to a lack of ionic species during the deposition process, the film produced at

low solution concentrations appeared exceedingly thin and irregular. Due to enhanced complexation, the presence of a complexing agent during the creation of films will reduce the rate of deposition. Numerous benefits of chemical bath deposition include low cost, simple setup, and suitability for massive deposition at low bath temperature [10-11]. This method, which may create binary, ternary, quaternary, and pen ternary metal chalcogenides, does not involve any harmful volatile elements. the development of thin films on appropriate substrates.

Experimental

Antimony doped Zirconium Sulphide thin films were deposited using chemical bath deposition method at the ambient temperature from the precursor solution by dissolving the salts of Zirconium Nitrate ($Zr(No_3)_4$), and thiourea (CH_4N_2S) and Antimony tri oxide nitrate ($Sb_4O_4(OH)_2(NO_3)_2$) in the molar ratio of 0.01M: 0.01M: 0.001M in double distilled water.. Under continuous stirring, triethanolamine was added into it. Triethanolamine (TEA) is a complexing agent to extract ions from the solution in a controlled condition. It also helps to reduce the speed of precipitate formation during synthesis. The complexing agent TEA controls the synthesis reaction by regulated and slow release of Zirconium Nitrate ions for better deposition of Zirconium Sulphide thin films on the glass substrate. The pH of the final solution was made to 5 by adding 5 mL of aqueous ammonia to enhance the reaction speed for fast nucleation of Antimony doped ZrS_2 onto the substrate without affecting the precipitation mechanism and homogeneity of thin films. The final solution of the bath was made to 100 mL by adding double distilled water. Films with doping (0.001M, 0.002M and 0.003M) level of Antimony tri chloride were also deposited by varying the concentration (0.001M) in the precursor solution without changing the other process parameter. The bath is placed in an oil bath that was maintained at a steady temperature of 80°C by a dimmer stat. A cleaned glass microscope slide was suspended in a reaction bath for 3 hours. After deposition time, the coated slides were rinsed with distilled water and dried in oven. For each molarity the reproducibility of the films was verified by repeating the experiments several times.

X- Ray Diffraction studies

XRD pattern of the Zirconium Sulphide films were studied at room temperature by using RIGAKU diffractometer (model RAD II A) with CuKα radiation (1.5418 Å) where other radiations are suppressed using Ni filter. The X-ray diffraction patterns of $Sb:ZrS_2$ thin film which were deposited at various Sb doping concentrations is shown in Figure 1. All samples have five diffraction peaks corresponding to the (101), (110) and (201) planes of Monoclinic crystal structure of the ZrS_2 phase, did not exist in the deposited thin film. It indicated that the O atoms were replaced by Sb atoms in the $Sb:ZrS_2$ thin film. For all samples, the intensity of (101) plane is more dominant than the intensity of other crystal planes, except for 1% $Sb:ZrS_2$ sample. This low intensity is more likely appears as the result of a very thin layer was formed.

