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Zinc oxide (ZnO) grown on flexible substrate using dual-plasma-enhanced metalorganic vapor deposition (DPEMOCVD)

Po-Hsun Lei *, Hsiang-Ming Wu, Chia-Ming Hsu

Institute of Electro-Optical and Material Science, National Formosa University, No. 64, Wunhua Rd., Huwei, Yunlin County 632, Taiwan

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ABSTRACT

This study investigates the temperature dependence of zinc oxide (ZnO) grown on polyestersulfone (PES) flexible substrates using the dual plasma-enhanced metal–organic chemical vapor deposition (DPEMOCVD) system. The proposed method uses a direct voltage (DC) and radio-frequency (RF) plasma system. The group-VI precursor, oxygen (O_2), can be completely ionized by the DC plasma system. The effect of optimal DC plasma power on ZnO thin films is thoroughly investigated using X-ray diffraction (XRD). The experimental results indicate that the crystalline structure and optical and electrical properties of ZnO thin films grown on PES substrates are dependent on the deposition temperature. The optimum deposition temperature for ZnO thin films deposited on PES substrates is 185 °C, whereas the DC and RF plasma power is 1.8 W and 350 W, respectively. Additionally, the wettability characteristic regarding the UV irradiation time was assessed by measuring the water contact angle. Under the UV irradiation for 60 min, the ZnO film grown at 185 °C represents a low contact angle of 5°, which approaches to a superhydrophilic surface.

1. Introduction

Zinc oxide (ZnO) with its wide bandgap and a large exciton binding energy at room temperature has attracted much attention because of its high conductivity, good optical transmittance, high thermal stability, abundance, and low-cost fabrication [1–4]. Due to these desirable properties, ZnO is a versatile material with excellent properties and highly useful in various applications such as gas sensor [5], field emitter [6], solar cells [7–9], light-emitting diodes [10,11], laser diodes [12], thin film-transistor liquid crystal displays (TFT-LCD), cell phones, personal digital assistants (PDAs), smart cards, and the future “electronic paper” [13–16]. For these applications, flexible or plastic substrates are useful as compared with conventional substrates due to its lighter weight, and lower cost. Several flexible substrate materials including polycarbonate (PC), polyarylate (PAR), polyestersulfone (PES), polyimide (PI), and polytetrafluoroethylene (Teflon) are used in these applications [14,17,18]. Some methods or technologies applied to fabricate ZnO films, such as sputtering deposition [19,20], molecular beam epitaxy (MBE) [21], pulsed laser deposition (PLD) [22], thermal CVD [23,24], metal–organic chemical vapor deposition (MOCVD) [25], atomic layer deposition (ALD) [26] and plasma-enhanced MOCVD (PEMOCVD) [27,28]. Among these techniques, sputtering deposition, PLD, ALD, and PEMOCVD can be used to fabricate ZnO films at a low growth temperature to avoid deformation of the flexible substrate. Excellent ZnO films can be achieved through sputtering technology, but the crystalline orientation of as-grown ZnO films is random, resulting in a low transmittance and high resistance. A (002) orientation ZnO film can be deposited using PLD and ALD systems. However, these technologies are inadequate for high throughput and large-area displays due to the low growth rate. The PEMOCVD system demonstrates a number of key advantages, including high growth rate, large area uniformity, low growth temperature, conformal, and easy integration within the preparation scheme of a complete device. Low-temperature-grown ZnO films with superior electrical and optical characteristics can be deposited on hard substrate by appropriate plasma power, but the reports about the ZnO films grown on flexible substrates are rare. In addition, substrate heating caused by ion bombardment effect in conventional PEMOCVD system can result in deformation of the flexible substrate. This study presents a modified PEMOCVD system with two plasma systems, including a RF plasma system and a DC plasma system to reduce the ion bombardment effect, low dissociation of oxygen (O_2), and growth temperature. The electrodes of a RF plasma system were parallel to the normal substrate in a DPEMOCVD system to alleviate the ion bombardment effect. The DC plasma system was used to enhance the dissociation of O_2. In addition, the deposition temperature is significant to ZnO thin films grown on PES. To avoid deformation of the PES substrate, the deposition temperature is maintained below 200 °C in this study.

The surface wettability of the ZnO film coating on the flexible substrate is very important while ZnO film is used as the window layer. However, the research in these applications is rare against large amount of publications on surface wettability. The surface wettability

* Corresponding author.
E-mail address: pohsunlei@gmail.com (P.-H. Lei).

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of a solid is a vital characteristic of surface physical chemistry, which has significant value both in fundamental research and industrial applications [29]. It is mainly controlled by the surface energy and the surface roughness. Recently, UV-caused hydrophilic TiO_2 was discovered [30]. The UV-induced hydrophilicity of TiO_2 was attributed to the attachment of more hydroxyl groups onto the surface [30,31]. In addition, the UV-induced hydrophilicity is the property of the metal oxide with the band-gap wider than that of TiO_2 [32]. From this point of view, a hydrophilic ZnO surface caused by UV-irradiation can be obtained. The UV-induced ZnO represents the properties of photo-activated self-cleaning, anti-fingerprint, and anti-oxidation, which are demanded from ZnO as window layer. There are several reports about the hydrophobility and hydrophilicity of ZnO film especially for ZnO nanorod film [33–35] on the hard substrate such as glass substrate. The discussion of hydrophilicity of ZnO grown on flexible is rare. In the study, we discussed the UV-caused hydrophilic property of ZnO film grown PES at specific growth temperature through the measurement of water contact angle (CA) and analyzed the reduction of CA according to the hydroxyl groups measured from Fourier transform IR (FTIR).

