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 polysiocyanate (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 \(~4.1 \times 10^{-3}\) to \(9.7 \times 10^{-4}\) 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...
electrical resistivity of $5.3 \times 10^{-4}$ 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 $1.6 \times 10^{-3}$ 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 $\sim 10^6$ 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 Antoine equation, in $P_v = A-B/(T_v + C)$, 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 $4.3 \times 10^{14}$ and $3.3 \times 10^{14}$ 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 $\sim 20$ 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
Across a step created in the film by masking a small region of the substrate. X-ray Diffraction (X’Pert Materials Research Diffractometer, PANalytical, Inc., Netherland) was utilized to characterize the crystallinity of the films by mounting in a vertical sample stage. XRD spectra were collected using a step width of 0.01° and step time of 0.1 s with a 2θ range from 30.0° to 60.0°. The visible transmittance of the films was measured by a UV–Vis–NIR spectrophotometer (Cary 6000i, Agilent Technologies Inc., US). The average transmittance was calculated by averaging the values obtained for the wavelength in the range of 380–830 nm. The composition of the film was evaluated by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe, Physical Electronics Inc., US). Prior to the measurement on the film surface, ion sputtering was applied to remove contaminants from the air. The microstructure of the films was examined by atomic force microscopy (AFM, XE-70, Park system Inc., US) and scanning electron microscopy (SEM, Sirion XL30, FEI Co., Ltd., US). Resistivity of the samples was measured using a four-point probe technique (200 mm Probe Station, Cascade Microtech, Inc., US) with a semiconductor parameter analyzer (4156C, Agilent Technology, Inc., US).

### 2.3. Adhesion measurement

Double cantilever beam (DCB) tests were carried out to measure the adhesion energy, \( G_c \), of the ZnO films on the plastic substrates. Details of the procedure can be found elsewhere \[21,22\]. To prepare the test specimen, a beam with the same dimensions as the substrate was bonded to the top of the film with a thin epoxy layer (<2 μm). A metal loading tab was also glued on each side of the specimen. The specimen was mounted into an adhesion testing system (Delaminator v8.2, DTS company, US). The initial crack was introduced from the edge of the sample by applying a tensile load. The specimen was then loaded repeatedly in tension with a displacement rate of 1.0 μm/s until film debond extension and then unloaded. The fracture energy, \( G_c \), was calculated using the equation \[23\]:


\[ G_c = \frac{12P_c a^2}{B'E'h} \left(1 + 0.64 \frac{h}{a}\right)^2 \]  

where \( P_c \) is the critical load at which debond growth occurs, \( a \) the corresponding debond length, \( E' \) the plain strain elastic modulus of the substrate. \( B \) and \( h \) are the width and thickness of the substrate. The debond length \( a \) was obtained from the compliance of the unloading curve [23]. This procedure was continued until the debond length became longer than \((L-4h)\), where \( L \) is the length of the substrate. All tests were carried out in laboratory air environment at room temperature. Following mechanical testing, the fracture path was determined by XPS and AFM.

3. Results and discussions

3.1. Film morphology

ZnO films with thicknesses of 100–450 nm were successfully deposited by atmospheric plasma in ambient air on PMMA, PC, and PET substrates. A SEM image of the ZnO film deposited on the PMMA substrate is shown in Fig. 3(a). The film transparency decreased with plasma power above \( \sim 30 \) W. For example, the films deposited with a plasma power of 20 W and helium flow rate of 40 L/min (Fig. 3(b)) was highly transparent, while the film deposited with 40 W and 30 L/min helium (Fig. 3(c)) became whiter and less transparent. Typical XPS spectra of the films are shown in Fig. 4. The solid line is for the film deposited with a plasma power of 20 W and helium flow rate of 30 L/min and the dotted line for the film deposited without plasma assistance. Only peaks associated with Zn and O were apparent in both cases and the Zn:O atomic concentration ratio was \( \sim 1:1 \). The absence of noticeable amount of residual carbon suggests complete oxidation of DEZ during deposition even without plasma assistance. In an ambient air environment, DEZ reacts violently with water to form ZnO and ethyl alcohol [24], and follow a fast autocatalytic chain reaction with oxygen, resulting in complete oxidation [20].

The average deposition rate, \( R_d \), of the ZnO films grown on PMMA is shown as a function of the plasma power in Fig. 5. The solid circles are for a helium flow rate of 30 L/min and the open circle for 40 L/min. The deposition rate with the 30 L/min helium flow rate was almost constant from 20 to 50 W, indicating that the deposition process was limited by the available precursor species in the power range from 20 to 50 W, and that 20 W plasma can generate enough oxidative species for the given amount of precursor molecules.

