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Properties of ALD Aluminum-doped ZnO as transparent conductive oxide

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Thin films of aluminum- doped ZnO are prepared by Atomic Layer Deposition (ALD). The properties of these films toward application as transparent conductive oxides are studied. It is obtained that doped films possess high optical transmittance (>85%) in the visible and near-infrared spectral ranges. A resistivity as low as $3x10^{-3}$ Ω.cm depending of the Al content in the doped film is measured. The observed high conductivity and high transparency fulfil the requirements for transparent conductors.

Keywords: ALD, doped ZnO, transparent conductive oxide, thin films

INTRODUCTION

Transparent conducting oxides (TCOs) are considered key materials for a range of applications in electronic screens and displays, LEDs and solar cells. These applications take advantage of the unique characteristics of TCOs, which include high electrical conductivity, transparency in the visible range and good chemical and thermal stability. TCOs usually are based on simple oxides as In_2O_3, SnO_2, Ga_2O_3 and ZnO – which are intrinsically or extrinsically doped in order to provide electrical properties similar to those of metals, and high transparency. Tin-doped indium oxide (ITO) is currently the most popular TCO, but concerns for the cost and supply of indium have resulted in increasing efforts to find alternatives. The most promising candidate for the replacement of ITO is aluminum-doped zinc oxide (AZO) which have low resistivity of the order of 10^{-4} Ω.cm, high transparency, and inexpensive non-toxic source materials [1].

The doping is a process in which impurities are intentionally introduced, in order to modulate the electrical properties and thus establish electrical conductivity as a result of free carriers. The process of extrinsic doping involves the addition of metal ions with different valences to the crystal lattice structures of the simple oxides in order to form these free carriers. For intrinsically doped TCOs, the electrons originate from intrinsic defects, or interstitial metal cations. In both cases, these structural imperfections give rise to the increased carrier concentrations and consequently electrical conductivity. Typical point defects observed in intrinsically doped ZnO are oxygen vacancies and Zn^{2+} in an interstitial while in AZO it is Al^{3+} occupying a Zn^{2+} site in the ZnO lattice [2].

Aluminum- doped ZnO thin films can be deposited by several techniques such as sol–gel, chemical spray, thermal evaporation, pulsed laser deposition, DC and RF magnetron sputtering. In our research ALD was used as method for preparation of AZO films with qualities appropriate for application as transparent conductive oxides.

EXPERIMENTAL

TCOs are deposited as thin films for a wide variety of applications demanding electrical conductivity and optical transparency. The desired qualities of a good TCO: transparency, conductivity, and surface texture, depend on the growth technique and the growth parameters. Atomic layer deposition (ALD) is a growth technique which has recently become very popular since it provides uniform and conformal coverage and control of the thin film by atomic layer precision. ALD is a self-limited deposition method that is characterized by alternating exposure of the growing film to chemical precursors, resulting in

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the sequential deposition of mono layers over the exposed sample surface. The self-limiting nature of the vapor-solid reactions ensures pinhole free coatings with a precise thickness controlled at the atomic scale and superb conformality onto large scale substrates with complex topologies. The main features which make the ALD distinctive technique for deposition of thin films are shown at Fig. 1. Although the growth rate of the ALD system is relatively low, the uniformity, conformality and the compactness of the film cross-section achieved from the ALD technique are superior to those from other techniques [3].

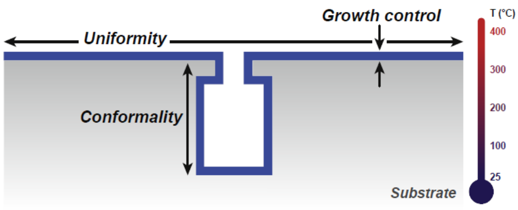

Fig. 1. ALD method features: precise growth and thickness control, high conformality/step coverage, good uniformity on large substrates, low substrate temperatures [4].

