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Effect of Substrate Temperatures on the Structural and Optical Properties of Na-Doped ZnO Thin Films

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ABSTRACT

ZnO thin films doped with Na have been prepared by chemical vapor deposition technique on the glass substrate at different temperatures (400, 450, 500 ˚C) for 20 min. By increasing the dopant Na from 0 to 20% in ZnO thin films were found to lead to pronounced changes in their structure. From optical properties the band gap energy of the Na-doped ZnO thin films is affected by increasing substrate temperatures and Na doping. X-ray diffraction (XRD) has shown that the maximum intensity peak corresponds to the (002) predominant orientation for ZnO films. Scanning Electron Microscope (SEM) images reveal the formation of Na-doped ZnO films having better crystalline behavior by increasing the substrate temperature at 500˚C. Energy dispersive X-ray analysis (EDXA) shows that the structure of ZnO contains Zn and O elements for undoped and Na for doping state.

Keywords: ZnO thin film, ZnO-Na doped, transparent conducting oxides

تأثير درجات حرارة الأرضية على الخواص التركيبية والبصرية لأغشية ZnO الرقيقة المطعمة بـ Na

الملخص

حضرت أغشية ZnO الرقيقة المطعمة بالصوديوم (Na) بواسطة تقنية ترسيب البخار الكيميائي chemical vapor deposition (CVD) على أرضية من الزجاج عند درجات حرارة مختلفة (400, 450, 500 ˚C) لمدة 20 دقيقة. عند زيادة التطعيم من Na (0-20%) في أغشية ZnO الرقيقة وجد حصول تغييرات واضحة في التركيب البلوري. من الخواص البصرية وجد أن فجوة الطاقة لأغشية ZnO المطعمة بـ Na تتأثر بزيادة درجات حرارة الأرضية وبنسب التطعيم بـ Na. من حيود الأشعة السينية (XRD) تبين أن قمة الشدة العظمى تقابل الاتجاه (002) وهو الاتجاه السائد في أغشية ZnO.

تبين صور المجهر الالكتروني الماسح (SEM) أن أغشية ZnO المطعمة بـ Na تكون ذات حالة بلورية أفضل بزيادة درجة حرارة الأرضية عند 500 ˚C. أما تقنية التحليل الطاقي (EDXA) فتوضح أن أغشية ZnO غير المطعمة تحتوي على عناصر الخارصين Zn والأوكسجين O وبالإضافة إلى ذلك فإنها تحتوي على عناصر Na في حالة التطعيم.

INTRODUCTION

Zinc oxide is a II–VI group compound semiconductor with a wide band gap. Recently, ZnO has been of great interest because of its direct band gap of (3.37) eV and relatively high exciton binding energy (60 meV) at room temperature. ZnO is used in many applications such as solar cells (Lee *et al.*, 2007), laser devices (Lee *et al.*, 1996), gas sensor devices (DeVoe, 2001) and short wavelength light emitting diodes (Tsukazaki *et al.*, 2005). The main purpose for doping ZnO in general is to modify its electrical and optoelectronic properties (Briscoe *et al.*, 2009). Various dopants are known to enhance the structural and optical properties of ZnO thin films (Chen *et al.*, 2010) (Henley *et al.*, 2004). However, less attention has been paid to Na doping in ZnO. The doping

of Na in ZnO is expected to modify the structure, surface morphology, luminescent and other physical or chemical properties of ZnO (Wang and Gao, 2009) (Karthikeyan *et al.*, 2009).

Less commonly, in situ doping can also affect ZnO growth and structure. To date, many growth techniques, such as pulsed laser deposition (PLD) (Zhao *et al.*, 2009), molecular beam epitaxy (MBE) (Chen *et al.*, 1998), spray pyrolysis (Ma and Lee, 2000), metal organic chemical-vapor deposition (MOCVD) (Sun *et al*., 2008) and Rf magnetron sputtering (Song *et al*., 2002) have been widely applied to prepare high quality ZnO films. Among these techniques, the chemical vapor deposition (CVD) method is popular due to its simplicity, safety and low cost (Purica *et al*., 2002).

The properties of ZnO films depend on various parameters such as deposition rate, substrate temperature, pressure and annealing temperature (Mohsen *et al*., 2012). One of the most important factors in preparing ZnO film by CVD is the substrate temperature.

In this paper, ZnO thin films of Na-doped were prepared by CVD method. The aim of this work is to study the influence of different substrate temperatures and Na doping on the structures and optical properties using by XRD, SEM,EDXA and transmittance spectra.

EXPERIMENTAL

ZnO and ZnO:Na thin films were deposited on the cleaned glass substrate by chemical vapor deposition with different substrate temperatures (400,450,500 ˚C) for 20 min. High purity (99.99%) zinc acetate powder ($Zn(CH_3COO)_2$. $2H_20$) was used as a source as CVD in our method.

Glass substrates were first rinsed in ethanol for 5 min. The substrates were then rinsed thoroughly in distilled water and dried in acetone just before they were loaded into the system for film deposition.

The temperature was controlled by an electronic temperature controller. Air flow through the experiment was about 0.5 L/min. Deposition time was kept constant at (10 minutes) for both the pure and doped samples.

The thickness of films was measured by the gravimetric method and it was around 1 μm. Then, the same explained method was used for the preparation of ZnO:Na thin film with various Na concentrations (0,10,20)% at substrate temperatures (400,450,500 ˚C).

