



Growth behaviors and film properties of zinc oxide grown by atmospheric mist chemical vapor deposition



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ARTICLE INFO

Article history:

Received 22 May 2014

Received in revised form 12 June 2014

Accepted 18 June 2014

Available online 26 June 2014

Keywords:

Mist CVD

ZnO

Thin film transistor

Atmospheric pressure

ABSTRACT

We evaluated the characteristics of ZnO grown by atmospheric mist chemical vapor deposition at temperatures ranging from 200 °C to 300 °C as a function of the water in the solvent. We also utilized ZnO thin films as an active layer of thin film transistors (TFTs) using the mist CVD process. The mobility measured in the thin-film transistor (TFT) increased with increasing water concentration in the solvent and increasing temperature. We believe that the fact that hydrogen is incorporated in ZnO due to the function of water in the solvent plays an important role in determining the transistor characteristics. The higher deposition temperature functions to increase oxygen vacancies which influences the mobility.

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1. Introduction

ZnO is a cheap and non-toxic material with excellent electrical properties. ZnO is applied as an n-type active semiconductor because of its wide band gap (~3.3 eV), large exciton binding energy (60 meV at room temperature), and high mobility. Its electrical conductivity is mainly due to oxygen vacancies or excess zinc at the interstitial position. Zinc oxide films exhibit a combination of interesting piezoelectric, electrical, optical and thermal properties, and are applied in the fabrication of a number of devices, including gas sensors [1], transparent electrodes in solar cells [2], light-emitting diodes [3], and the oxide semiconductor of thin film transistors (TFTs) [4]. Among the applications, ZnO-based oxide semiconductor has been already adopted as an active layer for active matrix liquid crystal displays (AMLCDs) and active matrix organic light emitting diodes (AMOLEDs) due to high mobility and low cost. Furthermore, the high transparency of ZnO-based oxide semiconductor could make the opportunity to the next generation of applications, including “flexible” and “see-through” display [5].

In recent years, various techniques have been used to deposit ZnO films, such as pulsed laser deposition [6], RF magnetron sputtering [7], chemical vapor deposition [8], ALD [9] and sol–gel processes [10]. Among the preparation techniques of ZnO films, the sol–gel process has become increasingly popular in recent years, because it has advantage of being an inexpensive, non-vacuum, and easy to

operate process. Various sol–gel processes involve spin coating [11], dip coating [12], spray pyrolysis [13], and mist CVD [14]. The weaknesses of spin coating and dip coating include non-uniformity and wrinkles resulting from spin speed imbalance or the viscosity of the solvent. Among several sol–gel processes, mist CVD and spray pyrolysis do not need a viscous solvent but require solubility of the precursors. Spray pyrolysis and mist CVD are different methods which generate aerosols. The aerosols consisting of small solvent drop, produce the films. Spray pyrolysis generates aerosols by pressure and mist CVD makes aerosols by ultrasound. The difference resulting from these methods is the aerosol size where aerosol produced by spray pyrolysis is larger than that from mist CVD by a factor of 10–1000. As a result mist CVD has the advantage of good uniformity.

The mist CVD process is a combination of spray pyrolysis and chemical vapor deposition. It uses solutions of constituent elements without a significant viscosity as the metal sources. The solutions are ultrasonically atomized, and produce aerosol or mist particles. For the growth of thin films, mist particles made by ultrasonic are transferred to the reactor by a carrier gas [15] (Fig. 1). The mist particles transferred to the reactor are decomposed on the substrate by heat energy. Then, the decomposed particles are oxidized to metallic oxide. The advantages of this process are that it is inexpensive, a non-vacuum process and easy to operate. Therefore, the mist CVD process offers the possibility of large-area deposition at a low cost. In earlier studies, ZnO, SnO [16], and TiO₂ [17] were produced using mist CVD. Only ZnO thin films were applied in solar cells [18].

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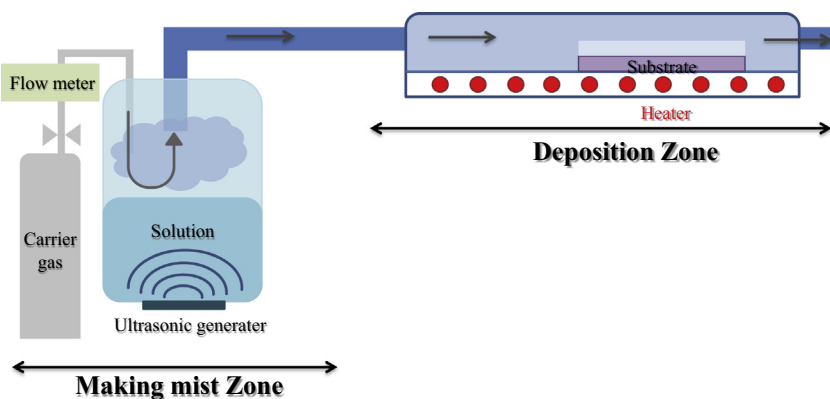


Fig. 1. Diagram of the mist CVD process.

In this paper, the electrical, physical, optical, and chemical properties of ZnO produced using a mist CVD process were investigated. The variables adjusted were the water concentration in the solution (0, 0.5, 1 vol%) and deposition temperature (200–300 °C). The ZnO thin films were applied as the active layer of thin film transistors (TFT). With increasing water concentration, the mobility of the ZnO films increased from 0.00016 cm²/V s to 0.02 cm²/V s at 200 °C.

