ELABORATION AND CHARACTERIZATION OF ZnO THIN FILMS
DEPOSITED BY DC SPUTTERING AT LOW PRESSURE AND LOW
TEMPERATURE:
APPLICATION TO PHOTOVOLTAIC AND GAS SENSOR

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ABSTRACT

DC reactive sputtering was used to deposit Zinc oxide (ZnO) films onto corning glass and
crystalline silicon substrates at both room temperature and 100°C with an argon/oxygen
mixture at sputtering pressure varying from 10 to 70 Pa. The dependence of films properties
including structure, microstructure as well as optical on deposition parameters (deposition
temperature and sputtering pressure) are investigated. The ZnO thin films were characterized
by X-ray diffraction (XRD), scanning electron microscopy (SEM), optical transmission,
electrical conductivity measurements.

All ZnO films exhibit an intensive (002) XRD peak, indicating that the films are highly
texturized along the c-axis perpendicular to the substrate surface. It is found that the nature of
the annealing atmosphere has a great influence on the ZnO film composition. Furthermore,
thermal annealing at 300°C have the effects of narrowing the diffraction peak and shifting the
(002) peaks to higher 2θ angles, which indicates that grain growth has occurred.
The transmission measurements have shown that all films exhibit high transmittance in the
400–2500 nm range. Post-deposition annealing influences the morphological, optical and
electrical properties of ZnO films. A very large increase in electrical conductivity, up to nine
orders of magnitude, was observed in as-grown ZnO films upon vacuum-annealing at 300°C
for one hour, reaching as high as 10Ω -1 .cm -1.

Keywords: reactive sputtering, transparent conducting zinc oxide, optical properties, structural characterization, electrical conductivity.
1. Introduction

Transparent conducting zinc oxide (ZnO) has received a vast amount of attention in the last few years. This material is both transparent and conductive with a wide variety of applications (solar cell, microelectronics, sensors) [1]. For solar cell applications, a strong c-axis orientation (002) perpendicular to the substrate is required. The single orientation in polycrystalline ZnO can easily be obtained by controlling the deposition parameters. The material properties (i.e. structural, optical and electrical properties) of the ZnO thin film are strongly dependent on the processing conditions, such as gas phase composition, plasma conditions, deposition temperature, geometry and the specific growth technique employed. ZnO can be deposited by a variety of techniques such as radio frequency (RF) sputtering, direct current (DC) magnetron sputtering [2,3], pulsed laser deposition (PLD) [4] and molecular beam epitaxy (MBE) [5]. However among the methods of deposition, sputtering is a promising technique to grow ZnO thin film at lower temperature with higher purity, better-controlled composition, greater adhesive strength, and higher density.

Deposition by DC magnetron sputtering is usually performed at pressures of $10^{-2}-10^{-3}$ Torr (0.13-1.30 Pa) in order to allow a larger mean free path for the sputtered atoms to reach the substrate. It can be used in reactive as well as non-reactive modes. There are, however, differences between reactive sputtering with an argon/oxygen mixture from a metallic Zn target than sputtering with pure argon from a ceramic ZnO target. The control of film stoichiometry has been found to be much easier with oxide targets, which avoids the need for high temperature and post-deposition annealing. In the case of reactive sputtering of metallic targets, the deposition rate and film stoichiometry are strongly dependant on the oxygen content in the sputtering chamber. To our best knowledge, DC reactive sputtering deposition of ZnO thin films at high pressures up to 30Pa has not been reported in the literature [6-7].

In this paper, we report the successful growth of highly crystalline ZnO thin films by DC reactive sputtering technique under high working pressure (70 Pa) of argon/oxygen mixture. The ZnO thin films were characterized by X-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM), optical transmission, electrical conductivity measurements, and photoluminescence.
2. Experimental details:

2.1. Thin films deposition

The zinc oxide films were deposited on corning glass 9075 (for optical transmission and electrical conductivity measurements) and crystalline silicon substrates by DC reactive sputtering in a home-made planar sputtering system. The quartz glass and silicon substrates were rinsed in acetone, ethanol and distilled water sequentially. The sputtering chamber was pumped down to about $5.10^{-6}$ mbar ($5.10^{-4}$ Pa) by using a diffusion pump and rotary pump combination. High purity (99.995%) argon and oxygen were used as sputtering and reactive gases, respectively. A disc of zinc (75 mm in diameter and 0.25 mm thick) with a purity of 99.95% was used as the sputtering target.

