

# Photoluminescence properties of ZnO:Al films deposited on flexible PET substrate by RF reactive magnetron sputtering

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Aluminium-doped ZnO (AZO) thin films have been deposited on flexible polyethylene terephthalate (PET) substrate by RF reactive magnetron sputtering process at low substrate temperature (room -100 °C), and their photoluminescence (PL) behavior at room temperature and the influence of O<sub>2</sub>:Ar ratio, substrate temperature, and deposition time were investigated. The strong near band-edge UV emission and the weak blue emission were observed, while the defect-related deep-level green emission was nearly absent, indicating that high optical quality AZO films, grown on flexible PET substrate, were obtained using the RF reactive magnetron sputtering technique. The origin of the emissions is discussed.

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**Keywords:** ZnO:Al (AZO), Thin films, Flexible PET, RF reactive magnetron sputtering, Photoluminescence

## 1. Introduction

New flexible light-weight display technologies are becoming more important in the development of smart portable devices such as personal digital assistants (PDA), pagers, cell phones, camcorders, digital cameras, smart cards, remote control circuits and also solar cells and future “electronic paper”. Flexible “plastic” displays often incorporate transparent conducting oxide (TCO) films grown on plastic substrates [1,2]. Plastic displays have several obvious advantages over those on glass surface, such as their flexibility to improve their function, robustness, lighter weight, thinness (which provides wide viewing angles) and their durability [3-5]. Industrially their production is easy to scale up to large volumes. The substrate materials, commonly used for the above applications include polycarbonate (PC), polyarylate (PAR), polyestersulfone (PES), polyimide (PI), polytetrafluoroethylene (Teflon), cellulose triacetate etc [3,6-8]. Poly-ethylene glycol terephthalate (PET) is, however, the most commonly used substrate in plastic display applications because of its low chemical reactivity, high optical transmittance, and high melting point (about 200 °C) [3].

In recent years, Sn-doped In<sub>2</sub>O<sub>3</sub> (ITO) films deposited on flexible substrates have been extensively studied. Compared to ITO, Al-doped ZnO films have many advantages, such as abundant raw materials, low cost, non-toxicity, and high stability in hydrogen plasma etching

processes [9,10]. ZnO:Al (AZO) film deposited on the flexible substrate is a promising material in new generation flexible optoelectronics devices. To characterize the AZO films and control their electrical and optical properties UV/vis spectroscopy and photoluminescence (PL) measurements are required. Elmas and Korkmas have studied the optical properties of AZO/PET system using UV/vis spectroscopy [11]. Nevertheless, to our knowledge, the photoluminescence properties of AZO films deposited on flexible substrates has not been reported.

In this letter, we report ZnO:Al films deposited on flexible PET substrates by radio frequency (RF) reactive magnetron sputtering systematically under different conditions where after their photoluminescence behavior is reported and discussed in details. This work should give insight to the applications of AZO-based flexible optoelectronic devices.

## 2. Experiments

ZnO:Al films were deposited on flexible PET substrate by the RF reactive magnetron sputtering system (JCP-200). A Zn: 2.0 wt.% Al alloy was used as a target. The distance between the substrate and the target was around 50 mm. High-purity argon and oxygen were used as the sputtering and reactive gas, respectively. Argon and oxygen were introduced via two separately controlled leak

valves in order to adjust the partial pressure of both Ar and O<sub>2</sub>. The PET substrates were ultrasonically cleaned first in acetone and then in alcohol for 15 min before being placed into the deposition chamber. Because the flexible PET substrates cannot bear high RF power and substrate temperature, we designed several deposition conditions based on different ratio of O<sub>2</sub> and Ar, deposition time, and low substrate temperatures of room temperature (RT) and 100 °C, while other sputtering conditions were kept identical. Table 1 lists the preparation parameters for the AZO film samples. Under the above conditions, high quality AZO films with good adhesion and optical properties were obtained without damage to the flexible substrates.

Photoluminescence (PL) spectrum measurements were carried out on an FLS920 fluorophotometer using a xenon lamp as the excitation source (with wavelength 325 nm and incidence angle 45 °) at room temperature. The power of the excitation for PL measurements was kept same (5 mW) when comparing the PL intensities from all the samples so that a direct EER comparison can be made among the three structures. By employing a 325 nm optical filter, PL signals were detected using a Red PMT equipped spectrometer (Acton SP2500i) from the top side geometry of the samples.

Table 1. Preparation parameters of AZO thin films samples.

