Study of transparent conducting ZnO:Al films deposited on organic substrate by reactive magnetron sputtering

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Abstract. A Zn-Al metallic target (Al 2 wt.%) has been used to prepare conductive and transparent aluminium-doped Zinc oxide (ZnO:Al) films on PI substrate by direct current reactive magnetron sputtering. The structure, crystallinity, optical properties, electrical properties and adhesion were investigated using a range of techniques, including AFM, XRD, spectrophotometry, four-point probe and adhesion tester. The optimal films were prepared with a substrate temperature of 150°C, O₂/Ar ratio of 2:38 and sputtering power of 80W. The infrared emission properties of films and the feasibility for military application were also discussed in this paper. All the results to date demonstrate that magnetron sputtering is a cost-effective and easy to fabricating technique.

1. Introduction
Nowadays there is a great interest in replacing indium tin oxide (ITO) with aluminium-doping ZnO (ZAO), because of this oxide low cost, abundant raw materials, non-toxicity, relatively low deposition temperature and stability in hydrogen plasma. Extensive research work has being done on ZAO films deposited on rigid substrates. Recently preparing ZAO films on organic substrate has generated a renewed interest in it’s potential use. Transparent conducting films deposited on polymer substrates have many merits compared with those deposited on glass and silicon substrate; they are lightweight, flexible, robust, of small volume and easy to carry, which are desired properties for a variety of applications such as flat panel display, heat-reflecting coating for energy saving use, low emissivity coating for stealth use etc. In this work, ZAO films were deposited on polyimides being with good heat resistance from Zn-Al metallic target. Detailed information about optical properties, electrical properties as well as structure and morphology were presented.

2. Experiment details
The substrate used in this work are polyimides foils from JinShan company with a thickness of 175μm. The main reason for choosing such polymer is that it can meet a number of different requirements including optical transparency, high temperature capability, chemical ruggedness, dimensional stability up to a maximum working temperature of 200℃. Before depositing the ZAO film, the substrates were ultrasonically cleaned in a detergent and ethanol baths, respectively. Subsequently they were rinsed with de-ionized water and dried with N₂ gas. Paralled to the target surface (φ6cm, thickness 3mm), the substrate with the same size was placed inside the chamber, and then evacuated until a base pressure of 1.3×10⁻³Pa. The ZAO films were produced by direct current (D.C.) magnetron sputtering from a commercially available alloy Zn:Al (98:2 wt.%) target.
with 99.99% purity. Sputtering pressure was kept at 0.4 Pa constantly. The flow rates of Ar and O₂ were controlled individually by a couple of mass flow controllers according to the demanded flow ratio. During the sputtering, the power was fixed as 80 W and the substrate temperature was controlled at 150 °C. The deposition time was 2 h for each example. The film thickness was measured with a Sloan Dektak 3D profilometer, while the film’s sheet resistance was measured by a four-point probe system. The crystal structure of the films was determined by X-ray diffraction (XRD) spectroscopy using a Siemens D 5000 system with CuKα radiation (λ = 1.540562 Å). The surface morphology was investigated by atomic force microscopy (AFM). A double-beam spectrophotometer (Varian Cary 5G) was used to measure the transmission and the reflectance spectra of the films in the wavelength range 200-3000 nm. The infrared spectral emissivity was measured by a special instrument based on FTIR.

3. Result and discussion

3.1. Structure and morphological analysis

Compared with the sputtering power and substrate temperature, the O₂/Ar flow ratio has little influence on the deposition rate. For 2 h sputtering time, with different O₂/Ar flow ratios, the thickness for all examples is in the range of 400 nm to 500 nm. Adhesion testing showed that all films have a good adhesion on the PI substrate.

![Figure 1](image)

**Figure 1.** The XRD patterns of the ZAO films for four different O₂/Ar flow ratios: (a) O₂/Ar flow ratio = 2:38, P(O₂) = 0.02 Pa; (b) O₂/Ar flow ratio = 2.5:37.7, P(O₂) = 0.025 Pa; (c) O₂/Ar flow ratio = 4.2:35.8, P(O₂) = 0.042 Pa; (d) O₂/Ar flow ratio = 5:35, P(O₂) = 0.05 Pa.
Figure 2. The AFM images of the ZAO films for four different O₂/Ar flow ratios: (a) O₂/Ar flow ratio=2:38, P(O₂)=0.02Pa; (b) O₂/Ar flow ratio=2.5:37.7, P(O₂)=0.025Pa; (c) O₂/Ar flow ratio=4.2:35.8, P(O₂)=0.042Pa; (d) O₂/Ar flow ratio=5:35, P(O₂)=0.05Pa.

From figure 1, for all examples, two main peaks, corresponding to the (002) and (103) reflections are observed. The (002) diffraction peaks are observed at a 2θ value of 34.23°, 34.29°, 34.28°, and 34.26° respectively, which agree with the value reported in the literature for films grown on silicon, glass, and sapphire substrates[1, 2]. The c-axis length of the polycrystal tends to increase for all films, as the (002) peak angle was smaller than that of the bulk crystal (34.45°). Furthermore, for all examples, additionally to the (002) peak the (103) orientation is evident. The similar results are also reported by other authors[3, 4]. The XRD measurements firstly reveal that these ZAO thin films are polycrystalline and retain the hexagonal wurtzite structure, having lattice parameters corresponding to that of bulk ZnO. Secondly, the XRD patterns suggest that the optimal films with improved crystallinity can be obtained at the O₂/Ar flow ratio range from 2:38 to 4.2:35.8. Particularly, the (103) peak decreases evidently and the (002) peak does not change significantly, which means that at the lower oxygen content the O₂/Ar flow ratio does not mainly influence the degree of crystallinity but the preferred orientation. When O₂/Ar flow ratio is up to 5:35, both the (002) peak and (103) peak decrease, which reveals that the ZAO film now has weak crystallinity. The full width at half-maximum (FWHM) of
(002) peak is 0.351 for example a. The grain size can be estimated using the Scherrer formula. The grain size is calculated to be of 41 nm.

