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Aluminum-doped ZnO polycrystalline films prepared by co-sputtering of a ZnO-Al target

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Aluminum-doped Zinc oxide polycrystalline thin films (AZO) were grown on 7059 Corning glass substrates at room temperature by co-sputtering from a ZnO-Al target. The target was designed as follows, high purity elemental Aluminum was evaporated onto a ZnO target covering small areas. The structural, optical, and electrical properties were analyzed as a function of Al content. The Al doped ZnO polycrystalline films showed an n-type conductivity. It was found that the electrical resistivity drops and the carrier concentration increases as a consequence of Al incorporation within the ZnO lattice. In both cases the changes are of several orders of magnitude. From the results, we conclude that, using these ZnO-Al targets, n-type Al doped ZnO polycrystalline films with high transmittance and low resistivity can be obtained.

Keywords: II-VI compounds; semiconductors; low resistivity; ZnO-Al films.

Películas delgadas policristalinas de óxido de zinc impurificadas con aluminio fueron crecidas en substratos de vidrio Corning 7059 a temperatura ambiente por Co-erosión catódica a partir de un blanco de ZnO-Al. El diseño del blanco fue el siguiente: Aluminio de alta pureza fue evaporado sobre el blanco de ZnO cubriendo pequeñas áreas. Las propiedades estructurales, ópticas y eléctricas se analizaron en función del contenido de Al. Las películas policristalinas de ZnO impurificadas con Al presentan una conductividad tipo n. Se encontró que la resistividad eléctrica de las películas disminuye y la concentración de portadores aumenta, como resultado de la incorporación de Al dentro de la matriz de ZnO. En ambos casos, los cambios son de varios órdenes de magnitud. Partiendo de estos resultados, se concluye que usando este tipo de blancos de ZnO-Al, se pueden obtener películas policristalinas de ZnO impurificadas con Al con una alta transmitancia y baja resistividad.

Descriptores: Compuestos II-VI; semiconductores; baja resistividad; películas de ZnO-Al.

PACS: 61.10.Nz; 68.37.Ps; 68.55.-a; 71.55.Gs; 81.15.Cd

1. Introduction

For the development of transparent electrodes in solar cells systems ZnO doped with Al (AZO) has received increasing attention due to its high optical transmittance in the visible range, and low electrical resistivity properties. Recently with the high cost of Indium-based materials, extensive research has been oriented on replacing Indium-tin-oxide (ITO) with AZO films [1]. AZO represents a valuable alternative due to abundance in nature and low cost of the raw components [2,3], nontoxicity, stability against H plasma environments and facility to texture in acidic solutions [2,4]. ZnO:Al thin films have been prepared with different processes such as chemical vapor deposition (CVD) [5], spray pyrolysis [6], pulsed-laser deposition [7,8], sol-gel process [9], sputtering [10,11], etc. Among them, the rf magnetron sputtering technique offers some advantages: the possibility of preparing a large-area coating of ZnO:Al thin films at low cost for technological applications [11], precise control in thickness, composition of the films close to the target. For this work we implemented a target where the Al doping material was evaporated on a high purity ZnO target covering small areas of the total surface. The percentage in area is proportional to the Al content in the deposited film. The scope of this paper is to evaluate the structural, optical and electrical properties of AZO thin films grown by sputtering from these targets. In solar technology where cost is a fundamental issue the design of this kind of targets could be an effective solution. The films grown from these targets had a decrease of five orders of magnitude in the electrical resistivity and an increase of four in the carrier concentration along with excellent transmittance in the visible.