The structure of the films was determined by X-ray diffraction measurements with 40 kV, 20 mA (XRD, Bruker/D8-advance with CuKα radiation (λ= 1.54178 Å), Germany), in the scan range of 2θ between 20˚-80˚. The surface morphology of the ZnO films was investigated by scanning electron microscopy (SEM) (FESEM, HITACHI S7900, Japan). Then the films were characterized by using the energy dispersive X-ray analysis (EDXA, HORIBA EMAX Energy EX-950, Japan) (in Sumy state university/ Ukraine).

The transmittance of the ZnO and ZnO:Na thin films was measured using a spectrophotometer in the range (320-1000 nm). Then the energy band gap of both ZnO and ZnO:Na films at three different substrate temperatures through the absorption spectra was calculated.

RESULTS AND DISCUSSION

Structural properties

1- X-ray diffraction:

The X-ray diffraction pattern of pure and Na-doped ZnO (Na=10% and 20%) films deposited at different substrate temperatures (400, 450, 500 ˚C) with a preferred orientation of (002) is shown in Fig.(1a-c). The presence of diffraction peaks indicates the polycrystalline nature of the films with hexagonal (wurtzite) structure.

The X-ray diffraction peaks appearing at $2\theta = 31.82^{\circ}, 34.48^{\circ}, 36.26^{\circ}, 47.62^{\circ}, 56.63^{\circ}, 62.88^{\circ}$ are due to (100), (002), (101), (102), (110), (103) planes respectively, were observed that for pure sample at 400 ˚C. The data are in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card for ZnO (Frank, 1976).

Fig.(1a) showed that there is no change in the intensity of all orientations (100, 002, 101, 102, 110, 103). However, we can see in these Fig. (1a-c) the appearance of other peak may represent the plane (004) at 2θ=72.5 when the ZnO doped with 10% and 20% Na and peak at 2θ=25 may be due to pure Na (Mariappan *et al.*, 2014). But for the ZnO films obtained at 450 ˚C, It is clear that the intensity of (002) increased in comparison with the films at 400 ˚C for pure and doped (10% and 20%). The increase in preferential orientation is attributed with the increased number of grains along the plane. From other side, the peak intensities of (100, 101, 102, 103 and 004) for pure and doped 20% appeared to be smaller in Fig.(1b). For the film deposited at 500 ˚C, the peak intensities of (100, 101 and 102) and Na peak are increased by increasing substrate temperature and Na doping in comparison with 400 ˚C and 450 ˚C, Fig.(1c).

