

Preparation and characterization of nano sized pure ZnTe and antimony doped ZnTe nano thin films by spray pyrolysis technique

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Tel.: +91 9842040515

Received : 30-01-2018

Accepted : 03-02-2018

ABSTRACT: Antimony doped ZnTe thin films developed by spray pyrolysis technique. The deposited thin films are characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive electron microscopy (EDS) and ultra-violet visible spectroscopy (UV-Vis). XRD studies indicate that antimony doping in host result a crystallinity change. The average particle size calculated from XRD values is in good agreement with the SEM results. EDS spectrum is a good evidence of confirm the formation of antimony doped ZnTe. An optical band gap calculated value varying from 2.3 eV to 1.9 eV. The extinction coefficient increases depending on the temperature 300° C, 350° C and 400° C.

Keywords: ZnTe thin films; Structural property; Optical bandgap; SEM

1 Introduction

The synthesis and characterization of thin film semiconductors has recently attracted a great deal of attention. Thin films are mostly II-VI compounds in which the host cations are replaced with impurities up to a few atomic percent. Thin films differ in characteristics from those of bulk materials. Due to numerous applications, studies on the synthesis, characterization and properties of thin films have received significant attention in the past several years. Among several of thin films, ZnO films have received more attention. ZnO is a wide band gap semiconductor having large excitation binding energy of 60 meV at room temperature and it has high transmittance and good electrical conductivity also. ZnO's resistance to radiation damages make it useful in various space application [1-3]. ZnO have widespread applications such as biosensor, gas sensors, solar cells, ceramics, nanogenerators, photo detectors, catalysts, active fillers for rubber and plastics, UV absorbers in cosmetics and

anti-virus agent in coating, pigments, optical materials, electrical and optoelectronics process and systems and additives in many industrial and in treatment of water and waste water [4-14].

Spray pyrolysis has been widely used to produce fine powders because it is an inexpensive and continuous, ambient pressure process. It involves the atomization of a liquid precursor containing metal salts, droplets transport towards a heated substrate and film formation on the substrate surface, evaporation of solvent and decomposition of the deposition material.

In present article depicts the spray pyrolysis process for the fabrication of antimony doped ZnTe thin films. The films are characterized by XRD, SEM, UV-Vis and EDS characteristics.

2. Experimental

Spray pyrolysis technique was adopted for the preparation of zinc tellurite (ZnTe) and Antimony doped zinc tellurite thin films. The chemicals used for the preparation were General reagent grade (99.5% purity procured from S.D fine chemicals, Mumbai) zinc chloride, sodium telluride, and antimony trichloride.

The working solution contains 0.136 g of Zinc Chloride (ZnCl₂) dissolved in 20 ml of deionized water and the second working solution contains 0.221g of Sodium Tellurite (Na₂TeO₃) dissolved in 20 ml of deionized water. The both solutions were added together and stirrer for 5 minutes. The ammonia solution was added until to get clear solution. Each 20 ml of the solutions mixture forms the sprayed ZnTe thin films. The pH of the spray solution is fixed at 10.20 after undertaking several depositions. The experimental was carried out at various Substrate temperatures (300°- 400° C).

Antimony doping was achieved by adding (5 wt %) of antimony tri-chloride. The antimony doped ZnTe thin films coated with various substrate temperatures (300°- 400° C). The sprayed solution containing 0.05M of zinc chloride (ZnCl₂), and 0.05M of sodium tellurite (Na₂TeO₃), the antimony doping was prepared by adding 0.5 wt% of antimony trichloride. The main preparatory parameters in the spray pyrolytic process are substrate temperature, concentration and the mole rated of Starting Solution. The distance between the spray nozzle and the substrate was 18cm; spray rate of solution 12cm³/sec through the nozzle ensures a uniform film thickness. The optimized preparative parameters for ZnTe and Sb:ZnTe thin films deposition are listed in Table1 and Table2.

X-ray diffraction data of the electrodeposited Undoped ZnTe and Antimony doped ZnTe samples were recorded with the help of X-ray diffractometer (XPERT PRO PAN anytical, Netherlands) with Cuk-alpha radiation (λ=0.1540 nm). Thickness of the deposited films was estimated using “Filmetrics F20”. The surface morphological studies were carried out using a scanning electron microscope (JEOL JSM 840).

The composition of Undoped ZnTe and Antimony doped ZnTe thin films way analyzed by the EDX microanalytic unit attached with scanning electron microscope. Optical

absorption spectrum was recorded using an UV-VIS-NIR spectrophotometer (Lambda35). Photoluminescence spectrograph was recorded in “FP-6500 spectro - flruometer”.

