



Plasma-aided hydrogenation and Al-doping: Increasing the conductivity and optical transparency of ZnO transparent conducting oxide

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ABSTRACT

Plasma-assisted magnetron sputtering with varying ambient conditions has been utilised to deposit Al-doped ZnO (AZO) transparent conductive thin films directly onto a glass substrate at a low substrate temperature of 400 °C. The effects of hydrogen addition on electrical, optical and structural properties of the deposited AZO films have been investigated using X-ray diffractometry (XRD), scanning electron microscopy (SEM), Hall effect measurements and UV–vis optical transmission spectroscopy. The results indicate that hydrogen addition has a remarkable effect on the film transparency and conductivity with the greatest effects observed with a hydrogen flux of approximately 3 sccm. It has been demonstrated that the conductivity and the average transmittance in the visible range can increase simultaneously contrary to the effects observed by other authors. In addition, hydrogen incorporation further leads to the absorption edge shifting to a shorter wavelength due to the Burstein–Moss effect. These results are of particular relevance to the development of the next generation of optoelectronic and photovoltaic devices based on highly transparent conducting oxides with controllable electronic and optical properties.

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1. Introduction

Transparent conductive oxides (TCOs) have been extensively investigated as they can be used in a wide variety of electronic and optoelectronic applications such as low-emissivity windows, electrochromic mirrors and windows, defrosting windows, electromagnetic shielding, photovoltaic cells and flat panel displays [1,2]. The most notable differences between TCOs and conventional semiconductors apart from transparency arise in the transport of charge carriers through the crystalline lattice. It is found that the effective masses and number density of carriers are in a higher order of magnitude as compared to conventional semiconductors. Therefore, the charge carriers move more slowly through the material and with a greater coupling to the lattice whilst maintaining a mobility of up to 20 000 cm² V^{−1} s^{−1} leading to remarkable electronic properties [3].

One of the most exciting properties of TCOs is their piezoelectric property enabling their use as self-powered devices (which convert mechanical energy to electrical energy). This property is particularly strong in ZnO nanowires, which were used to produce self-powered pH and UV sensors [4]. For example, it has been

demonstrated that by stacking 3 ZnO nanowire arrays on top of each other a voltage of 0.243 V and power of 2.7 mW cm^{−3} can be produced [4].

The peculiar properties of TCOs cannot be effectively implemented without the ability to control the electronic structure of the material and to this end donor/acceptor elemental doping is used. In this work we have focused on ZnO due to its broad range of properties and because it is found to be cheaper and more stable than other metal oxide materials [5–9]. The most common dopants for ZnO are group III elements such as boron (B) [10], aluminum (Al) [11], gallium (Ga) [12], and indium (In) [13]. Aluminum doped zinc oxide (AZO) has been investigated in this work as doping with Al usually produces a film with a lower resistivity when compared to the other mentioned dopants [14]. Moreover, Al-doped ZnO thin films show an increase in conductivity coupled with a decrease in transmittance and vice versa as the dopant concentration is varied. This contradictory trend is a common problem for many existing TCO films.

Incorporation of hydrogen in most semiconductors is generally found to produce an amphoteric impurity [15], acting in a fashion that counteracts conductivity. Recently however there has been interest in the effect of atomic hydrogen on the properties of ZnO. First-principle calculations based on the density-functional theory (DFT) that interstitial hydrogen in ZnO has a higher probability of appearing in a H⁺ (cation) state rather than H⁰ (neutral) or H[−]

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(anion) [16]. This indicates that hydrogen in ZnO acts as a shallow n-type donor [17]. Therefore, in this experiment the co-doping of hydrogen and Al is anticipated as a possible solution to the problem of either having low resistivity or high transmittance in Al-doped ZnO thin films.

Applications of low-temperature plasmas to enhance the growth of oxide materials (e.g., by using ionized physical vapor deposition, iPVD) are well established [17–19]. For instance, iron oxide can be produced over large areas and in large quantities with the use of a plasma and that the growth is rationalized and controllable by plasma parameters [20]. Niobium oxide materials have also found to grow efficiently in a plasma system with the structure and morphology of the deposits able to be controlled [21]. The common result found is that the plasma can be used to control the delivery of building materials onto the growing by varying the process parameters [22–24]. A somewhat similar result is found when a specific dopant element is added to the plasma. This has been found to be effective in producing n-type ZnO thin films where nitrogen is incorporated from an Ar + N₂ plasma as ZnO is sputtered onto a substrate [25]. In the experiments of this work, a Ar + H₂ plasma has been used to enhance the effectiveness of the doping. Similar plasma mixtures have been previously successfully used for the mask-less production of self-organized surface nanostructures [26]. Surface termination by hydrogen was found as the important mechanism of the surface energy control (e.g., reduction) and nanostructure shaping [26–28]. Incorporation of hydrogen atoms may also lead to structural transformations such as reorganizations of atomic networks to regular crystalline states [29].

