Preparation and Characterizations of NiS/ZnS Bilayer Thinfilm by Chemical Bath Deposition Method

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ABSTRACT

NiS/ZnS thin films were grown by Chemical Bath Deposition (CBD) technique using eqimolar aqueous solutions of zinc chloride, nickel chloride and thiourea as precursor. Silicon glass substrates were placed in glass bottles with polypropylene autoclave screw caps containing the precursors described above, and the bath temperature is maintained at 95°C. X-ray diffraction 28/8 scans showed that the only crystallographic phase present was the hexagonal wurtzite structure. Scanning electron microscopy showed the formation of nanostructures, consisting of hexagonal structures of a few hundred nanometers. The photoluminescence spectra of NiS/ZnS bilayer were recorded at 18-295 K using a cw He-Cd laser (325 nm) and pulsed laser (266 nm). The NiS/ZnS nanostructure exhibit an ultraviolet emission band centered at ;:::; 3.87eV in the vicinity of the band edge, which is attributed to the well-known excitonic transition in ZnS. The optical properties such as refractive index, electrical and optical conductivities were determined by using UV- VIS absorption spectrometry. The band gap energy was determined as 1.45 eV.

Keywords: NiS, ZnS, Bilayer, X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Optical property, Photoluminescence

INTRODUCTION

Alternating lattice-matched perovskite bilayer or ultrathinfilms have been investigated extensively in the search for new functionalities and behavior related to a broad range of materials properties [1]. During the last decade, the thin films of ZnS and NiS have received more attention due to their potential applications in various fields of science and technology. Metal chalcogenide films have been widely studied, because of their effective applications in electronic, optical, solar cell, photoconductor and superconductor device [2]. Two important

factors that should be considered in producing these materials are the band gap energy matching solar spectrum and the competitiveness of production cost. Devices based on this new concept are being realized both in the area of very fast circuits and in optoelectronics. This whole domain, however, is still in its infancy and promises a great deal for the future [3]. They have attracted growing attention over the past twenty years. The technological interest is due to their unique transport properties along the growth direction.

In this report we stated that the synthesis of NiS/ZnS bilayer thin films using a simple, reproducible, and cost effective technique called Chemical Bath Deposition [4], ZnS thin films deposited from Zinc chloride containing baths were observed to have average optical absorption for both below and above band gap energies. Therefore for this research work we selected zinc chloride as Zinc source. NiS thin films belong to group VII – VI compound semiconductor materials and have diverse applications in the areas of optoelectronics and electro-optic devices. [5-9].

EXPERIMENTAL DETAILS

NiS/ZnS bilayer thin films were prepared by Chemical Bath Deposition (CBD) method using (IM) of aqueous solution nickel chloride and (0.2M) of sodium thiosulphate as first precursor. The microscopic glass slides were washed with chromic acid followed by acetone and finally with double distilled water, was placed in beakers containing the precursor described above. The pH of 1.5 is maintained throughout the experiment with the aid of adding hydrochloric acid (HCl). Triethylamine (TEA) was added as a chelating agent. The time allowed for deposition is I h at 95°C. After the deposition, the film was cleaned with distilled water for several times and dried finally. After the deposition of single layer film was achieved, NiS/ZnS bilayer was fabricated by dipping the substrate into a bath containing the second precursor. The second precursor containing IM of zinc chloride, 0.2M of thiourea and pH of I I is maintained throughout the experiment by means of adding ammonia (Merck 30%). EDTA was added as a chelating agent. The deposition time and the cleaning process were the same procedure as mentioned above. The as deposited thin films were kept in a furnace and annealed at 400°C and 500 °C for about an hour.

The surface morphology of the NiS/ZnS nanostructures was examined by scanmng electron microscopy (SEM), while their crystal structure was determined by X-ray diffraction (XRD) using a Rigaku diffractometer with CuKa X-rays. The measurements were carried out using a He-Cd cw laser at 325 nm with full power 35 mW, and a 266 nm frequency quadrupled solid state-pumped YAG laser with 0.5 ns pulse width, 7.6 kHz repetition rate

and 5 mW average power in order to excite the photoluminescence of the samples. The spectra were recorded using a very sensitive LN2 cooled CCD camera and a UV-visible spectrometer.