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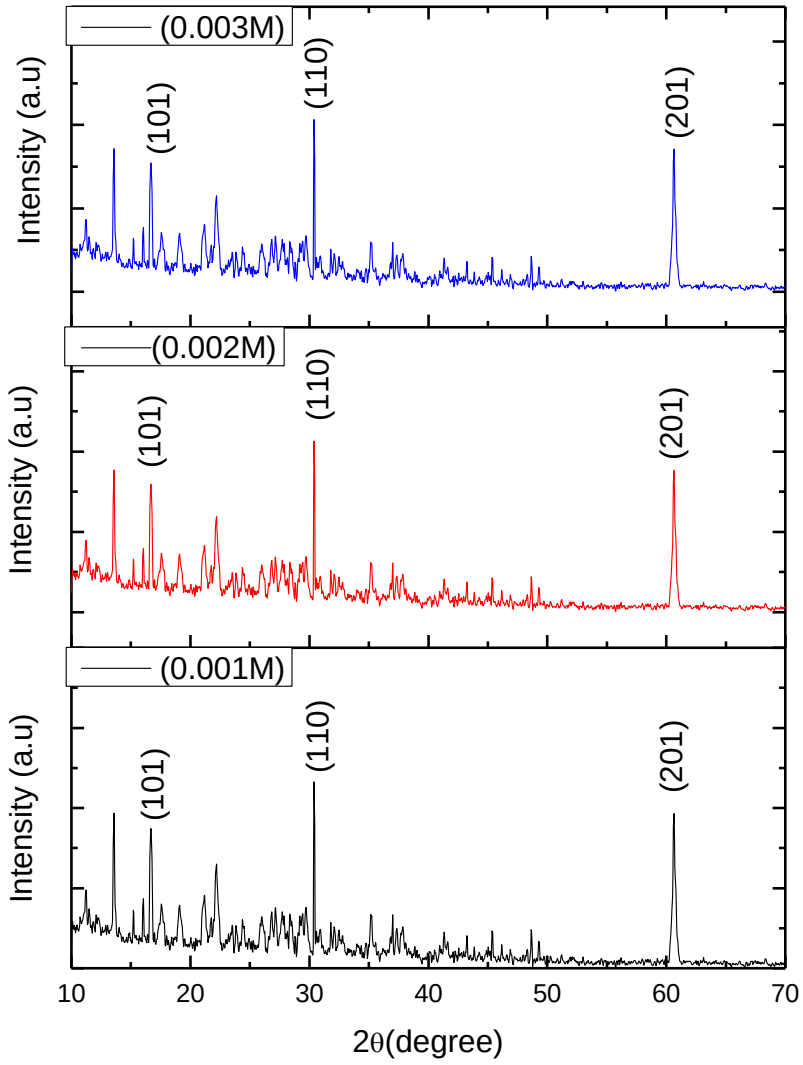

Fig 1. X- Ray Diffraction Spectrums of Sb doped ZrS_2 Thin films

Optical Studies

A computer controlled ELICO make (SL 159 UV-VIS) single beam spectrophotometer was used to obtain transmittance spectrums Antimony doped Zirconium Sulphide doped with different molarities of Antimony tri chloride (0.001M, 0.002M, and 0.003M).

