Thin Solid Films 594 (2015) 256–260

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Corrosion resistance analysis of aluminium-doped zinc oxide layers deposited by pulsed magnetron sputtering

E. G-Berasategui [a],*, R. Bayón [a], C. Zubizarreta [a], J. Barriga [a], R. Barros [b], R. Martins [b], E. Fortunato [b]

[a] IK4-Tekniker, Research Centre, c/Iñaki Goenaga, 5, 20600 Eibar, Guipuzcoa, Spain
[b] CENIMAT/I3N, Departamento de Ciência dos Materiais, FCT, Universidade Nova de Lisboa (UNL) and CEMOP/UNINOVA, 2829-516 Caparica, Portugal

ARTICLE INFO

Article history:
Received 12 November 2014
Received in revised form 8 July 2015
Accepted 8 July 2015
Available online 9 July 2015

Keywords:
Aluminum-doped zinc oxide
Thin films
Transparent conductive films
Direct-current magnetron sputtering
Electrochemical impedance spectroscopy
Corrosion properties

ABSTRACT

In this paper an exhaustive analysis is performed on the electrochemical corrosion resistance of Al-doped ZnO (AZO) layers deposited on silicon wafers by a DC pulsed magnetron sputtering deposition technique to test layer durability. Pulse frequency of the sputtering source was varied and a detailed study of the electrochemical corrosion response of samples in the presence of a corrosive chloride media (NaCl 0.06 M) was carried out. Electrochemical impedance spectroscopy measurements were performed after reaching a stable value of the open circuit at 2 h, 192 h and 480 h intervals. Correlation of the corrosion resistance properties with the morphology, and the optical and electrical properties was tested. AZO layers with transmission values higher than 84% and resistivity of 6.54×10^{-4} Ω cm for a deposition process pressure of 3×10^{-1} Pa, a sputtering power of 2 kW, a pulse frequency of 100 kHz, with optimum corrosion resistance properties, were obtained.

1. Introduction

Lifetime of optoelectronic devices is related to the durability of the transparent conductor front electrodes as they are the most exposed layers in the systems [1]. These front electrodes are currently tin-doped indium oxide layers but indium has been classified as a critical raw material by the European Union [2]. Thus, alternative conductor materials are being investigated. Al-doped ZnO (AZO) is a promising material due to its high transmittance, low electrical resistivity, resource availability, low toxicity, strong resistance to high radiation and thermal and chemical stability. It is an n-type semiconductor material with high conductivity caused by an increase in carrier concentration and in carrier mobility due to the aluminium impurities. Among the different techniques available to deposit AZO layers, DC pulse magnetron sputtering technology has been used as it is optimal for industrial applications allowing deposition of high quality films at large scale with automated processes with no toxic emission or waste [3]. To make AZO front contacts penetrate the market, it is necessary to further investigate the durability of these layers. To test the durability, an exhaustive analysis of the electrochemical corrosion response of AZO layers grown by DC pulse magnetron sputtering deposition as a function of pulse frequency has been performed. The corrosion resistance behaviour is correlated with the optical, electrical and morphological properties.

2. Experimental procedure

A DC magnetron sputtering industrial equipment (MIDAS 450 manufactured by Ik4-TEKNIKER) with a ZnO: Al_2O_3, 98:2 wt.% target was used to deposit the AZO thin films. The power density was 2.9 W/cm^2, which corresponds to 2000 W. The substrates were heated up to 350 °C. The power source was dual output pulsed-DC (5 to 350 kHz) from AEI Pinnacle Plus + 5/5 kW with a duty cycle of 96%. Two different process pulse frequencies were studied, 50 kHz and 100 kHz. Process pressure was fixed at 3×10^{-1} Pa. Layers of 1000 nm thickness were deposited on glass and silicon wafers. The structural characterization of the films deposited on glass was carried out by X-ray diffraction (XRD, PANalytical, model X'Pert Pro) in grazing incidence geometry in 2θ model with Cu Kα line radiation ($\lambda = 1.5406$ Å). Surface morphology was examined by scanning electron microscopy (Zeiss Auriga CrossBeam scanning electron microscope/focused ion beam SEM/FIB system) and surface roughness by atomic force microscopy in tapping mode (Asylum Research 3D Stand Alone). The transmission spectra (350–2500 nm) were measured by a Perkin-Elmer Lambda 950 spectrophotometer on glass substrates (using as a reference Spectralon labsphere certified reflectance standard). The electrical properties were evaluated by Hall effect measurements in a Van der Pauw geometry [4].

---

* Corresponding author.
E-mail address: eva.gutierrez@tekniker.es (E. G-Berasategui).

http://dx.doi.org/10.1016/j.tsf.2015.07.010
0040-6090/

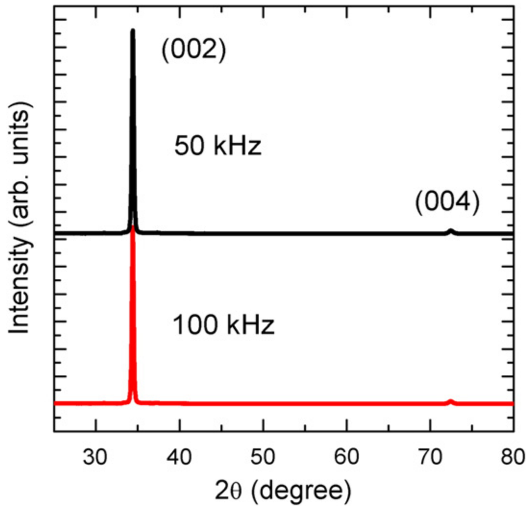

Fig. 1. XRD patterns of the AZO films at the two different studied frequencies.