2. Experimental details

Polycrystalline ZnO:Al films were grown on 7059 Corning glass substrates at room temperature (RT) in a radio frequency (rf) sputtering system with a water cooled cathode. The rf power employed in the growth process was 20 W and the distance between the target and substrate was 4 cm. The chamber was evacuated to a pressure of 1×10^{-5} Torr before the addition of pure Ar gas. During the growth the chamber pressure was kept at 1 mTorr. Depositions were performed for 60 min. The Al was introduced into the films by co- sputtering a ZnO-Al target. The ZnO target (99.999% in purity) was 4.92 cm^2 in area. Elemental aluminum (99.999% pure) was deposited by thermal vacuum evaporation onto the ZnO target. The Al area onto the ZnO target was varied to cover 0%, 2%, 3%, and 5% of the total target area. These samples, with increasing aluminum concentrations on the target, were denoted by A1 (undoped reference), A2, A3 and A4, respectively. To determine the amount of O and Zn in the films Si substrates were employed to avoid oxygen from the Corning glass substrates in EDS measurements. The Si substrates were placed side by side with the glass substrates during each growth. Film thicknesses were measured by means of a KLA Tencor P15 profiler. Atomic concentration measurements of the samples were obtained with a semiquantitative chemical analysis performed in an 1100/1110 EDX system from Noran Instruments installed in a Jeol equipment model JSM-7401F. The crystalline structure of the films was determined by X-ray diffraction (XRD) using an X-ray SIEMENS D5000 equipment, using the CuKα line (1.5406 Å). Atomic Force Microscopy (AFM) images were obtained with an Autoprobe CP (Veeco Metrology Group) Microscope. The resistivity, carrier concentration, mobility and type of conductivity of the films were measured at room temperature using the Van der Pauw method. To perform electrical measurements, high purity Silver Paint electrodes were deposited on the films. The optical transmittance spectra of the films were measured in an UNICAM 8700 spectrophotometer in the 250-800 nm range.

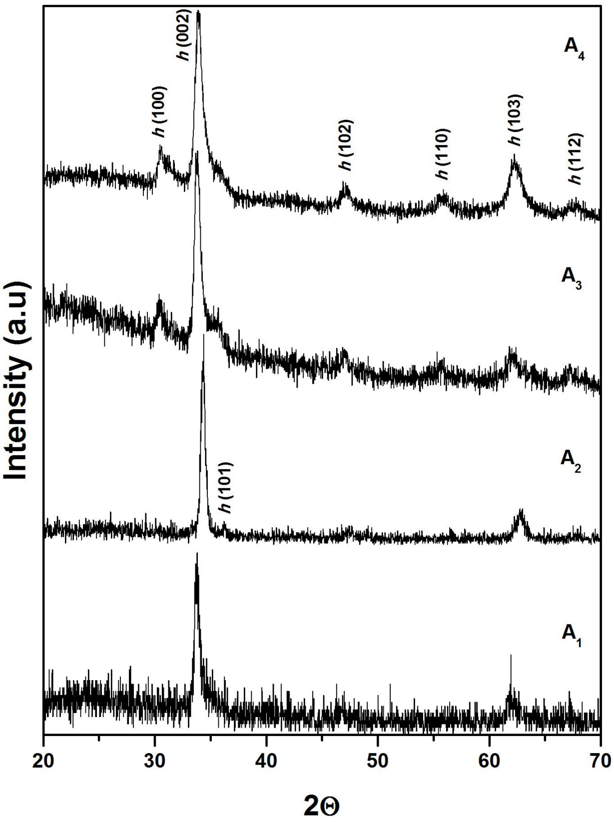

FIGURE 1. X-ray diffraction patterns of ZnO and ZnO:Al films deposited at RT by RF co-sputtering from a ZnO-Al target. The meaning of h on the plane indexes is hexagonal.

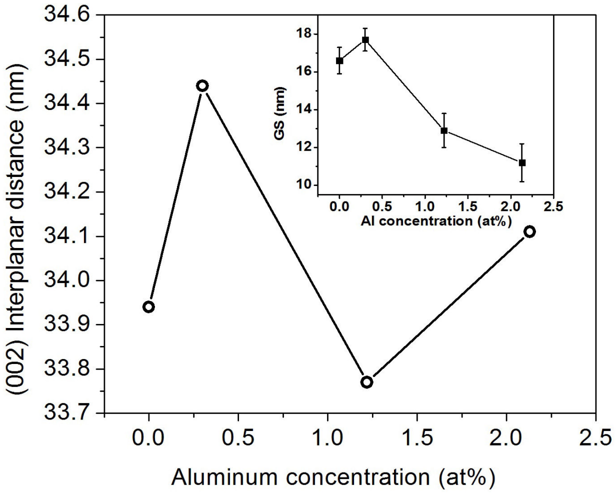

FIGURE 2. The (002) interplanar distance versus the Aluminum concentration. The inset illustrates the grain size as a function of the Al concentration.