RESULTS AND DISSCUSSION

An obvious change in the XRD peak intensity of NiS/ZnS bilayer thin films is observed with increasing annealing temperature which is shown in FIG 1. From this result, NiS/ZnS films annealed at 400°C exhibited a dominant peak at 28 = 27.92°(H) and 3 l.24°(H) and annealed at 500°C films exhibited a high intense dominant peak at 28 = 3l.767°(H) and other peaks at 19.96°(H), 52.81°(R), 66.276°(H) which has both the Hexagonal, Rhombohedra Wurtzite phase which is compared with the JCPDS card no(75-0612 and 89-2351) . In the present study the grain size of as-deposited and films was estimated from XRD peaks using Debye Scherer formula [10] and was found to be in the range of 40 nm – 50 nm. No data on the dependence of grain size on annealing temperature of NiS/ZnS films is available in the literature for comparison.

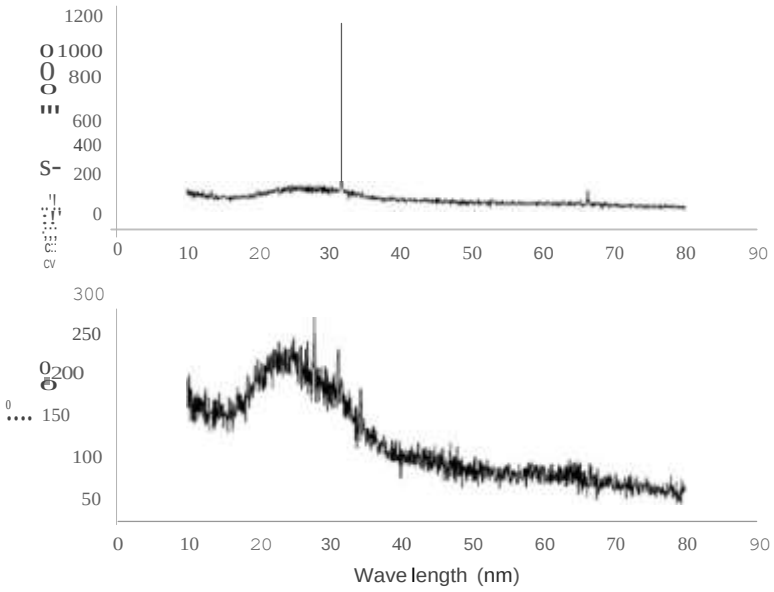

FIG 1. XRD pattern of NiS/ ZnS bilayer annealed at 400°C and 500 °C

FIG 2 shows a set of SEM images of the as grown NiS/ZnS bilayer thin films prepared assemblies at different magnifications. The structure was found to be compact and covered the surface of the substrate completely with micro holes, with the grain particles exhibiting granular morphology of the film annealed at 400°C. FIG 2 (b) shows the SEM

micrographs of NiS/ZnS bilayer thin films annealed at 500°C and it is observed as hexagonal structure. Chemical compositions of the constituents' in the coatings, obtained from EDAX spectra for the NiS/ZnS bilayer thinfilm annealed at 400°C and 500°C are shown in FIG 3 (a) and 3 (b). The other elements Ca, Al, Mg and Si that are not expected to be in the deposited films may be resulted from the glass substrates [10].

