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ELECTRICAL PROPERTIES OF ZNO:AL THIN FILMS FABRICATED BY PULSED LASER DEPOSITION METHOD

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Electrical properties of ZnO:Al thin films fabricated by pulsed laser deposition method

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Abstract

The possibility of the high quality AZO thin films fabrication by the PLD method using the second harmonic of the Q-switched YAG:Nd^{3+} laser is demonstrated. The investigations of dependence of the AZO thin films properties on the PLD conditions (concentration of Al in the target, buffer gas pressure) have been conducted. The optimum conditions of the ZnO:Al thin films deposition have been defined.

Introduction

Transparent conductive oxides (TCO) are widely used in thin-film and organic solar cells, optoelectronic devices, light emitting diodes, sensors, etc. The application of TCO in crystalline silicon solar cells passivate the surface and reduce the probability of emitter shunting through holes [1]. Nowadays the most applicable material for the transparent electrodes fabrication is tin-doped indium oxide (ITO). But the high cost of indium necessitates the research in the field of creation and characterization of the materials for the ITO substitution.

The zinc oxide is actively studied as a material that could replace ITO because ZnO is a widespread, inexpensive and non-toxic material. Impurity doping of ZnO with the elements of the third group of the periodic table (boron, aluminum, gallium and indium) produces n-type conductivity due to Zn^{+2} ion substitution. The most perspective materials for ZnO doping are Al (ZnO:Al or AZO) and Ga (ZnO:Ga or GZO) because of the high solubility and behavior during the growth, which allows obtaining the films of low resistivity (~ 10^{-4} Ohm × cm) and high transparency in the visible region of the spectrum [2-5]. Meanwhile AZO would be more preferable for industrial use due to the relatively low cost of the initial components. A principal interest in the study of these materials is caused by the dependence of their physical properties (band gap, concentration and mobility of charge carriers, transmittance, etc.) on the fabrication conditions [6-9]. In terms of the literature data, there are no definitive recommendations for the high quality AZO and GZO films synthesis. Therefore the research in this field (the influence of the growth parameters, and subsequent heat treatment on the properties and the stability of the films) is intensively conducted [10-13].

The pulsed laser deposition method (PLD) is effective for the synthesis of different materials: metals, semiconductors, dielectrics, low-dimensional structures, polymers, biological materials. Compared with other methods PLD reveals high energy (~ 1 eV-1 keV) and density (~ 10^{14}-10^{17} cm^{-3}) of particles in the ablation plasma plume [14], so it is particularly attractive for the synthesis of complex oxide thin films. The method allows synthesizing of thin films and multilayers of different compositions with high crystalline perfection, and reduces the demand to the level of use of vacuum. Managing of the film growth process is realized in the PLD method by controlling the gas composition and pressure of the buffer gas in the vacuum chamber, the target-substrate distance, substrate temperature and deposition rate. In addition, the particle energy of the laser plasma plume in the PLD method can be controlled by changing the energy fluence at the target and the laser wavelength. The above mentioned features of the method enable the control of physical and chemical properties of the films in a wide range [15-18]. As follows from the literature, the majority of experiments on the AZO PLD synthesis have been conducted using excimer lasers, because the use of UV laser radiation minimizes the number of microparticles arising on ablation of the ZnO:Al target and thereby impairing the quality of AZO thin films [19,20]. But the use of visible-light lasers in AZO thin film fabrication is interesting for the economical and scale production.

This work reports the investigations of the AZO thin films properties dependence on the PLD conditions (concentration of Al in the target, buffer gas pressure) involving the visible-light laser.

