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Structural and electrical properties of ZnO:Co thin films prepared by pulsed laser deposition

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ABSTRACT

The present paper is based on the study of polycrystalline ZnO:Co thin films deposited on glass substrates by pulsed laser deposition (PLD) technique using pulsed Nd-YAG laser with wavelength (λ=532 nm),duration (7ns) and energy flounce (1.4 J/cm^2) with different doping percentage (1 wt.%, 3 wt.% and 5 wt.%). The X-Ray diffraction patterns of the films showed that the ZnO films and ZnO:Co films exhibit hexagonal wurtzite crystal structure and high crystalline quality. Through the electrical properties: the dc electrical conductivity at a temperature range (27-300) ^{o}C for ZnO:Co films were studied to confirm that these films have two activation energies. Hall effect is studied to estimate the type of carriers, from the result we deduced that the ZnO:Co thin films are n-type. Seebeck measurements are used to obtain the thermoelectric power as a function of temperature.

KEYWORDS

Pulsed-laser deposition;
Zinc oxide thin films;
Structural and electrical properties.

INTRODUCTION

Zinc oxide (ZnO) is an n-type semiconductor of wurtzite structure, with a direct band gap of about 3.37 eV at room temperature[1,2]. It is a quite important oxide which exhibits near ultraviolet emission and transparent conductivity. ZnO is piezoelectric due to its noncentral symmetry, a property that makes it a major candidate for building electromechanical coupled sensors and transducers[3]. ZnO is also one of the most widely applied oxide gas sensing materials[4]. Various deposition techniques have been developed for depositing ZnO thin films, including chemical vapor deposition, radio frequency sputtering, magnetron sputtering, sol–gel, ion-beam-assisted molecular-beam epitaxy and pulsed laser deposition (PLD)[5]. Amongst them, the pulsed laser deposition technique is interesting because it offers an easy way to add other elements for alloying or for doping purposes. An important point is that PLD gives the advantage of carrying out the growth in a high-O partial pressure for better control of possible oxygen deficiency[6]. In this study we prepared Co-doped ZnO thin films deposited by PLD on glass substrates at 400 ^{0}C temperature. We also investigate the influence of laser (1.4) J/cm^2 applied during the deposition process on the structural and electrical properties of the films.

EXPERIMENTAL PROCEDURE

ZnO:Co thin films were synthesized by pulsed laser deposition system using a second harmonic Nd:YAG laser. Thin films were grown in a vacuum chamber with background pressure of ~$1x10^{-3}$ mbar. The Nd:YAG laser was operated at the wavelength of (λ=533 nm) with the repetition rate of (10Hz) and pulse duration of (7ns). The target to substrate distance was (3cm).

X-ray diffraction measurement has been done and compared with the ASTM (American Society for Testing and Materials) cards, using Philips PW 1840 X-ray diffracotmeter of λ = 1.54 Å from Cu-Kα. The resistivity is conventionally calculated from the measured electrical resistance. The activation energy is calculated from measuring the conductivity as a function of temperature using a cryostat. The temperature was maintained by (MANFREDI L7C). The bias voltage was supplied by (FARNELL E 350) power supply. (*Kithley-616 Digital Electrometer*) was used to measure the current.