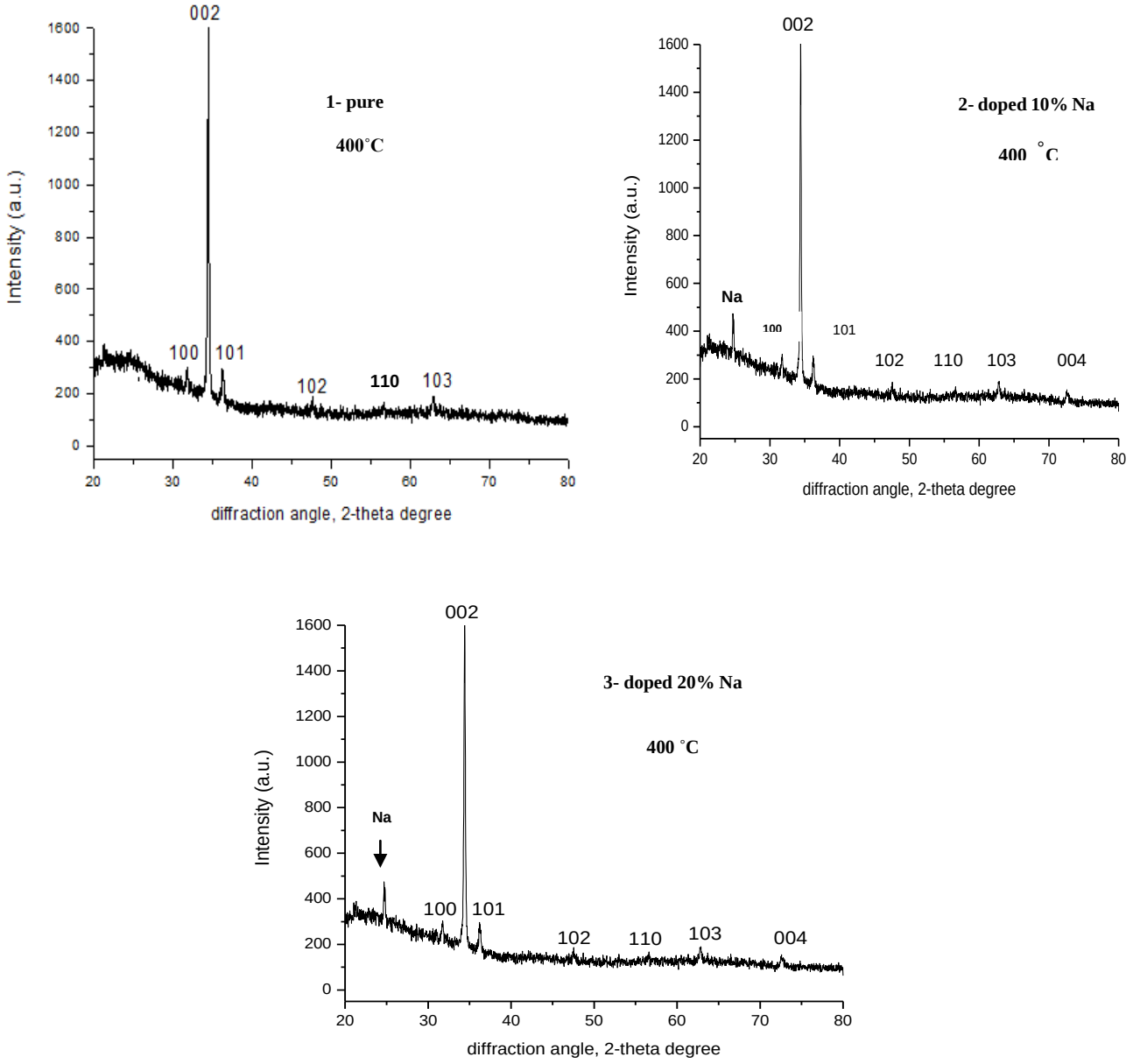


Fig. 1a: XRD pattern of ZnO films of (1-pure) andP doped (10%, 20%) Na at 400 ˚C.

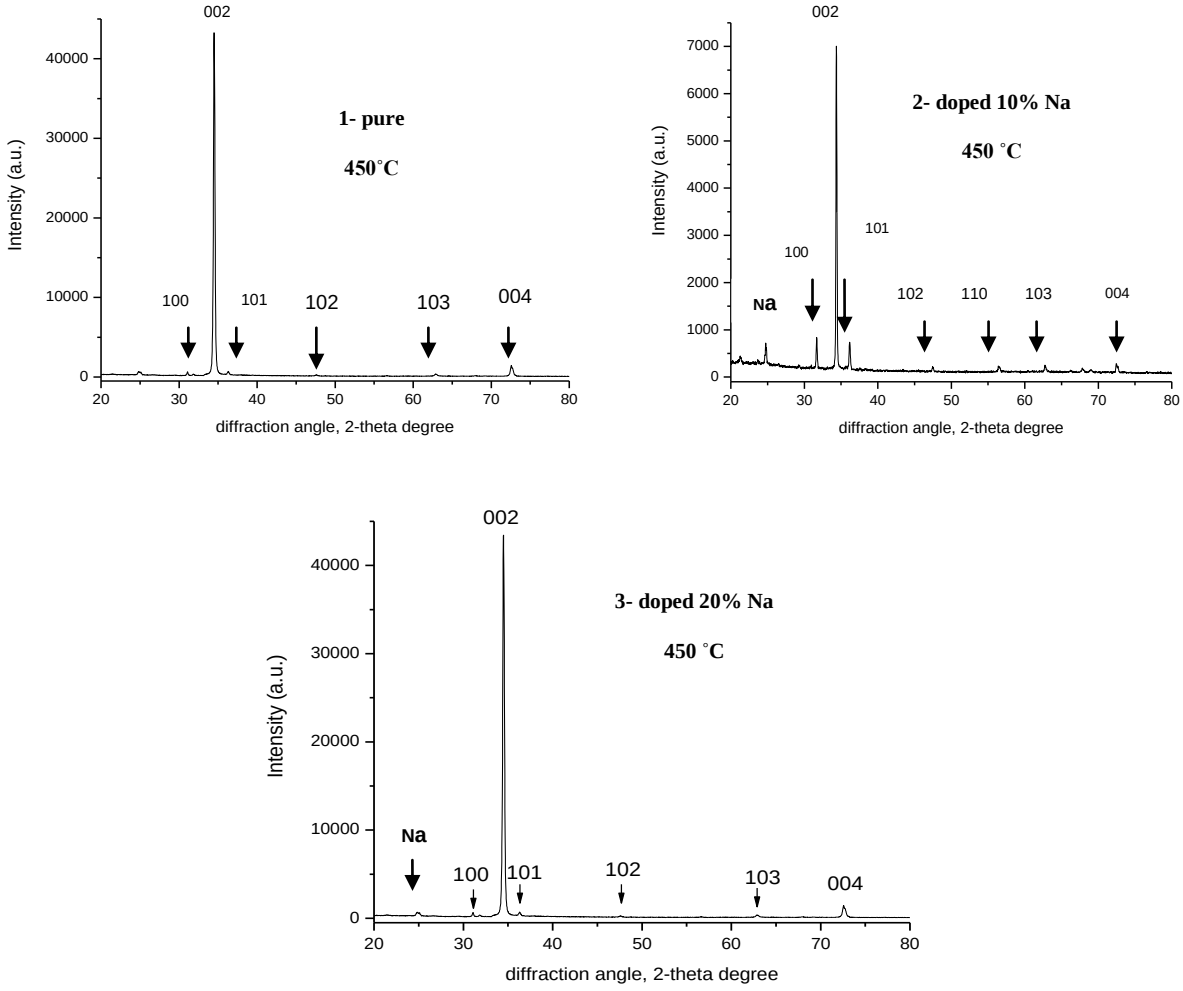
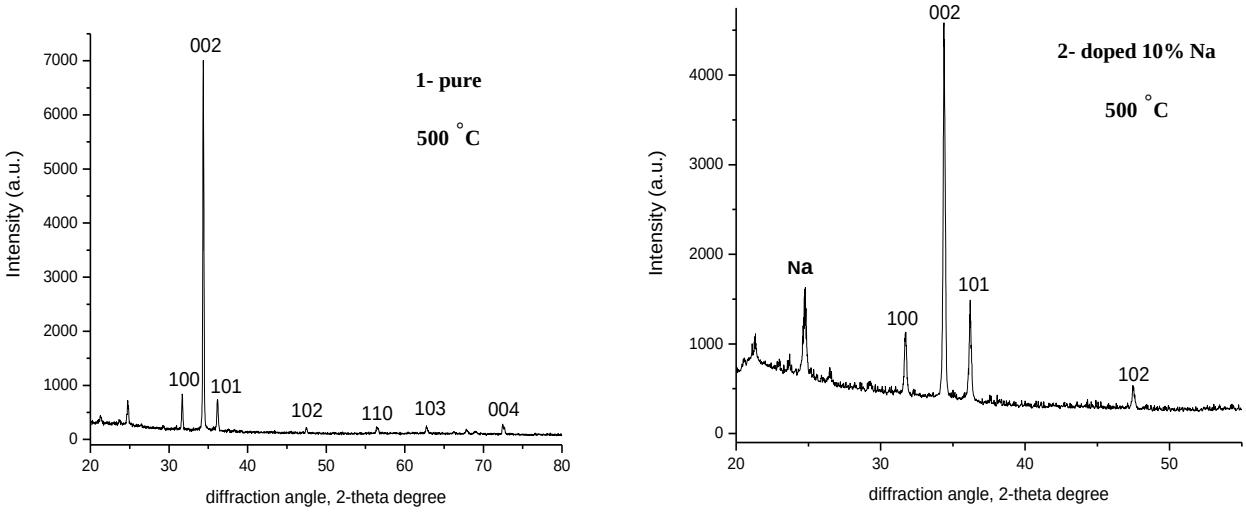