2. Experimental details

The reaction of DEZn and O_2 for ZnO thin film growth is given by

$$Ar^{+} + O_2 + \mathbf{e} \rightarrow Ar^{*} + O + O^{*} \quad (1)$$

$$(C_2H_5)_2Zn + 14\ O^{*} \rightarrow ZnO + 4\ CO_2 + 5\ H_2O. \quad (2)$$

A high ionization rate for O_2 is very important to react to the DEZn completely, allowing a high-quality ZnO thin film with well-controlled stoichiometry to grow on the sapphire substrate. However, the ionization rate in conventional PECVD systems is very low, especially O_2 with strong bond energy. To enhance the dissociation of O_2 and increase the concentration of oxygen free radicals (O^{*}), the proposed DPEMOCVD system was used to grow ZnO thin film. Fig. 1 shows a schematic of the DPEMOCVD apparatus, including dual plasma systems including a DC voltage driven and a RF plasma system, gas delivery system, heating system, and vacuum system. In this dual plasma system, the oxygen free radicals ionized by DC voltage driven plasma system diffuse to the substrate, which is surrounded by a RF plasma system to reduce the recombination of oxygen free radicals during the growth process. Unlike a conventional PEMOCVD system, the electrodes of the RF plasma system are parallel to the substrate surface normal (Fig. 1). An automatic-matched network controls the RF power coupled to the chamber to maintain a constant power. The experiments in this study used a working pressure of 2.25×10^{-4} Pa. The substrate temperature, which was controlled by a PID-controlled resistive heater mounted on the back-side of the substrate holder to maintain the deposition temperature. The flow rates of DEZn and O_2 were 13 and 100 sccm, respectively. The growth rate of the ZnO films was about 140 A/min, and the thickness of the ZnO films in this study was approximately 200 nm. The crystalline structure of ZnO thin film was characterized by X-ray diffraction (XRD) patterns using a Bruker D8 advanced diffractometer equipped with a CuKα ($\lambda = 0.154$ nm). The surface morphology of ZnO thin films on PES was measured using an atomic force microscope (AFM) (D13100, Digital instruments Veeco Metrology Group). The transmittance of ZnO thin films in the visual range was measured using a UV–vis–NIR spectrophotometer (UVD-350). The static contact angle (CA) was measured according to the sessile drop method using a CA analyzer with deionized water. An external UV ($\lambda = 365$ nm) lamp was used to examine the effect of the photoinduced hydrophilicity of ZnO thin films grown on PES. The electrical properties including carrier concentration, carrier mobility, and resistivity were measured by Hall measurements (HMS-5000) at room temperature.

3. Results and discussion

Fig. 2(a) displays the X-ray diffraction (XRD) patterns of ZnO thin films grown on PES at the DC power of 0, 1.8, and 3.2 W while the deposition temperature is maintained at 185 °C. The XRD patterns indicate a hexagonal crystalline structure in the ZnO thin films grown with/without the DC plasma system. A weak intensity of the (002) plane was found at the DC power of 0 W, which is attributed to the low growth temperature [27,36] and incomplete O_2 dissociation due to the large bond energy of O_2. As DC power increases to 1.8 W, the intensity of the (002) plane increases recognizably. This can be ascribed to the free surface energy of semiconductors strongly depending on the hybridized orbit [37,38] and the crystalline tendency to orient toward the (002) plane due to the minimal free surface energy. By introducing DC plasma power, the active oxygen free radicals from the O_2 dissociation can be enhanced. Therefore, numerous adsorbed

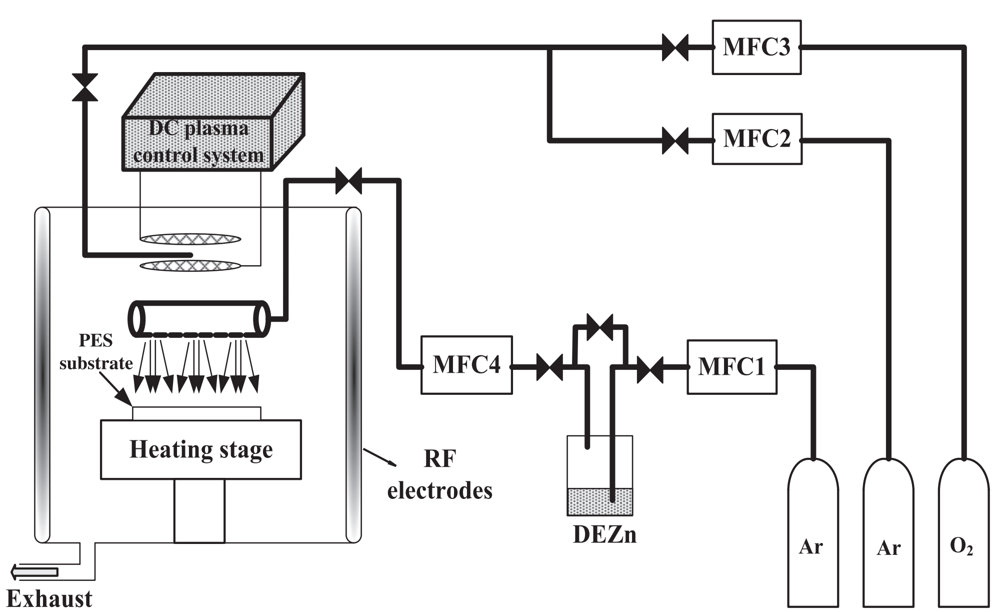

Fig. 1. A schematic of the DPEMOCVD system.