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Atmospheric pressure dielectric barrier discharge (DBD) for post-annealing of aluminum doped zinc oxide (AZO) films

Eithan Ritz, Yui Lun Wu *, Jungmi Hong, Daniel Andruczyk, Tae S. Cho, D.N. Ruzic

Center for Plasma Material Interactions, Department of Nuclear Plasma and Radiological Engineering, University of Illinois at Urbana — Champaign, Urbana, IL 61801, USA

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ABSTRACT

Aluminum-doped zinc oxide (AZO) is a material that can have high electrical conductivity while being highly transparent at the same time. It has been used in many applications such as displays, mobile devices and solar cells. Currently AZO films are considered as attractive alternatives to materials such as indium–tin oxide (ITO) due to its much cheaper cost and comparable high electrical conductivity. A process of depositing AZO film by dual DC magnetron and RF enhancement system has been developed. Film thicknesses were measured to be at about 200 nm by a stylus contact profilometer and transparency of greater than 90% in the visible range was measured with spectrophotometry methods. Film conductivities were on the order of 10^{-3} Ω-cm using the four-point probe method. By using a dielectric barrier discharge operating at atmospheric pressure, the conductivity of film can be further lowered. A 300 mm × 60 mm line source operating at a nitrogen flow of ~250 L/min was used and ~0.4 L/min hydrogen gas was also introduced into the discharge system to create hydrogen radicals for surface modification. A 10%–15% decrease in electrical resistance was observed with no changes in the optical properties of the AZO films.

1. Introduction

Transparent conducting oxides (TCOs) are an important class of metal oxide semiconductor materials that is used in photovoltaic, display and LED technologies [1]. In order to help in decreasing the cost associated with mass production of thin film and enable a flexible roll to roll production for these applications, low cost materials, such as plastic substrates, are needed [13]. The use of polymeric substrates, however, limits deposition temperature as well as post-deposition annealing temperatures that have been shown to significantly improve the quality of TCOs, such as aluminum–zinc oxide (AZO) thin films [2–5]. For example, polyethylene terephthalate (PET) is a common polymer substrate material that is suitable for these applications. However, it has a glass transition temperature of 100 °C which markedly limits the process temperature window.

Metal oxide semiconductors such as zinc oxide (ZnO) can replace the existing indium-based TCOs, as the supply of indium in the world market is depleting [7]. Thin ZnO films can be deposited via sputtering techniques with high optical transmission and low resistivity. Doped ZnO is used as a TCO window layer and has been identified to achieve high efficiency in thin film solar cells using copper–indium–gallium selenide (CIGS) as an absorber layer [6]. In laboratory trials, sputtering processes (DC or RF) have been identified as the best deposition methods to fabricate impurity-doped ZnO thin films such as AZO [7]. Thus, there is a need to further investigate sputtering processes that can produce high-quality ZnO films that are scalable to large-area substrates at low temperatures [7–10]. Also, since the as-deposited film will have a certain amount of structural defects, these microstructure defects will have an effect on the physical and electrical properties of the film. Currently, these properties could be improved by post-annealing. The process will improve the stoichiometry or the crystallinity of the film [12]. However, this process is normally done at around 300–400 °C and not suitable for many flexible substrates and they would melt and deform under these conditions. A cold plasma, such as a dielectric barrier discharge (DBD) plasma, could operate in conditions close to room temperature. This would avoid the heating issue and thus be ideal for annealing films on flexible substrates after deposition.

In this paper, the effects of supplemental RF power created plasma on AZO film properties were investigated to evaluate the viability of plasma enhancement for improved low-temperature TCO thin film processing. In addition, improvement with atmospheric pressure DBD plasma post-annealing on electrical properties of the ITO and AZO film was also investigated. Both the deposition experiments and the post-annealing experiments will be discussed. In the AZO deposition part, the effect of RF plasma enhancement on the magnetron plasma will be shown, then followed by the effect of oxygen and thickness variation of the deposited AZO samples; in the post-annealing part, ITO samples would first be treated as a demonstration of the effect of hydrogen-containing atmospheric plasma on TCOs, then the deposited AZO samples will be treated to see the effect of the annealing plasma on the AZO films deposited in the SHADE experiment.

* Corresponding author at: 216 Talbot Laboratory, MC-234, 104 South Wright Street, Urbana, IL 61801, USA. Tel.: +1 217 333 2295.
E-mail address: wu139@illinois.edu (Y.L. Wu).