Fig.1b: XRD pattern of ZnO films of (1-pure) and doped (10%, 20%) Na at 450 ˚C.



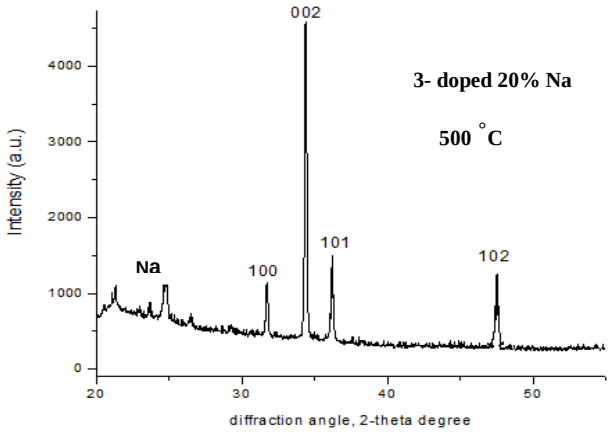


Fig. 1c: XRD pattern of ZnO films of (1-pure) &doped (10%, 20%) Na at 500 ˚C.

2- Scanning electron microscopy:

Scanning electron microscopy (SEM) was used for the study of surface morphological changes of pure and doped ZnO films prepared at different temperatures. Fig. (2a-c) shows the SEM images of pure and Na-doped ZnO films deposited at substrate temperatures 400, 450, 500˚C.

The surface morphology of the films is strongly dependent on the substrate temperature. High temperature favors rapid and defect free growth of crystallites due to oxidation of Zn atoms and optimum surface of diffusion of the species, whereas a low temperature results in the growth of disordered poorly crystallized structure. The development of a smooth, dense and uniform microstructural with good adhesion to the substrate is observed with the increase of substrate temperature (Mariappan *et al.*, 2014).

Fig. 2a shows the surface morphology formed with non-uniform distribution of the grains with agglomeration small crystallites in the case of Na- doped (20%) formed at 400 ˚C. The film deposited at 450 ˚C (Fig.2b) has slightly improvement in crystallinity from Fig. 2a. In Fig.2c the images indicate to better crystalline behavior and the grains are densely packed, having different sizes and figures.

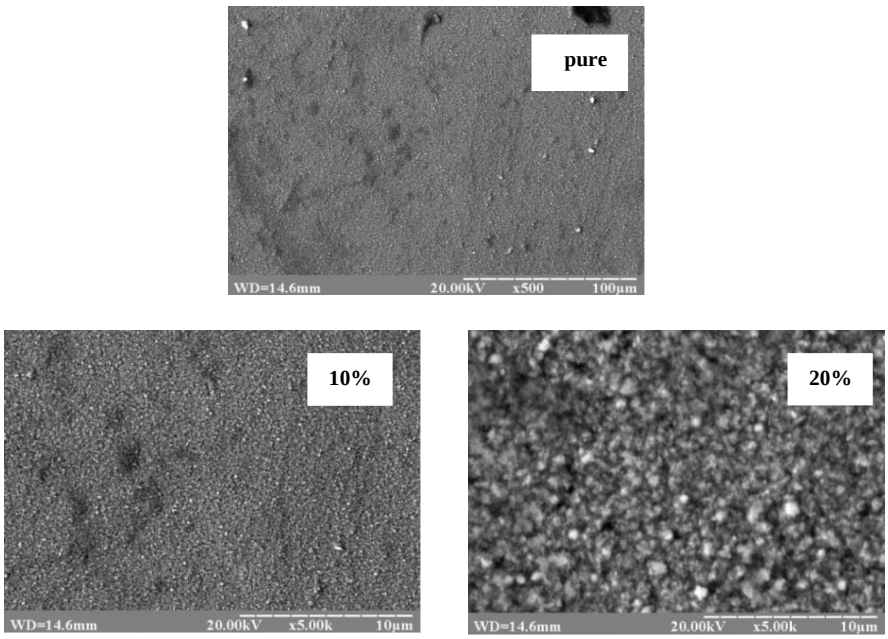


Fig. 2a: SEM of thin ZnO pure and doped with (10% & 20%) Na at 400 ˚C.

