Low temperature sequential PLD of Al-doped ZnO thin films

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Highly oriented (110) Al-doped ZnO thin films were deposited by sequential PLD at low temperatures (20 and 150°C) on amorphous substrate. The resulting structural properties were explained as a result of the film's surface bombardment with energetic particles arriving from the ablation plasma. A post-deposition laser annealing step was carried out with the aim of improving the optical and electrical performances. The findings prove that the method is capable of increasing the optical transparency and crystalline quality of the films.

1. Introduction

Tremendous efforts reflected by the great number of scientific papers on fundamental and applied research on ZnO and Al-doped ZnO properties will lead to the replacement of the traditionally used ITO in applications such as, organic light emitting diodes (OLED) [1], solar cells [2], surface acoustic wave devices [3] and gas sensing devices [4]. The emerging technologies would certainly need to be upgraded with this earth abundant and nontoxic material. There is still need to develop techniques that allow low temperature manufacturing processes in order to be deposited on temperature sensitive materials (i.e., polymers). In contrast with other used techniques (e.g., chemical vapor deposition [5], magnetron sputtering [6], etc.), Pulsed Laser Deposition (PLD) is a versatile method that may lead to a lower crystallization temperature due to the higher kinetic energies of the condensing particles [7]. Sequential PLD (SPLD) is a particular case of PLD that consists in alternating laser ablation of independent target materials, one for the host and another for the dopant [8]. Thus, SPLD eliminates the inconvenience of using sintered ceramic targets and allows to easily obtain AZO thin films with different doping concentrations.

As regarding the impurity-doped ZnO films, SPLD has been used for Co-doped ZnO [9], S-doped ZnO [10] and Er-doped ZnO [11]. For AZO films manufacturing SPLD was also used by Alauddin et al. [12] where the research was focused on doping concentration influences on AZO films properties obtained at relatively high temperature (i.e., 400°C), as well as the influence of deposition temperature for a constant doping concentration (i.e., 2% at.). In a previous paper we have demonstrated for the first time that SPLD can lead to AZO films with unusual (110) growing orientation [8]. This growing mode has been alredy observed by Takayanagi et al. [13] where (110) ZnO films were obtained on amorphous substrate in magnetron discharge capacitively coupled plasma. They demonstrated that the (110) ZnO orientation appeared in the cathode area due to a more effective oxygen ions bombardment when the deposition pressure decreased from 1 Pa to 0.1 Pa. In the case of OLEDs the quantum efficiency is directly affected by the electric field generated along the c axis when a spontaneous strain is applied on this piezoelectric material [14]. This is why it is suitable to have materials with the c axis parallel to the substrate. Moreover, materials with this particular orientation are important due to the anisotropy of the electrical and mechanical properties [15-17].

In this work, AZO thin films with uncommon (110) growing orientation were obtain through SPLD technique by alternating ablation of Zn and Al metal targets in a low oxygen atmosphere. We have investigated the influence of doping concentration and the number of pulses / sequence used for both targets ablation. In order to improve the material quality Al-doped ZnO samples were subjected to an *ex situ* laser annealing in air. From the obained data it appears that highly oriented (110) AZO thin films are obtained at relatively high dopant concentration and low oxygen deposition pressure. The mechanism responsable for this growth mode is investigated.

2. Experimental details

Al doped ZnO (AZO) thin films of were obtained by using the SPLD technique. Alternating excimer laser ablation (KrF, wavelength - 248 nm, pulse length - 20 ns) of the two separate targets of Zn (purity 99.9%, Goodfellow) and Al (purity 99.9%, Nilaco Corporation) mounted on an automated control system ATCC-101, we obtained samples with different dopant concentrations in oxygen

atmosphere by varying the Zn/Al pulses ratio (Table 1). The samples were deposited on glass substrates resistively heated at 150°C. For comparison one sample was deposited at room temperature. Prior to deposition, the glass substrate was cleaned in an ultrasonic bath of distilled water for 10 min, then washed with ethanol and acetone, and finally dried under nitrogen gas flow.

To avoid contamination before deposition the vacuum chamber was evacuated to a base pressure of 10^{-5} Pa and both metal targets were exposed to preablation for 1000 pulses. Then, the oxygen was introduced into the deposition chamber with a constant flow rate of 10 sccm and reducing the pumping speed the deposition pressure was set to 1.2 Pa. The target to substrate distance of 5 cm, the laser repetition rate of 5 Hz and the laser fluence of 3 J/cm^2 were kept constant during the deposition process for all samples.