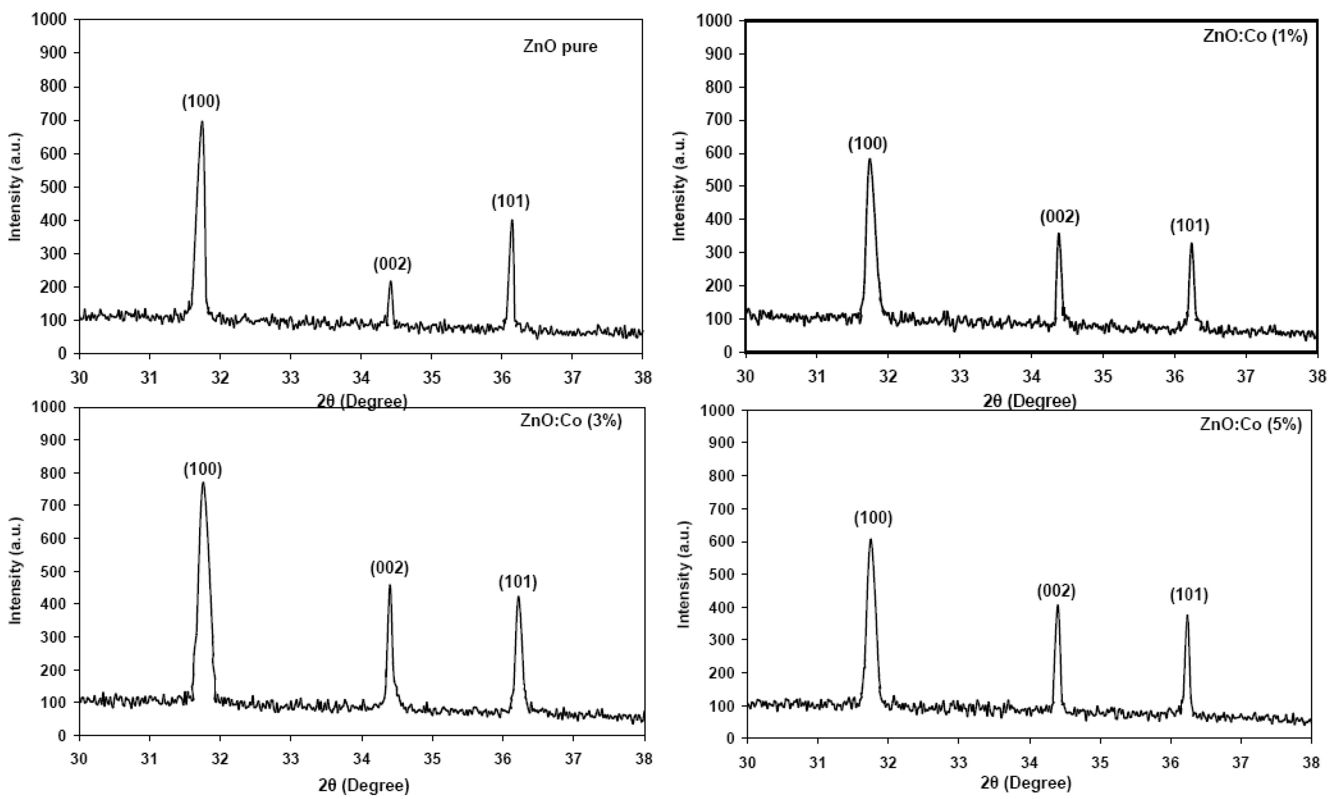
RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of ZnO:Co films. It can be seen that the structure of all the films are hexagonal with a strong preferred orientation a long (100) plane.

No diffraction peaks of Co or other impurity phases are found in these samples. The angle of the dominant peak corresponding to (100) plane is at 2θ=31.7° for the undoped ZnO sample and it increased as the concentration of Co content increased[7].

The conductivity of ZnO:Co films decreased as the value of 1/T increases at higher temperature (T > 27 ºC), suggesting a thermally activated conduction in this temperature range. The conductivity for undoped was about 1.587$(\Omega,cm)^{-1}$ as the Co content increase (1wt.% and 3wt.%) but the conductivity decrease to 1.052 $(\Omega.cm)^{-1}$ of Co (5wt.%),these data were shown in TABLE 1[8,9].

Figures 2 shows the electrical activation energy of ZnO:Co films which were calculated from lnσ versus (1000/T) plots for different Co-doping concentrations. Their values were tabulated in TABLE 2, it could be seen that the values of conductivity have increased up to 3 wt% then it become to decrease. The activation energy depends on the donor carrier concentration and the impurity energy levels. An increase in donor carrier concentration brings the Fermi level up in the energy gap and results in a decrease of activation energy val-



Figures 1 : XRD spectrum of ZnO pure and cobalt-doped ZnO thin films deposited on glass substrate.

