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ALD Deposited ZnO: Al Films on Mica for Flexible Liquid Crystal Devices †

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Abstract: In this work, high performance Al-doped ZnO (AZO) films are deposited on transparent and flexible muscovite mica substrates by using Atomic Layer Deposition (ALD) technique. AZO/mica films possess high optical transmittance at visible and near-infrared spectral range and retains low electric resistivity, even after continuous bending of up to 1000 cycles. Based on the performed optical and electrical characterizations AZO films are implemented as transparent conductive electrodes in flexible Polymer Dispersed Liquid Crystal (PDLC) smart devices.

Keywords: transparent conducting oxides; ALD; PDLC flexible devices

1. Introduction

Among transparent conductive oxide materials, Al-doped Zinc Oxide (AZO) are very attractive because of their high thermal stability, good resistance to damage by hydrogen plasma and low fabrication cost, compared to the nowadays commercially available ITO (indium tin oxide) layers [1]. Generally, AZO films can be deposited by various methods as magnetron sputtering, pulsed laser deposition, metal-organic chemical vapor deposition at large temperature interval between room temperature and 300 °C [2].

ALD technique is a self-limiting deposition method characterized by exposing the growing film to alternating chemical precursors resulting in the sequential deposition of monolayers over the substrate surface [3]. The self-limiting nature of the vapor-solid reactions ensures pinhole-free coatings with a precise thickness controlled at the atomic scale and superb conformality onto large scale substrates [4].

Owing to the above benefits of ALD technique and high performances of AZO layers it is important to implement them onto flexible and transparent substrates. The current leading polymer materials for flexible applications as polyethylene terephthalate (PET), polyethylene naphthalate (PEN) and polyimide (PI) show several limitations as low processing temperature, lack of dimensional stability during processing and significant differences in the linear coefficients of thermal expansion (CTE) between the polymer substrate and conductive electrode layer [5]. At the

same time mica is a well-known natural transparent crystalline material, which possesses high flexibility due to its sheet/layered structure. Due to the weak van der Waals interactions between the adjacent layers, it is easy to peel off resulting in facile cleavage along the {001} planes [6]. Moreover, mica possesses excellent optical transmittance in the ultraviolet–visible-infrared range, high temperature stability (up to 600 °C for muscovite mica), high dimensional stability and low cost [7]. In addition, mica is elastic (Young's modulus of 200 GPa) and flexible, chemically inert, non-toxic and, more importantly is compatible with almost all deposition techniques. Based on all above, mica appears to be an ideal substrate for flexible opto-electronic device applications and wearable optoelectronics [8].

Recently, PDLC based structures have attracted increasing attention for applications in outdoor displays, switchable privacy glasses, energy saving windows, light shutters, projection displays, and so on. The conventional PDLCs use transparent ITO as electrodes and due to the brittleness of the ITO [9] the applications in flexible devices is limited. For flexible electronic devices, the transparent conductive electrode (TCE) is the most important material for determining the flexibility of the devices therefore several alternative TCEs have been developed.

Herein, we report the properties of AZO films synthesized by ALD technique on mica substrates and their implementation in flexible polymer dispersed liquid crystal (PDLC) smart devices. After deposition of AZO films on transparent mica, highly transparent and extremely foldable AZO electrodes were obtained, which displayed high optical transmittance and stable sheet resistance even after extreme bending for 800 cycles. Next, the fabrication of the flexible PDLC smart devices using AZO/mica foldable structures and working performances before and after bending tests are demonstrated.

2. Materials and Methods

AZO films were prepared by ALD using Beneq TFS-200 ALD system on mica substrates at a deposition temperature of 200 °C. In addition, AZO films were deposited on polyethylene terephthalate (PET) (100 μm) substrate used for references. The deposition temperature for AZO/PET was 100 °C. A preliminary buffer layer of Al_2O_3 (~15 nm) was deposited by ALD to prevent the interdiffusion between PET and AZO. Diethylzinc (DEZ, $Zn(C_2H_5)_2$), trimethylaluminum (TMA, $Al(CH_3)_3$) and deionized water (H_2O) were used as Zn, Al and oxidant precursor, respectively. Pure nitrogen was used as a carrier and purge gas at a flow of 600 sccm. The Al-doping of ZnO was controlled by varying the number of DEZ/H_2O and TMA/H_2O pulses in a standard for ALD process procedure [10,11]: on each 24 cycles of DEZ/H_2O, a cycle of TMA/H_2O was applied consisting one so-called supercycle. The precursors pulse durations were the same for DEZ, TMA and H_2O—200 ms, while the purging time after each precursor was 2 s.

