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Atmospheric plasma deposition of transparent semiconducting ZnO films on plastics in ambient air

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ABSTRACT

Transparent zinc oxide (ZnO) thin films have been successfully synthesized on poly (methyl methacrylate) (PMMA), polycarbonate (PC), and polyethylene terephthalate (PET) substrates by atmospheric plasma deposition in ambient air at room temperature. The structural, optical and electrical properties of the ZnO films as well as their adhesion to the polymer substrates were investigated for various deposition conditions. The film surface exhibited a dome-shaped topography comprised of nanometer-sized grains. The size of both the domes and the grains became larger as the plasma power increased. The visible transmittance increased above 95% with decreasing plasma power. The resistivity exhibited a wide variation in the range of 10^2–10^8 ohm cm. The adhesion energies to PMMA varied from 0.2 to 1.5 J/m^2 with increasing plasma power. While a finer grain structure achieved with lower plasma power was preferable for higher transmittance, it resulted in lower adhesion to the plastic substrates. The study demonstrated the feasibility of depositing semiconducting transparent ZnO films on polymer substrates at low temperature in ambient air using atmospheric plasma deposition.

1. Introduction

Zinc oxide (ZnO) has attracted considerable attention as a transparent conducting oxide and one of the candidate materials for indium tin oxide (ITO) replacement due to its high visible transmittance, low electrical resistivity with metal-dopants, and abundant Zn-based mineral sources [1,2]. While ITO is the most widely used conducting oxide, low temperature deposition severely deteriorates the quality of the films [3]. Low temperature deposition is particularly desirable for deposition on plastic substrates which is required for the fabrication of flexible and roll-to-roll polymer electronics.

While many studies of ZnO deposition on polymer substrates have been, all of the procedures require vacuum/inert gas process environments [3–7] or wet-chemical approaches [8,9]. For example, Al-doped ZnO films were deposited on polyisocyanate (PI) or poly carbonate (PC) substrates using radio frequency (RF) magnetron sputtering in argon [4,5]. The films exhibited an optical transmittance higher than 80% and a resistivity in the range of $\sim 4.1 \times 10^{-3}$ to 9.7×10^{-4} ohm cm. ZnO films have also been deposited onto polyethylene terephthalate (PET) substrates using a wet-chemical process and conditions for preparation of ZnO crystalline films in aqueous solutions were investigated at near ambient conditions [8]. Direct-current (DC) magnetron sputtering in argon was also applied to deposit ZnO or Al-doped ZnO onto PET substrates, and the optical and electrical properties have been reported [3,6]. Finally, ZnO films have been deposited on polyimide (PI) and polytetrafluoroethylene (PTFE) substrates by pulsed laser deposition in vacuum at room temperature with an optical transmittance above 80% and an

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electrical resistivity of 5.3×10^{-4} ohm cm [7]. To date, however, atmospheric plasma deposition of ZnO at low temperature in an ambient air environment on plastic substrates has not been demonstrated.

Atmospheric pressure plasma enhanced chemical vapor deposition is an emerging large-scale and cost-effective deposition technique, which utilizes cold plasma in glow discharge state for deposition [10]. A unique feature of the process is the capability to deposit a film under atmospheric pressure and especially in ambient air at low temperature. Several attempts to deposit ZnO films with atmospheric plasma and elevated substrate temperatures have been reported. These were achieved with a bis(dipivaloylmethanato)zinc precursor in a non-equilibrium cold plasma [11], a bis(octane-2,4-dionato)zinc precursor [12], and by using a 5% ethanol solution of zinc acetylacetonate with a DC arc plasmatron in open air [13]. The substrate temperatures needed were 140 °C, 100–250 °C, and 120–150 °C, respectively. Alternatively by creating an inert environment with helium, atmospheric pressure plasma deposition of ZnO was also reported and the effect of deposition conditions on the film resistivity and transmittance was investigated [14–16]. In a recent study, un-doped ZnO films were successfully deposited at atmospheric pressure and low substrate temperature of 200 °C, with high deposition rate of 7 nm/s. After post-deposition exposure to near-ultraviolet light, the films exhibited a very low resistivity of 1.6×10^{-3} ohm cm [17]. While these studies have demonstrated the feasibility of atmospheric plasma processing of ZnO films, deposition on polymer substrates in ambient air at low temperature has not been reported.