Table 1. Optimized preparative parameters for spray pyrolysis of ZnTe thin films.

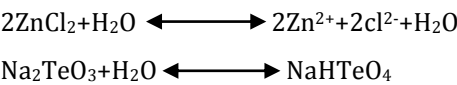
Deposition rate	1 ml/min
Solution Concentration	0.05 M
Substrate temperature(° C)	300-400
pH of the solution	10.20
Deposition time(min)	5 min
Nozzle to Substrate distance	18 cm
Carrier gas pressure	0.5

Table2: Optimized preparative parameters for spray pyrolysis of Sb: ZnTe thin films.

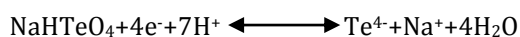
Deposition rate	1 ml/min
Solution Concentration	0.05 M, 0.1 wt% of sbcl ₃
Substrate temperature(° C)	300-400
pH of the solution	10.20
Deposition time(min)	5 min
Nozzle to Substrate distance	18 cm
Carrier gas pressure	0.5

3. Results and discussion
3.1. Kinetic studies

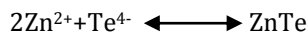
Deposition of ZnTe thin film occurs when the ionic product of Zn²⁺ and Te⁴⁻ ions exceeds the solubility product of ZnTe, and same is the case in the deposition of Antimony doped ZnTe thin film. The control of Zn²⁺ and Te⁴⁻ ions along with sb³⁺ ions in the case of in doped ZnTe film on Antimony doped substrate is speculated as follows.



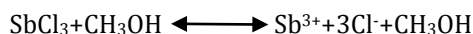
On reduction of NaHTeO_4



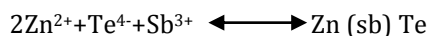
And the formation of ZnTe takes place according to the chemical reaction



Also the reduction of SbCl_3



This process can be explained why excess Te was observed on the surface of ZnTe films by EDAX measurement. When antimony trichloride is added to Antimony doped ZnTe thin film formation the following reaction takes place.



3.2. Optimization of deposition parameter

The properties of the materials prepared by the spray pyrolysis technique critically depend on various preparative parameters such as the sources and concentration of metal and chalcogenide ions, the pH of the solution, deposition time, temperature etc., In the present study, the pH of the spray pyrolysis was measured using digital pH meter (HANNA instruments). Initially the pH of the spray pyrolysis is at 10.20. By adding adequate amount of HCl, the pH of the spray was reduced from 11.00 to 10.20. At this pH value, there is a rapid growth of films followed by peeling out from the substrates. If the value is increased above 10.20 the solution became cloudy due to the precipitation of zinc chloride, sodium telluride. Hence, the optimum pH value of 10.20 plus or minus may be chosen for all depositions. The dissociation of zinc chloride, sodium telluride, ammonia, and depends on the temperature. The dissociation is greater and gives higher amount of Zn^{2+} , Te, Sb ions. However, in the present study, the films were deposited at spray temperature 300-400 °C respectively. In the present study, the deposition time was optimized as approximately 10 minutes, as which uniform and adherent films were obtained.

3.3. Thickness and rate of deposition

The deposition of ZnTe thin films was controlled by two independent variables such as

- Thickness and its uniformity and
- Surface morphology [15]

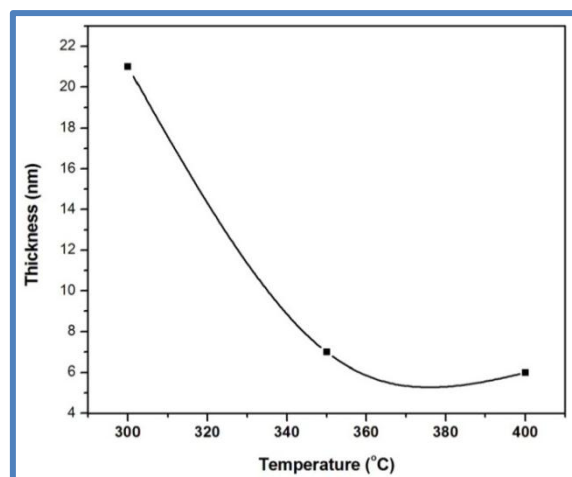
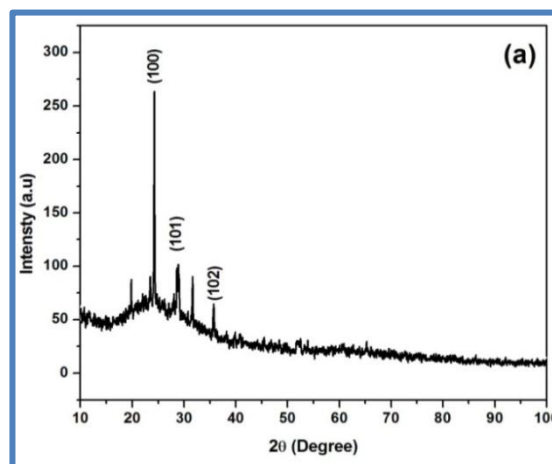