TABLE 1 : Electrical properties of ZnO thin films prepared at different Co dopant concentrations.

sample	ρ (Ω.cm)	σ (Ω.cm)$^{-1}$ at RT	R_H	N (cm)$^{-3}$	μ (cm^2/v.s)
ZnO-pure	0.630	1.587	48.8	1.28 x10^{17}	77.13
ZnO:Co (1%)	0.351	2.845	17	3.6 x10^{17}	48.36
ZnO:Co (3%)	0.366	2.731	0.13	4.56 x10^{19}	0.374
ZnO:Co (5%)	0.949	1.052	36	1.7 x10^{17}	37.87

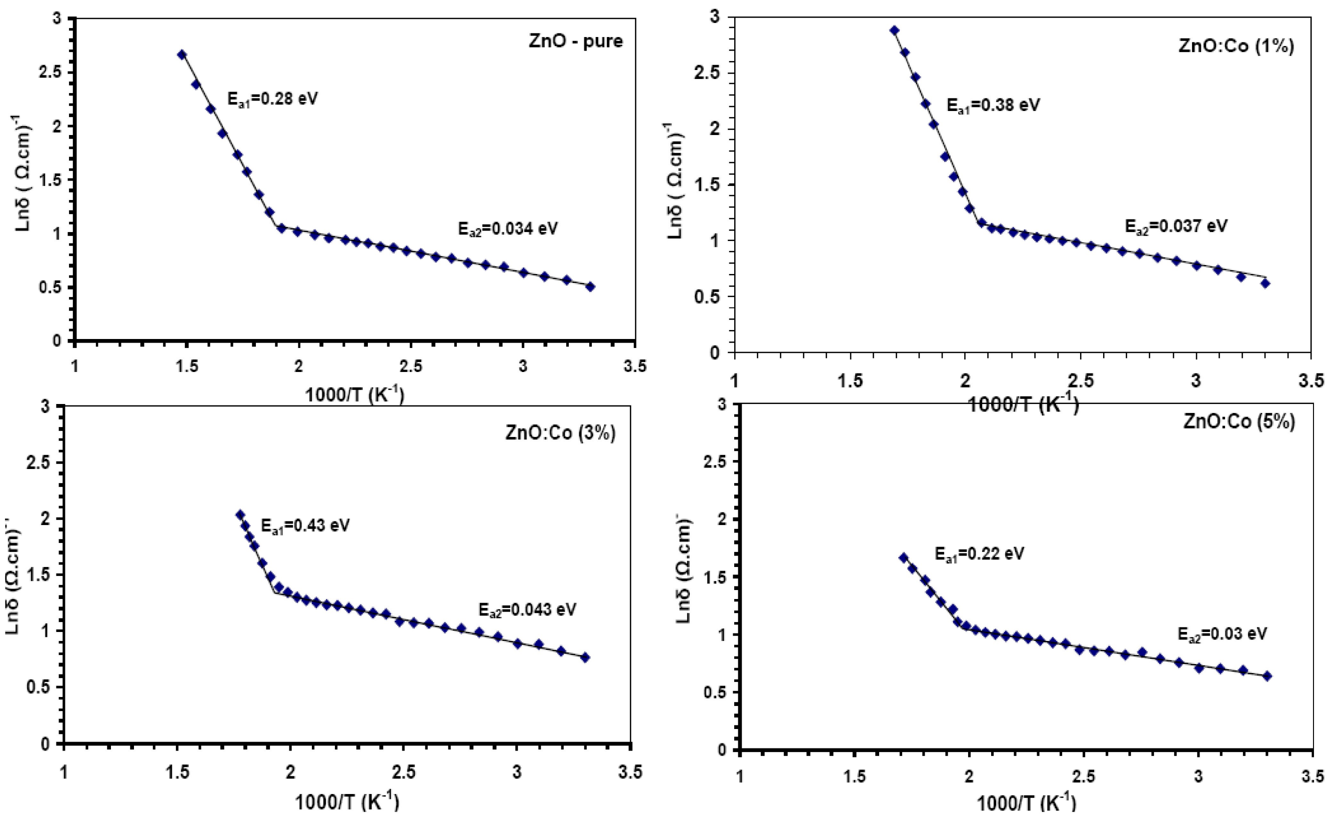


Figure 2 : Lnσ versus 1000/T for pure ZnO and ZnO:Co films at different doping concentrations and temperatures.

TABLE 2 : Activation energy of ZnO thin films prepared at different Co dopant concentrations.

sample	Ea_1 (eV)	Ea_2 (eV)
ZnO-pure	0.28	0.034
ZnO:Co (1%)	0.38	0.037
ZnO:Co (3%)	0.43	0.043
ZnO:Co (5%)	0.22	0.03

ues[10].

The results obtained from Hall effect show that the pure ZnO and ZnO:Co films were n-type, which are in good agreement with the previous work[11-13]. Hall voltage values decrease when the current increases, as shown in Figures 3.

It was noticed that the field applied at the film ends has a proportional relationship with Hall voltage. The values of Hall coefficient R_H at different concentrations of Co are given in TABLE 1, the variations of N and mobility μ_H with Co concentration in ZnO: Co films are shown in TABLE 1. It is seen from this TABLE that the carrier concentration (N) increase with increasing Co concentration. Maximum values of N (4.56 x 10^{19} cm^{-3}) are obtained for 3wt.% of Co, but the (N) decreases when increasing the doping to 5wt.%. The mobility μ_H of the ZnO: Co films decreases with increasing dopant concentration as in TABLE 1, and reaches a minimum around Co 3wt.% with a value of 0.374 cm^2 V^{-1} S^{-1}.

The measurement of thermoelectrical power as a function of temperature, is one of the most important characteristics of electronics, Seebeck coefficients (S_b) of undoped ZnO and doping films for cobalt are shown