The AZO film thicknesses were obtained by ellipsometric measurements using a Woollam M2000D (JA Woollam, Lincoln, NE, USA) rotating compensator spectroscopic ellipsometer. For AZO/mica the thickness was approximately 173 nm, while for AZO/PET the thickness was about 100 nm, respectively.

Crystal structures of AZO/Mica and AZO/PET were investigated by Powder X-ray diffraction patterns were collected within the range from 5.3 to 80° 2θ with a constant step 0.02° 2θ on Bruker D8 Advance diffractometer with Cu Kα radiation (1.54056 A) and LynxEye detector. Phase identification was performed with the Diffractplus EVA using ICDD-PDF2 Database. The surface topography and roughness of the as grown films were examined by atomic force microscopy (AFM) MFP-3D, Asylum Research (Goleta, CA, USA), Oxford Instruments (Abingdon, UK).

The optical transmittance spectra of AZO films in the wavelength range of 300 nm to 800 nm were measured at room temperature using an Ultraviolet-Visible-Near-Infrared (UV-VIS-NIR) spectrophotometer Cary 5E.

The sheet resistance was measured using four-point probe technique on Ossila apparatus before and after the bending test. The bending test was performed using a computerized home-built bending setup, with ESP301 control platform.

Based on the above characteristics, several AZO/mica films were selected for PDLC cells assembling. PDLC mixture was made by polymerization-induced phase separation method using UV-curable monomer NOA65 (Norland, $n = 1.524$) and E7 nematic liquid crystal (LC, Merck) at 30:70 wt.% ratio. The LC/monomer mixture was injected into an empty cell composed by two AZO/mica substrates separated with 12 μm Mylar spacer. Next, in order to polymerize NOA65, the cells were exposed with ultraviolet light ($\lambda = 365$ nm) with an intensity of 60 mW/cm^2 for 15 min at a temperature ~20 °C. As a result, the phase separation resulted to formation of randomly dispersed LC droplets in a polymer matrix, which determines the unique behavior of PDLC devices, discussed later on.

The electro-optical characteristics of fabricated AZO/mica PDLC devices were measured by He-Ne laser as light source and an applied root-mean-square (RMS) alternating current (AC) voltage at 1-kHz frequency. The transmittance was monitored as a function of applied voltage.

3. Results and Discussions

3.1. Structural and Morphological Properties

X-ray diffraction (XRD) patterns of AZO/mica and AZO/PET structures were shown at Figure 1a,b. The crystalline structure of mica allows the van der Waals epitaxial growth of oxide thin films [12]. The observation of only AZO (001) diffraction peaks on muscovite (00l) suggests the epitaxial nature of TCO thin films without other secondary phases (Figure 1a). In contrast the XRD pattern of AZO/PET shows mostly reflections from the PET substrates and weak (100) peak, (002) and (101) are not detectable, (110) was very weak presumably pointing to the inferior crystallinity of the low-temperature deposited AZO.

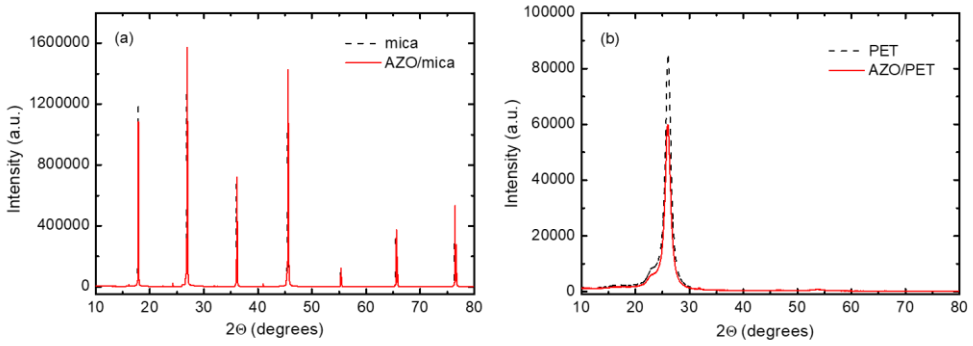

Figure 1. XRD of (**a**) AZO/mica and (**b**) AZO/PET structures.

