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Fabrication of ZnO-NiO nanocomposite thin films and experimental study of the effect of the NiO, ZnO concentration on its physical properties

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ABSTRACT

ZnO-NiO nanocomposites thin films were elaborated at different mixing concentrations using sol gel and spin coating methods. Their structural and morphological evolutions as well as the optical and electrical properties were investigated. XRD diffraction and Raman spectra allowed phase identifications of ZnO (zinc oxide) and NiO (nickel oxide) with no appearance of secondary phases and the crystallinity of elaborated nanocomposite films improved with doping concentration increase. The grain sizes of obtained ZnO-NiO nanocomposites are investigated by AFM (Atomic force microscopy); they increase in the range (10–65 nm) and they are observed to affect the optical and electrical properties. In fact, ZnO-NiO nanocomposites thin films optical reflectivity decreased in the range (10–5%) with the increasing of mixing proportion and their resistivity decreased up to 1.4 10^2 Ω cm. The optical band gaps were in the range (3.3–4 eV). The values obtained by UV–Vis spectroscopy and ellipsometry are quite similar. We remarked also that the NiO concentration increase on to the nanocomposite induced a red shift of the gap value while the ZnO increase led toward a blue shift

1. Introduction

Nanocomposites are a mixture of at least two phases which one of them or both is in the nanometer scale. They were extensively researched because of the nanocomposite thin films enhancements when compared to the study of the separate phases [1,2]. As an example, we can cite higher electrical conductivity, better interactions at phase's interfaces [3], lower density, better chemical and mechanical stability and better wear resistance [4,5]. The nanocomposite materials are used for many applications such as photovoltaic devices [6], gas sensors [7], and UV-Detectors [8].

Nanocomposites were divided in several types which were investigated by a multitude of researchers [3]. Among them, the semiconductor metal oxide nanostructured materials is the ZnO/NiO (zinc oxide/Nickel oxide) nanocomposite. In fact, when the n-type semiconductor metal oxide (ZnO) is mixed with the p-type semiconductor metal oxide (NiO) at a nanometer scale, the result is interesting for new applications in material sciences [2,9,10]. The nanocomposites are mixed with significant proportions of each phase. The purpose of the synthesis of such materials is to combine the properties of the original materials in order to obtain new and improved ones.

Both the semiconductors share a multitude of interesting properties. As an example we can site a wide band gap, the ability to be transparent and conductive in the same time and the possibility to be manufactured by a variety of techniques [11,12]. Besides, both are known to be stable, in fact the zinc oxide is known for its optical and electrical stability while the nickel oxide is known for its excellent durability and electrochemical stability [1,13]. The combination of these two materials allows us to exploit a combination of their morphological, optical, structural and electrical properties.

Various deposition techniques have been widely used to produce ZnO and NiO thin films. The most intensively studied techniques include, RF magnetron sputtering [14], chemical vapor deposition (CVD) [15], sol–gel method [16], and spray pyrolysis [17,18]. The Sol gel method was chosen to synthesize ZnO/NiO nanocomposite because it allows the final properties of the films to be tailored using various precursors and annealing temperatures, In addition to being a low cost method [19]. This technique presents the advantage to be applicable to a wide variety of materials and can be performed under ambient conditions [20]. Sol gel is an effective method to synthesize nanoparticles; nanocomposite materials is a rapidly growing and very promising research field in which it plays a central role; this method provides a good

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dispersion of the nano-phases into the matrix and proper adjustments of the nanocomposite final properties [21].

Several investigations were reported on ZnO/NiO nanocomposites [22–26]. The authors have insisted either on the morphological and structural aspect or on the conduction properties without insisting on the correlation between the observed phenomena. Whereas the novelty in the present work is a correlation between the results of each technique used that allowed us to understand and identify the physical properties of our elaborated layers. In fact, the study of the nanocomposites physical properties allows a better integration of these materials in several applications such as solar cells and gas detection. Besides, this work covers a wide range of ZnO-NiO concentrations and consequently aims for a wide range of applications while using a simpler and less expensive technique of elaboration. Moreover, our as-prepared ZnO-NiO samples are thin films unlike most studies that investigate them as powder. Furthermore, we can observe the effect of concentration variation on the structural and morphological properties. For instance, the XRD analysis show that from the variations of the ZnO/NiO mixtures concentrations, it appears that the incorporation of the Zn 2+ and Ni 2+ ions depends not only on the ionic radius but also on the concentration of the mixture, In addition it changes the thin films morphology from nanowalls (nickel oxide NiO), nano-rods (zinc oxide ZnO) to individual sphere-like particles (nanocomposites)

In this study, we elaborated the ZnO/NiO nanocomposites by the sol gel method and deposed them by spin coating to obtain thin layers. The structural properties investigations are conducted by XRD. The results are used for phase identification and so are the results of the Raman spectroscopy but also to identify the micro-strain and the crystallite size, AFM and SEM to observe the variation of the surface morphology and the four point probe method to measure the electrical resistivity. The optical characteristics were examined by NIR-UV–Vis spectrophotometry and spectroscopic ellipsometry.