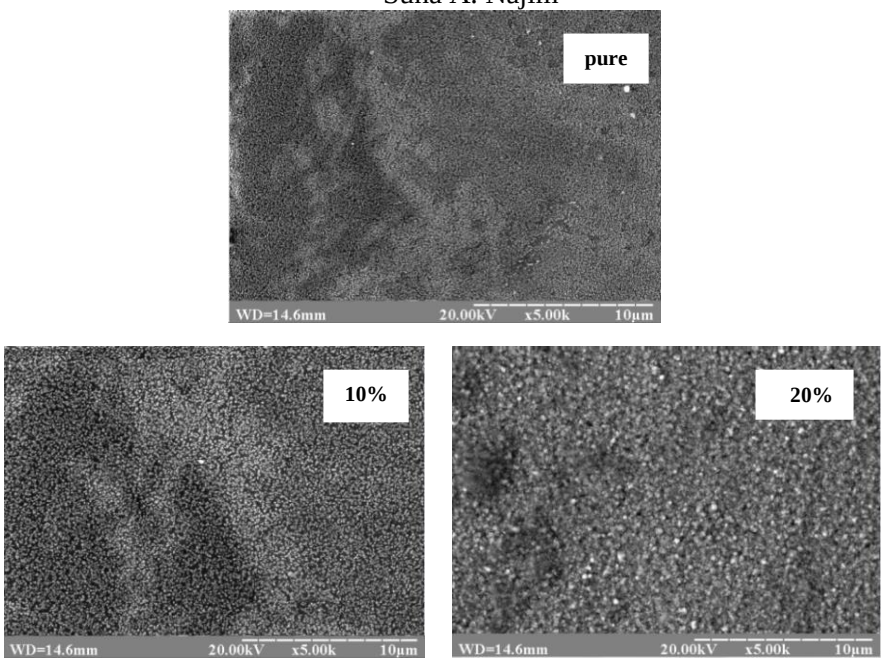


Fig. 2b: SEM of thin ZnO pure and doped with (10%&20%) Na at 450 ˚C.

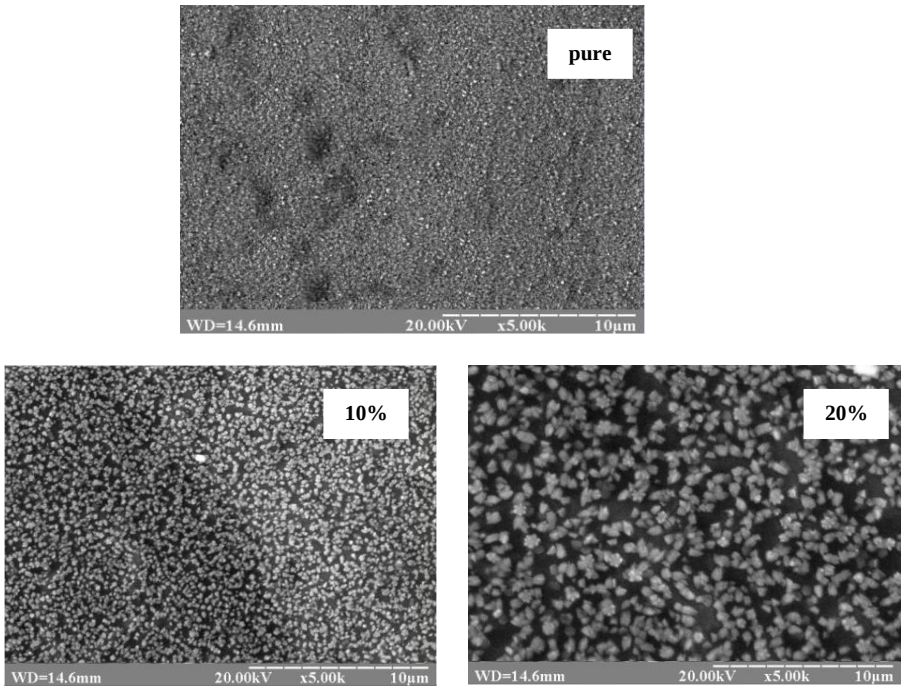


Fig. 2c: SEM of thin ZnO pure and doped with (10%&20%) Na at 500 ˚C.

3- EDXA analysis:

EDXA analysis for ZnO pure and doped thin films as shown in Figs.(3 a,b) respectively shows that the dominant composition of ZnO and the details of the relative analysis are depicted in (Table 1). Whereas the quantitative analysis of the as-deposited ZnO films shows two strong peaks corresponding to Zn and O elements, which refers the high purity of the ZnO thin films. However, in the doping state we observed the appearance of Na element with high intensity due to high concentration (20% Na) as well as two strong peaks corresponding to Zn element and another peak due to O element.

