Materials Science and Engineering B 176 (2011) 237–241

Contents lists available at ScienceDirect

Materials Science and Engineering B

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

The uniformity of Al distribution in aluminum-doped zinc oxide films grown by atomic layer deposition

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ARTICLE INFO

Article history:
Received 17 August 2010
Received in revised form
17 November 2010
Accepted 29 November 2010

Keywords:
Aluminum-doped zinc oxide
Thin films
Atomic layer deposition

ABSTRACT

We investigated the aluminum distribution in aluminum-doped zinc oxide films grown by atomic layer deposition. Surface morphology, structure, composition and electrical properties of obtained films were studied. For the aluminum content less than 2 at.%, a periodicity of Al distribution along the layer depth was observed. This periodicity diminished significantly after annealing the samples in nitrogen atmosphere at 300 °C. For the Al content higher than 2 at.%, its distribution in ZnO:Al films was uniform within the depth measurement accuracy of ~5–10 nm.

1. Introduction

One of the major issues determining optoelectronic and photovoltaic device applications is a cost reduction of the device technology. In such devices, indium tin oxide (ITO) films are widely used as transparent electrodes. However, due to still increasing cost of indium as well as its toxicity, one tends to replace ITO by other materials. Among them the very promising one is zinc oxide (ZnO) which is a wide band gap semiconductor (Eg ~ 3.3 eV at 300 K [1]) and can be doped with metals such as Al or Ga to achieve very low film resistivity [2,3]. It has been reported, however, that doping of ZnO with cations like aluminum can have some possible drawbacks. For Al-doped ZnO (AZO) films deposited by sputtering, Al diffusion is observed in higher temperatures and this deteriorates film and device stability [4]. Moreover, sputtering deposition of AZO films can result in Al cluster inclusions at the zinc oxide grain boundaries resulting in very high local currents which damage device structures, especially when the active layers are organic materials [5].

In the present work, we concentrate on the uniformity of Al distribution in AZO films grown by atomic layer deposition (ALD). ALD method is similar to MOCVD technique except the fact that precursors are sequentially introduced into the growth chamber. Precursor doses are separated by purging the chamber by neutral gas (e.g. N_2). It makes this technique advantageous fourfold. Firstly, chemical reaction occurs only on the substrate surface and thus prevents any reactions in the gas phase and enables using very reactive precursors. Secondly, this method does not require complex and expensive vacuum system as the film growth occurs in neutral gas atmosphere. Thirdly, using precursors that have sufficiently high vapor pressure enables thin film deposition at lower temperatures comparing to other techniques, such as magnetron sputtering [6] or pulsed laser deposition [7]. This is also true in case of ZnO and AZO film deposition [8,9]. Finally, the ALD method allows to cover very uniformly very large substrates of a few m^2 sizes. The first work on ZnO:Al deposition by ALD was reported in 1994 [10]. Na et al. [11] investigated aluminum incorporation into ALD-grown ZnO:Al films. They found out that that the depth profile of Al in ZnO:Al was periodic and corresponded to the dopant incorporation steps used during the film growth. We demonstrate, however, that uniform Al distribution can be achieved, when the ALD process as well as annealing conditions is optimized.

2. Experimental

To grow AZO films, we used diethylzinc (DEZ) and deionized water vapor as zinc and oxygen precursors, respectively. As aluminum precursor, trimethylaluminum (TMA) was used. The films were grown in Savannah-100 ALD reactor (Cambridge NanoTech) on glass substrates. The process pressure was ~10^{-1} Torr and the N_2 purging gas flow rate of 20 sccm. For ZnO pulse sequences, we chose growth parameters, under which we obtained the films possessing the lowest resistivities [12]. Among these parame-

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doi:10.1016/j.mseb.2010.11.014