The AZO films were grown on two different substrates: p-type single crystal Si (100) and fused silica using Beneq TFS-200 ALD system. The substrates temperature during deposition was 200 °C. Diethylzinc (DEZ, $Zn(C_2H_5)_2$), trimethyl-aluminum (TMA, $Al(CH_3)_3$), and deionized water (H_2O) are used as Zn, Al and oxidant precursor, respectively. Nitrogen was used as a carrier and purge gas. The general reaction sequence for ZnO ALD involves separate DEZ and H_2O exposures, and Al_2O_3 ALD utilizes separate TMA and H_2O exposures. Since H_2O is adsorbed on most surfaces, a formation of Si–O–H hydroxyl group on the Si substrate is expected. The growth sequence can be understood from the following surface reactions on a hydroxylated Si substrate.

$$Zn(C_2H_5)_2 + Si\text{-}O\text{-}H = Si\text{-}O\text{-}Zn(C_2H_5) + C_2H_6 \quad (1)$$

$$Si\text{-}O\text{-}Zn(C_2H_5) + H_2O = Si\text{-}O\text{-}Zn\text{-}O\text{-}H + C_2H_6 \quad (2)$$

$$Si\text{-}O\text{-}Zn\text{-}O\text{-}H + Al(CH_3)_3 = Si\text{-}O\text{-}Zn\text{-}O\text{-}Al(CH_3)_2 + CH_4 \quad (3)$$

$$Si\text{-}O\text{-}Zn\text{-}O\text{-}Al(CH_3)_2 + 2H_2O = Si\text{-}O\text{-}Zn\text{-}O\text{-}Al\text{-}(O\text{-}H)_2 + 2CH_4 \quad (4)$$

AZO films with targeted thickness were deposited using several supercycles. Usually n monolayers (cycles) of ZnO plus one monolayer (cycle) of Al_2O_3 represent one supercycle as shown in Fig. 2.

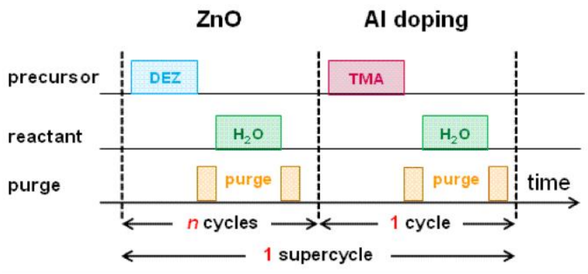

Fig. 2. Super cycle for Al doped ZnO ALD.

Transmittance spectra of samples deposited on fused silica substrate were measured in spectral range covering UV, VIS and NIR using a spectrophotometer. The sheet resistance was obtained by the standard four-probe technique on Veeco EPP-100 apparatus at room temperature and the resistivity was calculated using the thickness data from ellipsometric measurements. Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were used for study the morphology of the films with average thickness of 180 nm.

RESULTS AND DISCUSSION

The prepared AZO films were polycrystalline and predominantly *c*-axis oriented perpendicular to the substrate surface, as evidenced by x-ray diffraction analyses [5]. Al doping affects the crystallographic orientation of the grains in the ZnO film, causing the preferred orientation of the films to shift to the (100) direction.

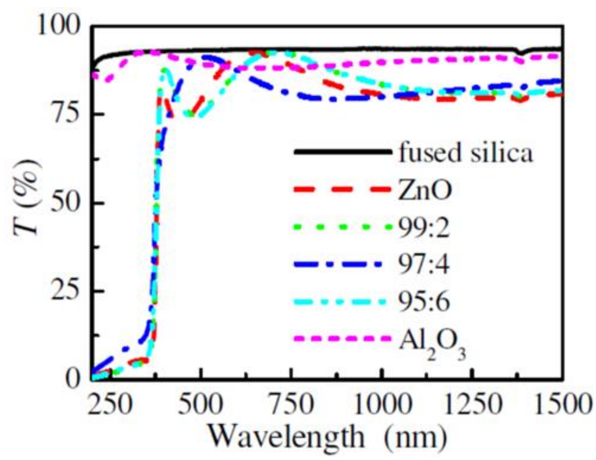

Fig. 3. Transmittance spectra of Al_2O_3, ZnO and samples with compositions ZnO: Al_2O_3 (cycles ratio shown)

Fig. 3 presents transmittance spectra of samples deposited on fused silica substrate. The substrate's spectrum is also shown for comparison. It is seen that all samples containing ZnO are transparent for wavelength higher than 370 nm and absorbs light with smaller wavelength, while the transparent window of Al_2O_3 extends towards UV range. The position of fundamental absorption edge is almost the same for all samples containing ZnO but more detailed analysis is needed including calculation of optical band gap thus accounting for slightly different thicknesses of the samples. The transmittance in the visible region normalized to that of the substrate oscillated between 90% and 100% due to constructive and destructive interference.