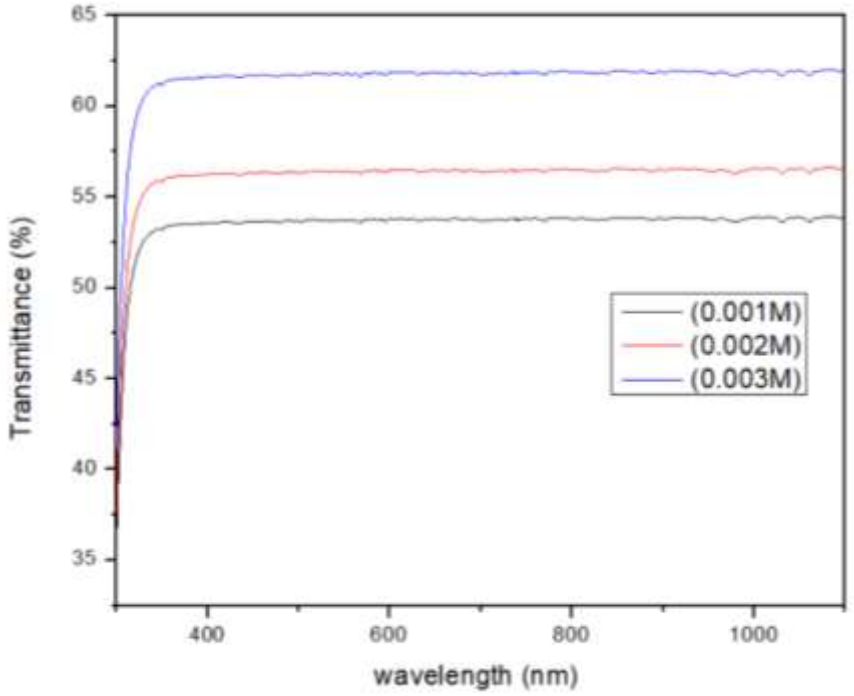

Fig. 2 Transmittance Spectra of Sb doped ZrS_2 Thin Films

Transmittance spectra of the as deposited film as a function of wavelength is shown in Figure 2. The plot shows a sharp rise in transmittance near the band edge attributed to the good crystallinity of the film. Transmittance spectra of the films show a narrow range of variation with the increase in dopant molarity. Here the film deposited with lower molarity of the dopant shows higher transmittance (>70%). Hence the transmission spectra recorded for different molarity levels of Sb in ZrS_2 shows a consistent decrease in transmittance with increasing doping molarities. The decrease in the transmittance with increase in molarity may be due to the increasing absorption and it is felt that doping of Sb in ZrS_2 may lead to increase in the degenerate (metallic) nature of the films, which results in light absorption. The transmission spectra reveals that ZrS_2:Sb films exhibits moderate transmittance between 50% and 70% in the visible region.. It can be seen from the transmittance spectra that the films are transparent even in the short wavelength region of the visible spectrum. Positive aspects transmittance of thin films causes them to be an excellent material for optical films. Transmittance in the apparent region is very essential for most optical applications [12]. In both crystalline and amorphous semiconductors, near the fundamental absorption edge there is the dependence of absorption coefficient on the photon energy. In high absorption region, the form of absorption coefficient with photon energy is given in a more general term by as

$$\alpha = A(\alpha h\nu - Eg)^{n}$$

where,

h is Planck's constant

A is a constant

Eg is the optical energy gap and n is the number which characterizes the optical processes. n has the value ½ for the direct allowed transition and has the value 2 for the indirect allowed transition[13]. Figure 3 shows the Tauc's plot for Sb doped ZrS_2 thin films and the energy gap is found to be in the range between (3.6 eV to 3.82 eV) for 0.001M, 0.002M, and 0.003M dopants of Antimony.

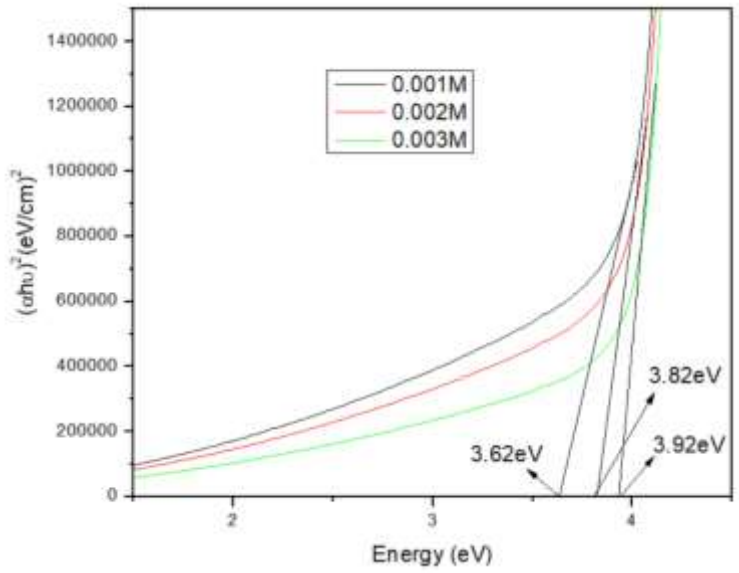

Fig.3. Tauc's plot $(\alpha hv)^2$ Vs hv. for Sb doped ZrS_2 Thin Films

FTIR Studies

FT-IR spectroscopy (4000-400 cm^{-1}) range with the Perkin-Elmer 1600) was carried out to study the potential existence of Sb doped ZrS thin film preparation. Figure shows the FT-IR spectra of the Sb doped ZrS_2 thin films. The FT-IR spectrum, heat treated at 200 °C, showed an absorption band at 465 cm-1. The peaks 465 and 484 cm-1 are attributed to presence of Sb ions. The bands observed at about 1450 to 1578 cm-1are characteristic of Zirconium species. The bands at 3400 to 3500 cm'* are characteristic of Sulphide groups. Absorption due to Zirconium vibrations were also observed at around 2380 and 1405 cm -1. The peak intensity is increased due concentration of antimony dopants [14].