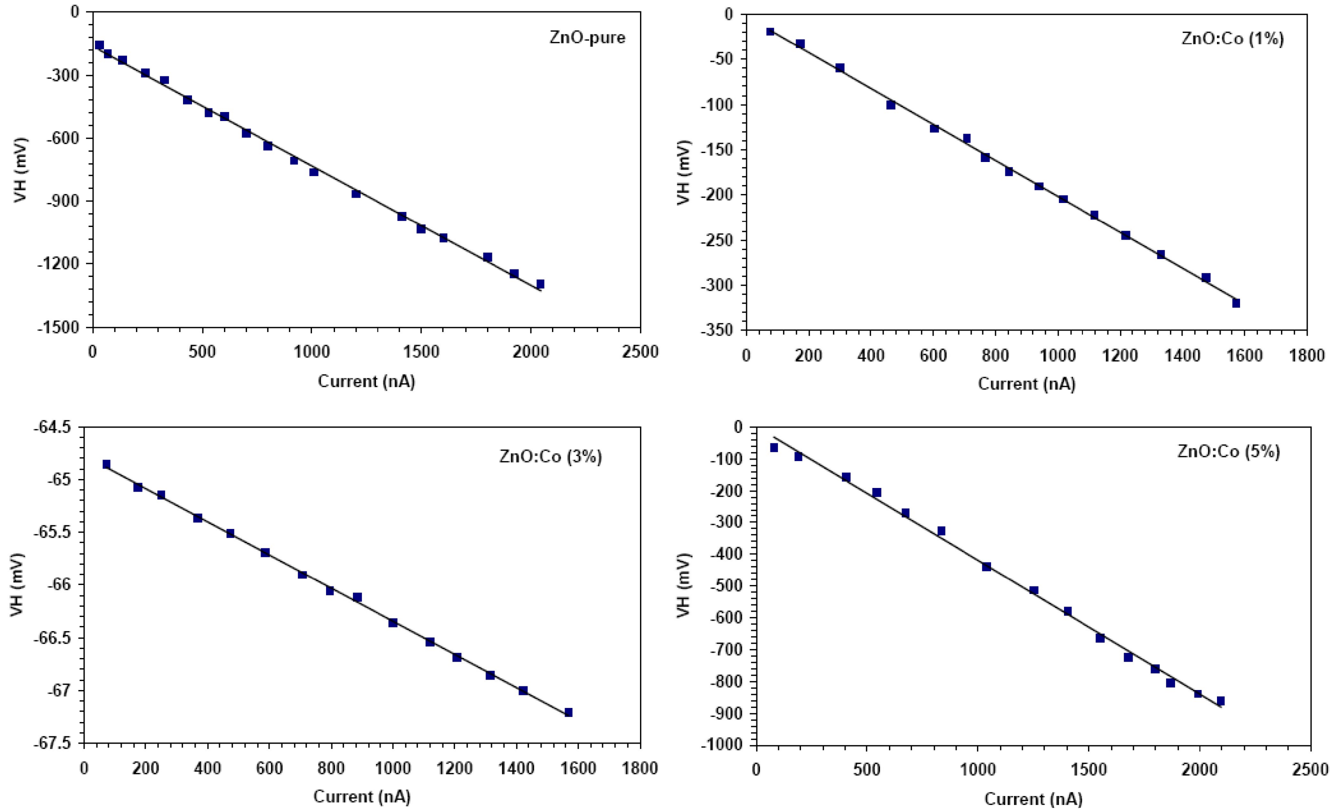


Figure 3 : Relation between Hall voltage (V_H) and the current (I) of ZnO thin films prepared at different Co dopant concentrations