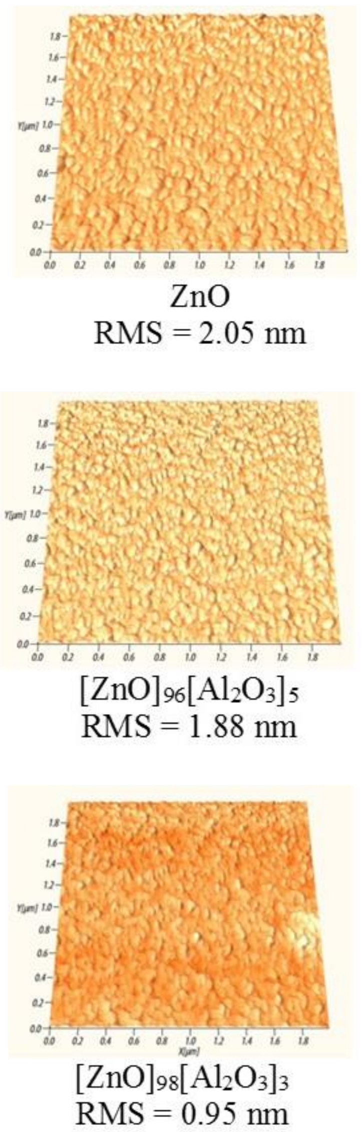

Fig. 4. AFM of ZnO and Al-doped ZnO (AZO).

AZO films are more transparent in the infrared (IR) than ITO films. IR transmission is very important because increasing the long-wavelength response is an approach to increase the efficiency of some solar devices [6]. Thus, AZO films are an appropriate replacements for ITO films in applications such as transparent electrodes for solar cells, flat panel displays, LCD electrodes, touch panel transparent contacts and IR windows [7].

The surface morphology of the thin films was studied by AFM and SEM as shown in Figs. 4 and 5, respectively. The as-grown films are relatively smooth with uniform distribution of grains which are around 60 to 100 nm long and 10–20 nm wide. Another important requirement for TCO electrodes in electronic devices is the formation of tailored interfaces with the active electronic material, which is normally a typical semiconductor [8]. As it shown on the SEM cross-sectional view, the interface between the AZO and Si substrate is very smooth. The incorporation of Al_2O_3 layers into ZnO significantly reduces the surface roughness of the film (from RMS= 2.05 nm to RMS = 0.95 nm, see Fig.4), and by varying the amount of Al_2O_3 layers it is possible to tune the ZnO films' roughness for gas sensor applications [9].

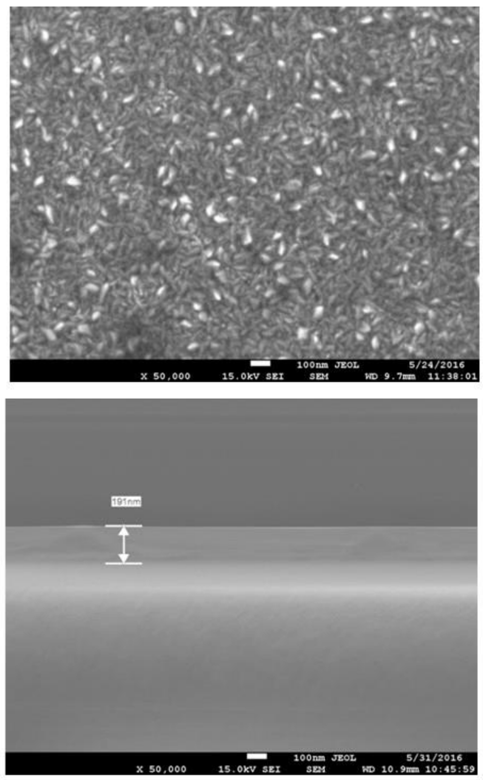

Fig. 5. SEM plan view and cross-section of AZO film showing polycrystalline morphology and smooth interface between the film and Si wafer substrate