Figure 1. Variation of film thickness with temperature of ZnTe thin film.

Thickness of the deposited films was estimated using Filmetrics. The average thickness of deposited layers can be directly controlled by controlling the pressure and the depositing time. The variation of film thickness with temperature for ZnTe thin films obtained under various temperatures of 300, 350, and 400 °C are shown in figure 1. It is observed from figure 1 that the film thickness decreases linearly with temperature and attains its maximum value at a deposition time of 5 minutes. When the temperature is increased up to 400°C, thickness of the deposited films slightly decreased. It is also observed figure 1 that the film a maximum thickness of 24 nm is obtained for films prepared at temperature 300°C.

3.4. X-Ray Diffraction analysis of ZnTe thin films

X-ray diffraction patterns of the ZnTe film deposited on to a glass substrates at a various temperatures of 300, 350, and 400 °C are shown in figure 2.



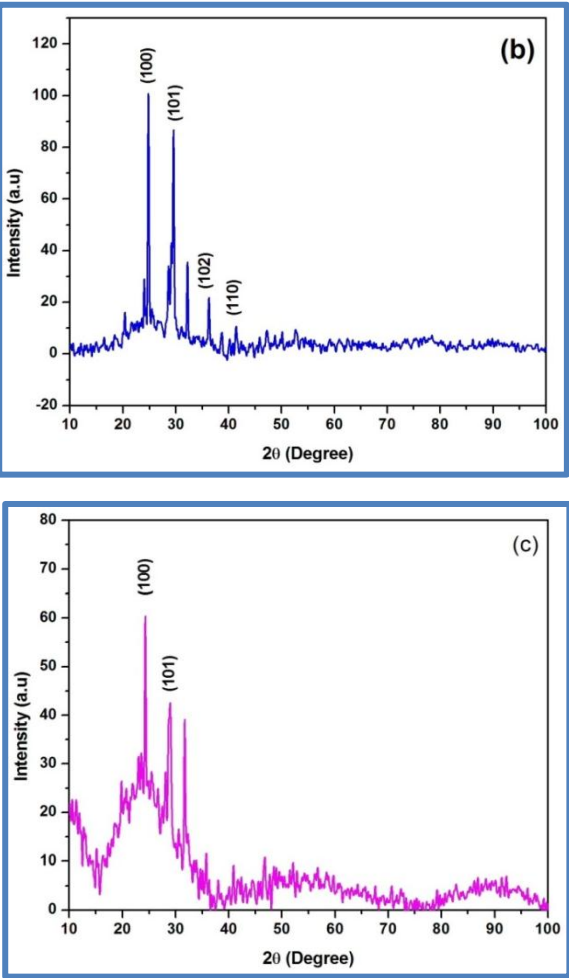


Figure 2. XRD patterns of ZnTe thin films deposited at different temperatures of (a) 300 °C, (b) 350 °C and (c) 400 °C.

The XRD patterns revealed that the deposited films are found to hexagonal crystal structure is widely accepted. The peaks at 25.15°, 26.90°, and 31.65° correspond to diffraction from (100), (101), and (102) planes of ZnTe hexagonal phase. The corresponding d-spacing are also in agreement with the JCPDS data (83-0966). All the films showed a most preferred orientation along (100) plane in addition, (101), and (102) reflections were also present. The (100) direction is the close-packing direction of the polycrystalline nature with a hexagonal structure. When the bath temperature is increased from 300 to 400 °C, the intensity of the peaks is decreased and some new peaks gradually appear, and the peaks in the sample deposited at 400 °C are the most obvious. The height of <100> peak in X-ray diffraction pattern for ZnTe thin films deposited at temperature 400 °C has shown sharper peaks with small

FWHM data, results better crystallinity for films deposited at 400 °C.