Base pressure	10 <sup>-4</sup> pa
Sputtering pressure	0.7~1.0 pa
RF power	80 W
Substrate temperature	RT and 100 °C
Ratio of O <sub>2</sub> :Ar	9:3, 6:6, and 4:8 sccm
Deposition time	1 and 2 h

### 3. Results and discussion

The Photoluminescence (PL) spectrum of ZnO is normally composed of two parts: excitonic related near band edge emission (NBE) with energy around the band gap of ZnO and defect related deep level emission (DLE) in the visible range induced by the impurities and structure defects such as oxygen vacancies or zinc interstitials [1,12,13]. It was generally accepted that PL behavior of ZnO depends essentially on the stoichiometry and the microstructure of the films.

Fig. 1 shows the room temperature photoluminescence (PL) spectra in the wavelength range of 350-600 nm of AZO films deposited on PET substrates for 1h at the substrate temperature of 100 °C, RF power of

80 W, and several ratios of O<sub>2</sub>:Ar. All the AZO flexible films show a typical photoluminescence behavior with the ultraviolet-blue emission band between 350 and 450 nm, and three emission peaks can be observed in this band. The most strong ultraviolet emission (UVE) peak dominating at about 390 nm (3.28 eV) is most likely due to the free exciton emission/recombination, one subsidiary peak is located at about 370 nm (3.35 eV) with energy around the band gap of ZnO (3.37 eV) and may be assigned to free exciton emission and bound exciton with high electronic density of state, and another weak purple emission peak at about 410 nm (3.03 eV) may be associated with certain exciton recombination and also probably due to the defects level existing at the grain boundaries in the ZnO:Al films. Besides, a very weak blue emission band at about 470 nm (2.64 eV) was observed, which can be regarded as the defect-related emission of AZO films possibly originated from the electron transition from both the Zn interstitial levels to the top of the valence band (2.87 eV) and the energy levels of Zn interstitial to Zn vacancies (2.57 eV) [14]. In our case, the visible emission (purple-blue) intensity is much weaker compared to the UV emission, and no defect-related deep level green emission is observed, which indicates that less oxygen vacancies and structure defects exist in the surface layer of our films. So a high optical quality AZO film grown on PET was obtained by RF reactive magnetron sputtering.

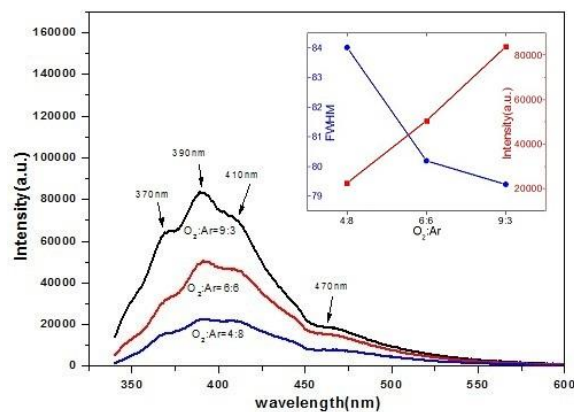


Fig. 1. The PL spectra of AZO films grown on PET for 1h at 100 °C, and various ratios of O<sub>2</sub>:Ar. The inset shows the intensity and FWHM of UV emission peak dominating at about 390 nm as a function of O<sub>2</sub>:Ar ratios.

As shown in Fig. 1, the UV emission of AZO films strongly depends on the ratio of O<sub>2</sub>:Ar, which influences essentially on the stoichiometry and the microstructure of the films. Under the same condition, as the ratio of O<sub>2</sub>:Ar increased from 4:8 to 9:3 sccm, although the thickness of the films decreased from 950 to 450 nm due to the decrease of the partial pressure of Ar sputtering gas, the intensity of UV emission peak monotonously increased

and the full-width at half-maximum (FWHM) decreased, reaching a maximum peak value and a minimum FWHM value when the ratio of  $O_2:Ar$  increased to 9:3 sccm, as seen in the inset of Fig. 1. This indicates that with an increase of oxygen partial pressure, the oxygen vacancies and non-radiative defects in the AZO films seem to decrease, resulting in the formation of ZnO exciton and then pronounced UV emission.

In order to further investigate the influence of other deposition conditions on the optical properties of the AZO films on PET substrate, the PL measurements of AZO films grown at  $O_2:Ar$  ratio of 9:3 sccm with varied substrate temperature and deposition time were carried out at room temperature and the results are shown in Fig. 2 and Fig. 3, respectively.