Six sets of ZnO thin films with thicknesses varying from 50 to 500 nm were elaborated at room temperature (RT) and 100°C in (Ar+O₂) plasma mixture at a sputtering pressure varying from 10 to 70 Pa. The target to substrate distance was 38 mm. The deposition sputtering current during the film deposition was 600 mA. The control of the stoichiometry of ZnO thin films is done through the control of oxygen percentage in Ar/O₂ gas mixture.

2.2 Film characterization

Optical emission spectroscopy (OES) measurements were carried out at room temperature in the wavelength range of 400–800 nm. The emission from plasma was collected by an optic fiber externally mounted on the vacuum chamber window and pointed to the center position between the cathode and the substrates. OES from the plasma was detected by multichannel photo-analyzer (Hamamatsu Photonics, PMA-12).

Structural and microstructural changes in the deposited ZnO films were characterized by grazing incidence (0.8°) X-ray diffraction (XRD) measurements on Brucker D8 Advance AXS diffractometer in a (θ–2θ) geometry using Cu-Kα radiation ($\lambda=0.1540$ nm). The θ - 2θ curves were measured in symmetrical Bragg-Brentano geometry in the (10–90°) 2θ range. Microstructural parameters (lattice parameters, crystallite size and microstrains) were obtained from the full pattern XRD Rietveld fitting procedure using the MAUD program which is based on the Rietveld method [8].

The surface morphology of the films was analyzed by scanning electron microscopy (SEM) in a JEOL-6360 electron microscope.

Room temperature diffuse absorption measurements were performed using a CARY 500 UV-Visible-NIR spectrophotometer in the range 250-2500 nm, with a resolution of 0.3 nm in
the UV-Visible wavelength region and 1 nm in the NIR. This spectrometer is equipped with an integrating sphere accessory coated with PTFE (Poly Tetra Fluoro Ethylene) white material. The optical transmission spectra allows evaluating the film thickness "d", the static refractive index "n_s" and the absorption coefficient "α".

Electrical conductivity measurements were performed in a coplanar configuration. The current measurement versus temperature is taken in the secondary vacuum cryostat at $10^{-5}$ mbar ($10^{-3}$ Pa) under constant bias polarization.

3. Results and Discussion:

   OES is a widely used diagnostic that provides information on the species present in the plasma. Optical emission spectra for the plasma were investigated in order to identify excited species according to varying experimental deposition parameters. OES show the presence of several reactive oxygen species including O⁺ (777 nm), O₂⁺ (645 nm), O₂⁺ (465 nm), molecular oxygen ions O₂⁺ (602 nm), and metal atomic Zn at 430, 472, 481 and 636.2 nm. A dominant emission peak at 777 nm induced by the atomic oxygen transition of 3p⁵P-3s⁵S⁰ was observed in the emission spectra. Because of the large number of emission lines associated with different species in the plasma and detected in the range 400-800 nm, we give an insight of the lines observed in the range 700-800 nm. Fig. 1 shows representative OES spectra obtained from O₂/Ar during the sputtering of Zn target. OES show the presence of 04 peaks of argon (Ar I) corresponding to the wavelengths 706.7, 738.4, 750.3 and 763.5 nm, a peak associated with oxygen (O*) located at 777 nm and a peak of zinc (Zn II) at 763.25 nm. These emission lines are generally those found in the literature on ZnO [9].