The obtainable electrical properties of doped ZnO films are strongly dependent on the deposition methods and conditions. Vacuum evaporation of AZO is difficult to achieve because the vapor pressure of Al_2O_3 is too low in comparison with that of ZnO. AZO films with a resistivity of the order of 10^{-5} Ω cm have been obtained by PLD, but preparing films on large substrates with a high deposition rate is very difficult to achieve. The deposition of AZO films on large area substrates by dc magnetron sputtering using an oxide target is particularly difficult because the resistivity follows a spatial distribution corresponding to the target erosion area pattern created on the substrate surface [10].

Table 1. Volume percentage of Al_2O_3 layer content, thickness and resistivity of AZO films

$[ZnO]_n[Al_2O_3]_m$	Al_2O_3 layer content, %	Thickness, nm	Resistivity, Ω.cm
ZnO	-	160	7.6×10^{-3}
$[ZnO]_{100}[Al_2O_3]_1$	0.55	196	4.2×10^{-3}
$[ZnO]_{99}[Al_2O_3]_2$	1.11	189	3.3×10^{-3}
$[ZnO]_{98}[Al_2O_3]_3$	1.67	186	3.9×10^{-3}
$[ZnO]_{97}[Al_2O_3]_4$	2.24	183	4.2×10^{-3}

Aluminum doping purpose is the lowering of resistivity as low as possible, and several studies report resistivity values in the 10^{-4} Ω.cm range. The optimal Al doping amount for minimizing resistivity varies from study to study, but is generally reported to be in the 2%–5% range. At higher Al contents the resistivity increases again as the solubility limit of Al into ZnO is exceeded, which is thought to lead either to the formation of separate Al_2O_3 phases or the spinel phase $ZnAl_2O_4$ [11]. The results of our measurements are presented on Table 1. Resistivity values of~$3x10^{-3}$ **Ω**·cm have been reached and the values could still be further optimized. The resistivity is mostly determined by the Zn/Al ratio in the film [12], however the process temperature has also an effect.

CONCLUSIONS

Al-doped ZnO films were grown using thermal mode ALD with DEZ/H_2O precursors for ZnO and Al_2O_3 ALD with TMA /H_2O. The composition of the doped films was controlled by adjusting the relative number of ZnO ALD and Al_2O_3 ALD reaction cycles in the pulse sequence. Films with physical characteristics that could be tuned over the full range of values defined by pure ZnO and Al_2O_3 were grown. A variety of film properties was investigated with Al content including the film optical transmittance, surface roughness, crystallinity, and resistivity. Optical transparency higher than 85% and resistivity up to $3x10^{-3}$ **Ω**·cm were measured. The obtained results show that AZO films are appropriate materials for functionality as transparent conductive oxide.

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СВОЙСТВА НА ПОСЛОЙНО АТОМНО ОТЛОЖЕН ЛЕГИРАН С АЛУМИНИЙ ZnO КАТО ПРОЗРАЧЕН ПРОВОДЯЩ ОКСИД

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(Резюме)

Чрез метода на последователно отлагане на атомни слоеве са получени тънки слоеве от ZnO легиран с алуминий. Изследвани са свойствата на тези слоеве за приложение като прозрачни проводими оксиди. Установено е, че легираните слоеве притежават висока оптична пропускливост (>85%) във видимата и близката инфрачервена области на спектъра. Измерени са ниски съпротивления до $3x10^{-3}$ Ω.cm, зависещи от съдържанието на Al в легираните слоеве. Получените висока проводимост и оптична транспарентност изпълняват условията за приложение на легираните с алуминий ZnO слоеве като прозрачни проводници.