In this work, we demonstrate that simultaneous hydrogenation (from a low-temperature thermally non-equilibrium Ar + H₂ plasma) and Al doping is beneficial to both the transmittance and the resistivity of the Al-doped ZnO thin films. It is shown that by utilizing the plasma as the source of hydrogenation the conductivity and transmittance can be made to simultaneously increase. The hydrogen flux is then optimized in the view to produce films with the desired optical and electrical properties maximized.

2. Experimental details

ZnO films were deposited onto a microscope slide glass substrate by reactive radio-frequency (RF) magnetron sputtering at 13.56 MHz using a CESAR rf power generator in a sputter-up configuration of the Integrated Plasma-Aided Nanofabrication Facility (IPANF) [30]. The samples were deposited at 400 °C using a rf power density of 5.0 W/cm². The base pressure in the chamber was kept below 2×10^{-5} Torr, and the distance between the target and the substrate was 5 cm. An Al₂O₃ chip (99.99% in purity) with a square area of 12 cm² placed on top of a ceramic ZnO target (99.99% in purity) served as the source for the doping impurity. This corresponded to an area percentage of Al₂O₃/ZnO sputtering target materials of 12 cm²/66.54 cm².

In order to dope the samples with hydrogen, the sputtering was carried out in the chamber containing Ar and H₂. Hydrogen gas was introduced into the sputtering chamber to co-sputter the Al₂O₃/ZnO target. The thin film deposition was carried out at a pressure of 35 mTorr with the Ar flow rate being set to 60 sccm; whilst the H₂ flow rate was varied. To investigate the effects of the hydrogen addition on the properties of ZnO:Al films, a series of samples were deposited with different H₂ flow rates of 0.0, 1.0, 2.0, 3.0, 5.0, 7.5, and 10.0 sccm.

The structural analysis was carried out by an X-ray diffraction (XRD, Philips X'Pert MRD) measurement (Cu K α wavelength, $\lambda = 1.540562$ Å, θ – 2θ scan mode). Surface morphology observation and film thickness measurements were performed with a JEOL JSM 6700F field emission scanning electron microscope (SEM). The film

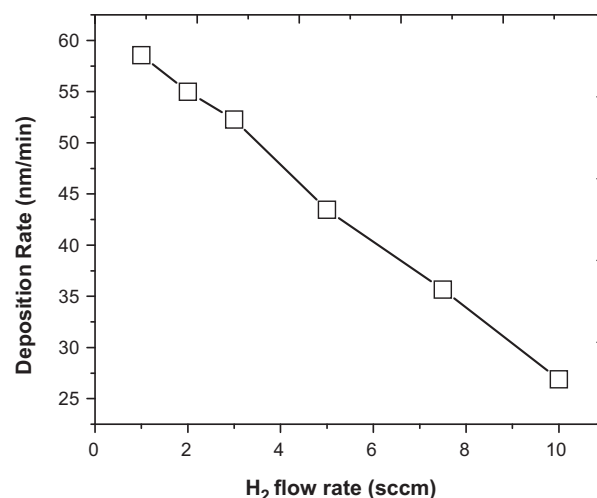


Fig. 1. Influence of the H₂ flow rate on the deposition rate.

thickness was estimated using cross-sectional SEM imaging. The electrical resistivity, Hall mobility and carrier concentration were determined at standard conditions using a Bio-Rad HL5500 system following the van de Pauw method. The optical transmission and reflection spectra were obtained using a Varian Cary 510 Bio UV–vis spectrophotometer over a wavelength range from 300 to 1100 nm.

3. Results and discussions

Here we analyze the structural, electronic and optical properties of the deposited ZnO films. The analysis is aimed at ascertaining the influence that the addition of H₂ to the plasma has on the properties of the films.

3.1. Structural properties

The thickness of the films deposited in this series of experiments was approximately 2.5 μ m. The deposition rate was found to decrease as the hydrogen partial pressure in the chamber increased as shown in Fig. 1. This indicates that hydrogen acts as an etchant and therefore by adding hydrogen to the system the film thickness decreases. The XRD spectra of the samples are displayed in Fig. 2 and show the shift of the ZnO (002) peak with increasing the amount of hydrogen. All films exhibit the (002) peak due to the self-texturing mechanism [31]. It can be seen in Fig. 2 that the samples deposited with less than 5 sccm of hydrogen feature 2 peaks, whilst only 1 peak is observed for the samples deposited using a hydrogen flow between 3 and 5 sccm. Indeed, an increase in the H₂ flow is found to cause the above 2 peaks to merge as a result of one of the peaks broadening. It is also observed that an increase in H₂ flow decreases the intensity of the XRD spectra. This is indicative of the crystalline grains becoming more randomly oriented with increased hydrogenation. These observations show that increasing the flow rate of hydrogen beyond 3 sccm leads to poor film crystallinity. This effect may be a result of the hydrogen acting as an etchant, which increases the overall etching occurring during the growth.

The increase in the H₂ flow thus leads to stronger etching of the growth surface, which increases the number of defects in the film, thereby reducing the crystallinity. From Fig. 2, it can be seen that the (002) peak shifts towards a smaller diffraction angle with an increase in the H₂ flow to 3 sccm. It may then be inferred that the H-atoms were initially successfully incorporated in the AZO thin films and that the location of H⁺ cations inside Al-doped ZnO thin

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