



## AZO (ZnO:Al) Transparent Conductive Film Prepared by Plasma Enhanced Chemical Vapour Deposition and its Performances in Comparison with ZnO Film†

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In this paper, AZO(ZnO:Al) polycrystalline thin films have been fabricated by PECVD (plasma enhanced chemical vapour deposition) method. Based on PECVD method, the fabrication process of AZO film is shown in detail. Furthermore, the measurements of the film electro-optical properties have been bringing forth, in comparison with ZnO film. The results suggested that based on PECVD method, AZO films with strong adhesion to the substrate, as low as 89  $\Omega/\%$  of square resistance and as high as 85 % of visible light transmittance have been deposited on the glass substrate and the silicon substrate, respectively.

**Keywords:** AZO (ZnO:Al), Plasma enhanced chemical vapour deposition, Transparent conductive film.

### INTRODUCTION

The transparent conductive film is one kind of film materials, which have the advanced performances with electric conduction and optic transmittance in the scope of visible light. In<sub>2</sub>O<sub>3</sub> film (*i.e.*, ITO) has occupied the leader position in the area of TCO films. Its application scope has involved in the majority of photoelectron component like the flat-panel display, the solar cell, *etc.* Tin oxide film was used as the TCO film early. But the early SnO<sub>2</sub> film has not been doped and then its electro-optical performance is inferior to the doped SnO<sub>2</sub> film afterward. Therefore, what obtains the application now is the doped SnO<sub>2</sub> thin film and what the doping effect is best are SnO<sub>2</sub>: Sb (*i.e.*, ATO) film and SnO<sub>2</sub>: F (*i.e.*, FTO) film. However, this two TCO film have many demerits involving: (1) In and Sn are fewer in nature storage, thus the cost of production will be very high; (2) The chemical properties of In and Sn are lively, the technological conditions will not be easily controlled; (3) The atomic weight of In and Sn are more, the substrate material will be poisoned in the process of the manufacture, especially for the component of the liquid crystal display, the phenomenon of pollution will be very serious. In comparison with

those TCO films, the cost of the ZnO:Al (*i.e.*, AZO) film is low cost, the source of the raw material is richer and non-toxic, its stability is finer than ITO or ATO film, but its electro-optical property can compare with ITO film<sup>1</sup>. Therefore, the research on AZO film has become hotly in TCO domain recently<sup>2-5</sup>.

The purpose of this paper is to produce AZO transparent conductive film based on the method of Plasma Enhanced Chemical Vapour Deposition (PECVD). In addition, comparing with the electro-optical property of ZnO film, the measurements of the film electro-optical properties have been operated.

### EXPERIMENTAL

**AZO film fabrication process based on PECVD method:** The present work is experiment on PECVD setup as shown in Fig. 1. This experiment adopt the solid state source (CH<sub>3</sub>COO)<sub>2</sub>Zn·2H<sub>2</sub>O and Al(OH)(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (doping source) as the reaction gaseous matter with carrier gas N<sub>2</sub> to the heated substrate. Many active atomic groups have come into being in the vacuum cavity with the plasma produced by the high frequency electric discharges. These groups deposited

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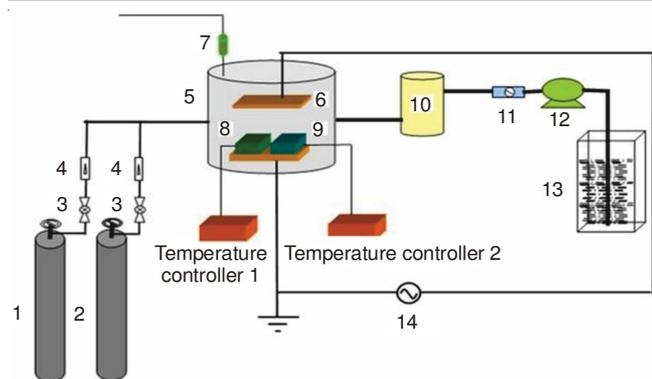


Fig. 1. Diagrammatic drawing of the PECVD system: 1 argon gas; 2 nitrogen gas; 3 relief pressure valve; 4 gas flow meter; 5 reaction cavity; 6 parallel plate electrode; 7 vacuum gauge; 8 platform for heating up the reaction source; 9 platform for heating up the substrate; 10 Filter; 11 Electromagnetic valve; 12 Vacuum pump; 13 waste gas treatment; 14 RF power source

increasingly on the substrate surface produce the AZO (ZnO:Al) film as a result of the chemical reaction with active groups on the surface of glass chip. The experimental parameters choose as follows: (1) Carrier gas: argon (Ar) and nitrogen (N<sub>2</sub>); (2) discharging frequency: 40.68 MHz; (3) discharging power: 200 W; (4) discharging voltage: 600 V; (5) Gas pressure: 200 Pa; (6) Substrate temperature: 620 K; (7) Solid state source sublimation heating temperature: 570 K; (8) depositing time: 0.5 h.