3. Experimental results and discussion

The X-ray diffraction spectra of the samples are shown in Fig. 1. The A1 sample corresponds to an undoped ZnO polycrystalline film (grown as reference). A strong peak located at 33.94° assigned to (002) planes of hexagonal wurtzite ZnO can be observed. Another peak with less intensity was registered in 61.94° due to (103) planes. The XRD spectrum for A2 sample showed a slight improvement in the crystalline structure of the AZO films. Besides the reflections at (002) and (103), a small peak at 36.25°, identified with the (101) planes, is observed in the diffractogram of A2. A1 and A2 films show a highly oriented growth along the (002) direction. The samples A3 and A4 exhibited reflections corresponding to (100), (002), (102), (110), (103) and (112) planes from AZO hexagonal phase. High preferred orientations are diminished with the Al doping. Table I summarizes the, Zn, O and Al content, thickness, energy band gap (Eg), resistivity, mobility, and carrier concentration of the ZnO:Al films studied in this work. The analysis of the chemical composition (Table I) suggests that aluminum atoms were incorporated into the ZnO films from 0.3 at% for A2 sample, to 1.22 at% in A3 until 2.13 at% for A4 sample. Notice that the (002) peak position, beginning with the undoped A1 sample, is located at 33.94°, the peak shifts to 34.44° for the A2 sample and then the peak shifts to the left for A3 and A4 where the reflection was located at 33.77 and 34.11° respectively. Figure 2 illustrates the displacement of the peak position as a function of the Al concentration. The standard value reported for the (002) reflection position is 34.442°, these data reveal that the undoped ZnO sample is strained due to polycrystalline nature of the film and to the amorphous structure of the substrate. The ZnO lattice shrinks when the peak position changes from 33.94° to 34.44° because Al^{+3} (ionic radius = 51 pm) occupies Zn^{+2} (ionic radius = 88 pm) sites, in such a way that the lattice relaxes almost completely when ZnO is doped with 0.3 at% of Al. The lattice is strained again for 1.22 at% Al, probably due the decreasing of the preferential orientation, and tends to relaxation again for 2.13 at% Al. Similar behavior in the AZO films has been reported previously and has been attributed to