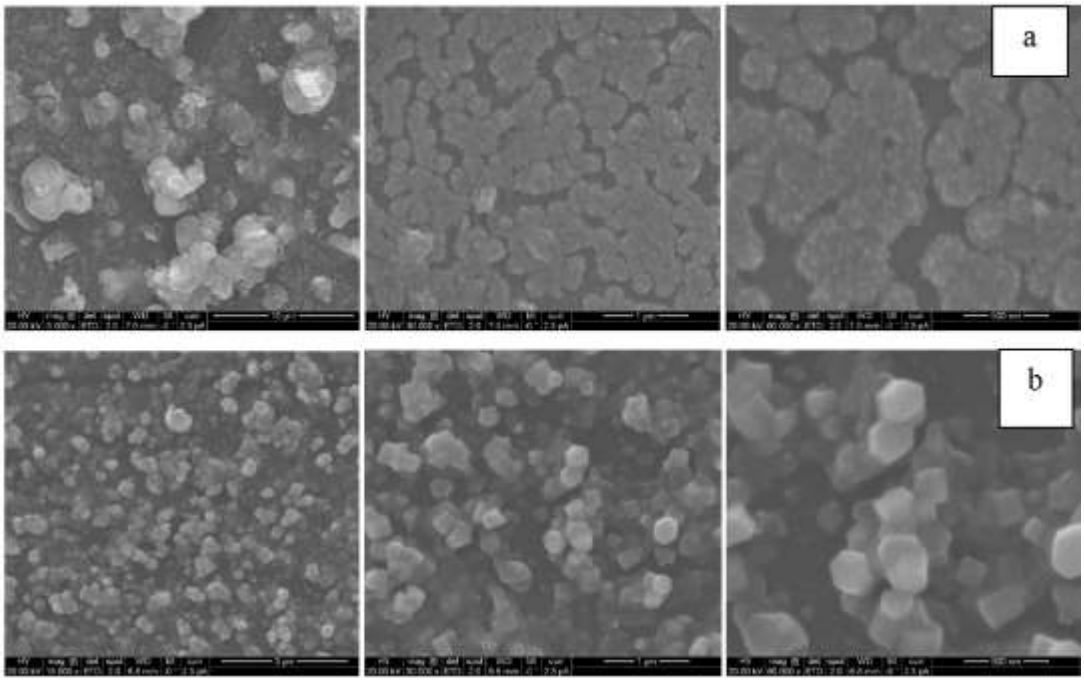

FIG 2. (a) to (b) SEM image of NiS/ ZnS bilayer annealed at 400°C and 500 °C

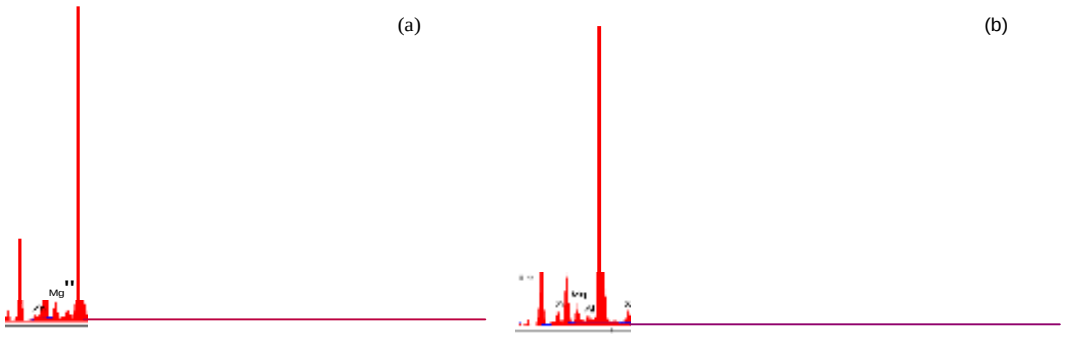

FIG 3 (a), (b) EDAX images of NiS/ ZnS bilayer annealed at 400°C and 500 °C

The optical properties of NiS/ZnS bilayer were determined from absorption measurement in the range 300nm to lOOOnm. From the spectra, it is observed that, the absorption is higher below 300nm and lower in the range of 400nm to 900nm.

