Development of ALD ZnO:Al as transparent conductive films

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Abstract. We report the deposition of ultrathin Al-doped ZnO (AZO) films by using atomic layer deposition (ALD) and results from X-ray photoelectron spectroscopy (XPS) and photoelectrical measurements. The AZO films were deposited on glass, silicon and polyethylene terephthalate (PET) substrates and their structural and photoelectrical properties were measured and discussed. Based on the results, selected AZO films deposited on PAT were implemented as transparent electrodes in a polymer dispersed liquid crystal display device (PDLC). The electro-optical modulation characteristics of these devices are comparable to those of devices using commercial ITO electrodes.

1. Introduction
The transparent conductive oxides (TCOs) are electrically conductive materials with low electromagnetic waves absorption within the visible region of the spectrum. They are used in a variety of applications, such as flat panel displays, thin film solar cells, light emitting diodes (LEDs), optoelectrical interfaces, touch screens, and automobile window de-icers and de-foggers. Indium tin oxide (ITO) is the most widely used transparent conductive oxide material; it has exceptional properties, such as low resistivity (\(\sim 10^{-4} \Omega \text{ cm}\)) and high transparency in the visible spectrum [1]. However, due to the indium scarcity ITO is an expensive material. A few material systems only offer simultaneously optical transparency and electrical conductivity, so that there is always a trade-off between these properties, which can be often tuned for specific applications. Highly-doped (degenerate) metal oxides, commonly known as TCOs, are the most widely used and studied transparent electrodes to date. The conventional TCO materials include tin-, zinc-, cadmium- and indium-based oxides (SnO\(_2\), ZnO, CdO, In\(_2\)O\(_3\)). Elements like Al, In, Ga, etc. could serve as a donor in the ZnO lattice and increase the bandgap width, which improves the electrical and optical properties of ZnO [2]. Designing new high-performance indium-free TCOs remains an important task in view of reducing the cost of the optoelectronic devices.

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Flexible displays are expected to play a key role in the next generation consumer electronics due to their lightweight and flexibility, which enables the fabrication on curved surfaces and transformed shapes. Thus, they show an enormous potential in mobile and wearable electronics, in foldable touch screens, paper-like displays, curved and flexible solid-state lighting devices. However, two main challenges are still remaining. First, new types of flexible substrates with mechanical flexibility, high optical transparency, low surface roughness and excellent bending capability, are in great demand. The second main challenge to flexible optoelectronic devices is the replacement of the brittle and expensive indium-tin-oxide (ITO) transparent conductive electrodes (TCEs) with other materials with similar performance and low cost. In addition to flexible substrates and TCEs, the design of novel device architectures is another crucial point in optimizing the device performance.

2. Experimental

Al-doped ZnO (AZO) thin films were deposited on silicon, glass and polyethylene terephthalate (PET) substrates at temperatures of 200 °C and 130 °C by ALD (Beneq TFS-200) using alternating pulses of Zn(C₂H₅)₂ (diethylzinc, DEZ), Al(CH₃)₃ (trimethylaluminum, TMA) and H₂O vapor in a N₂ carrier gas flow. The X-ray photoelectron spectroscopy (XPS) analyses were performed on a Kratos AXIS Supra spectrometer with a non-monochromatic Al X-ray source under vacuum better than 10⁻⁸ Pa at a 90 degree take-off angle. For the high-resolution analysis, the number of sweeps was increased, the pass energy was lowered to 20 eV at steps of 100 meV. The C1s photoelectron line at 285 eV was used for calibration of the spectra. The photoluminescence (PL) spectra of the films were measured at room temperature on a FluoroLog3-22 Spectrofluorometer (Horiba Jobin Yvon) with a double-grating monochromator and excitation in the range 200-950 nm.

For PDLC cell assembly on AZO/PET, first photo-curable adhesive (NOA65) polymer and liquid crystal (E7) were mixed at a 3:7 weight ratio. The mixture was injected using the capillary method. Finally, the cell was exposed to ultraviolet light (5 W UV lamp peak at 355 nm) for 15 minutes to polymerize NOA65. Copper tape wires were attached to the edge of the cell for electrical connections.

The light transmission of the PDLC/AZO/PET device was measured as a function of AC voltage (1 kHz) applied to the electrodes using a helium-neon laser (He-Ne) emitting at λ = 633 nm and a photo detector. The PDLC/AZO/PET cell was placed between a pair of apertures (since the polymer defines the LC molecules orientations, PDLC do not require the use of polarizers).