Fig. 2 displays the PL spectra of AZO films deposited at the substrate temperature of both RT and 100 °C and at an  $O_2:Ar$  ratio of 9:3 sccm for 1 h with the thickness of 450 nm. The two groups of spectra show a strong UV emission peak at the same position of 390 nm and two weak peaks located at about 370 nm and 410 nm, respectively, while a very weak blue peak at about 470 nm is also found. The positions of the spectral peaks did not change with the substrate temperature, whereas, compared with the AZO films deposited at 100 °C, the UV emission of the AZO flexible films deposited at the substrate temperature of RT is much stronger. The peak intensity is enhanced about 80%, and the line-shape of the UV emission band becomes narrower. This is different from the results where the UV emission intensity of ZnO films was increased with the increase of deposition temperature [15]. The deposition temperature-dependent PL behavior, exhibited by our AZO films grown on PET substrate, may be explained by the decreased substrate temperature quenching the generation of the defect level, created by the vacancies or interstitial atoms and Al oxides acting as non-radiative emission centers. Thus, the PL behavior may become significantly improved with the decreasing substrate temperature.

Fig. 3 shows PL spectra of the AZO films deposited on PET substrate at 100 °C and an  $O_2:Ar$  ratio of 9:3 sccm for sputtering time of 1 and 2 h with the thickness of 450 and 900 nm, respectively. It is noted that the position (band gap energy) of the PL peak is not affected by deposition period. However, by increasing the deposition time to 2 h, the intensity and FWHM of UV emission peak become higher and narrower, respectively, and the peak intensity is enhanced about 75%. The PL properties can be improved with increasing the deposition period, because of the increase of films thickness and then the improvement of the crystal quality of the AZO thin films. More detailed investigations are needed to predict the optimal AZO composition as future material for flexible optoelectronic devices.

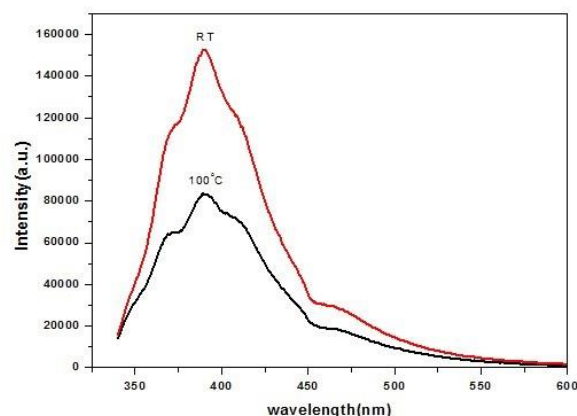


Fig. 2. The PL spectra of AZO films grown on PET for 1h at  $O_2:Ar$  ratios of 9:3 sccm, and substrate temperature of RT and 100 °C.

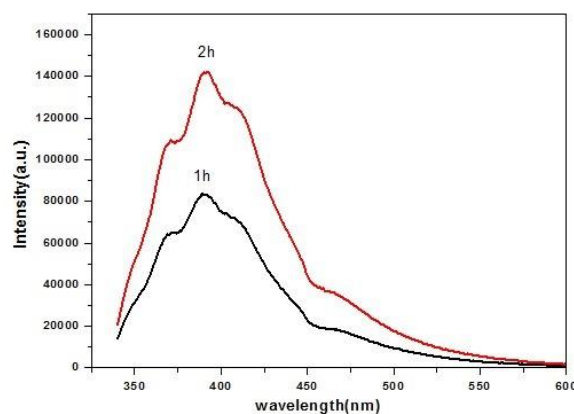


Fig. 3. The PL spectra of AZO films grown on PET at 100 °C and an  $O_2:Ar$  ratio of 9:3 sccm for 1 and 2 h.

#### 4. Conclusions

Al doped (2 wt.%) ZnO (AZO) thin films were deposited onto flexible PET substrate using RF reaction magnetron sputtering at low substrate temperature (room-100 °C). Room temperature PL measurements show that the AZO films exhibit strong excitonic related near band-edge (NBE) UV emissions centering about 390 nm and much weaker blue emission about 470 nm, without showing any accompanying defect related deep level green emission (here nearly absent), demonstrating that the obtained AZO films on PET are well close to the stoichiometry and of optically high quality. The UV NBE emission intensity of AZO films was enhanced monotonously with the increase of  $O_2:Ar$  ratio from 4:8 to 9:3 sccm (at 100 °C for 1 h). At  $O_2:Ar$  ratio of 9:3 sccm, as the substrate temperature decreased from 100 °C to RT (for 1 h), or deposition time increased from 1 to 2 h (at 100 °C), the intensity of the UV NBE emission peak increased greatly about 80 % and 75%, respectively, while the deep-level green emission is almost absent. In summary,

with a good control of the processing conditions, such as oxygen partial pressure, substrate temperature, and deposition time, AZO flexible films on PET with optimized optical properties by RF reaction magnetron sputtering technique can be obtained, which is encouraging for the application of AZO films on PET as new flexible material for different types of photoelectronic devices.

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