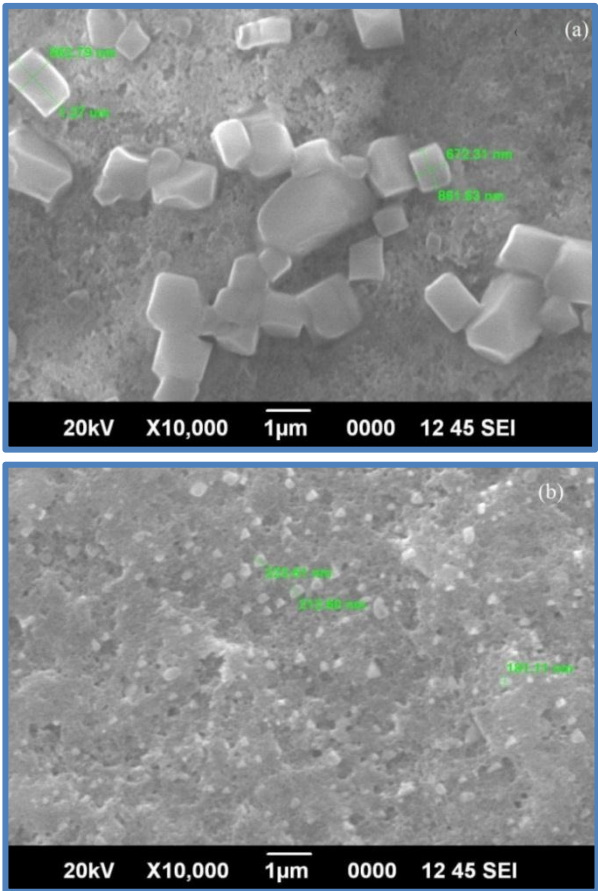
The grain size (D), dislocation density (δ), micro strain and lattice parameters of the hexagonal cell of the ZnTe phase were calculated using the XRD data for films deposited in the range of 300–400 °C, these values are shown in Table 3.

Table 3. Structural parameters of ZnTe thin film

Substrate temp (°C)	Grain size (A) (nm)	Dislocation Density (10^{15}) Lines/min ²	Strain in lines-m ² x10 ⁻³	Lattice spacing (d)in Å
300°C	44.94	0.4914	0.5652	3.082
350°C	49.80	0.4032	0.4380	3.022
400 °C	55.11	0.3292	0.4244	3.082

3.5. SEM analysis of ZnTe thin films

Scanning electron micrograph of ZnTe thin films deposited at different temperatures of 300°C, 350°C and 400°C is shown in figure 3 a to c of magnification 10,000 x.



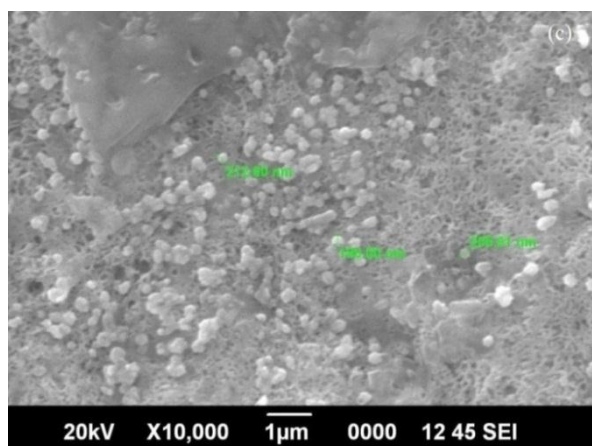


Figure 3. SEM spectrum of ZnTe thin films deposited at different temperatures of (a) 300°C, (b) 350°C, and (a) 400°C.

From the micrograph it was speculated that the agglomeration of spherical grains led to the formation of relatively big grains of uniform spherical shape but of different size.

It is found that nearly all grains are equal in size and cover over the entire surface of the substrate. The SEM images display that there is good surface coverage, good crystallinity and there is no pinholes, and average crystal size of the micro crystallites is about 190 nm. The grains are packed very closely and show a granular morphology as seen in figure 2b. However, the films exhibited a hillock like surface. Deposited at 400° C improved the surface smoothness, as is evident from figure 2c. Similar results were obtained for ZnTe thin films reported earlier [16].