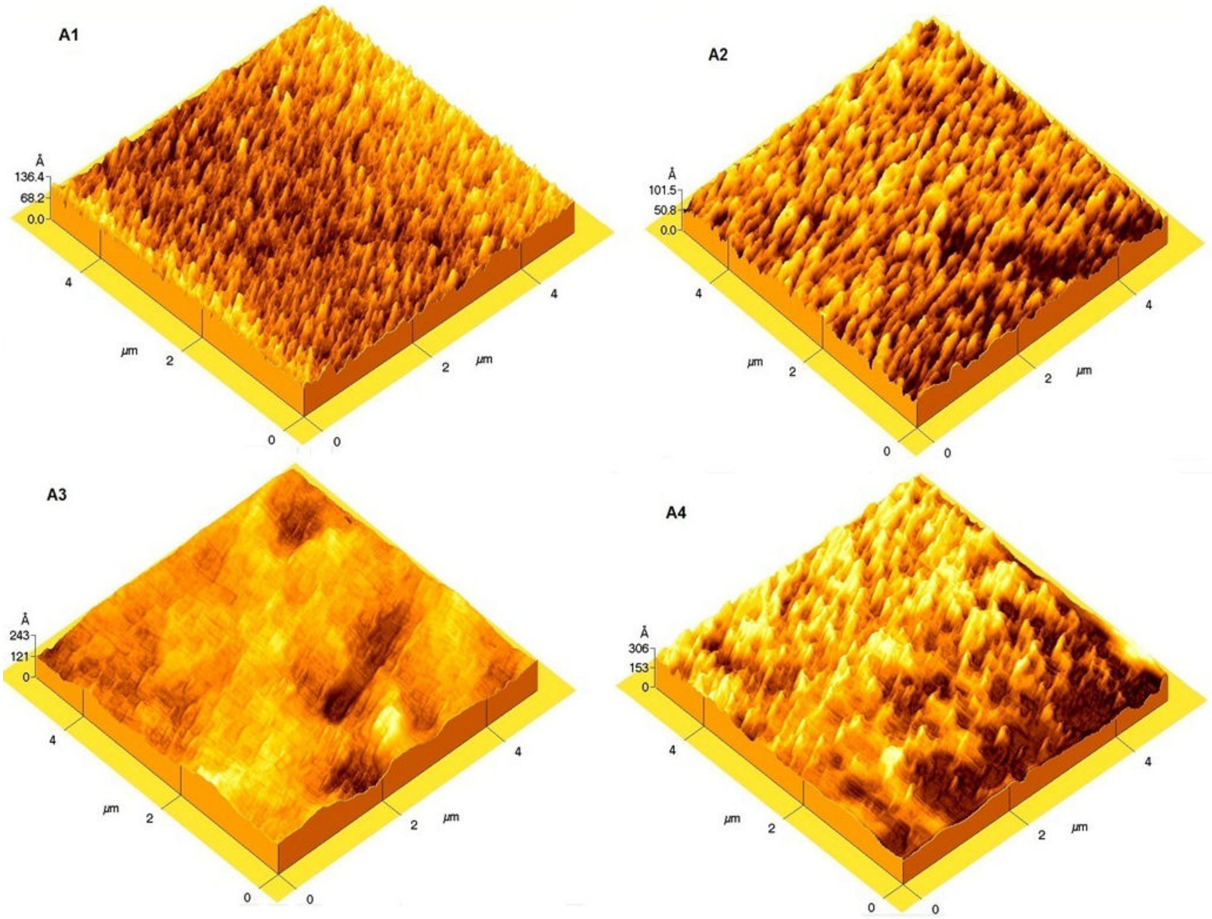

FIGURE 3. 3D AFM images of ZnO and ZnO:Al samples prepared at RT. The image scale is 5×5 μm.

stress in the samples and/or to a consequence of the Al content [12,13]. The inset of Fig. 2 shows the grain size (GS) versus the Al concentration. In general, the decreasing of the GS as the Al concentration increases is concluded.

A detailed analysis of the surface morphology of the samples was made by atomic force microscopy. Three dimensional 5×5 μm AFM images of ZnO and ZnO:Al samples prepared at RT are displayed in Fig. 3. In the AFM images there is an evident change of roughness in the A1 and A2 samples compared to A3 and A4. The A1 and A2 samples present root mean square (rms) roughness of 10.4 Å and 10.6 Å, while the samples A3 and A4 have rms values of 32.2 Å and 54.4 Å, respectively. The high value in roughness for samples A3 and A4 could be probably due to the increasing concentration of atomic aluminum in the ZnO films.

The room temperature electrical resistivity (ρ) and carrier concentration (cm^{-3}) of the ZnO and ZnO:Al samples prepared at RT are shown in Fig. 4 and Fig. 5, respectively. As can be seen, the incorporation of aluminum into the ZnO films has a strong effect in both electrical parameters. The undoped ZnO film A1 has a resistivity of $\rho = 74.10\ \Omega - \text{cm}$, sample A2 showed a $\rho = 5.58\ \Omega$-cm. The resistivity decreases to 2.83×10^{-2} Ω-cm for sample A3. The minimum value for resistivity was measured in sample A4 with $\rho = 1.1 \times 10^{-3}$ Ω-cm. It is important to mention that the samples were not thermally annealed after growth. Note that the resistivity of A2, A3 and A4 films drops one, three and five orders of magnitude; respectively, compared with that of A1 film. On the other hand, the carrier concentration varies from 10^{16} cm^{-3} in A1 to 10^{20} cm^{-3} in A4 film (see Table I).