The film preparation process is operated as follows: (1) Clean and dry the substrate, then lay aside on the substrate platform; meanwhile, install the solid state source in the quartz boat, then put it on the heating up platform; (2) Turns on the total power switch; (3) Opens the vacuum system and turns on the vacuum gauge. Once the reader of the gauge can achieve 10 Pa, the vacuum system work normally; (4) Turns on the valve of the Ar gas and then turns on the power switch to clean the substrate and the entire reaction cavity; (5) Adjusts the supply power and the voltage to produce the stable plasmas; (6) Opens the substrate heating system to achieve the constant substrate temperature; (7) Opens the solid state source sublimation heating system (control the temperature in 570 K), turns on the valve of the N<sub>2</sub> gas and the film starts to grow; (8) under the scheduled time, shuts down the plasma generator power switch and closes all heating systems; (9) Keep the valve of the N<sub>2</sub> gas opening and continually pump the gas (10 min) for eliminating the acidic gas in the cavity; (10) Closes the valve of the N<sub>2</sub> gas and then turns off the vacuum system and the total power switch; (11) Waits the sample to the room temperature, then takes out and puts it in a cleanly and aseptic airtight culture dish for result examination.

## RESULTS AND DISCUSSION

**Comparison of the film surface appearance:** ZnO film and AZO film have been deposited separately on Si substrate, under the similar experimental condition. From the FSEM (field emission scanning electronic microscope) image (Fig. 2), few Al doping has affected the film superficial appearance greatly. Pure ZnO film is even with clear crystal boundary and regularly crystal strip, the strip length is 300 nm and the

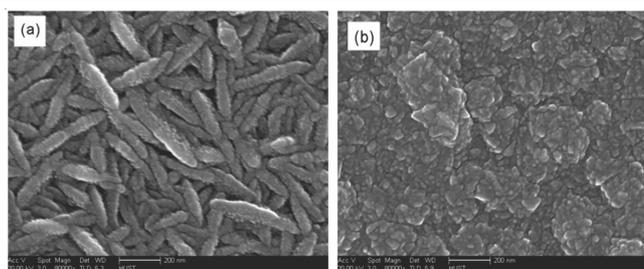


Fig. 2. FSEM image amplified by 80000 times: (a) ZnO film and (b) AZO film

strip diameter is 40 nm approximately. But the AZO film presents the reunion phenomenon and becomes the crystal laminated shape.

**Comparison of the film crystal structure:** As shown in Fig. 3, the X-ray diffraction (XRD) graph: ZnO film is poly-tropism structure and each diffraction peak position match well with the standard hexagonal system diffraction peak position; after Al doping, the spiauterite structure of ZnO film has not changed, the half peak width reduces obviously, the surface diffraction peaks like (100), (002) and (110), all traverse to the high angle compared with pure ZnO film, besides (101) diffraction peak. That may be deferred that the crystal constant reduces as a result of the Al introduction and the crystal lattice contract to be distorted, but there have not enough evidence to prove this mechanism at present.