3.6. EDAX analysis of ZnTe thin films

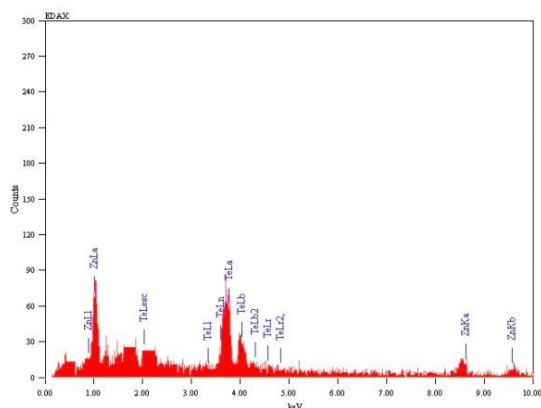


Figure 4. EDAX spectra of ZnTe thin film

Quantitative analysis of the film was carried out using the EDAX technique for ZnTe thin films deposited at different temperatures of 300, 350 and 400°C to study the composition in the film. Figure 4 shows the elemental analysis was carried out only for Zn and Te, the average atomic percentage of Zn:Te was (34.2)Zn; (65.8)Te for deposited at 400°C sowing that the sample was slightly tellurium rich, which is in good agreement with the reports of V.S.John et al [17].

3.6. Optical analysis of ZnTe thin films

The optical transmittance spectra of spray deposited ZnTe thin films is recorded as a function of wavelength in the range 300-900 nm for temperature of 300°C, 350°C and 400°C respectively as shown in figure 7a to c.

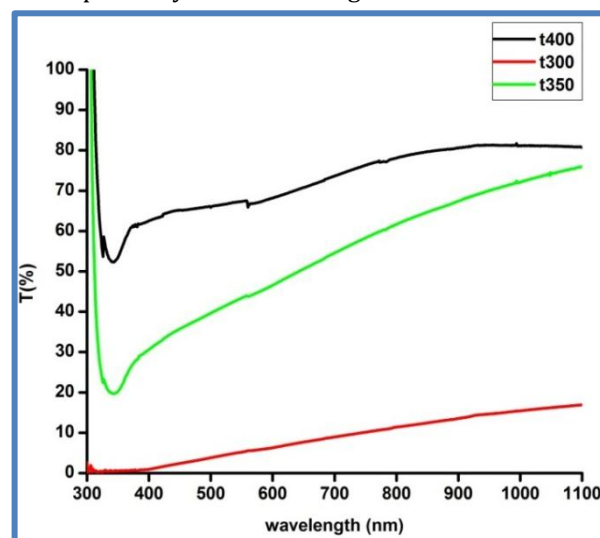


Figure 7. Transmittance spectra of ZnTe thin film deposited at various temperature of (a) 300°C (b) 350°C (c) 400°C.

The transmittance is very low in the range of 300-900 nm, but it increases rapidly with the increasing of the wavelength when the wavelength is longer than 900 nm. The transmission T through an absorbing slab is related to its reflectivity R , thickness d , and absorption α by,

$$T = (1 - R)e^{-\alpha d}$$

Here, the thickness d of the film is about 4-24 nm for the ZnTe films. Therefore, the absorption coefficient (α) can be calculated by the above formula from the data of T , and R . The energy gap E_g can be determined [18]

$$\alpha = \frac{A(h\nu - E_g)^{\frac{1}{2}}}{h\nu}$$

Here A is a constant, and n characterizes the transition process. We can see $n=2$ and $2/3$ for direct allowed and forbidden transitions, respectively, and $n=1/2$ and $1/3$ for indirect allowed and forbidden transitions, respectively. Figure 8a-c shows curves of $(\alpha h\nu)^2$ vs. $h\nu$ for the SnS films. Each curve has a good straight line fit over higher energy range above the absorption edge, indicative of a direct optical transition near the absorption edge. Figure 8a-c, the direct energy gap E_g of each sample has been calculated and it is changed from 2.3 eV to 1.9 eV.

The optical constant, extinction coefficient (k) of ZnTe film are given by the formula [2]

$$k = \frac{\alpha \lambda}{4\pi}$$

The extinction coefficient spectra of Zn Te film are shown in figure 10. It is determined from there figure 6 that the extinction coefficient increases depending on the temperature 300° C, 350° C and 400° C. decrease of the extinction coefficient indicates that the film density decreased.