To identify the surface structure characteristics of films mentioned above, atomic force microscopy (AFM) perspective images are shown in figure 2. It can be easily observed that the films deposited for various O₂/Ar flow ratios show a uniform grain size with a columnar structure. Comparatively, example b, c, and d consist of a more dense array of grains than example a, which is coincident with the XRD measurement result that film a being have a conspicuous (002) preferred orientation. And the grain size of example d is smaller than that of the other examples. This also can be concluded from XRD resurmept. Example d has a relatively weak diffraction peak.

### 3.2. Optical properties

The optical transmittance T and reflectance R curves of ZAO films mentioned above are shown in figure 3 and figure 4 respectively. It is clear that in the given sputtering condition of this work the O₂/Ar flow ratio has a very strong impact on the optical property and an insignificant influence below 1000 nm. Each example has a high transmittance to visible light, with an average value over 80%, and a fundamental absorption edge lying in the near-ultraviolet part of the visible spectrum. The examples that have been determined above with relatively good crystallinity have lower IR transmittance and higher IR reflectance.

![Figure 3](image1.png)

**Figure 3.** The transmission T of the ZAO films for four different O₂/Ar flow ratios:
(a) O₂/Ar flow ratio = 2.38, P(O₂) = 0.02 Pa;
(b) O₂/Ar flow ratio = 2.5:37.7, P(O₂) = 0.025 Pa;
(c) O₂/Ar flow ratio = 4.2:35.8, P(O₂) = 0.042 Pa;
(d) O₂/Ar flow ratio = 5:35, P(O₂) = 0.05 Pa.

![Figure 4](image2.png)

**Figure 4.** The reflectance R of the ZAO films for four different O₂/Ar flow ratios:
(a) O₂/Ar flow ratio = 2.38, P(O₂) = 0.02 Pa;
(b) O₂/Ar flow ratio = 2.5:37.7, P(O₂) = 0.025 Pa;
(c) O₂/Ar flow ratio = 4.2:35.8, P(O₂) = 0.042 Pa;
(d) O₂/Ar flow ratio = 5:35, P(O₂) = 0.05 Pa.

### 3.3. Resistivity and emissivity

Figure 5 exhibits the electrical resistivity of ZAO examples. In figure 5 as the ratio O₂ increases, the conductivity of ZAO films is reduced slowly at the beginning then increased abruptly. This may result from the difference of films’ crystal structure at different sputtering conditions. The electrical resistivity for all films is in the range of 10⁻⁵ Ω cm. And this result is also in accordance with the reflectance measurement result showed in figure 4. According to the Drude theory, there is a close relation between IR reflectance and sheet resistivity. The sheet resistivity will increase when the IR reflectance decreases. Compared with figure 3 with figure 5, it is observed that IR transmission increases when the ratio O₂ increases, a behavior accompanied by an increase of the electrical resistivity. All these test results can be explained through a quantitative relation of transmission and reflection associated with free electrons [5].
Figure 5. The electrical resistivity of the ZAO films for four different O₂/Ar flow ratios: (a) ratio = 2:38, P(O₂) = 0.02 Pa; (b) O₂/Ar flow ratio = 2.5:37.7, P(O₂) = 0.025 Pa; (c) O₂/Ar flow ratio = 4.2:35.8, P(O₂) = 0.042 Pa; (d) O₂/Ar flow ratio = 5:35, P(O₂) = 0.05 Pa.

Figure 6. The IR emissivity of the ZAO films for four different O₂/Ar flow ratios: (a) ratio = 2:38, P(O₂) = 0.02 Pa; (b) O₂/Ar flow ratio = 2.5:37.7, P(O₂) = 0.025 Pa; (c) O₂/Ar flow ratio = 4.2:35.8, P(O₂) = 0.042 Pa; (d) O₂/Ar flow ratio = 5:35, P(O₂) = 0.05 Pa.

Figure 6 showed the IR spectral emissivity of ZAO examples. It is well known that it is difficult to measure the material’s spectral emissivity. In this work, a modified instrument based on FTIR was used to measure the emissivity of ZAO films. It can be seen that each example gives a lower emissivity value in the IR spectrum range. The example having lower electrical resistivity also has a lower IR emissivity. A very interesting phenomenon is that in the region of 5 μm to 22 μm the emissivity reduces considerably with the increase of wavelength. Detail research work should be done in the future.

4. Conclusions

Transparent and conductive ZAO films were deposited on PI substrate successfully by reactive magnetron sputtering system. The effect of O₂/Ar flow ratio on the structure, optical and electronic properties of ZAO films was mainly investigated. All films deposited at the given condition in this experiment showed a strong crystallographic c-axis orientation (002) perpendicular to the substrate surface although (103) diffraction peak was observed. In this case, the O₂/Ar flow ratio mainly influence the orientation of crystallization. The ZAO films demonstrate transmittance of above 80% in the range of visible spectrum and a lowest electrical resistivity of 1.17 × 10⁻³ Ω cm. The lower IR emissivity of ZAO films obtained in this work proved that the ZAO film may be a promising material for military application.

Reference

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