TABLE I. Thickness, composition, optical and electrical experimental data of the ZnO and ZnO:Al films.

Films	Thickness (Å)	Zn	O (At. %)	Al	E$_g$ (eV)	Resistivity (Ω-cm)	Mobility (cm^2 V^{-1} s^{-1})	Carrier (cm^{-3})
A$_1$	1335	34.56	65.44	–	3.31	74.10	4.3	$n = 9.50\text{e}^{16}$
A$_2$	1286	35.33	64.37	0.30	3.32	5.58	3.1	$n = 3.93\text{e}^{16}$
A$_3$	1347	36.92	60.64	1.22	3.40	2.83×10^{-2}	5.6	$n = 6.07\text{e}^{18}$
A$_4$	1370	35.67	62.20	2.13	3.56	1.1×10^{-3}	4.7	$n = 3.32\text{e}^{20}$

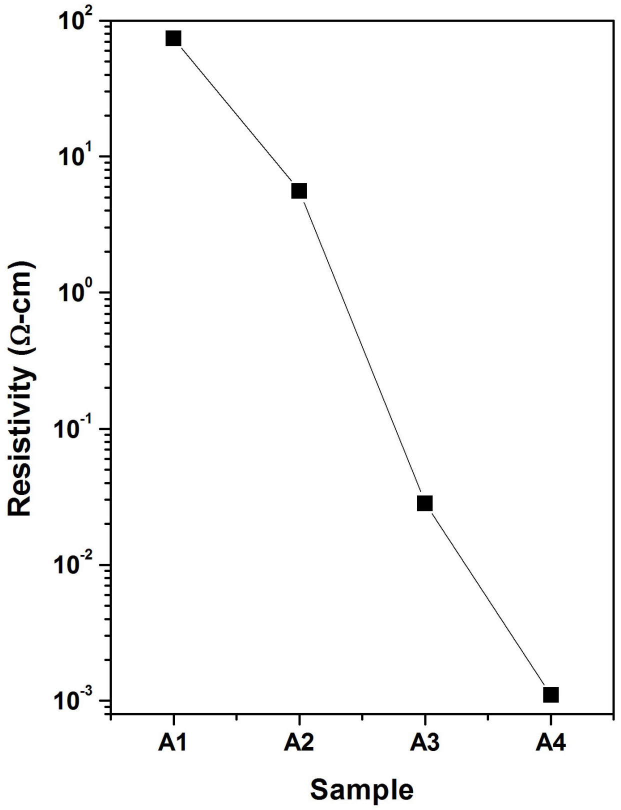

FIGURE 4. Resistivity of ZnO and ZnO:Al films grown by RF sputtering on glass substrates.