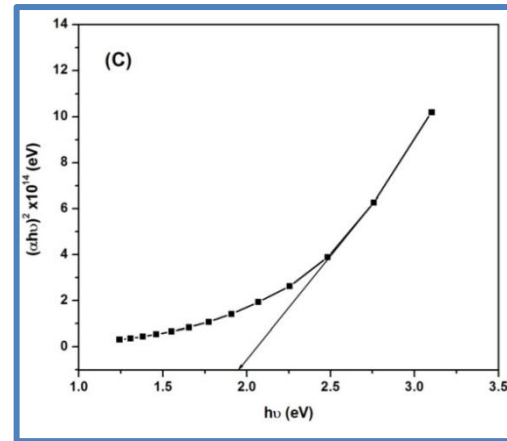
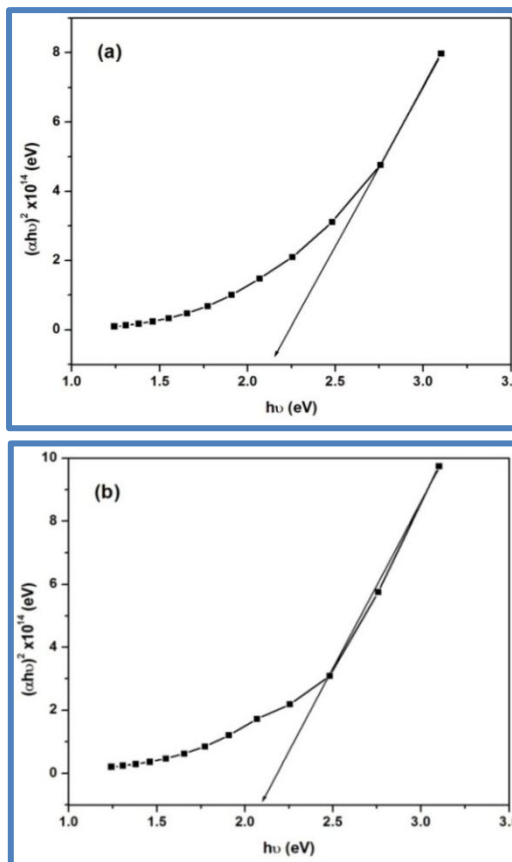


Figure 8. Plot of $h\nu$ vs. $(\alpha h\nu)^2$ for ZnTe thin films deposited at different temperatures (a) 300°C (b) 350°C and (c) 400°C.

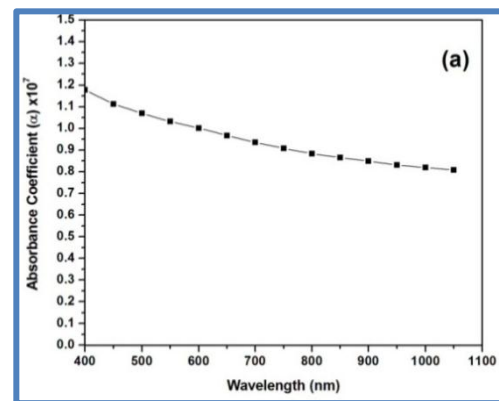


Figure 9. Absorbance coefficient spectra of ZnTe thin film deposited at 400°C.

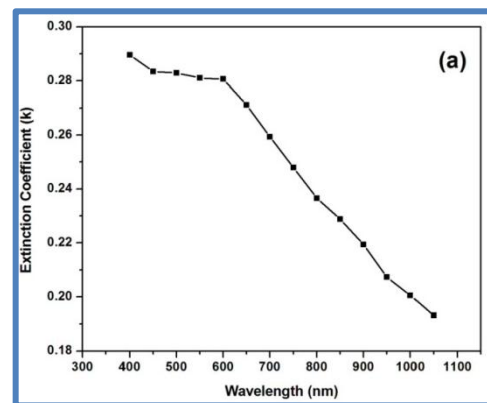


Figure 10. Extinction coefficient spectra of ZnTe thin film deposited at 400°C.

4. Conclusion

The ZnTe and antimony doped ZnTe thin films were successfully developed by the spray pyrolysis

technique at substrate temperature 300°C-400°C. X-ray diffraction patterns revealed that the particles exhibited hexagonal structure and particles size found to be in the range of 44-56nm. The SEM images display that there is good surface coverage, good crystallinity and there is no pinholes. EDX spectrum shows the presence of Zn and Te elements. The UV-Vis results depicted that the shorter wavelength indicates a much smaller particle size and strong particle confinement. Hence, the results suggest the possible potential application of ZnTe and antimony doped ZnTe thin films in solar cells and optoelectronic devices.

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Acknowledgement

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Competing Interests:

The authors declare that they have no competing interests.

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