   X-ray diffraction (XRD) 0/20 patterns of the ZnO films are shown in Fig. 2. It was apparent that all layers are composed of ZnO phase oriented along the c axis with a significant (002) peak, indicating that the layers are highly textured along the c axis perpendicular to the substrate surface. The same peaks are observed with a greater intensity for the sample deposited under primary vacuum (sample K4), and therefore at a greater oxygen pressure (inset of Fig. 2). This result can be explained by the fact that [002] plane requires a lowest energy formation [10]. With the increasing oxygen partial pressure an improvement in the crystallographic structure is seen, which can be explained by a reduction of the bombardment of the growing films by high-energy particles in (O₂+Ar) plasma. The XRD patterns reveal another diffraction peaks assigned to the ZnO crystals in the sample deposited at RT and 100°C. No diffraction from randomly oriented grains or impurity phases can be observed from the X-ray patterns related to the as-grown ZnO films. The crystalline structure of ZnO
thin films indexed by XRD reveals hexagonal lattice with cell parameters \(a=b=3.2499\,\text{Å}\) and \(c=5.2066\,\text{Å}\). The nature of the annealing atmosphere has a great influence on the ZnO film composition. When the heat treatment is performed in air the oxygen concentration increases with temperature. In contrast, heating under nitrogen or vacuum produced a loss of oxygen. The XRD spectra reveal the influence of post-treatment on the structure of the ZnO thin film. Fig. 3 clearly shows that thermal annealing at 300°C have the effects of narrowing the diffraction peak and shifting the (002) peaks to higher 2\(\theta\) angles, which indicates that grain growth has occurred. This increase in the intensity can be attributed to increased thermal energy provided to the atoms during the annealing step, thereby improving their mobility and also a reduction of the defects density in ZnO [11]. At the same time, a refinement of this peak and its shift to larger angles is clearly shown, it is characteristic of a decrease in the inter-planar distance. These results reflect an increase in the crystallinity of the material. It is found that the (002) peak located at 2\(\theta=34.26^\circ\) before annealing moves to the position related to the ZnO powder (2\(\theta=34.40^\circ\)), indicating that ZnO film is in a state of stress with a traction component parallel to c-axis. This shift of the peak indicates a reduction in tensile stress [11]. The full width at half maximum (FWHM) of the (002) diffraction peaks of as-grown and annealed films have the value of 0.58 and 0.24°, respectively. From the integral width and peak position of the (002) peak, the grain size in the films is calculated. The average grain size of the film can be estimated by Scherrer formula, using FWHM value of the XRD diffraction peaks as follows [12]:

\[
D = \frac{0.9\lambda}{B \cos \theta}
\]  

(3)

Where \(D\), \(\lambda\), \(\theta\) and \(B\) are the mean grain size, the X-ray wavelength (0.154nm), Bragg diffraction angle and the FWHM of the (002) diffraction peak located at 2\(\theta=34.26^\circ\) for ZnO films, respectively.

The grain size of the films increased from 14.3 to 34.6 nm upon air-annealing at 300°C due to the improvement in the crystallinity of the films [13]. This size increase can be attributed to a gradual disappearance of small crystallites that merge to form larger crystallites [14]. This change of lattice originates from the coalescence of small crystallites and the reduction of grain boundaries.
The surface morphology of the layers was analyzed by scanning electron microscopy (SEM) in order to know the influence of deposition conditions on the microstructure of the samples. The secondary electron image of ZnO thin film deposited on silicon at RT (sample K4) shown in Fig. 4a reveals a compact and a uniform surface with a presence of crystallites distributed over the surface. Significant changes are observed after vacuum-annealing at 300°C for one hour, resulting in the appearance of sticks distributed over the surface (Fig. 4b). Fig.4b clearly evidenced a smooth surface of low roughness with small rounded grains with an average diameter of about 100 nm.

The optical transmission and reflection spectra measured for the ZnO films deposited at room temperature and 100°C are presented in Fig. 5. All studied films were uniform and transparent to the naked eye. The transmittance spectra in the 400–1200 nm range, neglecting the losses in the corning glass substrate, have shown that all films exhibit high transmittance of the order 76–91%. Transmission, however, falls very sharply in the UV region due to the onset of fundamental absorption. This result indicates that the films prepared under these conditions are homogeneous and smooth surfaces. The optimal sputtering pressure to obtain transparent ZnO films, uniforms and stoichiometric is around 0.7 mbar (70Pa). The inset shows the transmittance spectra for the as-grown ZnO film and annealed film in air at 300°C for one hour, respectively, revealing that post-deposition annealing in air influences the optical properties of ZnO films.

The optical band gap ($E_g$) was calculated using the Tauc plot. According to Tauc, the photon energy dependence of absorption coefficient $\alpha$ can be described by the following relation [14]:

$$\alpha h\nu = B(h\nu - E_g)^r$$

(1)

Where $B$ is a parameter that depends on the transition probability, $h$ is Plank’s constant, $\nu$ is the frequency of the incident photons, and $r$ is an index which depends on the nature of the electronic transition responsible for the absorption. Since ZnO films are direct transition-type semiconductors, $E_g$ can be determined by plotting $(\alpha h\nu)^2$ versus $h\nu$. The $E_g$ values can be evaluated by extrapolation of the linear portion near the onset of absorption edge to the energy axis. The absorption coefficient was calculated using the relation [15].

$$\alpha = \frac{1}{d} \ln \left( \frac{1 - R}{T} \right)$$

(2)
Where $d$ is the thickness, $R$ is the reflectance and $T$ is the transmittance.