Deposition with a higher helium flow rate of 40 L/min resulted in a lower deposition rate compared to the 30 L/min condition. The resulting films had the highest optical
transmittance as discussed in the next section. The deposition rate was strongly affected by the density of the excited helium species in the plasma and the residence time of DEZ molecules in the plasma afterglow region. The higher helium flow rate reduced the concentration of the excited helium species due to the limited amount of free electrons generated at a fixed power. Higher flow rates also shorten the residence time of the precursor molecules in the afterglow region thus lowering the sticking probability of DEZ to the substrate surface. The deposition rate was therefore lower with the higher 40 L/min helium flow rate. Without plasma assistance ($P = 0$ W), the deposition rate was also significantly lower. In this case, film growth was through oxidizing the precursor by ambient air in the gas phase and on the substrate surface, which had a much lower reaction rate than that in a plasma afterglow environment.

With a plasma power of 20 W and a helium flow rate of 40 L/min, an average deposition rate of 12–15 nm/min was obtained on the three PET, PC, and PMMA substrates (Fig. 6). The substrates had little effect on the film deposition rates and the quality of the resulting films.

SEM surface images of the ZnO films deposited on PMMA with different plasma conditions are shown in Fig. 7. The surface morphology of the films was strongly dependent on the plasma power. The film deposited without plasma assistance at room substrate temperature had a smooth surface at low magnification (Fig. 7(a)), although randomly distributed grains ($\sim$14 nm dia.) and pin holes were revealed in the higher magnification image (Fig. 7(b)). With plasma assistance, the films exhibited an equiaxed domed surface topography, with each dome comprised of smaller nanometer-sized grains. Both the domes and grains increased in size with increasing plasma power. At 20 W plasma power, the diameters of domes and grain were $\sim$150 nm and $\sim$16 nm, respectively (Fig. 7(c and d)), and they increased to $\sim$390 nm and $\sim$31 nm, respectively, at 30 W plasma power (Fig. 7(e and f)). The substrate temperature during deposition also showed a marked effect on the film morphology. By increasing the substrate temperature to 68 °C, the morphology of the film deposited at 20 W exhibited a larger grain size of $\sim$25 nm compared to the $\sim$16 nm size at room temperature (Fig. 7(c)) and the dome structure disappeared.

It is generally accepted that the film microstructure has a strong dependence on the thermal mobility of the depositing species and that a domed surface topology is typically formed due to limited surface diffusion when the ratio of the substrate temperature ($T_s$) to the melting point of the film ($T_m$), $T_s/T_m$, is less than 0.3 [25]. Under these conditions, the film also tends to have lower crystallinity with more defects or to be amorphous. In the present study, $T_s$ during deposition was in the range of 293–373 K and $T_m$ for ZnO is $\sim$2273 K resulting in $T_s/T_m$ of $\sim$0.13–0.16, so the domed morphology was expected.

XRD was used to study the crystallinity of the films. For the films deposited on room temperature substrates, no peaks were observed (Fig. 8(a)), indicating an amorphous structure. Increasing the plasma power did not result in any observable crystalline structure. On the other hand, with heated substrates of 68 and 87 °C (20 W and 30 L/min helium) during deposition, (100) and (101) wurtzite ZnO peaks appeared, indicating crystalline growth during film deposition (Fig. 8(b)). There was no obvious crystal orientation of the films compared to a powder diffraction reference. These results suggest that the substrate temperature is more important than plasma power in forming crystalline films. Although higher plasma power increased the gas temperature (Fig. 2), it had a limited effect on the substrate surface temperature due to the short exposure time. Directly heating the substrate was much more effective in increasing the mobility of surface species and promoting crystalline growth.

### 3.2. Film properties

#### 3.2.1. Optical transmittance

Optical transmittance spectra in the wavelength range of 380–800 nm for the ZnO films with thickness of 200–400 nm on PMMA are presented in Fig. 9(a) and the average transmittance $T_s$ is shown as a function of the plasma power in Fig. 9(b). The films deposited without plasma and with plasma assistance of 20 W exhibited a transmittance above 95% over the entire visible wavelength range. With increasing plasma power, the average transmittance decreased. Similar visible transmittance was observed for the films deposited on PC and PET. The optical properties of thin films are mainly affected by the film surface morphology and the optical energy band gap which depends on dopants and impurities [26]. In the present study, neither dopants were introduced, nor were impurities detected by XPS. Thus the surface roughness which was observed to change significantly with deposition conditions is the main cause of the marked reduction of the transmittance of the films deposited with higher plasma power. Fig. 10 shows the variation of transmittance $T_s$ as a function of the surface roughness $R_a$ (arithmetical mean roughness) evaluated by AFM. The transmittance decreased monotonically with increasing surface roughness. The films with smooth surface ($R_a < \sim$10 nm) exhibited the highest transmittance $T_s > 98%$. 

