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Amorphous phase as possible origin of additional absorption bands in polycrystalline ZnO films

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ABSTRACT

The optical absorption edge characteristics of undoped zinc oxide (ZnO) films with varying thickness (~100 to ~1000 nm) prepared by means of polymeric precursor method (Pechini) on glass substrates have been investigated. Besides the normal absorption edge at about 3.3 eV, related to the transition between the valence and the conduction bands, the films feature additional absorption bands in the energy region around 4 eV. The experimental results show that this band is redshifted with increasing film thickness approaching a value of ~3.7 eV for the thickest films (~1000 nm). In contrast, increasing film thickness resulted in a significant blue shift of the bulk absorption edge stabilizing at ~3.3 eV for the thickest films which corresponds to the single-crystal value. Although the appearance of additional absorption bands in ZnO has been attributed to excitonic resonances as those related to the exciton/longitudinal optical (LO) phonons, this argument is hardly sustainable for ZnO films with a high concentration of defects as those reported in the present investigation. The achieved results suggest that this phenomenon is rather linked to reduced crystallinity of the films. Certainly, the redshift of the additional optical band gap back towards the single-crystal value with increasing film thickness was strong evidence that the additional absorption bands should be related to an amorphous phase. Particularly, it is possible that the amorphortization of the film increases the localized states in the conduction band. The improvement of the crystal quality with increasing film thickness was distinctly verified by X-ray diffraction analysis.

1. Introduction

Recent developments in gallium nitride (GaN) optoelectronic devices have been impressive with blue light emitting diodes (LEDs) or blue lasers in commercial production [1]. Interestingly, zinc oxide (ZnO) is a material very similar to GaN [2] with hexagonal structure and in-plane lattice constants being almost the same as those of GaN [3]. In addition, ZnO is very interesting as luminescent material as it exhibits an exciton binding energy of ~60 meV and a very bright luminescence in the UV-region [3]. The band gap of ZnO amounts to ~3.3 eV at room temperature and the crystals are unintentionally *n* type [4]. Grain boundaries (GBs) in ZnO have led to many interesting phenomena in electrical as well as optical applications [5]. In addition, the strong optical scattering that occurs at the GBs has paradoxically assisted the formation of self-assembled laser cavities [6]. In the last decade, a great deal of effort has been devoted to the research of the local atomic and electronic structures of GBs [7]. In doing so, microscopic probes with high precision have allowed the exact determination of the electronic structure with the scale down to the submicron level [8]. In this regard, electron probes such as spatially resolved electron energy loss spectroscopy (EELS) have been used to investigate the energy loss of the GBs. The majority of such studies considered the high-energy near-edge regime where only the unoccupied states in the conduction band are available [9]. Nevertheless, the low loss study provides information of the interband transitions and may offer an alternative to examine the local electronic structure at high spatial extent [10]. These studies have provided deep insight into the structure, chemistry, and electronic properties of the GBs in ZnO. Compared with indium-tin-oxide (ITO), ZnO is a lower cost material with no toxicity, and stable at high temperature, easy to be fabricated and patterned. Normally, physical methods as rf or dc sputtering or pulsed laser deposition (PLD) have extensively been used for the preparation of ZnO films [7–10]. Most reports focus on methods of obtaining single-crystal ZnO thin films, while there is little attention paid to amorphous and nanocrystalline ZnO. In this regard, soft chemical methods as sol–gel processes [11–14] or polymeric precursor method (Pechini) [15] particularly adapt to produce ZnO colloids and films in a simple, low-cost and highly-controlled way. In the sol–gel technology there are several methods of preparation which depend on the employed

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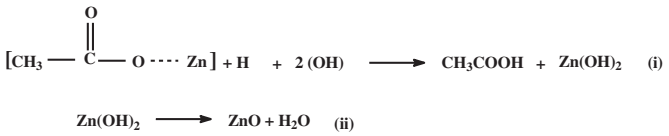
inorganic alcoxides [16]. Some methods are more versatile than others and involve determined organometallic compounds in an alcoholic dissolvent followed by a series of chemical reactions of hydrolysis, condensation and curing to produce a gel which is formed by a continuous inorganic network [17]. The most important step in this route is the formation of an inorganic polymer by means of hydrolysis reactions. The hydrolysis of a solution of tetraethyl orthosilicate (TEOS) in a dissolvent as the ethanol allows the formation of silanols which form a sol. A gel is then obtained by means of the curing by subsequent condensation [18].

Investigations over the years of various semiconductors thin films have established that their optical properties are determined by the interplay between the epitaxy, the microstructure, and the state of strain achieved in them [19]. Each of these parameters may be influenced by the substrate on which the film is deposited. Particularly, the epitaxy and the microstructure of ZnO films may be controlled by the choice of the substrate. Thus, *c*-axis oriented epitaxial and *a*-axis oriented ZnO films may be obtained when deposited on *c*-(0001) and *r*-(1102) sapphire substrates, respectively. The choice of substrate affects the final state of strain by directly determining the lattice mismatch and thermal expansion mismatch. Apart from this, the film thickness has considerable effect on the structural, electrical and optical properties. However, rather little attention has been devoted to this aspect.