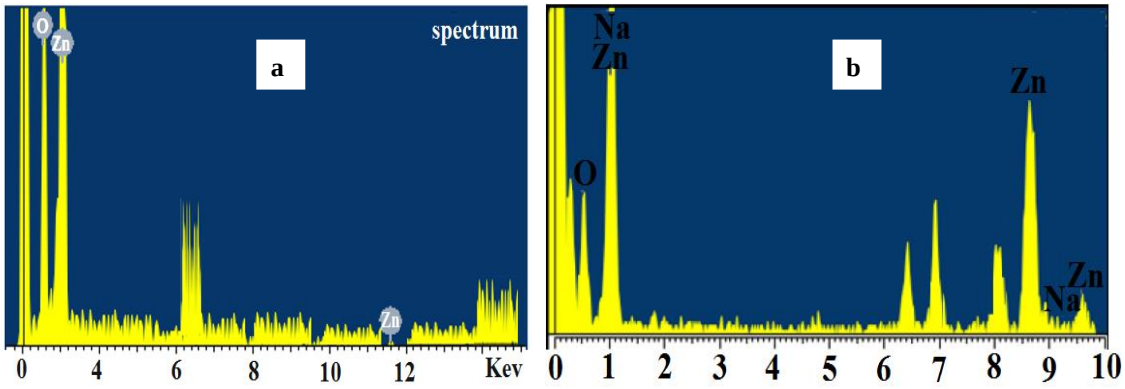


Fig. 3: EDXA of ZnO thin films a- pure , b- doped 20% Na

Table 1: Elemental analysis of ZnO doped at 20% Na

ELEMENT	WEIGHT %	ATOMIC %
O	25.80	57.48
Zn	71.45	39.03
Na	2.75	2 .49

Optical Properties:

1- Optical transmittance:

Figure (4a-c) shows the optical transmittance spectra of Na-doped thin films in the wavelength range between 320 to 1000 nm. It is observed that the transmittance has a tendency to increase with Na content. The highest transmittance edge was recorded at 62% for a sample with 20% Na while the lowest transmittance edge was obtained for 0% Na sample at 43%, over the same wavelength (400nm). An increment in the transmittance percentage is due to the progression of Na in the thin film that enlarges the particle size and it slightly contributes to this phenomenon. The variation of thickness (d µm) with Na concentration at different substrate temps. is shown in (Table 2).

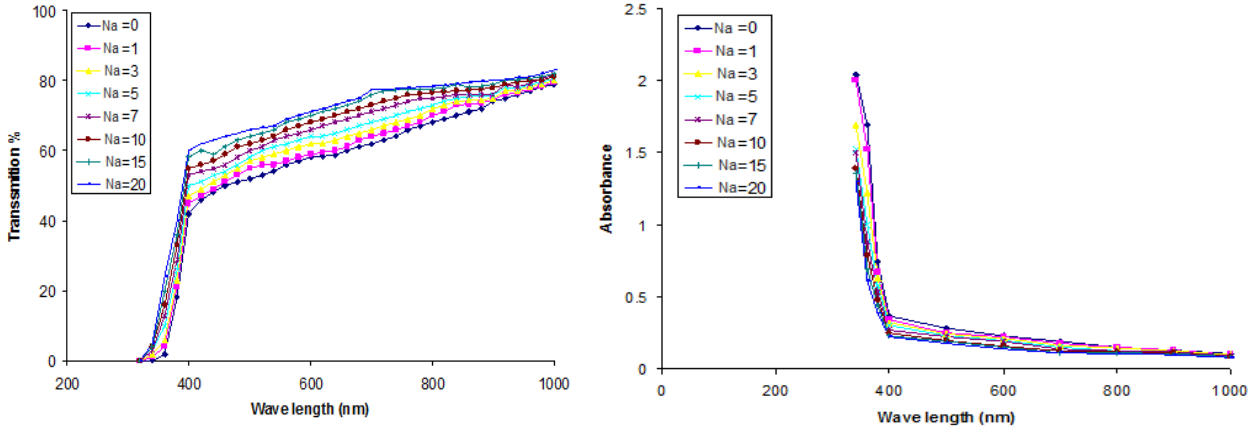


Fig. 4a: Transmittance & Absorbance spectra of ZnO:Na films at 400 ˚C.