Table 1. Experimental parameters for SPLD of AZO samples.

Sample	$[Zn\ pulses/Al\ pulses]_n$	N	P [Pa]	t (°C)
AZO1	$[30/10]_{99}$	11880	1.2	150
AZO2	$[12/4]_{247}$	11856	1.2	150
AZO3	$[12/1]_{304}$	11856	1.2	150
AZO4	$[12/1]_{304}$	11856	1.2	20

N (total number of pulses) = (Zn pulses + Al pulses) x 3n (sequence number)

To improve the quality of the deposited material some of the samples were submitted to an *ex situ* laser annealing process in ambient air by using a XeCl excimer laser (wavelength - 308 nm, pulse length - 20 ns). The samples were submitted to the laser beam radiation at normal incidence for a laser fluence of 100 mJ/cm^2, the laser frequency of 20 Hz during 12.5 minutes. The annealing laser is coupled with VarioLas system whose purpose is to guide, homogenize and focus the laser beam on the sample on the entire sample surface, i.e., 15 x 15 mm.

The structural, optical and electrical parameters were determined by using the following investigation techniques: X-ray diffraction - XRD (Shimadzu 6000), X-ray photoelectron spectroscopy - XPS (AXIS Nova, Kratos Analytical UK), profilometry (Alpha-Step IQ), UV / Vis / NIR spectroscopy (Evolution 300, Thermo Scientific) and four points probe in linear configuration coupled with a Keithley (2616). The thickness of the samples was determined by profilometry as an average of three values measured in different regions along the edge of the sample. Crystallographic structure was studied by XRD measurements using Kα radiation (λ = 0.15406 nm) for a voltage of 40 kV and an operating current of 30 mA. XPS measurements were made using a AlKα type energy source (1486.6 eV). To determine the dopant concentration all samples were cleaned for 10 s by Ar ion bombardment (acceleration voltage 500 V) to remove the carbon and other impurities that can inherently contaminate the sample surface.

3. Results and discussions

Generally, when ZnO films are deposited by using SPLD from metallic targets, the (002) diffraction plane is observed by XRD, describing a wurtzite structure [8]. With increasing dopant concentrations and at low oxygen deposition pressures (1.2 Pa, see Table 1) the Al-doped ZnO thin films exhibit a polycrystalline structure with a preferential (110) orientation, as evidenced by the XRD patterns shown in Figure 1. By comparison to the results presented in our previous reported work [8], the changes in the structure of the films are not remarkable even if the present AZO samples are obtained at higher dopant concentration, from 7 to 10% at. (Table 1) instead of 4.4% at. of Al [8]. The deposition temperature seems to have little influence on the overall aspect of the XRD patterns. Higher temperatures should promote or enhance the crystallographic orientation. Indeed, working at 150°C (AZO1, AZO2 and AZO3) instead of 20°C (AZO4) leads to an intensification of the (110) diffraction peak.

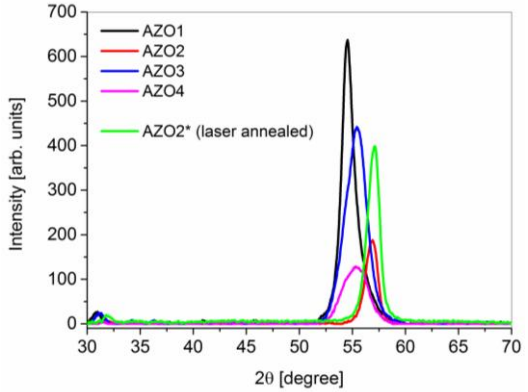

Figure 1. XRD diffractograms of obtained SPLD AZO samples.

The emergence of the (110) growth mode can be explained by taking into account that the kinetic energies of the ablation plasma species increase with decreasing deposition pressure [18]. The energetic particles that reach the already deposited layer act in a destructive manner, with the effect being most intense when the films initially grow along the *c* axis. This happens because the top surface in this particular case has the highest density

of atoms, thus leading to an enhanced number of interactions with the incoming particles. The (002) growth is inhibited and an orientation of the films for which particle bombardment is less damaging can be promoted instead. The obtained (110) oriented films have a lower atom density on the surface.