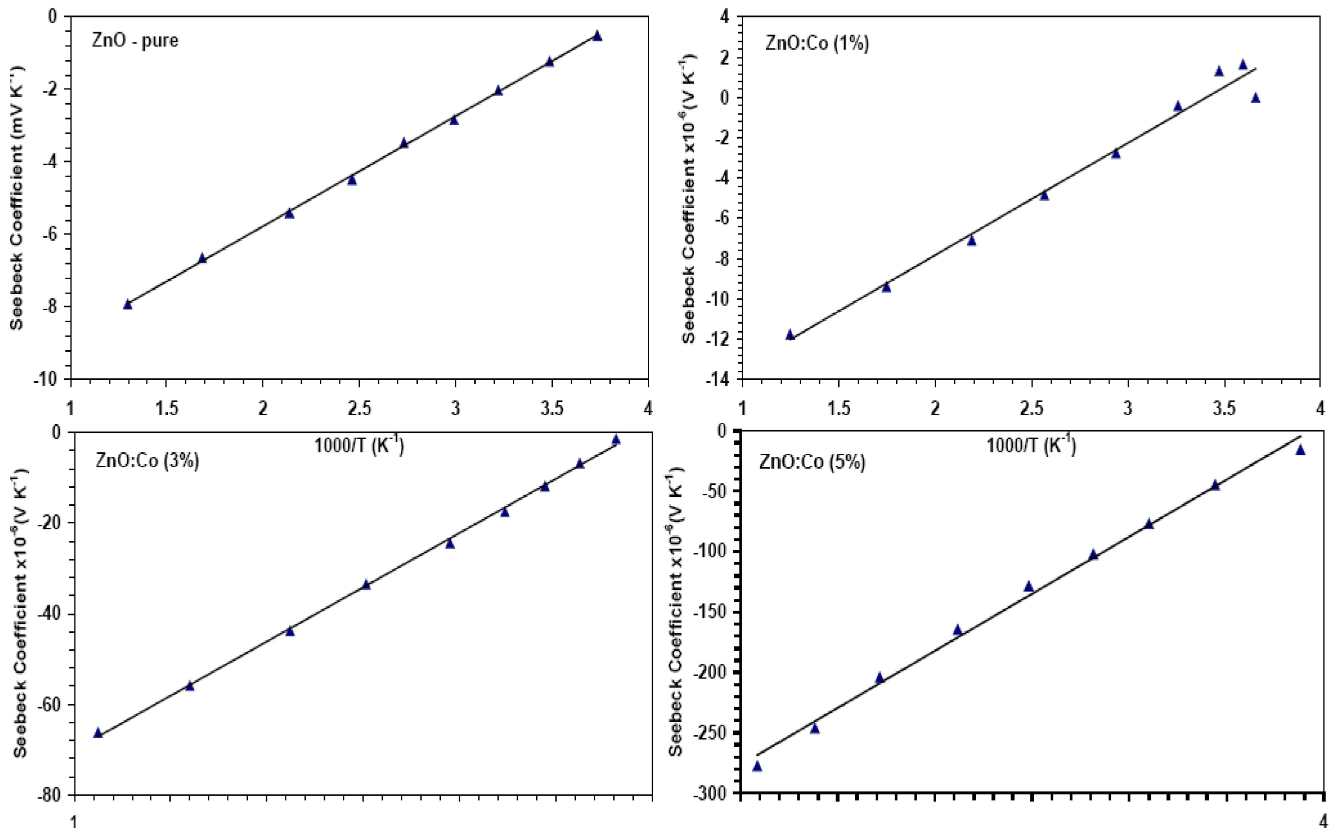


Figure 4 : The Seebeck coefficients of ZnO thin films prepared at different Co dopant concentrations as a function of temperature

in Figures 4. The Seebeck coefficients values of all the samples are negative within the whole temperature range examined, indicating n-type conduction. Seebeck coefficient of undoped ZnO has large and negative values of (-0.02 to -8) mV K^{-1} from room temperature up to 100ºC, on the other hand, ZnO:Co films give smaller but still moderate S_b values, with a general trend in which the absolute value increases gradually at room temperature up to 100ºC[8]. The calculated values of E_s (Seebeck) are tabulated in TABLE 3 for pure ZnO and ZnO:Co films. We have calculated the Seebeck energy (E_s),

TABLE 3 : Seebeck effect of ZnO thin films prepared at different Co dopant concentrations.

Sample	Carrier type	E_{a1} (eV)	E_s (Seebeck) (meV)	E_{a1} - $E_{Seeb.}$(eV)
ZnO-pure	n	0.28	0.26	0.2797
ZnO:Co(1%)	n	0.38	0.47	0.3795
ZnO:Co (3%)	n	0.43	2.05	0.4279
ZnO:Co (5%)	n	0.22	8.12	0.2118

which is found undoped ZnO around 0.26 meV increases with increasing Co concentration.

Maximum values are obtained for 5wt.% of Co and were around 8.12 meV, Seebeck effect based on the idea that different temperatures generate different carrier densities and the resulting diffusion causes the thermal emf, so any change in carrier concentration can cause significantly different transport behaviors and Seebeck coefficient[14].

CONCLUSIONS

ZnO:Co thin films were deposited on a glass substrate by pulsed laser deposition at a temperature of 400°C and at 10^{-3} mbar oxygen background gas. The structural and electrical properties are found to be dependent on the laser fluence. The crystal structure of the films is hexagonal wurtzite. All the films are polycrystalline and (100) oriented. By studying the electrical properties, dc electrical conductivity at a temperature range (27-300) ºC for pure and different doping (1 wt.%, 3 wt.% and 5 wt.%), we realized that these films have two activation energies. Hall effect is studied to estimate the type of carriers, from the result we deduced that the pure ZnO and the doped ZnO:Co films are n-type. The calculated values of Es (Seebeck) pure ZnO and ZnO:Co films re around 0.26 eV while its value increased to 8.12 for Co 5wt% doped ZnO

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