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# Influence of substrate on structural, morphological and optical properties of ZnO films grown by SILAR method

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**Abstract. ZnO films were obtained by successive ionic layer adsorption and reaction (SILAR) method from four different substrates: glass microslides, corning glass, quartz and silicon with and without oxide layer. For films deposition, a precursor solution of $ZnSO_4$ was used, complexed with ammonium hydroxide. Prior to the film deposition, wettability of the substrates was analysed using a CCD camera. It was found that the Si without the oxide layer substrate shows hydrophobic behaviour, which makes the films less adherent and not uniform, while in the other substrates, the behaviour was optimal for the growing process. ZnO films grown on glass microslides, corning glass, quartz and Si with oxide layer were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV–Vis techniques. According to the XRD patterns, the films were polycrystalline, with hexagonal wurtzite structure and the patterns mentioned showed significant differences in crystallite sizes, microstrain and texture coefficient with respect to the employed substrates. The morphology of the ZnO films constituted by rice-like and flower-like structures shows differences in form and size depending on the substrate. The UV–Vis spectroscopy results show that the substrate did not influence the band gap energy value obtained from films.**

**Keywords. ZnO; substrates; X-ray diffraction; scanning electron microscopy; SILAR.**

## 1. Introduction

Zinc oxide (ZnO) in powder, in bulk and in thin films has been widely studied due to the combination of its unique properties such as non-toxicity, good electrical properties, transparence in visible range, direct band gap, hardness, piezoelectric behaviour, chemical stability, abundance in nature and low cost. Among several metal oxide semiconductors, ZnO nanostructure has been identified as a potential material for future device applications like solar cells (Keis *et al* 2002), photo detectors (Liang *et al* 2001), transparent ultraviolet protection films (Saito 2002), gas sensor elements (Pizzini *et al* 1989) and light emitting devices (Srivastava *et al* 2007), among others.

Different methods have been used for ZnO thin films synthesis, including pulsed laser deposition (PLD) (Cao *et al* 2007), thermal evaporation (Shen *et al* 2005), spray pyrolysis (Saito 2002) and metal-organic chemical vapour deposition (MOCVD) (Egerton *et al* 2005). Chemical bath deposition (CBD) and successive ion layer absorption and reaction (SILAR) have been used by several authors (Ortega-López *et al* 2003; Gao *et al* 2004; Shinde *et al* 2005; Vargas-Hernández 2008) to produce good ZnO structures. These methods have attracted special interest because of their simplicity, low cost and capability to achieve large area coatings. They have also been used to obtain a large variety of semiconductor materials, as have been reported by Pawar (2011).

The research results on fabrication and application of ZnO films have proved the fact that their morphology plays a key role in their application for specific fields. Until now, a special wide variety of ZnO morphologies (complex structured films) have been grown using physical or chemical methods. Some studies related to morphology of ZnO thin films have been published and some of the reported structures are needles, tubes, flowers, stars, bars and strings, among others (Kim *et al* 2004; Shinde *et al* 2005; Villanueva *et al* 2006).

Although there are some studies related to the influence of the substrate temperatures on the structural properties of ZnO thin films, the real effect on the structural

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properties of the films related to the type of substrate has not been identified (Shan *et al* 2004; Rambu *et al* 2012). Recent results of ZnO thin films obtained by thermal oxidation of metallic Zn suggest a dependence of the nature of the substrate and the temperature of oxidation on the structural and electrical properties (Rambu *et al* 2012). The roles and effects of additives, the different condition of growth and the substrate types are established in order to develop ZnO films with high quality for devices with good performance. For example, the substrate in the emitting device structure has been found to be important on the surface plasmon (Cheng *et al* 2008). Besides, the degree of (0 0 2) plane orientation of ZnO films is directly related to the piezoelectric property, which is an important issue on related devices of surface acoustic wave (SAW) (Bai 2010).