The surface morphologies of mica and PET substrates and AZO/mica and AZO/PET films are presented in Figure 2. Freshly cleaved muscovite mica has very flat surface substrate- a prerequisite for growth of high quality AZO films. The root mean square (RMS) roughness values of blank mica and PET substrates as well as AZO/mica and AZO/PET films- as deposited and after bending test are shown in Figure 2. The surface roughness of the AZO/mica does not change significantly after bending testing. However, those of AZO/PET increased almost twice presumably due to the surface deformation during bending.

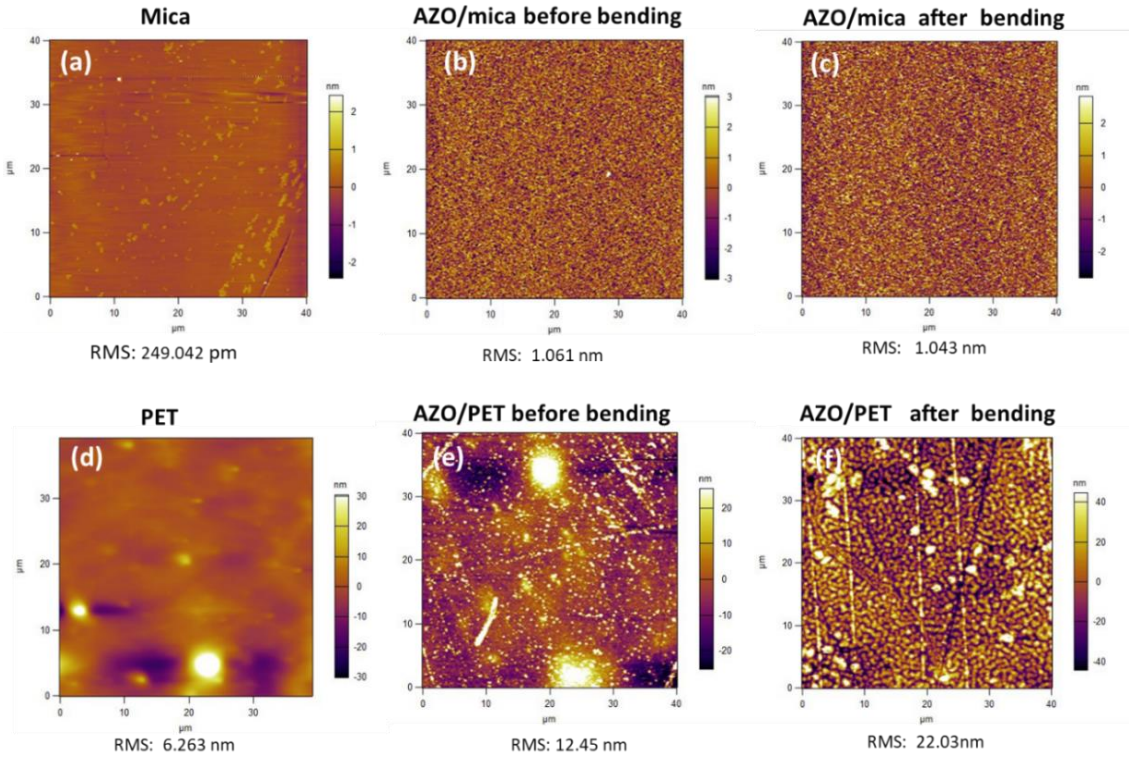

Figure 2. AFM images of (**a–c**) AZO/mica and reference mica and (**d–f**) AZO/PET and reference PET respectively.

3.2. Optical Properties

Transmittance spectra of AZO/mica and AZO/PET are shown at Figure 3. The spectra of blank mica and blank PET are also included for reference. As it is seen in comparison to blank mica and PET, the absorption edges of AZO/mica and AZO/PET are shifted to the longer wavelengths (red shift). The transparency of AZO/mica is higher than those of AZO/PET together with the benefit of improved conductivity.

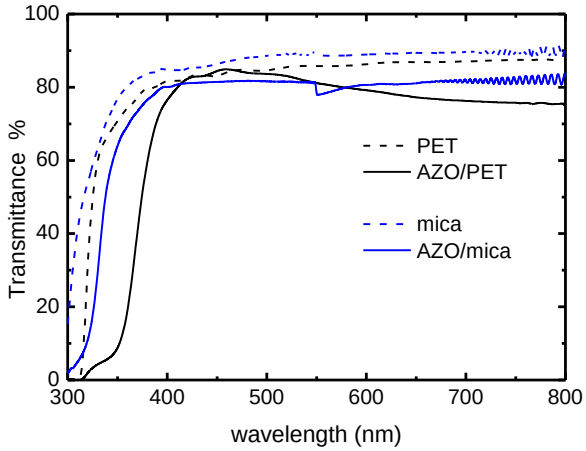

Figure 3. Transmittance spectra of AZO/mica and AZO/PET. Blank mica and PET spectra are also shown for reference.

