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# Advantage of dual-confined plasmas over conventional and facing-target plasmas for improving transparent-conductive properties in Al doped ZnO thin films

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ABSTRACT

Al doped ZnO films are prepared in dual-confined plasmas (rectangular side-ways and one top-side) in DC magnetron sputtering system without intentional substrate-heating. Present confinement shows improved transparent-conductive properties in Al doped ZnO thin films, when compared to those of deposited by conventional and facing-target confinement. As a function of working pressure and power density, plasma diagnostics is carried out at substrate location using optical emission spectroscopy, thermal energy transfer and net current density measurements. The optical, and electrical properties of the synthesis AZO films were studied and correlated to plasma conditions. It is found that high electron temperature, higher plasma density and highly ionization of oxygen play a key role in enhancing the deposition rate and transmittance ~90% along with minimizing resistivity in the order of $10^{-4}$ Ω cm.

## 1. Introduction

Well-established importance of transparent conducting oxide (TCO) materials in the optoelectronics and energy conversion devices has led to the development of highly performing materials, the most widely employed being indium tin oxide (ITO) [1–4]. ITO materials need to be replaced because of expensive cost of raw indium, and also limitation against thermal stability and flexibility. One of its replacement, doped ZnO film faces still hurdles due to relatively higher resistivity and poor transmittance, despite its unique advantages in low-cost and high toughness over those of ITO films. ZnO is a wide band-gap (3.37 eV at room temperature) multi-functional material, owing to its emerging applications in photocatalytic, sensing, piezoelectric transducers, varistors, phosphors, blue emitters, UV light emitters, and 'high-temperature, high-power' transistors [5–8]. ZnO show high electrical property as well as a high transmittance in the visible region, and when doped with group III elements such as Al, In, Ga and B [9–11]. Among these dopants, Al is extensively doped in ZnO films, for variety of advanced applications i.e. organic light-emitting devices [1], gas sensing [12], solar cell [13,14], NIR transformative applications [15], apart the conventional TCO applications [16–31].

Common synthesis techniques to deposit Al–ZnO thin films involve atomic layer deposition [17,18], laser molecular beam epitaxy [19], chemical vapor deposition [20], sol–gel [21], pulsed laser deposition [22] and sputtering [23–33]. Among the different thin film deposition processes, magnetron sputtering, characterized by a high kinetic energy of sputtering particles, especially for dc-discharges, is widely used technique for preparing AZO films [23–25] due to its advantages of good film quality, easy control and high efficiency. Conventional magnetron sputtering (CMS) [26,31] and facing target sputtering (FTS) [27–29] have been earlier employed to prepare Al–ZnO films by our group at CAPST. CMS uses a magnetic field to trap electrons above a cathode, which allows operation at low neutral pressures than similar unmagnetized plasmas [26]. Whereas, FTS uses two magnetrons facing targets to confine the plasma, resulting in high density plasma and significantly reduction of the damage, by suppressing of impinging high-energy particles during the film growth [27–29]. The deposition rate, structural, optical and electrical properties of deposited films are influenced by processing parameters such as pressure and power provided to targets in sputtering. It is of great value to study the plasma parameters (radicals/ions, plasma density, electron temperature etc.) and how they lead to obtain optimum properties of AZO films. It has been noted that it is critically important to control the high-energy recoiled atoms and ions, in order to create necessary O vacancies for enhancing the conductivities of films along with the doping of Al. However, the observed

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values of resistivity and transmittance are too far to be competent to ITO, particularly using DC-powers and without substrate heating.

We recently developed a new magnetron providing dual-confinement of plasmas, sideways as well as from top side (for deposition in bottom side substrate), and reported the dependence of power density on chemical and electrical properties of Al–ZnO thin films [30]. This work extends our preliminary findings to elucidate the in-depth plasma diagnostics studies under various pressure and power conditions in this system, and their effect on properties of prepared films. We have presented plasma diagnostic study using optical emission spectroscopy (OES), net current density and thermal energy transfer measurements, followed by film analysis using UV–visible spectroscopy and Hall measurements study. Using the obtained results, the growth of the films under various conditions has been discussed with relevant mechanisms applicable for the conductivity enhancement.

## 2. Experiments details

Thin films were deposited on soda lime glass substrates without additional substrate heating by modified magnetron sputtering systems using DC power, as shown in Fig. 1. The sputtering system for AZO film deposition consisted of two parts. One part has 4 targets in rectangle size; the other part is top target. The sputtering targets used in the experiment were 2 wt.% $Al_2O_3$ doped in ZnO ceramic targets (procured from Biz-material, Korea). The experimental conditions used in present experiments are summarized in Table 1. Before the process, the substrates were cleaned with acetone and alcohol to remove the contaminations. The cleaned substrates were placed on the center of the substrate holder, 4 cm distant from the lower ends of sideways rectangle targets. The chamber was evacuated using a turbo molecular pump and a rotary pump with a booster. The base pressure was less than $5 \times 10^{-6}$ Torr and the working pressure was varied from 4 mTorr to 8 mTorr with adjusting appropriate Ar gas inflow. The DC power was applied to side-ways targets with varying power density from 0.5 W/cm$^2$ to 2.5 W/cm$^2$ in steps of 0.5 W/cm$^2$.