3. Results and discussions

3.1 X-ray photoelectron spectroscopy (XPS)

Figure 1 shows high-resolution XPS spectra of Zn 2p, O 1s and Al 2p for pure and Al-doped ZnO. The ZnO 2p peaks for pure ZnO are observed at binding energies of 1021.7 eV and 1045.0 eV, respectively, corresponding to the spin–orbit interaction of Zn 2p₁/₂ and Zn 2p₃/₂, which suggests that Zn in the samples only exists in a divalent oxidation state. The high symmetry energy peak of Zn 2p₁/₂ located at 1021.7 ± 0.1 eV is approximately equal to the value of Zn in bulk ZnO [3]. It indicates that Zn in AZO films exists in oxidized states. From figure 1c, the main peak located at 530.0 ± 0.1 eV is assigned to lattice oxygen bonded as O²⁻ ions in the ZnO matrix [4]. The energy peak of Al 2p₁/₂ is symmetric and is located around 74.5 ± 0.1 eV, which corresponds to the characteristic peak of Al₂O₃ [5].

Furthermore, the binding energies for the Al-doped ZnO samples are slightly shifted compared with the pure ZnO sample (from 1021.7 eV to 1021.6 eV for Zn 2p₁/₂, and from 1045.0 eV to 1044.8 eV for Zn 2p₃/₂) The chemical shifts of the binding energies reflects the electronic interaction between the ZnO and the dopant. The Al 2p₁/₂ photoelectron peaks for the two AZO thin films shown in the figure appear at binding energy around 74.5 eV, typical for the Al³⁺ state. The O1s photoelectron lines were fitted with three components. The first one at 530.3 eV was attributed to O²⁻ in a fully stoichiometric ZnO [6]. The other two components at 531.5 eV and 532.5 eV are related, respectively, to the presence of oxygen-deficient regions or oxygen vacancies within the ZnO matrix [7, 8], and to another type of oxygen species, such as carbon–oxygen bonding, or other adsorbed molecules on the surface [9]. It is
obvious that the Al-doped ZnO has more O\textsubscript{2} species than pure ZnO; in other words, it has a higher donor content (V\textsubscript{O}) in comparison with pure ZnO. These results indicate that Al doping can modify the surface state, e.g., by increasing the oxygen vacancies.

**Figure 1.** XPS spectra of ZnO and AZO thin films (deposited on glass and silicon substrates).

3.2. **Photoluminescence (PL)**

The emission spectra of the Al-doped ZnO films deposited on a PET substrate at different excitation wavelengths are shown in figure 2. The emission of the undoped ZnO film consists of a strong UV emission peak at 378 nm and a weak blue emission shoulder peak at 424 nm. The UV emission is usually ascribed to the bandgap emission, and the blue emission, to Zn interstitials [10]. In AZO films, the UV emission peaks broaden and shift to the interval 389-392 nm. The UV emission intensity decreases dramatically with an increase in the Al concentration. This suggests that the Al doping widens the film bandgap and introduces non-radiative recombination centers and/or defects.

3.3. **LC device fabrication using AZO films as transparent conductive electrodes**

Figure 3 (a) shows schematically the structure of a PDLC cell using AZO deposited on a PET substrate. The transmitted light intensity dependence on the applied voltage is presented figure 3(b). The main operation principle of a PDLC display relies on the electro-optically controlled birefringence of the LC molecules inside the polymer droplets. Under application of an electric field, an induced dipole moment arises and all the molecules start to reorient along the direction of the applied field.

**Figure 3.** (a) Schematic diagram of a PDLC device on AZO deposited on a PET flexible substrate and (b) voltage-transmittance characteristics of device.
As seen, the AZO layers demonstrate opportunities for applications on flexible substrates for a new generation of photonic devices. Moreover, the preliminary bendability data of AZO on PET show very stable sheet resistance values.

4. Conclusions
Al-doped ZnO thin films were prepared on silicon, glass and PET substrates and their structural and optical properties were measured. Based on the characteristics measured, a PDLC device consisting of a AZO transparent conductive layer deposited on a PET substrate was successfully fabricated. The electro-optic modulation properties measured indicated that the AZO/PET is a promising candidate for uses in the next generation of flexible optoelectronics and display applications.

Acknowledgments
This work is supported in part by the Bulgarian National Science Fund under project DN-08/9.

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