2. Experimental

We used a mist CVD process to fabricate ZnO thin films. Fig. 1 shows a schematic of the mist CVD process. Mist CVD is composed of two zones, the making mist zone and the deposition zone. Each zone is important for controlling the deposition. The first zone is the making mist zone which consists of the mist generating system containing the liquid source and misted aerosol carrying system which uses air as the carrier gas. The second zone is the heating zone in which the misted aerosol is pyrolyzed in a reactor maintained at 200 °C.

ZnO thin films were deposited using the mist CVD process on a heavily p-type doped silicon substrate with a thermally grown SiO₂ layer which had a thickness of 100 nm. The source was zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O), and the dissolved solvent with a concentration of 15 mM. We prepared two types of solvent: 1) pure methanol (CH₃OH) and the methanol and deionized water mixture (0, 0.5, 1 vol%). The carrier gas which transfers the mist particles was N₂ at a flow rate of 5000 standard cubic centimeters per minute (sccm). The ultrasonic generator used to make the mist particles was operated at 1.5 MHz. The substrate temperature was varied in the range of 200–300 °C.

To analyze the thickness of the ZnO thin films, spectroscopic ellipsometry (SE, Elli-SE(UV)-FM8) was performed. The thickness of the ZnO layers for the TFT and analysis was approximately 20 and 40 nm, respectively. The surface morphologies of the films were examined by atomic force microscopy (AFM). The structures and chemical states of films were analyzed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. The optical properties of the films were measured using an ultraviolet–visible spectrophotometer and ellipsometer spectroscopy. The electrical properties of the devices were analyzed using a HP 4155A semiconductor parameter analyzer in a dark room under ambient conditions. The channel width and length were 100 and 50 nm, respectively. A highly doped Si substrate was used for the gate, and thermally oxidized SiO₂ (100 nm) was used for the gate insulators.

The TFT parameters such as field effect mobility (μ_{FE}) and sub-threshold voltage swing (S.S) are extracted by the following equations:

$$I_{DS} = \frac{\mu_{SAT} C_i W}{2L} (V_{GS} - V_{th})^2 \quad (1)$$

$$S = \left[\frac{d \log_{10} I_{DS}}{dV_{GS}} \right]^{-1} \quad (2)$$

where C_i , W , and L are the capacitance of the gate insulator per unit area, the channel width, and the length, respectively.

3. Results and discussion

Fig. 2(a) shows the growth rate as a function of the water concentration in the solvent at a substrate temperature of 200 °C. The growth rate decreased with increasing water concentration

in the solvent. We believe that this is due to difference between the growth rates of ZnO and Zn(OH)₂. At a water concentration of 1.5 vol% in the solvent, the solution becomes cloudy due to undesired ion reaction in the solution. The cloudy solution was not used for this work because of its heterogeneous concentration. Also, the ZnO film was not deposited with a higher water concentration solvent (pure water, 100 vol%). Fig. 2(b) shows the growth rate as a function of the substrate temperature. Here, the water concentration in the solvent was 0.5 vol%. The growth rate decreased at lower temperatures. At a deposition temperature of 200 °C, deposition is difficult because of the low growth rate. Chemical vapor deposition is a typical deposition method using thermal decomposition. Thus, the growth rate of the thin film at high temperatures is larger than at low temperatures because high temperatures accelerate the thermal decomposition reaction of the reactant. In other words, low temperature slows down the reaction among the reactants.

Fig. 3 shows the film morphology grown at 200 °C as a function of water concentrations (in the solvent): (a) 0 vol%, (b) 0.5 vol%, and (c) 1 vol%. The rms (root-mean-square) roughness values were 0.592 nm, 0.845 nm, and 0.951 nm, respectively. The sample prepared without DI water in the solvent shows a smooth surface compared to the samples made with DI water in the solvent. The increase in the roughness of the ZnO thin films may originate from an increase of the crystallinity. This was confirmed by the XRD patterns shown in Fig. 4, where the sample prepared with 0 vol% DI water is relatively less crystallized compared to the films fabricated with 0.5 vol% and 1 vol%. In addition, the rms roughness values of ZnO films deposited at 250 °C and 300 °C are 1.039 nm and 1.287 nm, respectively. The surface roughness increased from 200 to 300 °C, which is also related to the growth of crystallinity.

Fig. 4 shows the X-ray diffraction (XRD) peaks of the ZnO film. In Fig. 4(a), the (002) peak of the ZnO films and the (002) peak of the Zn(OH)₂ films appeared with an increase of the water content in the solvent. In the solvent, Zn ions exist in Zn–OH or Zn–(OH)–Zn forms [19]. Water in the solvent interrupted the production of ZnO from Zn(OH)₂. Therefore, the samples with DI water in the solvent have more Zn(OH)₂ than the sample without DI water. In Fig. 4(b), the (002) peaks of the ZnO films and the (002) peak of the Zn(OH)₂ films are observed in the XRD measurements. The (002) peak of the ZnO films becomes very strong while on the other hand, the (002) peak of the Zn(OH)₂ films disappears as the growth temperature was increased from 200 to 300 °C. At lower temperatures, the films tended to contain Zn(OH)₂ rather than ZnO. At high temperatures, it is easy to change Zn(OH)₂ to ZnO and H₂O or H₂.

The X-ray photoelectron spectroscopy results revealed the presence of Zn and O without other elements demonstrating that the

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