The optical band gap of undoped ZnO films did not change very much with varying $O_2/Ar$ ratios; they are between 3.27 and 3.37 eV (Fig.6). The energy bandgap are in good agreement with the values announced by other authors [16, 17] and remain close to that ZnO bulk: 3.3 eV.

Fig. 7 summarizes the dark conductivity $\sigma_d$ versus temperature in the Arrhenius plot from ZnO thin films deposited at RT and 100°C upon vacuum annealing at 300°C for one hour. The variation of the dark conductivity $\sigma_d$ versus temperature follows a linear variation. It corresponds to a thermally activated conduction mode which can describe by the following expression:

$$\sigma_d = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right)$$

Where $E_a$ is the thermal activation energy and $k_B$ the Boltzmann constant. An important decrease of $E_a$ after annealing is observed, except for the sample deposited at very low oxygen pressure, accompanied by a very large increase in electrical conductivity, by nine orders of magnitude, reaching as high as $10 \ \Omega^{-1}.cm^{-1}$. This resistivity value is accordance with that of ZnO bulk, which is typically as high as $1–100 \ \Omega.cm$ due to less oxygen deficiency [18].

The evolution of optical emission properties of ZnO layers after vacuum annealing at 300°C for one hour has been studied by photoluminescence. In Fig. 10 the PL intensity is significantly increased, thus demonstrating a marked improvement in the film quality as confirmed by XRD and electrical conductivity measurements. A small shift of the 380nm emission band towards the higher wavelengths is observed after vacuum-annealing at 300°C. The emission band located in the visible, due to the presence of interstitial oxygen is always present before and after annealing. We observed at the same time that the annealing does not alter the level of 517 nm emission attributed to the presence of vacancies in the crystal lattice. This oxygen loss can be explained by the fact that annealing is performed in deficient oxygen-atmosphere.
4. Conclusions:
Transparent conductive ZnO thin films have been deposited on corning glass and silicon substrates by DC reactive planar sputtering with an argon/oxygen mixture from a metallic Zn target. ZnO thin films were deposited at RT and 100°C, and subsequently annealed at 300°C for 1 h in vacuum or air.

The transmission measurements have shown that all films exhibit high transmittance in the 400–2500 nm range. The crystalline structure of ZnO thin films indexed by XRD reveals hexagonal ZnO phase with cell parameters a=3.2499 Å and c=5.2066 Å. From the scanning electron microscopy images, a uniform and compact surface with a presence of crystallites distributed over the surface is revealed. Significant changes are observed after vacuum-annealing at 300°C for one hour. A very large increase in electrical conductivity, up to nine orders of magnitude, was observed in as-grown ZnO films upon vacuum-annealing at 300°C for one hour, reaching as high as $10 \Omega^{-1}.cm^{-1}$.

References:
Figure 1: Representative OES spectra obtained from O$_2$/Ar plasma during the DC reactive sputtering of Zn Target.
Figure 2: XRD patterns of ZnO thin-film deposited on corning-glass at RT and 100°C. The inset shows the evolution of (002) diffraction peak according to the different ZnO samples.
Figure 3: Optical transmission and reflection spectra of ZnO thin film deposited at 100°C (sample K2) before and after air-annealing at 300°C for 1 hour.
Figure 4: Secondary electron images of ZnO thin film (sample K4) deposited at RT: (a) before and (b) after vacuum-annealing at 300°C for one hour.
Figure 5: Optical transmission and reflection spectra of O thin films deposited on corning glass substrates at room temperature and 100°C. The inset shows the optical transmission spectra of ZnO thin film before and after annealing in air at 300°C, 1 hour.
Figure 6: The $(\alpha \cdot h\nu)^2$ versus photon energy $h\nu$ plot of as-grown ZnO films deposited on corning glass at RT and 100°C.
Figure 7: Variations of the dark conductivity $\sigma_d$ versus temperature in the Arrhenius plot from a ZnO films deposited at RT and 100°C (open symbol: as-deposited, full symbol: after vacuum-annealing at 300°C, 1 hour).