ZnO thin film preparation using RF sputtering at various oxygen contents

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In recent years, nanostructured ZnO films have been receiving particular attention because not only do they show many valuable properties as semiconducting materials, but also due to their relatively easy methods for synthesis. In this paper, ZnO thin films were prepared with RF sputtering at constant total gas pressure, with different oxygen and argon contents. Different working parameters such distance between the cathode and sample, sample dimensions, as well as variable interelectrodic spaces were investigated. Our aim is to define the optimum percentage of oxygen contents for ZnO thin films production. Thicknesses, refractive index, thickness homogeneity, UV spectra, band-gap energy, absorption spectra of the obtained thin films were carried out in this study.

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1. Introduction

Zinc oxide (ZnO) is a strategic material for various photonic applications. One of the most important binary II-VI compounds, ZnO is a direct semiconductor of wurtzite structures that is suitable for short wavelength optoelectronic applications. ZnO exhibits a direct bandgap of 3.37 eV at room temperature and efficient radiative recombination [1-4] The large exciton binding energy of 60 meV, which makes it transparent in visible light and operates in the UV to blue wavelengths, paves the way for an intense near band edge excitonic emission at room and even higher temperatures.[5,6] ZnO thin films present many remarkable characteristics due to their large bond strength, good optical quality, extreme stability of excitons and excellent piezoelectric properties. For this reason, ZnO thin films have many potential applications in various technological domains such as transparent conducting films/electrodes in display devices and solar energy cells, surface and bulk acoustic wave devices (SAW) and acoustic-optical devices, light emitting diodes (LEDs) and laser diodes (LDs) [7-10]. It finds applications not only in various photonic associated technologies but due to its piezoelectric nature, it can be used effectively as a sensor in various MEM related devices e.g. in force sensing, acoustic wave resonator, acousto-optic modulator.

The ZnO thin film can be deposited by various methods such as spray pyrolsis, chemical vapor deposition (CVD), sol-gel process, sputtering techniques, chemical spray, plasma enhanced CVD and pulsed laser deposition [11-16].

Most of reports underlined that the ZnO films produced by RF films had better quality than those deposited by DC techniques. It is believed that RF excitation provides a higher degree of ionization/dissociation, which leads to a greater oxidation rate at the substrate surface. RF discharge itself also generates more intensive ions densities [2].

The quality of thin films deposited by sputter technique depends by following parameters: the applied power, the temperature of substrate, sum of the partial pressure of oxygen pressure and argon pressure, substratetarget material distance and the stoichiometry of the target material.

In this paper RF sputter technique was carried out for ZnO thin films synthesis using RF power supply of 13.56 MHz. Physical properties of ZnO thin films deposited were investigated at various percentages of O_2 and Ar as working gases. Optical properties of the growth thin films were performed in terms of UV spectra, band-gap energy, absorption spectra. Thickness homogeneity was also evaluated using a Cressington thickness monitor.

2. Experimental set up

Reactive RF sputter system includes four parts namely. These parts are vacuum chamber, vacuum pumping system, radio frequency power supply and network unit and gas mixing system and filling system.

Schematically view of the growth film is presented in Fig. 1. The target material is represented by Zn particles, with $1x1x0.2 \text{ cm}^3$ dimensions prepared from square plate by us. As buffer gases a combination of x% Ar+ (100-x) % O₂ gas mixing was used, where x is the Ar contents in used Ar-O₂ gas mixture, In our experimental conditions x has the following values: 50 and 70, respectively.

The distance between the target and sample holder was maintained at 3 cm.



Fig. 1. Schematically view of the growth of ZnO thin films by using RF sputter system.

Photo image of the RF plasma produced with 50% Ar+ 50% O_2 gas mixing is illustrated in Fig. 2.



Fig. 2. Photo image of the produced RF plasma in 50% Ar+ 50% O_2 gas mixing

The RF sputter power supply of 160 W of 13.56 MHz has been applied for 65 minutes in Ar-O₂ gas composition at a working pressure of 1.1×10^{-1} Torr. The O₂ gas rates were 50% and 30%, respectively. Our aim was oriented on oxidation process and then on the growth ZnO thin films on the glass substrates.