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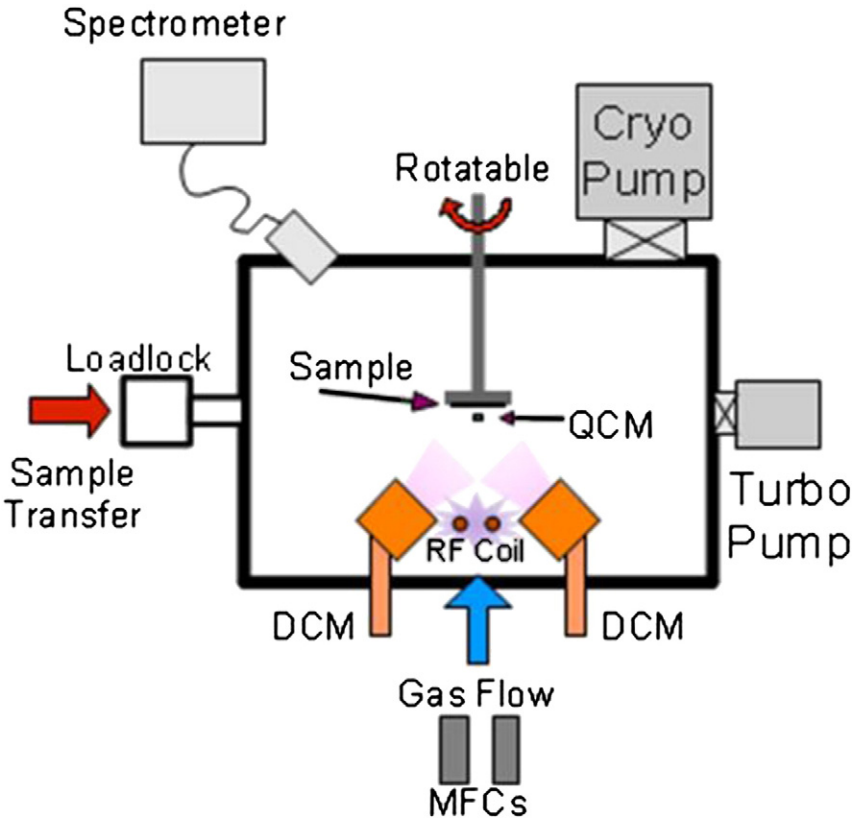

Fig. 1. Schematic of the SHADE vacuum chamber used to produce AZO films, showing the locations of the sample load lock, vacuum pumps, dual magnetrons and RF antenna.

2. Experimental

Samples were made in the Sputtering High-purity Atomic Deposition Experiment (SHADE) (Fig. 1). It has a dual magnetron setup for depositing thin films under an ultra-high vacuum (UHV) environment. A secondary RF antenna is also used in order to tailor the properties of the deposited films. The RF antenna is placed in between the two magnetrons with opposite polarity and the plasma is formed in between (Fig. 2). By using an unbalanced dual magnetron configuration, closed field lines can be generated that trap plasma over a large volume, thus allowing more ionizations to take place in the plasma. Base pressure of the vacuum system was 5×10^{-7} Torr. Standard microscope glass substrates were used in all the samples deposited and annealed in SHADE except for the purchased ITO samples (Sigma Aldrich, surface resistivity 300 Ω/sq, 749796) where the substrates were made with polyethylene terephthalate (PET). The purchased film has a 100 nm ITO sputter coated on top of the PET making the total thickness of the film as 5 mil (0.127 mm). The AZO targets used in the dual magnetron setup were sputtering ceramic targets (98 wt.% ZnO + 2 wt.% Al_2O_3) and the processing gas was Ar/O_2. Oxygen flow varied from 0 to 0.6% of argon flow and the total pressure was kept at 5 mTorr during deposition. The magnetrons were operated in constant current (DC)

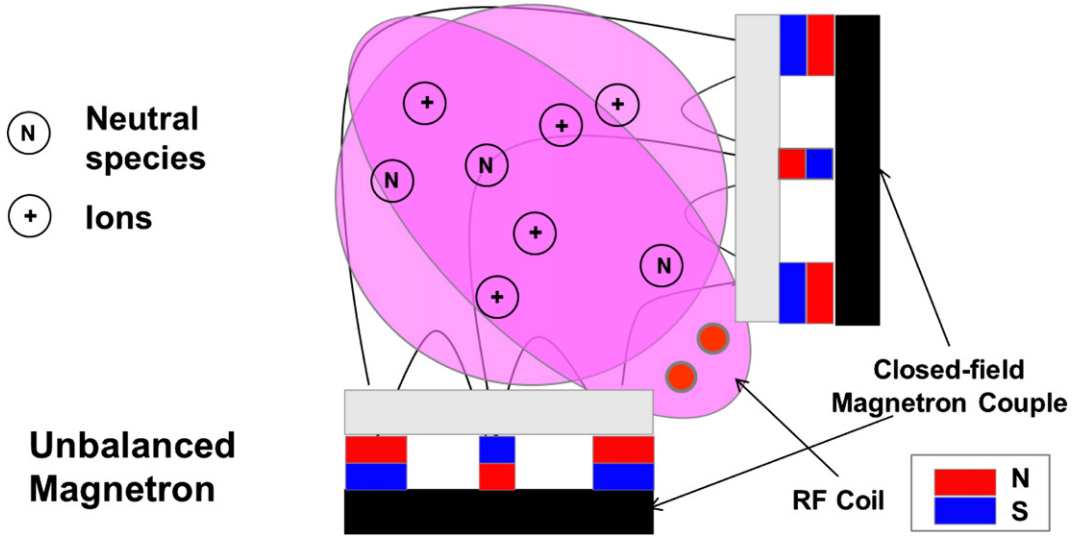

Fig. 2. Schematic of the dual magnetron setup and the RF plasma inside the SHADE vacuum chamber. The unbalanced field lines originate from one magnetron and terminates at the other, and the RF coil is placed in the middle between the two magnetrons to generate a secondary plasma in the region between.