The aim of this paper is to study the effect of four different and common types of substrate on the structural, morphological and optical properties of ZnO films grown by the SILAR method. The wettability study was conducted to determine the hydrophilic characteristics of substrates. XRD was used to observe changes within the crystalline structure, and SEM to identify how morphology changes with the substrate. Finally, UV–Vis was used to find whether the band gap changes as a result of different substrates.

## 2. Experimental

ZnO films were deposited by the SILAR process on four different substrates: glass microscope slides, corning glass, silicon (Bromont-Canada, 5 ohm-cm, 500 $\mu$m thickness) with oxide layer and quartz. Substrates were treated before deposition. For this, first, they were boiled in diluted sulfuric acid (1 : 10 v/v) for 1 h, then, ultrasonically rinsed in ethanol and acetone for 30 min, and finally stored in double-distilled water until use. The corning substrates were not treated in sulfuric acid to avoid chemical attack. Silicon substrates were treated as mentioned before, one of them was then submerged in a solution of diluted hydrofluoric acid ($HF : H_2O$ = 5 : 100) for 1 min to remove chemical and native oxides and to study its wettability characteristics.

The SILAR process used to obtain the films includes alternating by dipping the substrate in $Zn^{2+}$ source at room temperature and in hot water near the boiling point. Aqueous zinc sulfate solution (0·1 M) was used as source of Zn ions, which was made alkaline by addition of concentrated ammonia hydroxide (28%) in molar ratio of 1 : 10.

Glass substrates were successively immersed for 2 s in alkaline zinc sulfate solution so as to get zinc complex adsorbed onto the substrate. After 2 s of immersion of substrate into the hot $H_2O$, the reaction occurs at substrate surface to form ZnO. One hundred deposition cycles were conducted to obtain a visibly detectable and lustrous ZnO layer. After the growth process, the samples were air dried for 1 h and annealed in air at 200 °C for 2 h.

The experimental procedure was carried out by employing a stepper motor that provided a constant velocity for the sample immersion within the chemical baths. The system allowed the simultaneous growth of four samples under the same conditions. A commonly used procedure (Mitra *et al* 1998; Mitra and Khan 2006) has been automated to obtain the films; a detailed description of this experimental procedure to obtain ZnO films has been described in a previous paper (Jiménez-García *et al* 2010).

The contact angle was measured by using a CCD camera for each substrate in order to study the wettability of the substrates. The substrate was placed on a movable stage in front of the CCD camera. Drops of precursor solution were put onto the substrate using a vertical syringe; its volume was approximately 20 $\mu$L. Images of the drops were recorded with the CCD camera, on establishing the contrast, magnification and focal were set as well. The experiments were performed at room temperature (23 °C).

The structural characterization of ZnO films was carried out by XRD patterns, obtained in the range of the diffraction angle between 15 and 80°, with CuK$\alpha$ radiation by using a Siemens D5000 diffractometer ($\lambda$ = 1·5406 Å). An SEM model JEOL JSM-6060 LV (Japan) with energy of 15 kV was used to study the morphology of the samples. The chemical composition (semi-quantitative) of the thin films was obtained by means of an INCA Oxford-X-ray energy dispersive spectroscopy (EDS) to 20 kV. A spectrometer (double beam Perkin Elmer) was used to obtain the optical transmittance spectra. The measurements were done between 300 and 500 nm ($\lambda$). The same substrates (glasses and quartz) were used as a reference. All measurements were done at room temperature.

## 3. Results and discussion

### 3.1 *Wettability analysis*

Surface wettability is an important parameter to be controlled and modified because it involves the interaction between liquids and solids. Some applications include photo-activated self-cleaning and anti-fogging materials. The surface adsorption and hydrophilic/hydrophobic properties have to be carefully controlled to achieve optimal functionality (Hashimoto *et al* 2005). The wetting behaviour is characterized by the value of the contact angle $\theta$, a macroscopic parameter. If the wettability of the system increases, $\theta$ decreases and the interaction becomes hydrophilic, and vice versa. The contact angle is an important parameter in surface science and its measurement provides a simple and reliable technique for the interpretation of surface energies (Lokhande 2003).

The images obtained by the CCD camera serve to measure the contact angle of each substrate. These results