

Characterization of pure ZnO thin films prepared by a direct photochemical method

G.E. Buono-Core^{a,*}, G. Cabello^a, A.H. Klahn^a, R. Del Río^a, R.H. Hill^b

^a Instituto de Química, Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile

^b Department of Chemistry, Simon Fraser University, Burnaby, BC, Canada V5A 1S6

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Abstract

In this paper, amorphous ZnO thin films were obtained by direct UV irradiation of β -diketonate Zn(II) precursor complexes spin-coated on Si(100) and fused silica substrates. ZnO films were characterized by means of XPS, X-ray diffraction (XRD) and Atomic Force Microscopy (AFM). These analyses revealed that as-deposited films are amorphous and have a rougher surface than thermally treated films. Optical characterization of the films showed that these are highly transparent in the visible spectrum with an average transmittance of up to 95% over 400 nm, and an optical band-gap energy of 3.21 eV for an as-deposited film, and 3.27 eV for a film annealed at 800 °C. Low resistivity values were obtained for the ZnO films ($1.0 \times 10^{-2} \Omega \text{ cm}$) as determined by Van der Pauw four-point probe method.

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1. Introduction

Zinc oxide (ZnO), is a semiconducting and photoconducting material with a wide range of applications such as surface acoustic wave (SAW) devices, ultrasonic transducer devices, chemisorption gas sensors, mass-loading sensors and optical waveguides [1]. ZnO is a classical n-type wide band gap ($E_{\text{gap}} \sim 3.2 \text{ eV}$) semiconductor showing a variety of potential scientific and technological applications. ZnO thin films have been deposited by a variety of techniques such as spray pyrolysis [2–4], chemical vapor deposition (CVD) [5,6], sol–gel process [7–9], sputtering techniques [10–12], chemical spray [13], plasma enhanced CVD [14] and pulsed laser deposition (PLD) [15]. In general, good quality ZnO films are obtained when deposited

on heated substrates and annealed after deposition at high temperature in oxygen atmosphere. However, usually for commercial applications pure ZnO films must be prepared at much lower substrate temperatures. In the last few years, we have developed a simple photochemical method which has the advantage that good quality metal oxides thin films can be deposited at room temperature from simple precursor compounds [16–21]. In this method, thin films of inorganic or organometallic precursors upon irradiation are converted to amorphous films of metals or oxides, depending on the reactions conditions. The development of this method requires that the precursor complexes form stable amorphous thin films upon spin coating onto a suitable substrate and that photolysis of these films results in the photoextrusion of the ligands leaving the inorganic products on the surface.

In this paper we report the direct photodeposition and characterization of ZnO thin films on glass and

* Corresponding author. Tel.: +56 32 273176; fax: +56 32 273422.

E-mail address: gbuonoco@ucv.cl (G.E. Buono-Core).

Si substrates using β -diketonate complexes as source materials.

2. Experimental

2.1. General procedure

The FT-IR spectra were obtained with 4 cm^{-1} resolution in a Perkin Elmer Model 1605 FT-IR spectrophotometer. UV spectra were obtained in a Hewlett-Packard 8452-A diode array spectrophotometer. X-ray diffraction patterns were obtained using a D5000 X-ray diffractometer. The X-ray source was Cu 40 kV/30 mA. X-ray photoelectronic spectra were obtained in a XPS-Auger Model PHI 1257 at the Department of Physics, Universidad de Chile. Atomic Force Microscopy was performed in a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) in contact mode. Film thickness was determined using a Leica DMLB optical microscope with a Michelson interference attachment. Resistivity of the films was determined by the 4-point probe method using a Signatone S-301 4-point probe, a Keithley 2000 Digital Multimeter, and a Keithley 224 programmable current source. Films were annealed at $800\text{ }^\circ\text{C}$ for 2 h under a continuous flow of synthetic air in a programmable Lindberg furnace and allowed to return to room temperature slowly.