2. Experimental details

2.1. Preparation of the ZnO-NiO thin films

The ZnO/NiO thin films were prepared as follows:

We started by manufacturing the oxide sol gel solutions by dissolving, for ZnO preparation, the zinc acetate dehydrate [Zn $(CH_3COO)_2{\cdot}2H_2O$] in 2-methoxyethanol ($C_3H_8O_2$) so that we obtain a concentration of 0.5 M; the mixture is then stirred magnetically for a 15 min at room temperature. After that we added a few drops of diethanolamine (MEA) as a stabilizer up to a point where we maintained its molar ratio equal to that of the Zinc in the solution. Then, the solution is heated at 80 °C for a duration of 2 h to complete the process. Finally we leave the solution to rest for 24 h. The same procedure is used to synthesize the nickel oxide NiO from the nickel acetate tetra hydrate ($C_4H_6NiO_4{\cdot}4H_2O$) and the 2-methoxyethanol ($C_3H_8O_2$).

After that, the solutions marked S_1, S_2, S_3, S_4, S_5 are mixed using different ZnO/NiO volumetric concentrations (Table 1). The results are spin coated onto glass substrates with a speed of 3000 rpm for 30 s Up to four layers. The thin films are dried at 200 °C after deposing every layer and ultimately annealed for an hour at 600 °C.

2.2. Materials characterization

The structural study was investigated by a Bruker D 8 advance (Both Bragg-Brentano) X-ray diffractometer; the study using Xpert analytical program includes, particle size and the microstrain calculations and phase's identification also examined by Raman spectroscopy. The morphological study was conducted by using an atomic force microscope AFM type Nanoscope III in the tapping mode and Nanotech program; the AFM and SEM results allows the nanostructure study and the determination of the average grain size and the surface roughness. The optical study was conducted using two methods: The UV–Vis–NIR Spectrophotometer (Lambda 950) was used to study the thin films reflectivity, transmission and calculate the optical band gap, whereas the spectroscopic ellipsometry, carried with GES 5 device and Winnelli program allowed us to determine the refractive index, extinction coefficient and confirm gap energy results. The electrical resistivity was determined using the four point probe method. All measurements were carried out at room temperature.

Table 1
mixing percentages of the ZnO-NiO nanocomposites thin films.

Thin films/content (%)	S_1	S_2	S_3	S_4	S_5
ZnO	100	75	50	25	0
NiO	0	25	50	75	100

3. Results and discussion

3.1. Structural studies

Fig. 1 reveals the XRD patterns for S_1, S_2, S_3, S_4 and S_5. All diffraction peaks marked (*) for all films are indexed to the ZnO (Zinc oxide) polycrystalline hexagonal wurtzite phase, identified using JCPDS card (JCPDS, No. 79-0206) [27]. Diffraction peaks marked (¤) correspond to the polycrystalline NiO (nickel oxide) face centered cubic phase according to the standard spectrum (JCPDS, No. 04-0835) [28]. It is worthwhile to notice that no additional peak due to secondary phase or impurities is detected. The effect of NiO concentration increase into the mixture can be traduced by the shifting of the preferred orientation; for instance from the orientation (101) for S_1 to the orientation (002) for S_2. In fact Ramona et al. reported that since the dominant orientation is a result of growth or rearrangement process, the preferred orientation favor crystallographic direction corresponding to the lower strain energy density [29].

We noticed in (Table 2a, Table 2b) that peaks positions ($2\theta_{hkl}$) and intensity (I_{hkl}) are strongly dependent on the mixing ratio. The shift in ZnO,NiO peaks observed in the ZnO/NiO nanocomposite (S_2, S_3, S_4) compared with their original positions on the non-doped thin films (S_1, S_5) might be due to Ni^{2+} incorporation into ZnO matrix or Zn^{2+} in NiO.This type of incorporation causes a structural rearrangement [29] all the more so the question has been raised when investigating Ni doped ZnO [30,31], CO-doped ZnO [32], or Al doped ZnO [33]. The crystallites orientations were investigated through the texture coefficient (TC). Its values have been estimated using the XRD results as follows

$$TC(hkl) = \frac{\frac{Ihkl}{\mathring{I}hkl}}{\frac{N^{-1}\sum I(hkl)}{\mathring{I}(hkl)}} \quad (1)$$

where I(*hkl*) is the measured relative intensity of (*hkl*) plane, $\mathring{I}$ (*hkl*) is the standard intensity taken from the JCPDS data. And N is the reflection number. Looking at the evolution of TC as a function of the NiO percentage increase in Fig. 2 we deduced the maximum preferred orientation

We remark that the preferred orientation varied with the mixing ratios of the nanocomposites. The increase of TC (S_2) is related to high structured ZnO along a given orientation (002). The TC decrease with mixing ratios variation suggests poly crystallinity especially for S_3.

The lattice parameters for all elaborated thin films are calculated using the bragg Eq. (2). Where n is the order of diffraction and λ is the wavelength. The interplanar spacing was calculated as followed for both NiO cubic (3) and ZnO hexagonal (4) phases.

$$2dsin(\theta) = n\lambda \quad (2)$$