3.3. Electrical Properties and Bending Test

AZO/mica remains its sheet resistance almost constant, even after continuous bending of up to 1000 times—see Figure 4, due to the unique layered structure of mica and flexibility of the AZO films.

The sheet resistance of AZO/PET monotonously increases with bending cycles. As shown above the RMS data of AFM suggested some deformations (cracks) during the bending test of AZO/PET causing probably breaks in the conductivity channels i.e., sheet resistance increase with bending cycles.

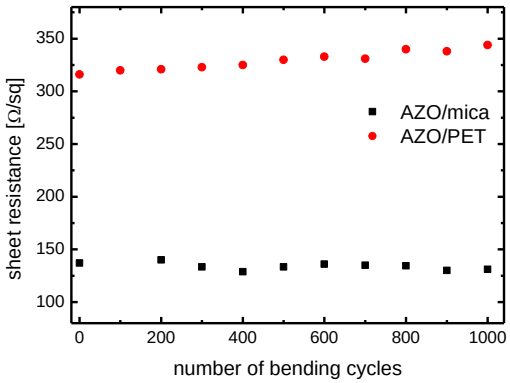

Figure 4. Sheet resistance dependence of the number of bending cycles for AZO/mica and AZO/PET.

3.4. AZO/Mica for Smart PDLC Devices

Based on the above performed optical and electrical characteristics, AZO/mica were selected for PDLC device assembly (Figure 5a). In general, PDLC structure can be switched between a light-scattering state and a transparent state by applying an external electric field, which results from mismatch or match of refractive indices between the LC molecules and the polymer matrix. The effect is due to the ability of applied voltage to re-orient the LC molecules inside the droplets in order to match the LC's refractive index to that of the polymer matrix. An optical setup and subsequent transmittance dependence of AZO/mica PDLC device as a function of the applied voltage are shown in Figure 5b. Without an applied voltage, the LC molecules are randomly oriented, which cause light scattering and as a result, the "diffuse" ("off") state appears. When the voltage is applied, the electric field forces the LC's nematic director to align along the direction of the electric field, allowing light to pass through the LC droplets. As a result, the "transparent" ("on") state appears.

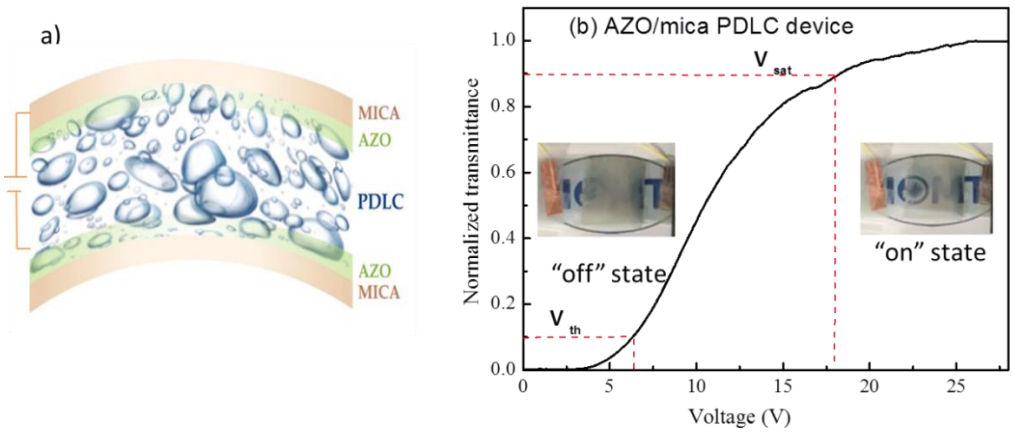

Figure 5. Schematic structure of: (**a**) AZO/mica PDLC cell and (**b**) Voltage-transmittance curve and image of AZO/mica PDLC device at "off" and "on" states.

4. Conclusions

In summary, we demonstrated a highly flexible smart device using PDLC and AZO/mica as transparent conductive film. Structural, optical properties and the sheet resistance stability after

bending of AZO/mica were systematically examined. Several flexible PDLC devices were successfully fabricated. The present results reveal the great potential for the integration of AZO transparent contacts on mica substrates into the next generation ITO-free flexible and stretchable devices.

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Conflicts of Interest: The authors declare no conflict of interest.

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