Thicknesses of the thin films were monitored by using Cressington thin film analyzer. The deposition rate was about 1.8 nm per minutes during the processes. Optical properties of the growth thin films were investigated by using Perkin Elmer UV/ VIS Spectrometer Lambda 2S. The glass slides were selected for the deposition after it had cleaned by pure ethanol.

3. Results and discussions

3.1. Optical properties of the ZnO thin films

The transmission spectrum of the grown ZnO thin films by RF sputtering is shown in Figure.3. As can be revealed from the mentioned figure, the results indicated good values for transmissions.



Fig. 3. Transmission spectra of growth ZnO thin film in $\%50 O_2$ concentration.

Thickness and transmissions of the growth thin film at 700 nm for different composition of gases can be summarized in Table 1.

Table1.	Thickness and transmissions of the growth ZnO
	thin film at 700 nm wavelength.

Material	Composition	Thickness (nm)	T (%)
ZnO	50% Ar+ 50%	70	76
	O_2		
ZnO	70% Ar+ 30%	110	69
	O_2		

For the determination of the ZnO thin film band gap energy optical method was used. The graph from which can be measured the value corresponding to the bad gap energy is shown in Fig. 4. A line is plotted from the linear part of the graph to x-axis (axis of hv). The intersection of this line with the horizontal axe corresponds to the value of the band gap energy.



Fig. 4. Graph of the $(\alpha hv)^2$ *versus hv.*

The calculated band gap energies values are represented in Table.2 for ZnO thin films prepared by different O_2 concentrations - 50% and 30% respectively. As can be seen from this table, when O_2 concentrations decrease, the values of the band gap energies also decrease.

*Table2. Band gap energies for the different concentrations of O*₂

Material	Concentration of	Band gap
	O_2 (%)	energy (eV)
ZnO	50	3.95
ZnO	30	3.80

Knowledge of the dispersion of the refractive indices of semiconductor materials is necessary for accurate modeling and design of devices. Refractive index of ZnO thin films is calculated [3] using following equation:

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \sqrt{\frac{E_g}{20}}$$

The results of the calculated values based on the previous equation can be summarized in the Table 3

Table 3 Refractive index of ZnO for the differentconcentrations of O_2 .

Material	Concentration	Band	Refractive
	of O ₂ (%)	gap	index
		energy	
		(eV)	
ZnO	50	3.95	2.18
ZnO	30	3.80	2.21

The value of the ZnO thin films refractive index shown in literatures (n =2.35) are very close to the values obtained by this method in our experimental conditions.

The graph of the refractive index values via wavelengths performed by Filmetrics F20 is depicted in Fig. 5.





Moreover, the graph of the refractive index in solving details modes (Fourier search for thickness) revealed that the mean refractive index of ZnO thin films is n=2.10.

3.2. Electrical Properties of growth ZnO thin films

Electrical properties of the ZnO films were evaluated by I-V characteristic shown in Figure 6. The intensity of the current value of film was measured in room temperature and half open in the range of voltages up to 2000 V.

Conductivity is governed by the excitation of electrons from trap levels between room temperatures and T=420K.



Fig. 6. I-V characteristic of ZnO thin film.

The resistivity and conductivity values were measured and listed in Table 4.

Table 4. Resistivity and conductivity values for ZnO thin films

	Resistivity	Conductivity
Material	ρ(Ω.cm)	$\sigma(\Omega.cm)^{-1}$
ZnO	8.75 E+5	1.14 E -6

The deposited ZnO films show metallic conductivity above T=420K, and semiconducting at temperatures below it.

4. Conclusion

ZnO material has been a subject of varying degrees of research effort over the decades. Its optical properties have been studied extensively motivated by some of its unique properties and some advantages over other wide-gap materials. In this study, ZnO thin films were produced RF sputter plasma oxidation process at various oxygen percentages. Band gap energy was changed according to O_2 gas contents directly proportional. From optical measures, we found that the forbidden energy space was nearly 3.8 eV and the ZnO films displayed high permeability rates in the noticed area.

Further studies will be devoted to reach a value of 3.3 eV for the band gap energy. In this way, ZnO thin films produced by our RF sputter technique will be used in application such as solar cells, solar thermal collectors, gas sensors or optic communication systems [15-16].

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