Table 1
Values of the position of the (002) peak, FWHM, grain size and deposition rate.

Freq (kHz)	$2\theta_{(002)}$ (°)	FWHM (rad)	Grain size (nm)	Deposition rate (nm/m)
50	34.37	0.00384	39.40	13
100	34.36	0.00350	43.31	17

The corrosion behaviour of AZO layers was evaluated using electrochemical impedance spectroscopy (EIS) and polarisation techniques on silicon substrates. The measurements were performed in a three-electrode electrochemical cell using a Ag/AgCl (KCl 3 M) reference electrode (SSC) and a platinum wire counter electrode. Tests were performed at room temperature under aerated conditions on an exposed area of 0.2 cm^2 in a standard solution of NaCl 0.06 M. Three immersion times were selected to test the electrochemical evolution of the coatings over time. The first measurement was after 2 h of immersion when the open circuit potential becomes stable. After this, 192 and 480 h of immersion were used to estimate the evolution of the corrosion resistance over longer immersion times.

For each immersion time a sinusoidal AC perturbation of ±10 mV of amplitude at a frequency range from 10 kHz to 10 mHz under open circuit potential conditions was applied. After the impedance measurements (480 h immersion), the potentiodynamic polarisation curves were registered for each sample from −0.4 V to 1.2 V (versus open circuit potential) at a scan rate of 0.5 mV/s. All the potentials are referred to Ag/AgCl electrode (0.207 V vs SHE).

3. Results and discussion

The X-ray diffraction patterns (Fig. 1) show a strong ZnO (002) peak typical of the hexagonal wurtzite crystalline structure orientated with the c-axis perpendicular to the substrate for both studied frequencies. A weak (004) peak is also observed.

The position (2θ) of (002) peak is 34.37° and 34.36° for process frequency of 50 kHz and 100 kHz respectively, smaller than 34.45° corresponding to the ZnO crystal. This shift towards lower diffraction angles shows that the (002) interplanar spacing of these layers is larger than the 002 interplanar space for ZnO crystals because of the increase in the compressive stress of the crystals when doping due to substrate heating [5]. No other phases, such as Al or Al_2O_3 were detected in these films. So, Al^{3+} ions substitute Zn^{2+} ions into the ZnO hexagonal wurtzite structure. Al ions may also occupy the interstitial sites of ZnO or Al segregates to the non-crystalline region in the grain boundaries and forms Al–O bonds.

The full width at half maximum (FWHM) of the XRD peaks depends on the crystalline quality of each grain and on the distribution of grain orientation [6]. Table 1 shows the analysis of the FWHM for the (002) XRD peak and the derived grain size through the Scherrer's equation [7]. The film grown at 100 kHz presents the highest crystallinity associated with the lowest FWHM value and the highest grain size of 43.31 nm [6].

Morphology of the layers changes with pulse frequency as observed in Fig. 2. For 100 kHz process pulse frequency, the grains are uniformly stacked up and compact, so no grain boundaries are visible (Fig. 2b), while for 50 kHz pulse frequency the grains grow loosely and they are clearly notable (Fig. 2a). These changes in morphology slightly affect the roughness values, with roughness varying from 23 nm for 50 kHz pulse frequency to 17 nm for 100 kHz pulse frequency.

There are no significant changes in resistivity for both studied samples (Table 2), although the sample grown at 100 kHz shows slightly lower values of resistivity correlated with the highest carrier mobility. The free carriers in the AZO films are mainly provided by oxygen vacancies, zinc interstitials and Al dopants. This correlates with the highest grain size, so the number of grain boundaries decreases facilitating the mobility of the free carriers.

There are no significant changes in transmittance spectra (Fig. 3), with an average transmittance in the visible range (400–800 nm) above 84% for both pulse frequencies. The bandgap of AZO films is higher than that of ZnO films (3.37 eV). The absorption edge shifts towards higher energy with an increase in carrier density due to Burstein–Moss effect [8].

The durability of these layers was tested through corrosion resistance analysis. Three electrochemical impedance measurements were registered after 2, 192 and 480 h of immersion. Electrochemical impedance spectroscopy (EIS) is a non-destructive technique that allows

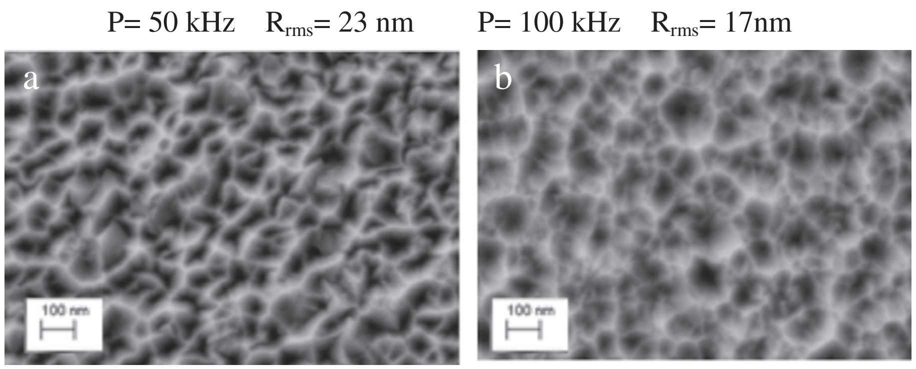

Fig. 2. SEM micrograph of AZO films for the two studied pulse frequencies.