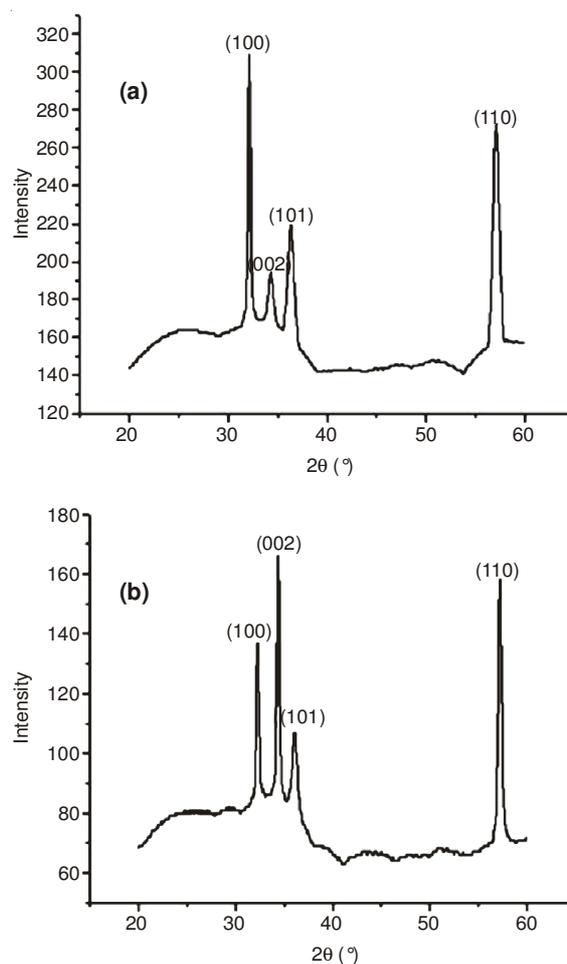


Fig. 3. XRD diagram: (a) ZnO film and (b) AZO film on the Si substrate

**Comparison of the film optics performance:** The intrinsic excitation cannot be occurred and the films are transparent in the visible light scope because that the energy gaps of AZO or ZnO film is larger than the visible light photon energy (3.1 eV). As shown in Fig. 4(a), it infers that the average transmittance of AZO film or ZnO film surpasses 80 % in the wavelength band from 400 to 800 nm; the only difference is the ultraviolet absorption of the AZO film slightly traversing to the short wavelength compared with ZnO film. This kind of absorption migration may be summed up with BM effect (Burstin-MOSS effect)<sup>6</sup>, namely the density of the current carrier elevates and causes the Fermi energy level carrying to the conduction band.

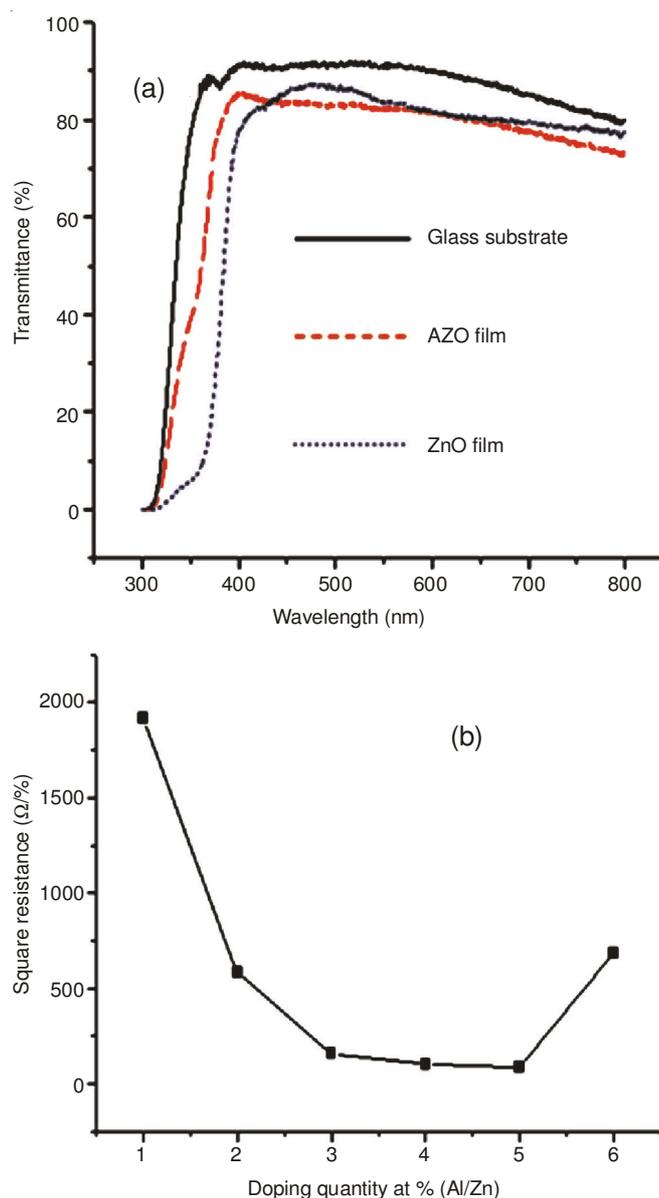


Fig. 4. (a) Optic transmissivity and (b) square resistance

#### Influence of the doping quantity for the conductivity:

The survey discovered that the square resistance of the AZO film is smaller than the ZnO film without doping as shown in Fig. 4(b). The doping quantity affects obviously the electrical conductivity. When the doping quantity increases from 1 to 3 %, the film resistivity reduces largely with lowest square electronic resistivity 89 Ω/%. But the film resistivity cannot reduce infinitely and will increase with higher doping quantity. It is reported in the literature<sup>7</sup> that the best doping quantity is 4.67 % with the lowest film resistivity. In the AZO crystal film, Zn ions with positive two chemical valences are displaced by Al ions with positive three chemical valences. According to the theory of the energy band, the free carrier concentration increase and the resistivity reduce correspondingly due to the electron located at the bottom of the valence band being excited to the conduction band by thermal stimulation<sup>8</sup>. When the doping quantity is excessive, the excessive Al atoms gather at the crystal boundary, the density of the flaw increase, the ionization scattering strengthens, the Hall transport ratio of the current carrier reduce and finally the film square resistance elevate, as shown in Fig. 4(b).

#### Conclusion

This paper presents the AZO film produced by PECVD method. This experiment adopted the solid state source  $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$  and  $\text{Al}(\text{OH})(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$  (doping source) as the reaction gaseous matter. The ZnO film with some degree of Al doping have caused film performance changes in the electricity, optics, structure and surface appearance. These results may be used to explore the optimization design of the solar cell and provide some constructive advice for the next generation of the film photovoltaic products.

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