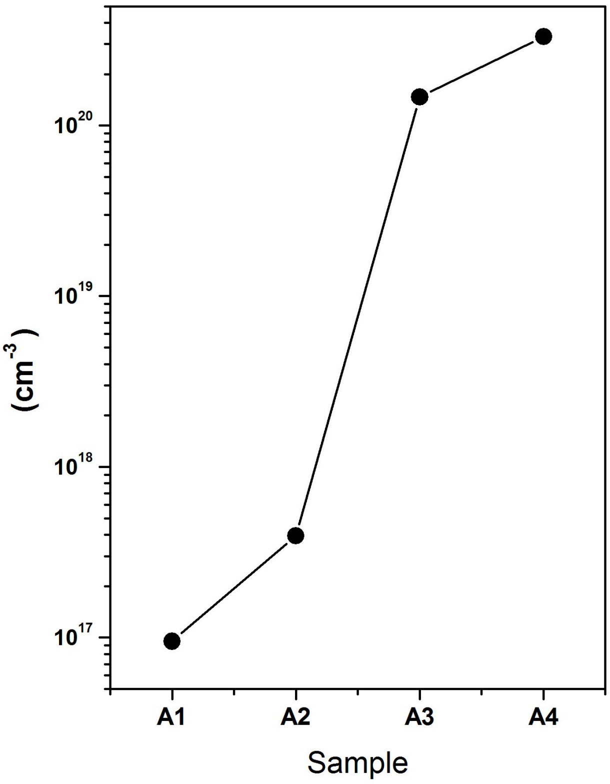

FIGURE 5. Carrier concentration of ZnO and ZnO:Al films studied in this work.

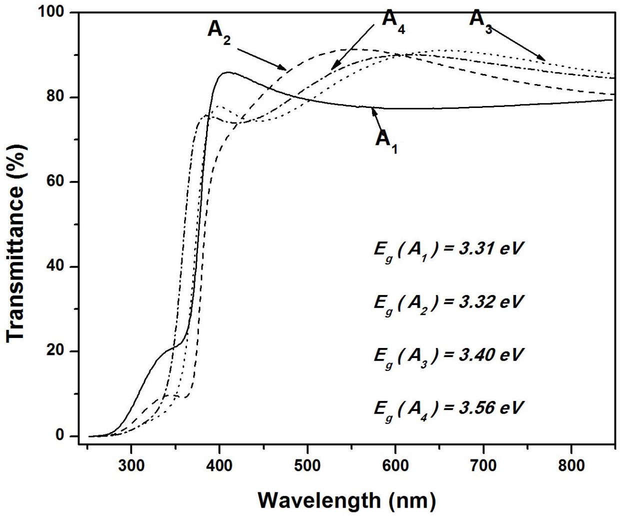

FIGURE 6. Transmission spectra of A1-A4 films. Energy gaps of the films are also displayed.

The electron mobility, calculated by the Hall Effect, has a maximum for A3 of about 5.6 cm^2 V^{-1} s^{-1}. The above mentioned results indicate that Al, according to the Hall measurements, is n-type, due to oxygen vacancies. For A2 to A4 the majority electron density is reinforced because an element of group III acts as donor when substitutes the Zn atoms. It is important to mention that the low resistivity figures reported in this work were measured in samples grown at room temperature and are comparable to those grown in different conditions even in annealed samples [1,11]. Figure 6 compares the optical transmittance of the films. The average transmittance (Tavg) in the 250-850 nm wavelength range of the undoped ZnO film (A1) was 79.1% while for the doped ZnO films (A2, A3 and A4) was 82.8%, 84.5% and 85.5%, respectively. This difference in transmittance is attributed to increasing concentration of atomic aluminum in the ZnO. The forbidden optical energy band gap (Eg) of the ZnO thin films was calculated from Tauc plots. The squared absorption coefficient was plotted versus photon energy, and the band gap was obtained by extrapolating the linear part of the curve intersecting with the photon energy axis. The point of intersection gives the optical band gap of the films [1,11,13]. The band gap of the A1-A4 films was measured to be 3.31, 3.32, 3.40 and 3.51 eV, respectively. The increase in the band gap as the Al content increases in the AZO films is due to the Burstein- Moss effect [14,15]. The increasing of transmittance is consequence of the increase of Eg when the Al-at% increases.

4. Conclusions

The incorporation of Al in ZnO films produces changes in their structural, morphological, electrical, and optical properties. Resistivity values up to 1.1×10^{-3} Ω-cm were obtained in sample A4 grown at RT, that is five orders of magnitude lower than that of the corresponding A1 undoped sample.

The electron mobility for the A4 sample is in the order of 4.7 $\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$. The carrier concentration increased by at least four orders of magnitude with respect to undoped ZnO films. An increase from 3.31 eV for undoped film to about 3.51 eV for the A4 film was observed in the energy band gap, these results indicate that the growth of AZO films from a target where metallic Al was sputtered into a ceramic ZnO matrix produces AZO films with good electrical properties to be considered as transparent electrodes.

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