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Effects of the deposition condition on the microstructure and properties of ZnO thin films deposited by metal organic chemical vapor deposition with ultrasonic nebulization

Choon-Ho Lee *, Min-Seok Choi

Department of Materials Engineering, Keimyung University, 1095 Dalgubeol-daero, Daegu 704-701, Korea

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ABSTRACT

ZnO thin films were deposited on glass substrates by metal-organic chemical vapor deposition with ultrasonic nebulization at different substrate temperatures and source solution concentrations, and the effects of the deposition conditions on the microstructure and properties of the ZnO films were investigated. The deposition rate was controlled by the rate of the surface reaction at low substrate temperatures and by the rate of mass transfer of the reactants at high substrate temperatures. The transition temperature between the surface-reaction-controlled condition and the mass-transfer-controlled condition increased with increasing concentration of the source solution. The microstructure and crystallographic properties of the films were largely affected by the deposition conditions. The ZnO thin films grown under the surface-reaction-controlled conditions were composed of columnar grains with a plate–pillar structure and some open spaces between the columnar grains. The crystal direction of the grains was oriented randomly. On the other hand, under the mass-transfer-controlled condition, the ZnO films adopted a dense rock-like structure composed of very large grains, whose crystal directions were highly [001] oriented perpendicular to the substrate surface. The resistivity of the films depended mainly on the mobility of the charge carriers, which varied significantly with the microstructure. The resistivity of the films with the columnar structure was much higher than that of the films with the rock-like structure because of the open space between the columnar grains. The mean transmittance of the films in the visible range was more than 80%. The optical band gap of the films was approximately 3.3 eV.

1. Introduction

Thin films of pure or doped ZnO have attracted considerable attention because of its potential use in many piezoelectric or optoelectronic devices, such as surface acoustic wave filters, transparent electrodes, transparent transistors, and ultraviolet light emitting devices [1–6]. A range of deposition techniques have been used to deposit ZnO thin films, such as sputtering [7–9], atomic layer deposition [10], pulsed laser deposition [11], and metal-organic chemical vapor deposition (MOCVD) [12–14]. Among these methods, MOCVD is the most desirable method in practical use because it has many advantages, including high deposition rate, uniform deposition in large areas and high step coverage. Furthermore, the apparatus can be scaled-up easily for large area deposition. Until now, diethyl-zinc was used only as the Zn-source precursor in the deposition of ZnO thin films by chemical vapor deposition (CVD) because of its properties appropriate to the CVD source, such as an appropriate vapor pressure at low temperatures, thermal stability at the vaporizing temperature, and adequate difference between its vaporizing temperature and its decomposition temperature. Although Zn alkyl compounds, such as dimethylzinc and diethylzinc, satisfy these requirements, they are too reactive to be treated and are very expensive. The temperature dependence of the equilibrium vapor pressure is so high that it is difficult to transport their vapors at a constant rate via a carrier gas.

Recently, ZnO thin films were deposited on soda lime glass substrates at low substrate temperatures of 225–325 °C by MOCVD using an ultrasonic nebulization technique to carry the source precursor, where zinc acetylacetonate, which is not a suitable source material for normal CVD because of the small difference between its vaporizing temperature and decomposition temperature, was used as the Zn source precursor. Zinc acetylacetonate has a melting point of 136–138 °C and evaporates adequately above 190 °C. These properties make it difficult to carry the zinc acetylacetonate vapor to the substrate using a conventional bubbling technique via a carrier gas. On the other hand, zinc acetylacetonate is inexpensive and moderately stable in air, and soluble in many organic solvents. In the MOCVD used in this study, the source precursors were transported up to the vicinity of the heated substrate in the form of an aerosol of the solution containing the precursor that evaporated instantly upon exposure to the radiant heat from the heated

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* Corresponding author.
E-mail address: chl594@kmu.ac.kr (C.-H. Lee).

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substrate near the substrate. In these respects, zinc acetylacetonate is believed to be a good source precursor for the deposition of ZnO thin films by MOCVD with ultrasonic nebulization.

The thin films made by CVD have a range of microstructures depending on the deposition conditions, which affect the properties of the deposited films. A previous study [15] found that the microstructure of ZnO thin films was largely affected by the total gas flow rate, which controlled the deposition rate, and a variation of the microstructure was caused by the difference in deposition mechanism between the surface-reaction-controlled condition and mass-transfer-controlled condition. In this study, ZnO thin films were deposited by MOCVD using ultrasonic nebulization at different substrate temperatures and source solution concentrations, and the effects of the deposition conditions on the microstructure and properties of the ZnO films were examined.

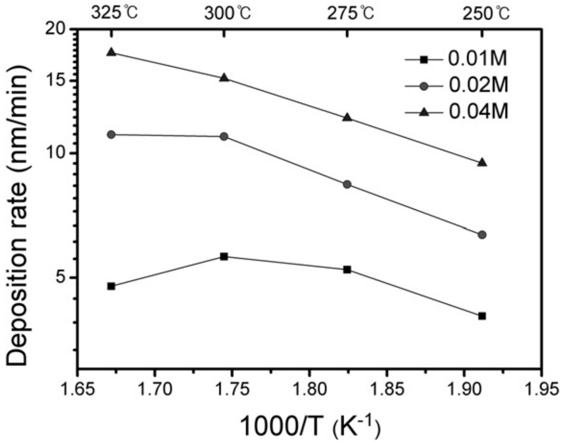

Fig. 1. Deposition rate of the ZnO thin films deposited with various concentrations of the source solution as a function of substrate temperature.