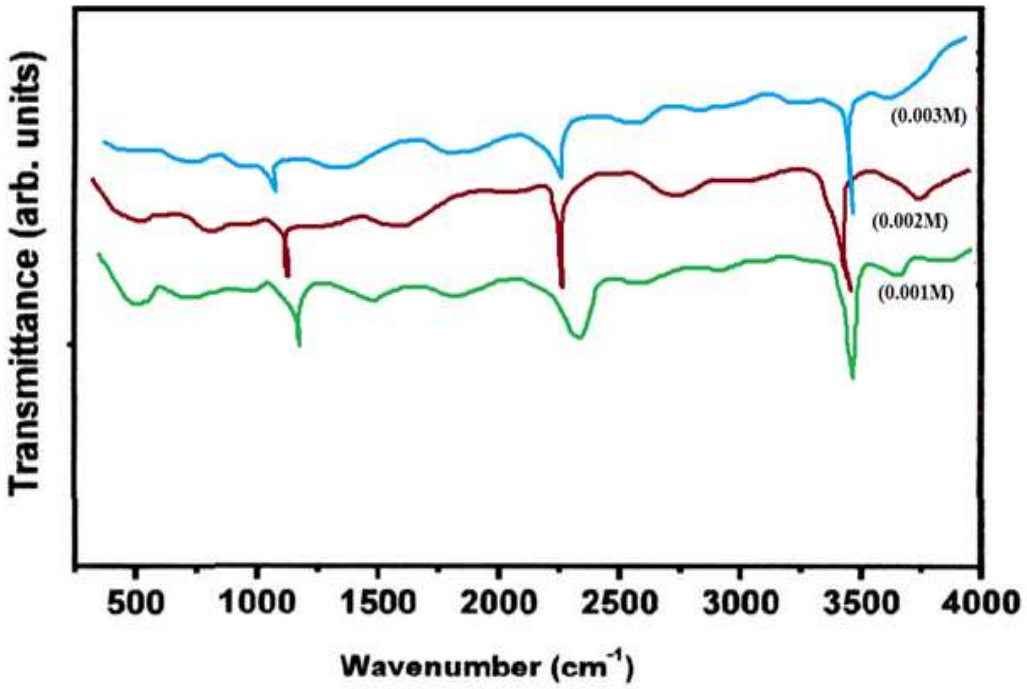

Fig 4. FTIR Spectrum of Sb doped ZrS_2 Thin Films

EDS Analysis

The electrical measurements were performed on the as-deposited Sb doped ZrS_2 films to know the resistivity, activation energy of the charge carriers. The electrical characterization of Sb doped ZrS_2 films was done by means of temperature dependent resistivity and the four probe van der Pauw technique. The conventional EDS spectral range of the as deposited Sb doped ZrS_2 films is recorded and depicted in Figure 5. The measured S/ Zn ratio is lower than the theoretical stoichiometry in all thin films. The existence of Sulphur opportunities (surplus zinc) is indicated by this result.