The optical transmission spectrum of the NiS/ZnS bilayer thinfilms annealed at 400°C and 500°C shows good transmission (>60) for wavelengths larger than 500 nm FIG 4, which is one of the prerequisites' for opto-electronics devices, especially for solar cell window layers. The band gap energy (Eg) and the parameters such as refractive-index (n), dielectric constant (£), optical conductivity (cr_0) and electrical conductivity (cre) were determined by various equations based on UV- absorption spectrum.

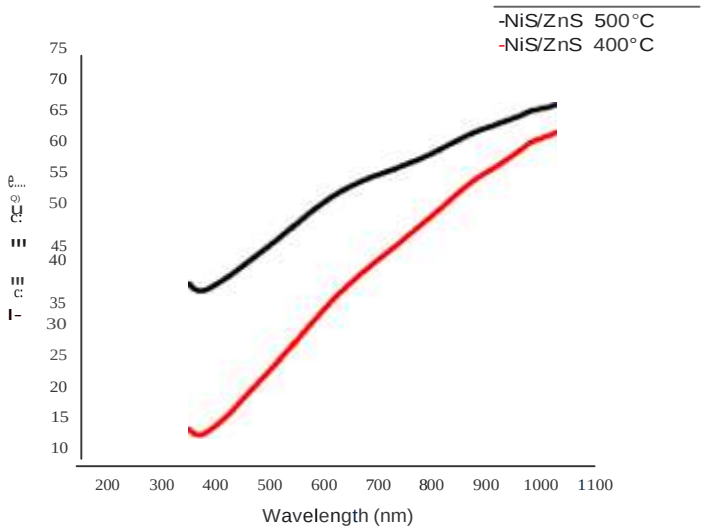

FIG 4 Plot of Transmittance % Versus Wavelength for NiS/ZnS bilayer annealed at 400 °C and 500 °C

Absorption coefficient a associated with the strong absorption region of the film was calculated from transmittance (T) using the relation,

Absorption coefficient $a = \frac{\ln(1/T)}{t} = \ln(;::) \times 10^6\ m^{-1}$ [11]

The band gap was determined from the intersection of straight portion of a^2 versus eV graph which is shown in FIG 5 for NiS/ZnS bilayer thin film. The observed band gap value of the thin films annealed at 400 °C and 500 °C are leV and 1.45 eV respectively.

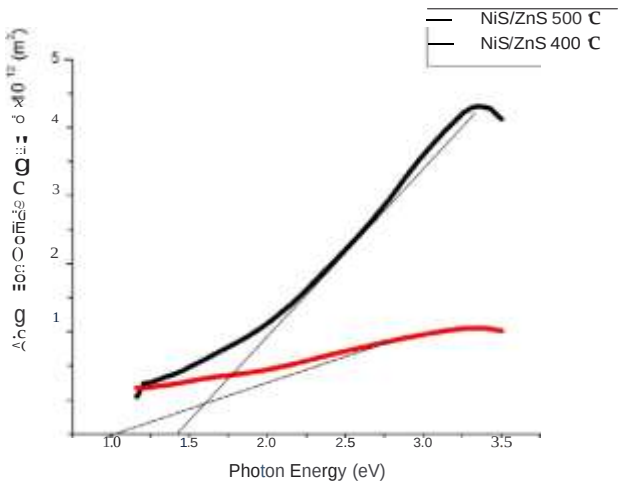

FIG 5 Plot of square of absorption Coefficient a^2 Versus Photon energy for NiS/ZnS bilayer annealed at 400 °C and 500 °C

The coefficient of absorption a is also related to extinction coefficient K by,

Extinction coefficient $K = \frac{ail}{47T}$ [12]

FIG 6 potrays a plot of extinction coefficient versus photon energy. The extinction coeficient for NiS/ZnS, is observed that there is a gradual increase from leV to 3eV and found a sudden decrease from 3eV to 5eV.