In the present investigation, we describe the successful preparation of ZnO films on amorphous glass substrates using the polymeric precursor method (Pechini). The structural and optical properties of films with different thicknesses are discussed in detail. Especial attention is devoted to discussing the origin of additional absorption band near 300 nm which seem to be linked to reduced crystalline quality of the polycrystalline films.

2. Experiment

The preparation of the coating solution is based on the Pechini method [15]. A metallo-organic precursor was mixed with stoichiometry esther in the appropriate ratio in order to complex the selected cation. Zinc acetate dehydrated [$Zn(CH_3COO)_2.2H_2O$] (Carlo Erba 99.9%) was used as metal organic compound. Zinc acetate dehydrated was first dissolved in ethanol at room temperature (concentration: 0. 6 M). The solution was subjected to reflux for 3 h and then triethanolamine (Merck, 99%), in a molar ratio to zinc acetate of 6:5, was added as stabilizer. The solution was stirred at 60 ° C for 30 min to yield a clear and homogeneous solution which served as the precursor solution. At this stage, it was observed that the times needed to get the appropriated coating solution were not too long as those involved in the traditional sol–gel procedure (sometimes more than 24 h) [13]. The chemical reaction to prepare the precursor solution using the polymeric precursor method may be described as follows:



Firstly, a zinc hydroxide is formed which transforms into ZnO after heat treatment at 500 ° C as it is described below. The heat treatment led to complete evaporation of the solvents and removing of organic residuals allowing thus an optimal adherence of the film to the substrate. Previous to the coating, the glass substrates were treated with a standard wet cleaning procedure. The ZnO films were prepared from the precursor solution using the spin-coating method. After setting the glass substrate on the disk or the spin-coater, the coating solution (approx. 0.2 ml) was dropped and spin-coated with 200 rpm for ~20 s in air. This process made a precursor film on the substrate. The precursor film was then air dried at 80 °C for 10 min in an electric oven and then annealed to 500 °C for 20 min. This ZnO film-making process was repeated several times (2, 4, 10 and 12 times) obtaining ZnO films with different thicknesses (the thickness of a single layer amounted to ~80 nm, as verified by transversal section SEM analysis and RBS spectroscopy).

The crystal structure of the as-prepared ZnO films was analyzed by X-ray diffraction (XRD) measurements with Cu *K*α radiation in a standard θ-2θ configuration at room temperature. The composition and thickness of the films were determined by Rutherford backscattering spectrometry (RBS) with 2 MeV $^4He^+$ beam in random geometry. Microstructure morphology was analyzed by atomic force microscopy (AFM). The optical absorption spectra were measured using an ultraviolet–visible (UV–VIS) spectrophotometer (Perkin-Elmer) at room temperature.

3. Results and discussion

Fig. 1 (a) shows the XRD pattern measured on a representative ZnO film formed by 10-cycle (~1000 nm) spin-coating of zinc acetate films on a glass substrates. The pattern reveals that the film is polycrystalline with no additional peaks corresponding to any secondary crystalline phase. The crystal lattice parameters were obtained by Rietveld refinement (open symbols) and ended up being $a = 3.2508$ Å and $c = 5.2059$ Å. For a ZnO film formed by twelve ZnO single layers, the *c*-lattice parameter resulted to be 5.2069 which corresponds to the c_{bulk} reported for ZnO (JCPDS card No. 36–1451). Evidence of the improvement of the crystalline quality of the ZnO films with increase in the film thickness is provided by the XRD-pattern presented in Fig. 1 (b). Here, the main peaks of two films with thicknesses equivalent to 10 and 12 ZnO single layers, along with the respective Rietveld refinements are shown. The diffractograms recorded on nano-sized ZnO

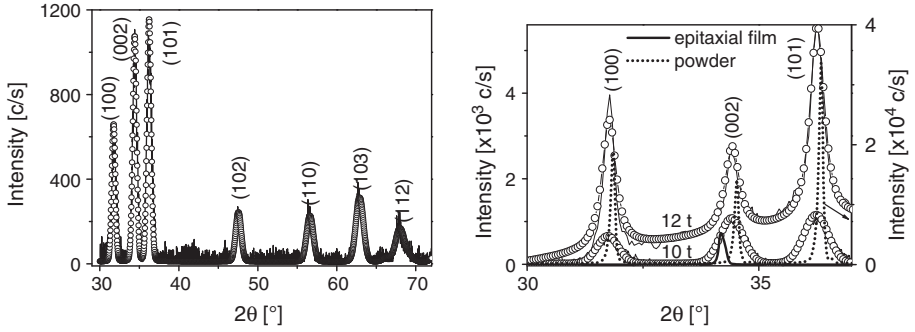


Fig. 1. X-ray diffraction patterns of ZnO films with different thickness on glass substrates (experimental data as solid line and Rietveld simulation as open symbols). The XRD diffractograms corresponding to an epitaxial ZnO film grown on a C-sapphire substrate by PLD and ZnO powder synthesized by Pechini's method are also plotted for comparison.