To obtain information about radical excitations in plasmas under different conditions during the deposition process OES study is carried out at the substrate location. All the spectral data are acquired using Acton Spectra pro 500i spectrometer through optical fiber (M/s. Ocean optic). The spectrometer having resolution ~0.05 nm, 10 μm wide entrance slit, 1200 grooves mm$^{-1}$ grating, is used in conjunction with a PIMAX Princeton Instrument CCD camera connected to a computer. The software for the spectra acquisition is WinSpec32™. Ion current density is measured using an oscilloscope (Tektronix TDS 3052B) assisted with a current probe amplifier (Tektronix TM502A). Plasma induced thermal energy transfer is measured using a thermocouple placed at substrate location.

**Table 1**
The detailed conditions for Al–ZnO film deposition.

| | |
|---|---|
| *Fixed parameters* | |
| Number of targets: | 5 rectangular shaped |
| Base pressure: | $<5 \times 10^{-6}$ Torr |
| Power: | DC |
| Target to substrate distance: | 4 cm |
| Gas: | Ar |
| Substrate: | Soda lime glass |
| *Variable parameters* | |
| Power density: | 0.5, 1.0, 1.5, 2.0 and 2.5 W/cm$^2$ |
| Pressure (partial): | 4, 6 and 8 m Torr |

We tried to keep the films thicknesses to be same, around 200 nm (±5 nm), by controlling the deposition time. The metal tipped pen was used to draw a line of whitener fluid (procured from Pentel, Japan), which readily dries without spread at center of substrate. After the deposition, the drawn line can be easily detached, which makes a sharp step (a valley) in the film. After which the film thickness was determined using an α-step profilometer (KLA Tencor Alpha-step IQ). The thickness of a given film was measured at five different positions for each sample, and averaged for determining the deposition rates. The optical transmittance was measured by UV–visible spectroscopy using a UV-1800 ENG 240 V, SOFT spectrometer in the wavelength range of 200–1000 nm. The electrical properties of resistivity, carrier concentration and mobility of films were measured using the Hall-effect measurement (ECOPIA HMS-3000) with van der Pauw method at room temperature.

## 3. Results and discussion

Fig. 2 shows the OES study of plasmas as a function of pressure variation and power density. Fig. 2(a) shows the spectra (recorded in 200–900 nm region at fixed power density 2 W/cm$^2$) with varying the pressure from 4 mTorr to 8 mTorr. It is evident in the spectra that spectral location of peak remains similar for each pressure, however the intensities of peaks are different. Similar trend has been observed with variable power densities at fixed pressure 4 mTorr (not shown here). Here, significant lines arisen from Zn and Ar electronic transitions are indexed. Strong emission lines are observed from Zn *I* at 307.6 nm and Ar *I* transition in the range of wavelengths 750–811 nm. With pressure and power densities, the intensities of these lines vary. We have shown the variation of Zn *I*/Ar *I* ratio and Ar *II*/Ar *I* ratio as a function of pressure (at fixed power density 2 W/cm$^2$) in Fig. 2(b). Also, the variation of Zn/Ar ratio and Ar *II*/Ar *I* ratio as a function of power densities (at fixed pressure 4 mTorr) is shown in Fig. 2(c). It is clear from these plots that Zn *I*/Ar *I* ratio as well as Ar *II*/Ar *I* ratio increases with pressure, however exhibit different trend with power density. Zn *I*/Ar *I* ratio shows a

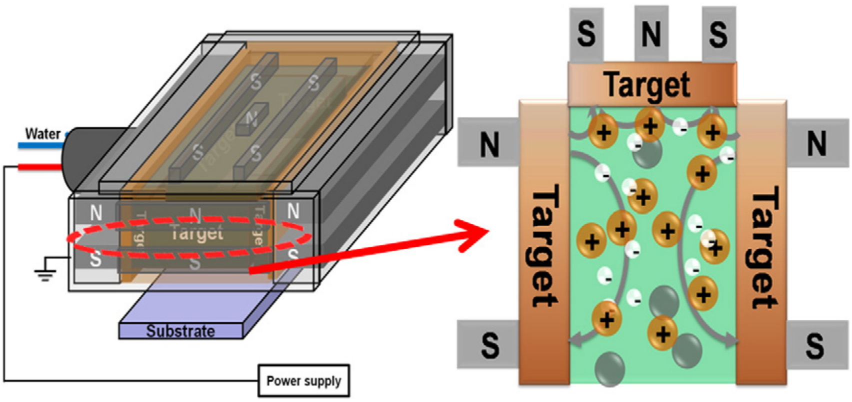

**Fig. 1.** Schematic diagram of the targets configuration in magnetron sputtering system.