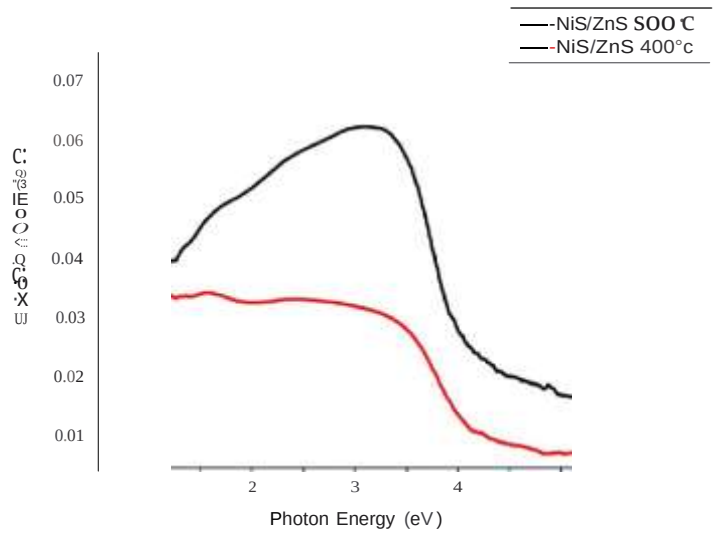

FIG 6 Plot of Extinction Coefficient Versus Photon energy for NiS/ZnS bilayer annealed at 400°C and 500°C

The refractive index of film 1s calculated using Modified envelope method [13]. Refractive index

$$n = [N + (N^2 - n_0^2 n_1^2)^{\frac{1}{2}}]^{\frac{1}{2}}$$

Where $N = \frac{n_{o2} + n_{12}}{2} + 2n_o n_1 \frac{[T_{max} - T_{min}]}{T_{max} T_{min}}$

n_0 is the refractive index of air, n_1 is the refractive index of the substrate, T_{max} and T_{min} are the maximun and minimum transmittances respectively for a particular wavelength.

The variation of refractive index (n) with wavelength for the as depositied thin films is shown in FIG 7. The high refractive index of 0.7 to 0.1 for wavelength range 200nm to 400nm and increases to 0.8 for values wavelength range 390nm to lOOOnm, which shows variation in the refractive index values. The bilayer of NiS/ZnS with the values of low refractive index which could be useful in applications of antireflection coatings. [14].

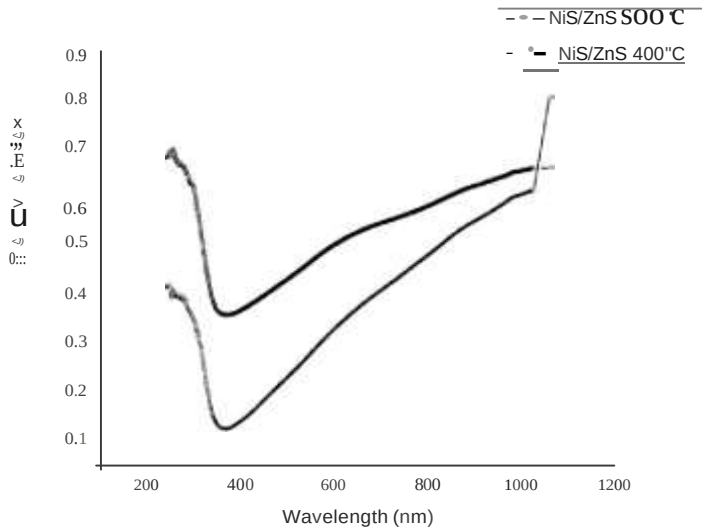

FIG 7 Plot of Refractive Index Versus Wavelength for NiS/ZnS bilayer annealed at 400 °C and 500 °C

The optical conductivity is given by

Optical conductivity $\sigma_{opt} = \frac{anc}{4\pi T}$, where c is the velocity of light in vacuum.