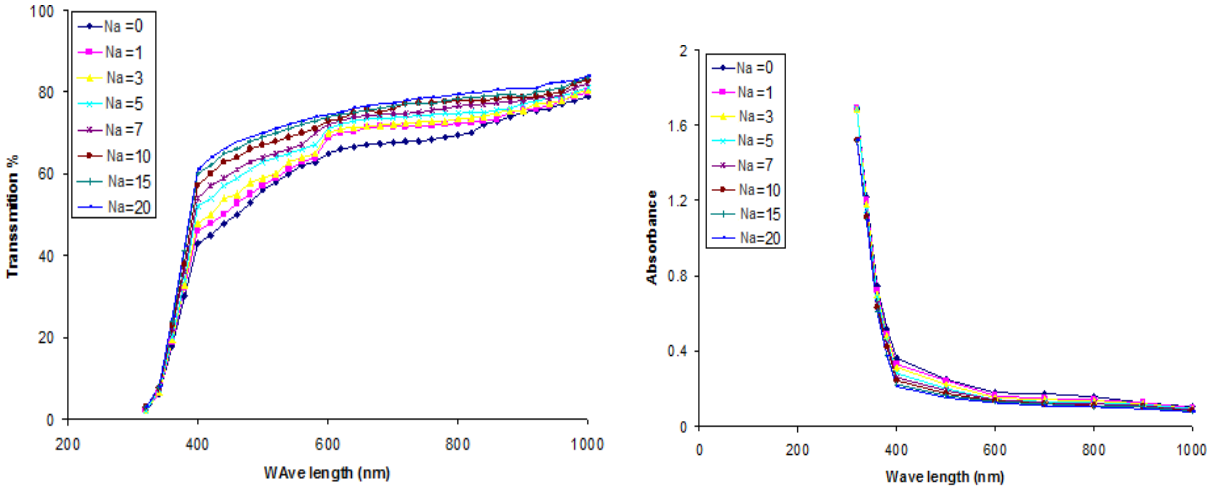


Fig. 4b: Transmittance & Absorbance spectra of ZnO:Na films at 450 ˚C.

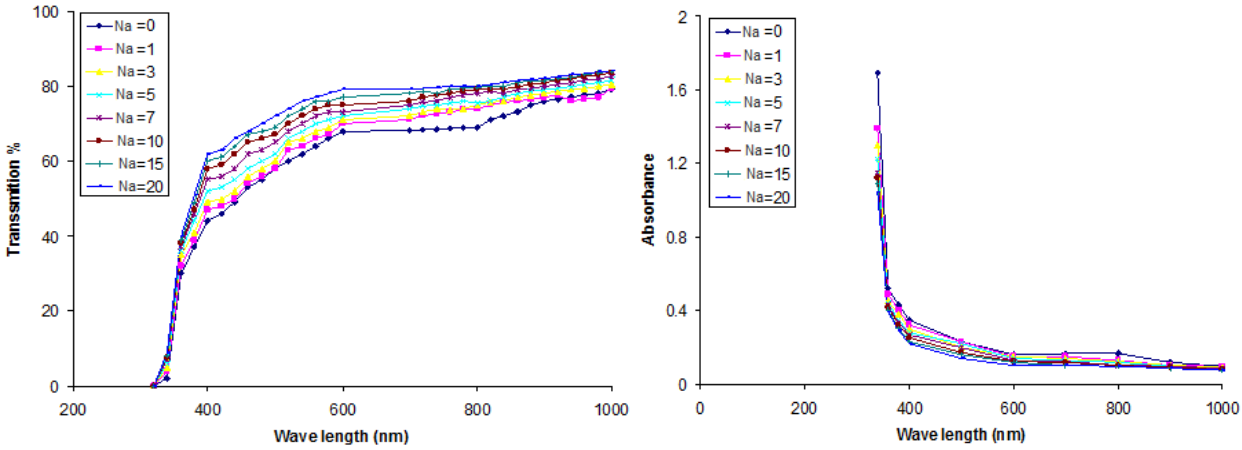


Fig. 4c: Transmittance and Absorbance spectra of ZnO:Na films at 500 ˚C.

Table 2: Variation of thickness (d μm) with Na percentage at different substrate temps. (400, 450, 500 ˚C)

Na %	d (μm)		
	T=400 ˚C	T=450 ˚C	T=500 ˚C
0%	0.95	1.01	1.04
1%	0.954	0.97	0.97
3%	1.05	1.05	1.05
5%	0.99	0.99	0.99
7%	0.103	1.05	1.01
10%	0.97	0.99	0.99
15%	0.99	1.02	1.03
20%	1.05	1.05	1.05

2- Optical absorption:

The relation between absorption coefficient (α) and photon energy for direct transitions is given by [Azimirad *et al*., 2006].

$$\alpha h\nu = A(h\nu - Eg)^{1/2}$$

where, h is the Plank constant, ν is the frequency of the incident photon, A is a constant depending on the electron-hole mobility and E_g is the optical band gap energy. The plots of $(\alpha h\nu)^2$ versus hν

will have a linear region and extrapolation of the straight line to zero absorption gives the energy gap for different substrate temperatures and Na concentrations, are shown in Fig.5.

For pure ZnO thin film, the optical band gap energy was 3.29 eV at 400 ˚C. This was followed by 3.3 and 3.31eV at 450 ˚C and 500 ˚C respectively. An increment of 0.02 eV in the optical band gap was obtained from 0 to 20% Na content in ZnO thin film. This evidently shows that the band gap of ZnO thin film can be altered. Approximately, the band gap alteration of ZnO:Na thin film can be deduced from Fig. 6. Here, it evidently shows that changes in the band gap are in parallel with the Na concentration in the thin film at 400, 450, 500 ˚C respectively.