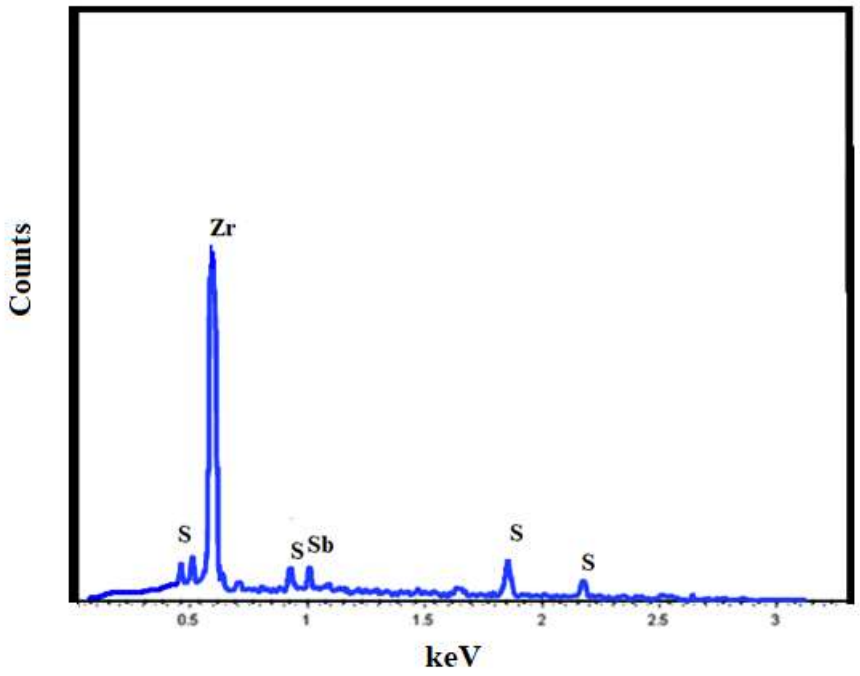

Fig. 5. EDAX profile of Sb Doped ZrS_2 thin films

Photoluminescence Spectra

Figure 6 shows the photoluminescence spectra of Sb doped ZrS_2 thin films. All the films were excited with 468 nm (Excitation and emission slit width of 2.5 nm). The emission peaks were observed at 304 (4.07 eV), 392.5 (3.15 eV), 604 (2.05 eV) and 766 nm (1.61 eV). Here the PL intensity of ZrS_2 thin films increased with increase in Sb concentration (Figure 6). Sb doped ZrS thin film with wide band gap and short wavelength luminescence emission can serve as a better luminescent material for photonic applications [15].

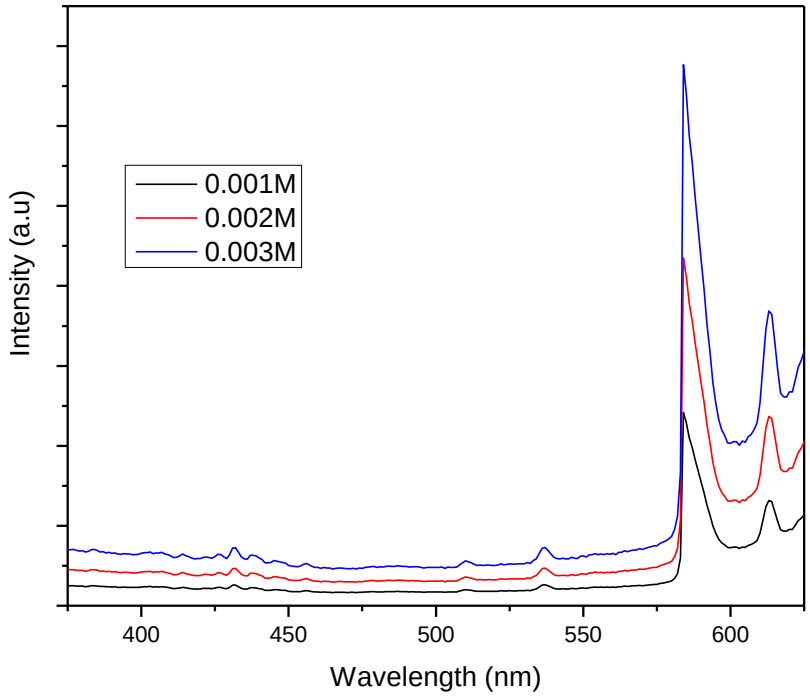

Fig 6. PL Spectra of Sb Doped ZrS_2 Thin films

Electrical Properties

The electrical resistivity values are plotted and depicted in Figure 7. It shows that the increase of Sb concentrations could significantly reduce the resistivity, because Sb has been well known as an effective electron's donor, so that it might decrease the electrical resistivity of the thin film [16].