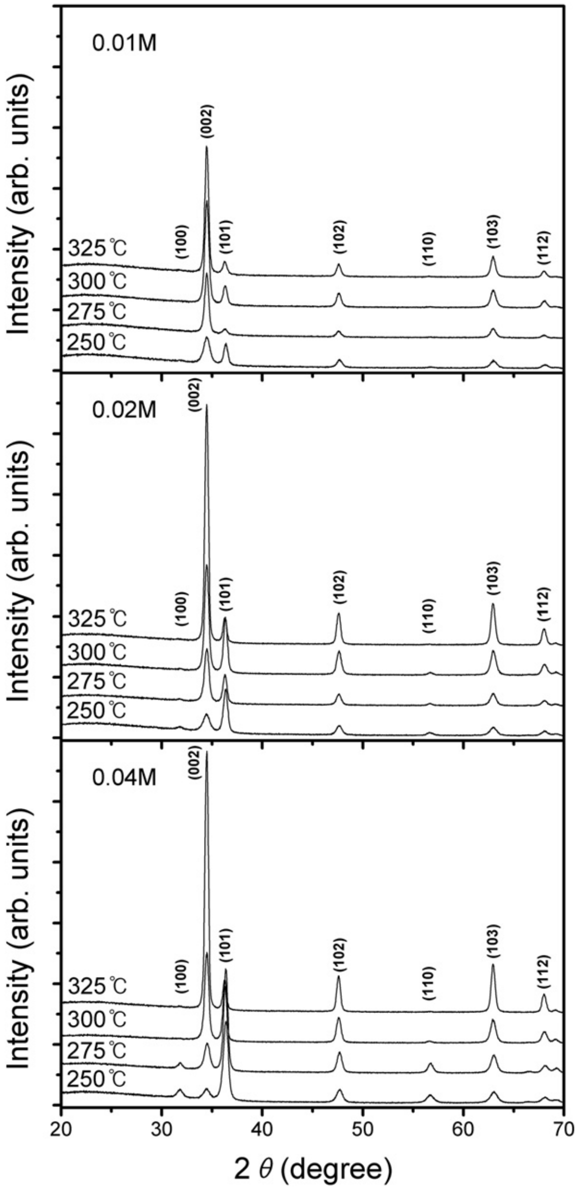

Fig. 2. X-ray diffraction patterns of the ZnO thin films deposited at various substrate temperatures with various concentrations of the source solution.

2. Experimental procedure

ZnO thin films were deposited by MOCVD using an ultrasonic spraying technique to carry the source materials. Details of this process and apparatus used are described elsewhere [16]. The reactor was made of quartz glass and was T-shaped. The substrate was attached to the substrate holder located on the upper side of the reactor in an upside-down posture. The glass substrate was heated by contact with a silicon wafer that was heated by the infrared radiation of halogen lamps. The substrate temperature was controlled by a K-type thermocouple located on the substrate surface and a precise control unit. The carrier gas containing a mist of the source solution, which was nebulized by an ultrasonic wave, flowed upwards to the substrate surface from a glass nozzle with a Φ 15 mm inner diameter.

The source solution was prepared by dissolving zinc acetylacetonate [$Zn(C_5H_7O_2)_2$] in a mixture solvent of 70 vol.% normal butyl alcohol and 30 vol.% butyl acetate. Soda lime glass (L.C.D. TEC), 3 cm × 3 cm in size with 0.7 mm thickness, was used as the substrates for ZnO thin film deposition after cleaning using an ultrasonic cleaner. All depositions were carried out at atmospheric pressure. Table 1 lists the deposition conditions.

The crystallographic properties of the films were examined by X-ray diffraction (XRD, MPD, PANalytical) using Cu Kα radiation in θ-2θ mode. The morphological characteristics of the surface and fractured cross-section of the films were examined by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800) with an operating voltage of 3.0 kV. The electrical resistivity, charge carrier concentration and Hall mobility of the films were measured using the Van der Pauw method (Ecopia, HMS-3000). The optical transmittance was measured using a spectrophotometer (Varian Inc., Cary500) over a wavelength range of 200–800 nm.

3. Results and discussion

Fig. 1 shows an Arrhenius plot of the deposition rate of the ZnO thin films deposited with various concentrations of the source solution. In the case of 0.04 M, the deposition rate showed a rapid increase with increasing substrate temperature over the entire range of substrate temperatures. In the case of 0.02 M and 0.01 M, however, the deposition rate showed a rapid increase only at the low temperature region and the deposition rate changed slightly with increasing substrate temperature

Table 1
Deposition conditions of ZnO thin films.

Concentration of source solution	0.01–0.04 M
Substrate temperature	250–325 °C
Total gas flow rate	7 l/min
N_2 gas flow rate	5 l/min
O_2 gas flow rate	2 l/min
Flow rate of mist solution	0.5 ml/min