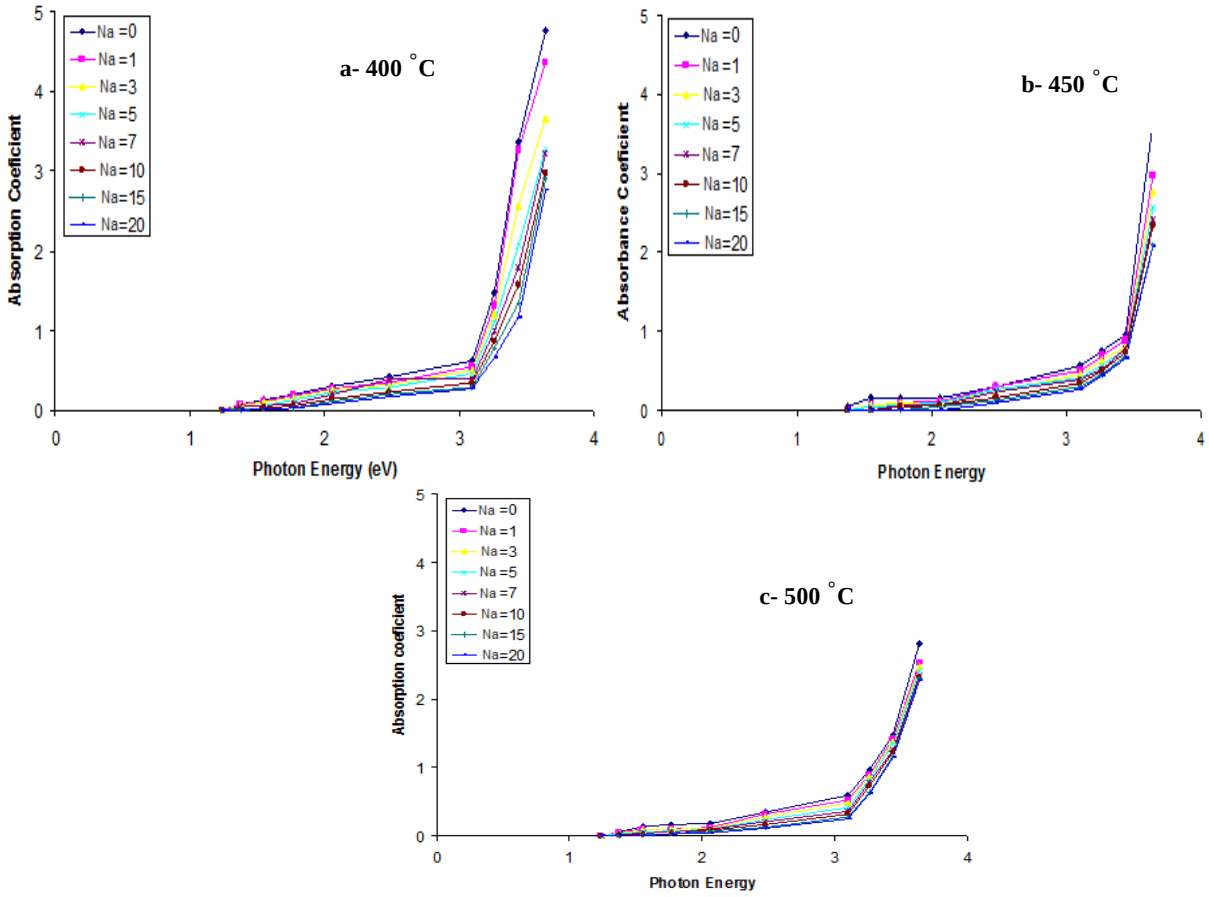


Fig. 5: Absorption coefficient vs. photon energy of representative thin films (0,1,3,5,7,10,15,20 of Na) at a-400, b-450, c-500 ˚C.

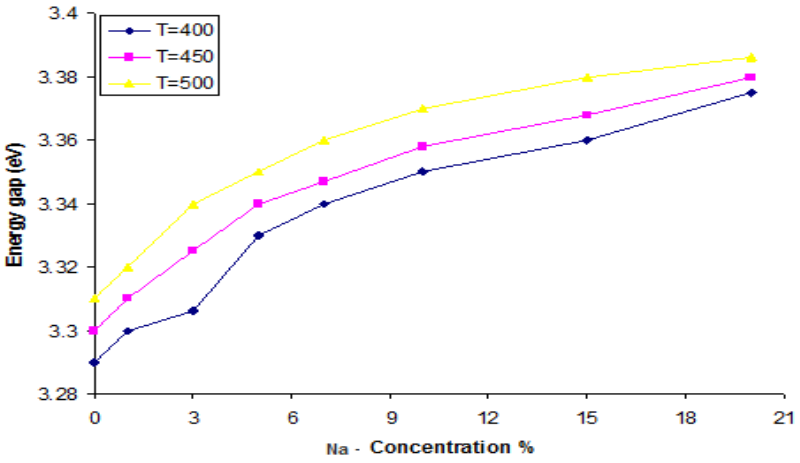


Fig. 6: Variation of energy gap with Na concentration at 400, 450 and 500 ˚C.

CONCLUSION

In summary, pure and Na doped ZnO thin films were successfully synthesized by CVD technique at different substrate temperatures. The influences of substrate temperature and doping on the structural and optical properties of the samples are studied. XRD measurements indicate that the synthesized ZnO and ZnO:Na films are in the hexagonal phase with a preferred orientation (002). SEM images show that better crystalline behavior for the films by increasing substrate temperatures and doping. EDXA analysis shows the chemical composition of pure and doped films with 20% Na. A direct optical band gap was found from the transmittance spectra. As the concentration of Na in the films and the substrate temperature increases, the band gap energy is affected.

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