In this paper, we show that ZnO transparent thin films can be deposited onto polymer substrates by atmospheric plasma in ambient air at room temperature. Three different polymers, poly (methyl methacrylate) (PMMA), polycarbonate (PC), and polyethylene terephthalate (PET), were employed. The optical and electrical properties of the films were investigated and related to the film microstructure, composition, and process conditions. Undoped films with resistivity as low as $\sim 10^2$ ohm cm were achieved. Additionally, the adhesion energies of the films with the polymer substrates were evaluated. We show that the adhesion energies increased with plasma power.

2. Experimental procedure

2.1. Film deposition

An atmospheric pressure plasma deposition system with a 25 mm dia. cylindrical plasma source (Atomflo 400D system, Surfx Technologies LLC, Los Angeles, CA) was used to deposit the films. The deposition system employed radio frequency (RF) power to generate the plasma and also controlled the flow rate of the primary and secondary plasma gases. The plasma source was mounted on a three-axis stage to enable scanning over the substrate during deposition. The plasma was generated with 30 or 40 L/min of high purity compressed helium (99.995%). Diethylzinc (DEZ, 96%, Alfa Aesar Gmbh & Co., KG.) was selected as the precursor and stored in a bubbler. DEZ was vaporized at room temperature during deposition. The high purity helium was used as the dilution and bubbler gas in the precursor delivery system with a flow rate of 3.0 and 0.03 L/min, respectively. A schematic drawing of the deposition setup is shown in Fig. 1. The vapor pressure of DEZ can be calculated from the Antonie equation, $\ln P_v = A - B/(T_v + C)$, where P_v is vapor pressure (unit: Pa), T_v is temperature (unit: K), A, B and C are constants and reported as 21.77377, −3480.588, and −50.79704, respectively [18]. In this study, the DEZ vapor pressure is $\sim 2 \times 10^3$ Pa at 23 °C, the vaporizing rate is 23.7 μmol/min, and the Zn atom concentrations in the mixture of plasma and precursor gases are 4.3×10^{14} and 3.3×10^{14} -atoms/cm^3 for 30 and 40 L/min helium flow, respectively. The detailed calculation procedure can be found elsewhere [19].

Poly (methyl methacrylate) (PMMA, MIL P 25690), polycarbonate (PC, Makrolon® GP, Bayer Material Science AG, Germany), and polyethylene terephthalate (PET, Clear PETG, McMaster-Carr Supply corp, US), were used as substrates. The substrate dimensions were $70 \times 10 \times 6.5$ mm^3. The substrates were degreased using isopropanol before deposition. The distance between the plasma source to the substrate surface was 1.0 mm. Prior to deposition, the surface of the substrates were plasma treated by scanning the plasma source with a plasma power P of 20 W, helium flow rate of 30 L/min, a scan velocity of 100 mm/s, and a step size of 10 mm. After pre-treatment, the film was deposited with a single pass at a scan speed of 10 mm/s and step size of 0.3 mm. Three substrates were sequentially deposited.

In order to investigate the effect of plasma power, ZnO films were deposited onto PMMA substrates with various plasma power conditions (20–50 W). For comparison, films were also deposited without plasma (i.e. 0 W) using only flowing helium gas. Without plasma, film formation was expected to occur through reaction with water and oxygen due to the pyrophoric nature of DEZ [20]. Since the film deposition rate was substantially lower without plasma assistance, two passes were applied in this case. The deposition conditions are summarized in Table 1.

The temperature of the plasma gas was measured at the center of the plasma source outlet (Fig. 1) using a thermocouple (Model Bare-8-J-12, Omega Engineering Inc., US). The gas temperature stabilized 10 min after the plasma was ignited. The steady state gas temperature is plotted as a function of the RF power in Fig. 2. The local substrate surface temperature fluctuated under the plasma source during deposition and was much lower than the plasma gas temperature due to the plasma source scanning speed. The cumulative exposure of ~20 s for any location on the substrate surface did not result in any detectable heating. To study the substrate temperature effects on the film structure, some depositions were conducted by heating the substrates to temperatures of 68 or 87 °C during deposition.

2.2. Film characterization

Film thickness was measured by scanning with a surface profilometer (Veeco Dektak 150, Veeco Instruments

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