The electrical conductivity σ_{ele} is given by the expression [15]

Electrical conductivity $(Je = \frac{znuo}{a}$

The complex dielectric constant

$$\varepsilon_r - \varepsilon_r + \varepsilon_0 ,$$

where $E r = n^2 - K^2$, $Eo=ZnK$ [16, 17]

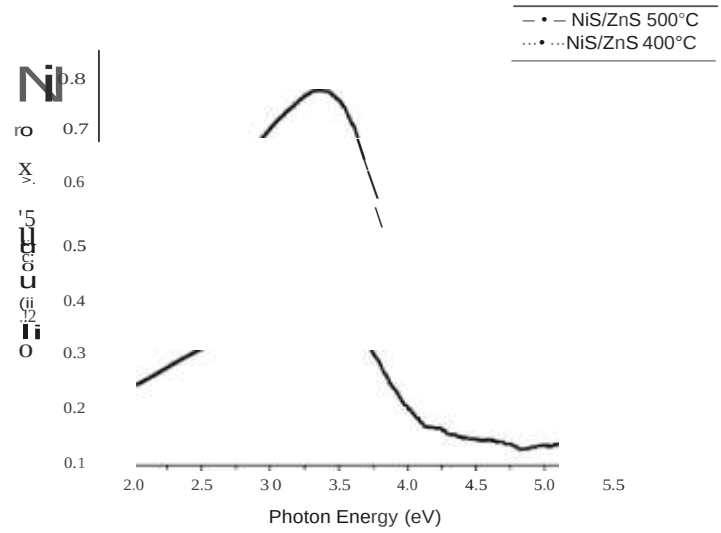

FIG 8 Plot of Optical Conductivity Versus Photon energy for NiS/ZnS bilayer annealed at 400 °C and 500°C

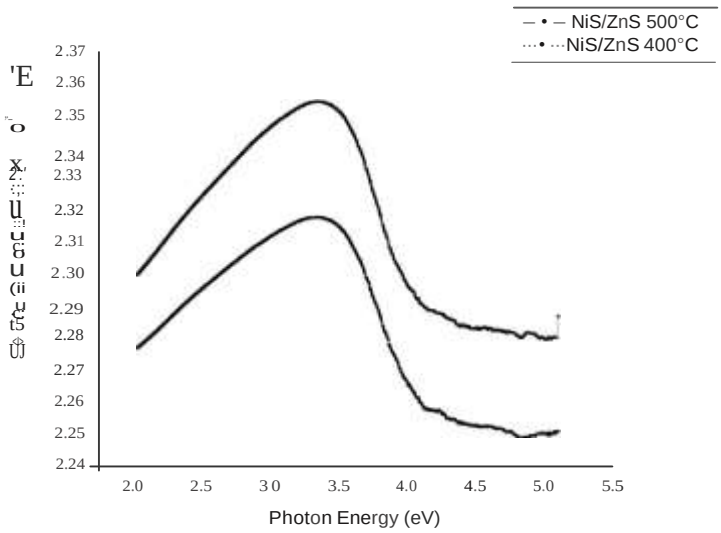

FIG 9 Plot of Electrical Conductivity Versus Photon energy for NiS/ZnS bilayer annealed at 400 °C and 500 °C

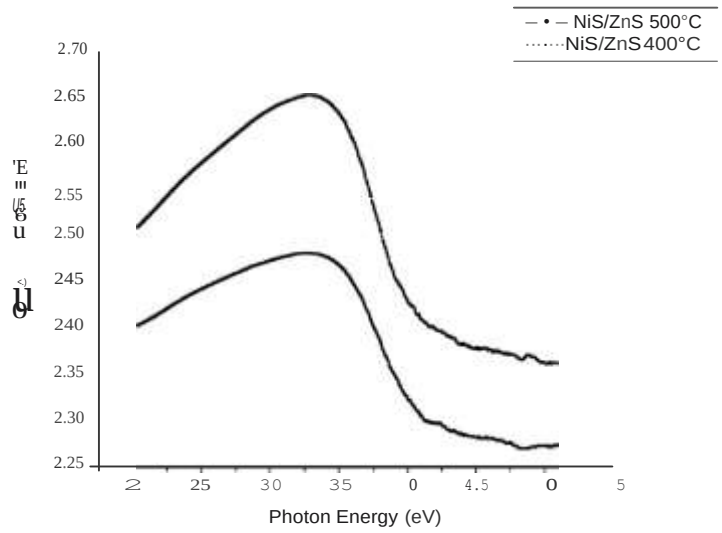

FIG 10 Plot of Dielectric constant Versus Photon energy for NiS/ZnS bilayer annealed at 400 °C and 500°C