![Fig. 6. Deposition rates of the ZnO films on PMMA, PC, and PET with the plasma 20 W and 40 L/min helium flow rate.](image-url)
3.2.2. Film resistivity

The dependence of electrical resistivity $\rho$ on plasma power is shown in Fig. 11. The standard deviation of the resistivity measurements was only slightly larger than the size of the data symbols and is not included for clarity. Resistivity exhibited a wide variation from semiconducting ($\sim 10^2$ ohm cm) to insulating ($\sim 10^8$ ohm cm). We also found that the film resistivity varied significantly even for the same plasma power. For example, the resistivity of the films with a plasma power of 20 W was $\sim 10^2$–$10^7$ ohm cm. In the figure, the upper and lower bounds of the resistivity are indicated with dashed lines. The highest resistivity for each plasma power was in the range of $\sim 10^6$–$10^8$ ohm cm and those values increased with increasing plasma power. The lower bound of resistivity versus plasma power exhibited a minimum of $\sim 10^2$ ohm cm at 20 W, and increased up to $\sim 10^7$ ohm cm at 50 W. Without plasma assistance ($P = 0$ W), the films also exhibit a moderately high resistivity of $\sim 10^5$ ohm cm.

For the films deposited with an increased substrate temperature of 68 and 87 °C at 20 W plasma power and 30 L/min helium, the resistivity was $2.3 \times 10^2$ and $1.2 \times 10^7$ ohm cm, respectively, indicating that changing the microstructure of the film alone was not enough to reduce resistivity.

Film resistivity is inversely proportional to carrier concentration and their mobility. The carrier of un-doped ZnO is often explained by oxygen vacancies ($V_o$) and zinc interstitials (Zn$_i$). However, according to the first-principles calculations, oxygen vacancies form a deep donor and should not contribute to the conductivity of ZnO films [27,28]. Zinc interstitials can form shallow donors, but not stable at room temperature [27]. Instead, hydrogen impurities are suggested as an electron donor for the n-type conductivity observed in ZnO for various processes [28,29]. In the present atmospheric plasma deposition, hydrogen exists in the DEZ precursor and the laboratory air environment with a constant relative humidity level of $\sim 40\%$. It is likely that during film growth hydrogen impurities were incorporated in the films either at interstitial or substitutional sites [30].

The concentration of hydrogen impurity is sensitive to the concentrations of oxidative reactive species during deposition.
deposition. At low plasma power, the oxidative species concentration decreases, leading to more hydrogen impurities in the films. Thus, the upper and lower bounds of the resistivity decreased with decreasing plasma power from 50 to 20 W. However, the film deposited without plasma assistance exhibited a relatively high resistivity of $\sim 10^5$ ohm cm. This is due to the possible carbon remnants beyond the XPS resolution of $\sim 1$ atm.% and the high grain densities and pin holes in the film, both of which reduce the carrier mobility.

Low resistivity of $\sim 10^2$–$10^3$ ohm cm was observed in several films deposited at 20 W where low plasma power led to high intrinsic defect concentrations. The largest spread of resistivity was also observed at 20 W because the intrinsic defect concentration is highly sensitive to oxygen content in the deposition environment, as reported for several different deposition methods [26,27,29,31,32]. For example, a wide variation of resistivity versus oxygen partial pressure was reported for ZnO films deposited by RF magnetron sputtering [32], in which the film resistivity underwent an abrupt transition from semiconducting ($\sim 10^{-2}$ ohm cm) at low oxygen partial pressure ($\sim 10^{-6}$ – $10^{-5}$ torr) to semi-insulating ($10^6$–$10^8$ ohm cm) at higher pressure ($\sim 10^{-2}$ torr). Similarly, a marked increase of resistivity for hydrogen doped ZnO films was reported with increasing oxygen content during sputtering [27]. In the current study, the carrier concentration and mobility of the films deposited at 20 W are likely in the transition regime and thus their resistivity exhibited a large spread. Given the relatively high oxygen partial pressure of $\sim 160$ torr in this study, it is not surprising that a slight variation of the plasma or environmental condition can result in significant fluctuation of the oxidative reactive species concentrations and thus large spreads of film resistivity.

Other possible factors for the large spread of the resistivity may include an ageing effect whereby intrinsic...
dopants in un-doped ZnO films are not stable and can vary quite significantly with time [30], variation of the partial pressure of water or oxygen in the lab air, and even electrode contamination in the plasma source leading to trace amounts of unintended doping.