Since we used two targets, thus there were two distinct bombardment phases; additional samples were deposited in order to investigate how each of the species affects the resulting structure. Aiming to deposit (110) AZO films for potential applications, data obtained so far shows that a higher number of pulses per sequence is indicated, for the same Zn/Al pulse ratio (30/10 corresponding to AZO1 yields a better oriented film than 12/4 for AZO2, Table 1). Moreover, Zn particles arriving from the plasma have repercussions on the ZnO lattice growth along the out of plane (c axis) crystallographic direction perpendicular to the substrate surface. When reducing dopant concentration (AZO2 vs AZO3), the results suggest that particles arriving from the Al target ablation also play an important role in promoting the (110) crystalline phase growth. Further investigations are needed to better clarify this issue and establish an optimum deposition sequence.

Table 2. AZO thin films measured parameters.

Sample	a [Å]	BG [eV]	d [nm]	ρ [Ω cm]	Al [%]
AZO1	3.382	3.83	357	1.9×10^{-2}	9
AZO2	3.238	3.87	355	5.6×10^{-3}	10
AZO2*	3.229	3.49	364	5.3×10^{-2}	9.8
AZO3	3.315	3.88	360	1.7×10^{-3}	7
AZO4	3.320	3.84	358	3.7×10^{-3}	7

UV-Vis obtained results (Figure 2) have shown that the average values for the transmittance were between 72% and 89 % in the visible spectrum, while the resistivities determined by the four point probe method varied between 1.7×10^{-3} and 1.9×10^{-2} Ω cm. For typical Al-doped ZnO applications like transparent electrodes, both of these characteristics should be improved. For this reason, we carried out a post-deposition *ex situ* annealing using a pulsed laser. AZO2 sample was irradiated with 15000 shots at a frequency of 20 Hz, in air. The annealed film was investigated to see the changes induced by the laser treatment.

While the optical transparency increased (as it can be seen in Figure 2) from 84% to 89% the resistivity was found also to increase by about one order of magnitude, from 5.6×10^{-3} to 5.3×10^{-2} Ω cm (Table 2). This behavior is likely the result of a reduction of free carriers concentration, and it corroborates well with the optical band gap (BG) shift that can be seen in the inset of Figure 2. After annealing, the BG of AZO2 decreased from 3.88 eV to 3.49 eV. The initial increase to high values (undoped ZnO has a BG of about 3.2 eV) can be attributed to the Burstein-Moss effect. The additional electrons result not only from doping with Al^{3+} donors, but also from the formation of oxygen vacancy type donors, expected when carrying out the deposition in an oxygen deficient atmosphere.

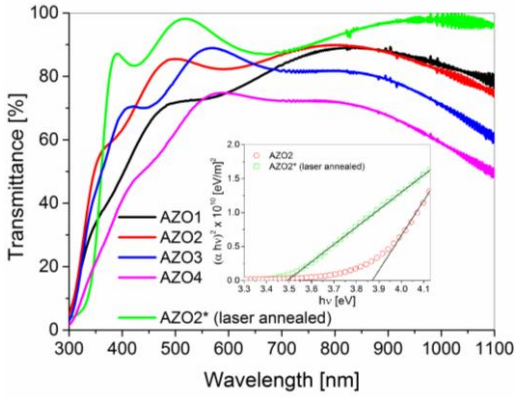

Figure 2. UV–vis spectra of SPLD AZO samples; the inset represents the Tauc plots for BG determination for as deposited (AZO2) and laser annealed (AZO2*) samples.

The laser annealing process mainly reduced the number of vacancies. While as deposited AZO2 had a dark tint common to both doped and undoped ZnO films obtained at low pressures, after annealing the film became highly transparent and similar in appearance to samples deposited at high oxygen presures. The improved stoichiometry of the material also resulted in an increased XRD signal. Thus, the ex-situ laser annealing method could prove useful in improving some of the characteristics of Al-doped ZnO. It preserves and enhances the initial crystalline orientation while also leading to an increased transparency. On the downside, the resistivity is negatively affected, but carefully chosing the number of pulses for annealing could lead to a satisfactory compromise.

4. Conclusions

Highly oriented (110) AZO thin films were obtained by SPLD on amorphous substrate at low substrate temperature. The uncommon (110) growing orientation is the main feature of the obtained material as revealed by structural characterization. This particular crystallographic structure was encountered for low oxygen deposition pressure (1.2 Pa) and relatively high aluminum doping concentration (≥ 7% at. of Al).

The highest mean value of the optical transmittance in the visible domain is 89 %, while the electrical resistivity falls down to $1.7x10^{-3}$ Ω cm. In order to improve the film properties an *ex situ* laser annealing procedure was tested. XeCl laser treated sample exhibits a better crystalline quality with a higher optical transparency, while the electrical resistivity raises one order of magnitude. These results reveal that SPLD is promising method for high quality oxides films manufacturing with a tailored orientation.

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5. References

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