The optical conductivity cr_0 against photon energy, electrical conductivity Cie against photon energy and dielectric constant versus photon energy for NiS/ZnS are shown in FIG 8,9 and 10 respectively. The nature of the curve of optical, electrical conductivity and dielectric constant has a gradual increase upto 3.5eV and a sudden decrease from 3.5eV to 5.0eV and the observed values are tabulated in Table I.

NiS/ZnS	At 2.00 (eV)		At 3.50 (eV)		At 5.00 (eV)	
Optical Conductivity	400 °C	500 °C	400 °C	500 °C	400 °C	500 °C
(cro xl 0^{13} s^{-1})	0.25	0.4	0.35	0.8	0.1	0.3
Electrical Conductivity (cre xl 0^{7} s/m)	2.27	2.30	2.30	2.36	2.25	2.29
Dielectic constant (Ee)	2.40	2.51	2.45	2.65	2.25	2.40

TABLE 1 Optical conductivity, Electrical conductivity and Dielectric constant of the Samples

Photoluminescence (PL) spectra of NiS/ZnS bilayer thin films excited with a 320 nm Xe lamp source at room temperature are presented in FIG 11. A dominant emission peak centred at 3.75eV (330 nm) and 3.87eV (320 nm) respectively. This shows strong ultraviolet (UV)

peak is attributed to the recombination of free excitons through exciton-exciton collision process [18]. The strongest peak is comparatively broad and gives near blue emission bands. The intensity of photoluminescence decreases significantly with increasing temperature.

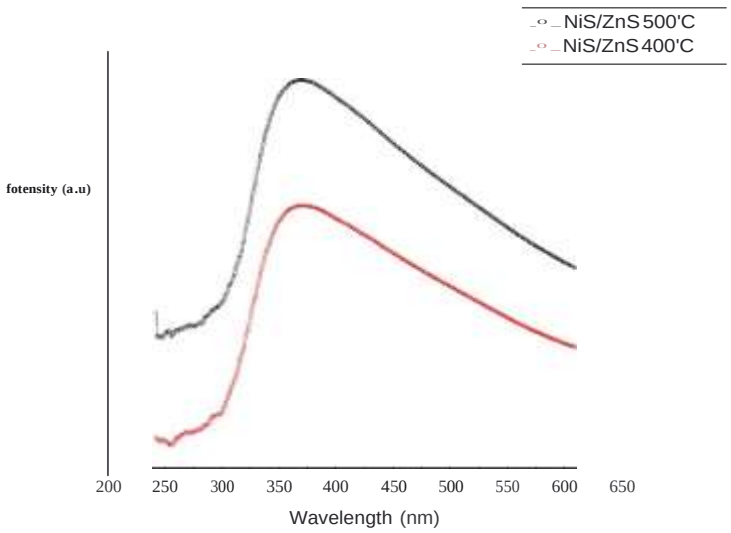

FIG 11 Photoluminescence spectra of NiS/ ZnS bilayer annealed at 400°C and 500 °C

CONCLUSION

NiS/ZnS bilayer thinfilms were sucessfully depositied on glass substrates by CBD technique. The as depositied films posses the wurtzite hexagonal structure and show very good crystalline quality. The atomic composition is confirmed by EDAX spetrum. The photoluminenscences spectra of NiS/ZnS bilayer thin films exhibit a strong UV excitonic peak The band gap energy of bilayer thinfilms were found to be leV and l .45eV respectively.

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