While we were unable to characterize the hydrogen content in the present study, future studies should address this and other important aspects of electrical conductivity. In addition, there are several possible avenues awaiting further studies to reduce the film resistivity. One avenue is to increase the carrier density by aluminum doping [16,30] with an aluminum containing precursor, nitrogen doping [30] using a nitrogen atmospheric plasma, or by post UV treatment to induce more intrinsic doping [17]. Another avenue is to increase the carrier mobility via grain size at elevated precursor delivery temperatures which has been shown to strongly affect the structure and properties of atmospheric plasma deposited silica [19] and polymer films [33]. Finally, further studies in the plasma power transition regime of 10–30 W with smaller incremental power steps and a lower minimal power may reveal conditions leading to lower resistivity films.

3.2.3. Adhesion energy

The adhesion energy, $G_c$, of ZnO films on PMMA substrates varied in the range of $\sim$0.2–1.5 J/m$^2$ and are presented as a function of the plasma power, $P$, in Fig. 12. The lowest value was obtained for the film deposited without plasma. The adhesion energy increased with increasing plasma power and the film deposited with $P = 50$ W exhibited the maximum value of $\sim$1.5 J/m$^2$. The relatively low adhesion values likely result from the weak dispersion interactions (van der Waals interactions) as well as interdigitation at molecular length scales between film and substrate as discussed below. No noticeable difference was apparent for the film deposited with higher plasma gas flow rate (40 L/min).

Optical images of the fracture surfaces on the substrate sides are shown in Fig. 13 for films deposited without plasma assistance (Fig. 13(a)) and with plasma of 20 W and 30 L/min helium flow rate (Fig. 13(b)). In the former case, adhesive failure at the interface between the ZnO film and the substrate was observed and no residual film was left on the substrate. In the latter case, a scattering of ZnO films remained on the substrate, indicating a mixed adhesive/cohesive failure. For the films deposited with plasma power above 20 W, mixed adhesive/cohesive failure was also observed. The ratio of cohesive to adhesive fracture area increased and the fracture surface became rougher at higher plasma power (Fig. 14), indicating enhanced adhesion.

The increase of film adhesion with plasma power likely results from three effects. Firstly, higher plasma power results in higher gas temperature and mobility of the reactive species on the surface, so that films with fewer defects at the interface are formed. In addition, increased van der Waals interaction between the film and the substrate occur along with increased interdigitation of the film and substrate at molecular length scales. Secondly, the films deposited with plasma assistance consist of nanometer-width grains as shown in Fig. 7 and the size increased with the plasma power. When a crack extends at the boundary of those grains in a mixed adhesive/cohesive failure mode, larger grains can enhance crack deflection, resulting in increased fracture energy. This explains the higher roughness of the fracture surface for the films with higher plasma power (Fig. 14). Finally, higher plasma power leads to more reactive species in the plasma gas. These reactive species can react with polymer substrate surfaces forming more polar groups and increasing the substrate surface roughness, both of which enhance the adhesion of film. We note finally that the lower adhesion of the ZnO film deposited without plasma assistance is consistent with the observation that PECVD coatings usually have better adhesion than the spray or sol–gel coatings deposited without effectively activating the substrate surface [33].

A comparison of the adhesion energies, $G_c$, for the ZnO films to the three different substrates, PMMA, PC, and PET, is presented in Fig. 15. All the films were deposited at 20 W and 40 L/min helium flow rate, the condition to achieve the highest visible transmittance. The adhesion energy was in the range from 0.2 to 0.75 J/m$^2$. The difference

![Fig. 11. Variation of resistivity of the ZnO films on the PMMA substrates as a function of the plasma power.](image1)

![Fig. 12. Adhesion energy of the ZnO films on the PMMA substrates as a function of the plasma power.](image2)
of the adhesion to the three substrates is only slightly out of the scatter of the data. The relatively low adhesion at the ZnO/polymer interface may be enhanced by plasma pre-treatment of the polymer substrate surface as we recently demonstrated for silica films deposited by atmospheric plasma [33]. Nevertheless, to the best of our knowledge, the current study is the first quantitative report of the adhesion energy of ZnO/polymer interface.

4. Conclusions

Transparent semiconducting ZnO films were successfully deposited by atmospheric plasma in ambient air at room temperature on PMMA, PC, and PET polymer substrates. XPS analysis confirmed the formation of ZnO and revealed no carbon residue in the films even without plasma assistance. Deposition rates of 25–30 nm/min were achieved with plasma assistance on the PMMA substrates and similar deposition rates were observed on PC and PET. The visible transmittance of the films varied from 40% to 98% and lower plasma power resulted in higher transmittance with smoother surface morphology. The resistivity was in the range of $10^2$–$10^8$ ohm cm for the films with plasma assistance and $10^5$ ohm cm for the film without plasma assistance. The adhesion energy varied from 0.2–1.5 J/m$^2$. Higher plasma power resulted in higher adhesion. The study demonstrated the feasibility of atmospheric plasma deposition of transparent semiconducting ZnO films on polymer substrates at low temperature in ambient air and reveals directions for future research to achieve lower resistivity with high visible transmittance.

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References