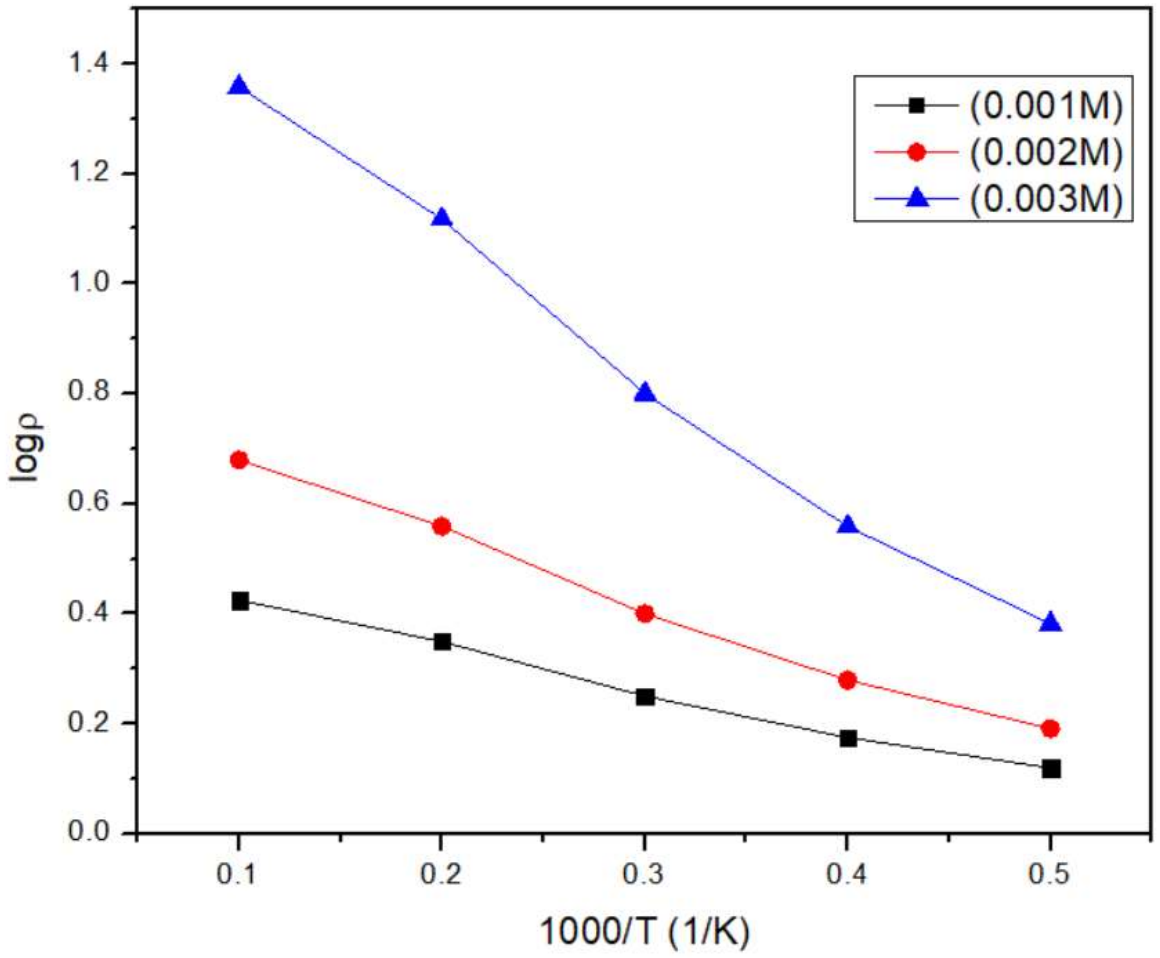

Fig.7. Plot of log ρ vs. 1/T *1000 for Sb doped ZrS_2 Thin films

Conclusion

The antimony doped zirconium Sulphide thin film with three different Sb concentrations (1, 2 and 3 wt %) were deposited by using Chemical Bath deposition method. Afterwards, the characterization and analysis were conducted and the effect of Sb doping concentrations on the structural, optical, FTIR, PL, electrical properties was reported. XRD pattern confirmed that the thin film was polycrystalline with tetragonal crystal structure. All samples show a preferential growth along the (101) (110) (201) crystal plane, while there is no linear relationship between Sb concentrations with the crystallite size. Optical spectra of Sb doped ZrS_2 thin contain direct-band transitions with good transmittance window between 60 – 80%. The energy band gap increased (3.6-3.824 eV). This is associated with the variations in grain sizes. Photoluminescence spectra gave intense emission bands at 576 nm is used blue light emitting diodes. The resistivity and the activation energy were estimated as a function of temperature which exhibits the semiconducting nature.

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