Solution photochemistry was carried out in 1 cm quartz cells, which were placed in a Rayonet RPR-100 photoreactor equipped with 254 nm lamps. Progress of the reactions was monitored by determining the UV spectra at different time intervals, following the decrease in UV absorption of the complexes. The solid state photolysis was carried out at room temperature under a UVS-38 254 nm lamp equipped with two 8 W tubes, in an air atmosphere.

The substrates for deposition of films were borosilicate glass microslides (Fischer, $2 \times 2\text{ cm}$) and p-type silicon(100) wafers ($1 \times 1\text{ cm}$) obtained from WaferNet, San Diego, CA. Prior to use the wafers were cleaned successively with ether, methylene chloride, ethanol, aqueous HF (50:1) for 30 s and finally with deionized water. They were dried in an oven at $110\text{ }^\circ\text{C}$ and stored in glass containers.

2.2. Synthesis of β -diketonate Zn complex

For the synthesis of the Zn complex, a modified procedure reported by Belford was used [22] using the commercial diketone 1-phenyl-1,3-butanedione (Aldrich). To 1.0 g (7.33 mmol) of ZnCl_2 dissolved in 3 ml of distilled water, is added in small portions with magnetic stirring, a solution of 2.38 g (14.67 mmol) of ligand (1-benzoylacetone), 4 ml of distilled water and 0.8 ml of 5 M NH_3 . The mixture is taken to pH 8–10 by adding 5 M NH_3 , after which a precipitate is formed. After stirring for one hour, the solution is filtered under reduced pressure. The crude product is recrystallized from ethanol to give a white powder (85% yield), m.p.: $105\text{--}109\text{ }^\circ\text{C}$; IR data (film): ν_{CO} 1592(s);

1561(s); 1512(s) cm^{-1} ; UV data λ ($\log \epsilon$) in CH_2Cl_2 : 324 nm (4.56), 252 nm (4.20), 232 nm (4.03). Anal: Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_4\text{Zn}$: C, 61.95; H, 4.68. Found: C, 61.90; H, 4.72.

2.3. Preparation of amorphous thin films

The thin films of the precursor complexes were prepared by the following procedure: A silicon chip was placed on a spin coater and rotated at a speed of 1500 RPM. A portion (0.1 ml) of a solution of the diketonate complex in CH_2Cl_2 was dispensed onto the silicon chip and allowed to spread. The motor was then stopped and a thin film of the complex remained on the chip. The quality of the films was examined by optical microscopy (1000x magnification) and in some cases by SEM.

2.4. Photolysis of complexes as films on Si (100) surfaces

All photolysis experiments were done following the same procedure. Here is the description of a typical experiment. A film of the diketonate complex was deposited on p-type Si(100) by spin-coating from a CH_2Cl_2 solution. This resulted in the formation of a smooth, uniform coating on the chip. The IR spectrum of the starting film was first obtained. The chip was then placed under a UVS 254 nm lamp. After the IR spectrum showed no evidence of the starting material, the chip was rinsed several times with dry acetone to remove any organic products remaining on the surface, prior to analysis.

3. Results and discussion

The electronic spectra of thin films of the Zn^{+2} β -diketonate complexes exhibited bands at 252 and 324 nm approx. The observed absorption bands have been assigned to the various electronic transitions, the band at 252 nm corresponding to LMCT transition (ligand-to-metal charge transfer) while the absorption at 324 nm being assigned to an intraligand $\pi \rightarrow \pi^*$ transition. Although the photochemistry of several transition metal 1,3-diketones has been extensively investigated [23–27], no reports can be found in the literature concerning Zn complexes. We therefore carried out experiments to evaluate the photosensitivity of the Bis(1-phenyl-1,3-butanodionate)Zn(II) complex in solution and as a film. When dichloromethane solutions of this complex were photolyzed with 254 nm UV light, a complete disappearance of the absorption bands of the complex could be observed after 110 min of irradiation (Fig. 1). This result demonstrates that the Zn diketonate complex is highly photoreactive in solution and that the photochemistry is initiated through the irradiation of the LMCT band at 252 nm.

In order to investigate the solid state photochemistry, films of the Zn complex were deposited on Si wafers by spin-coating and irradiated under air atmosphere with a

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