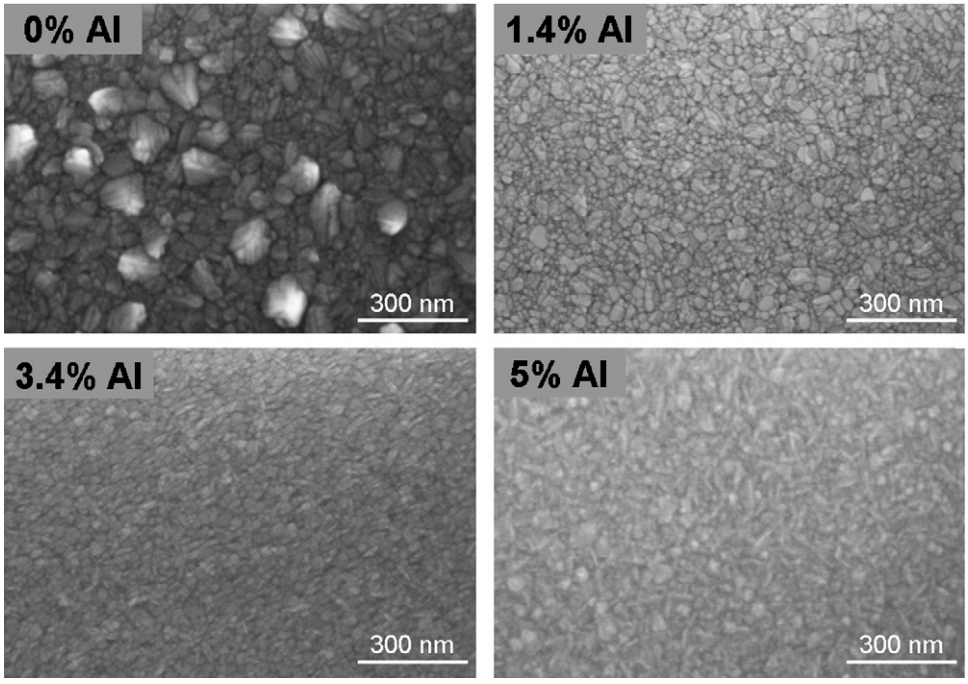

Fig. 1. Surface morphologies of ZnO and AZO films.

ters, one of the most important one was the growth temperature which optimal value was found to be 200 °C. To obtain AZO films with different Al contents, we applied one TMA + H_2O cycle between the varied number of DEZ + H_2O ones in the following way: $[i \times (TMA + H_2O) + j \times (DEZ + H_2O)] \times k$, where $i = 1$, j varied between 9 and 99, and k was adjusted to obtain the films with a thickness of approximately 200 nm. The total number of cycles, c, was then: $c = (i_{Al2O3} + j_{ZnO}) \times k$. Note that we firstly used one cycle of Al_2O_3 following by ZnO cycles, which means that the films were not terminated by Al_2O_3 cycle. The corresponding precursor pulse and purge times were kept constant for all deposited films.

The layer thickness was approximately 200 nm, as was checked by Micropack Nanocalc 2000 reflectometer for samples grown on Si substrates. The further characterization of the films was carried on for samples grown on glass only.

The surface morphology as well as chemical composition of obtained samples was investigated using Hitachi SU-70 scanning electron microscope (SEM). The final concentration of Al in AZO films was determined by electron dispersive X-ray (EDX) method and is given in atomic percents.

The crystallographic structure of ZnO and AZO films was identified by X-ray diffraction (XRD) measurements using a Philips *X'* Pert diffractometer with Cu Kα (λ = 1.54 Å) monochromatic radiation.

Secondary ion mass spectroscopy (SIMS) method was used to investigate aluminum depth profiles in the obtained AZO films. Cs^+ incident ions with an energy of 5.5 keV and incident angle of 36° from normal to the surface were applied. The depth resolution of SIMS measurement was in the order of 5–10 nm.

Room temperature Hall measurements were carried on in the Van der Pauw mode using the RH2035 PhysTech GmbH system with a magnet field $B = 0.4$ T.

3. Results

We obtained AZO films with the Al content up to 7.8 at.%. Fig. 1 presents surface morphology of the films. For undoped ZnO sample, the grains with different sizes and shapes are seen. They can be essentially divided into two categories. The first one consists of the grains which are rather wide (diameter of ~100 nm), and the other—the grains with a mean size of ~50 nm. The density of the larger grains is much smaller than the smaller ones, and diminishes gradually while the Al content increases.

One can relate the grain shape to the crystallographic structure of the films. Fig. 2 shows XRD patterns for ZnO and AZO films. All the samples are polycrystalline, but the crystallographic quality improves with the increase of Al composition, up to 3.4 at.%. For the 3.4 at.%-Al sample, (0 0 0 2) peak dominates. Together with the increase of (0 0 0 2) reflection intensity, the lateral mean grain size decreases. Based on XRD data, we calculated mean grain size, D, perpendicular to the film surface. From FWHM values for (0 0 0 2) diffraction peaks, the obtained D value increases from ≈20 nm (for undoped sample) to ≈41 nm (for 2.5 at.% of Al) and then it decreases to ≈20 nm (for 5 at.% of Al) and ≈8 nm (for 7.8 at.% of Al). The higher values of D indicate more oriented and columnar growth of AZO films for Al content up to ~3 at.%. Therefore, introduction of Al facilitates the growth in c-axis mode, however, for higher Al con-

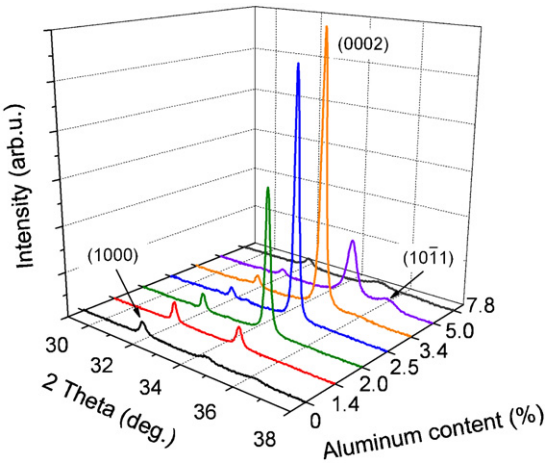

Fig. 2. X-ray diffraction patterns of ZnO and AZO films.