Experimental details

The AZO thin films were deposited on quartz glass substrates preliminarily cleaned in an ultrasound bath for 15 min at a temperature of 45°C in an

acetone–isopropyl ethanol mixture (1:1 by volume). Ablation of the ceramic AZO targets was performed using the second harmonic of Q-switched YAG:Nd^{3+} laser (532 nm, 15 ns, 10 Hz, 250 mJ). The volum and high vacuum turbomolecular pumps provided an initial vacuum in the vacuum chamber at a residual pressure level not exceeding 10^{-7} Torr. The scheme of experimental setup was described previously [15,18]. The AZO ceramic targets with Al contents from 2 to 11 at. % and the ZnO targets were obtained from ZnO and Al_2O_3 powders of 99.9 and 99.99% purity. For more details of ceramic targets fabrication see the paper [15]. During the deposition the substrate temperature *Ts* was kept constant at 300°C. The deposition was performed in a molecular oxygen atmosphere in the pressure range *p* = 0–20 mTorr. The transmission spectra of the films were measured using a Cary-50 (Varian) spectrophotometer; the electrical properties were studied by the Hall method using the HSM 3000 automated system (Ecopia) under a permanent magnet field of 1 T. The growth rate and morphology of the film were studied by means of the optical interferometer MII-4 (λ=543 nm) and the atomic force microscope (ACM) DME DualScope 2401.

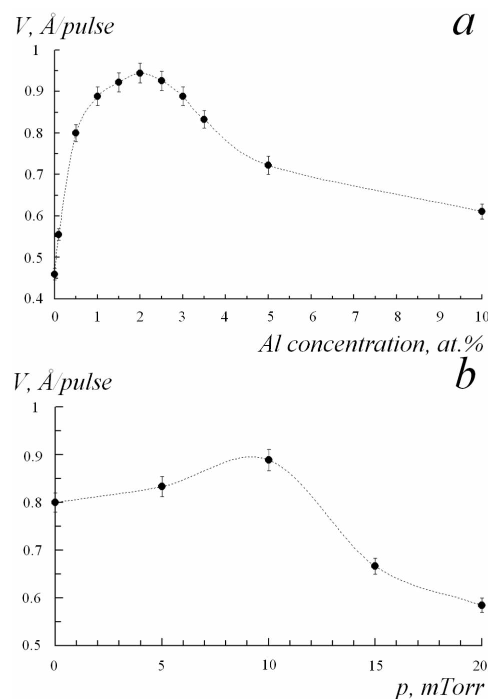

Fig. 1. The dependences of the AZO films growth rate on: (*a*) the concentration of Al in the film, (*b*) the oxygen pressure p.

Results and discussion

1. Growth rate of the AZO thin films

First we have conducted the experiments which allowed us to determine the effect of the dopant concentration and the buffer gas pressure on the AZO thin films growth rates. Fig. 1 presents the curves showing the effect of the Al concentration (*p* = 10 mTorr) and oxygen pressure (the concentration of Al in the target is 3 at. %) on the films deposition rate.

Fig. 1*a* shows that with the change in the Al concentration in the range of (0-2) at. % the growth rate of the AZO thin films increases and reaches a maximum (V = 0.94 Å/pulse) at the concentration of Al 2 at. %. This rate is as large as twice that of the undoped ZnO (V = 0.46 Å/pulse). It can be assumed that an increase of the Al_2O_3 content in the target consisting of ZnO and Al_2O_3 oxides causes a buildup of the concentration of oxygen ions in the laser plume formed during the ablation process. With further increase in the Al concentration the rate of AZO thin films growth reduces.

Fig 1*b* demonstrates that the growth rate increases slightly with rising of the oxygen pressure and achieves the maximum value of 0.89 Å/pulse at the oxygen pressure of 10 mTorr. With further build up oxygen pressure the rate of AZO thin films growth in considerably reduces. This behavior can be explained by the action of two mechanisms: the achievement of the stoichiometry composition in the AZO films and scattering of laser erosion by the plume buffer gas [21], which significantly reduces the laser plume energy. The first mechanism dominates in the range of the buffer gas pressure 0-10 mTorr, the second prevails if the oxygen pressure is higher than 10 mTorr.

2. Electrical properties of the AZO thin films

The conductivity of the undoped zinc oxide films is provided by the oxygen vacancies acting as donor impurities. The concentration of charge carriers will

fall over time because of the diffusion of atmospheric oxygen in the film [22,23]. The ZnO films application in optoelectronic devices is possible if a dopant is introduced. Therefore the experiments were performed to determine the optimal Al dopant concentration. Fig. 2. demonstrate the dependence of the charge carrier density n_e and resistivity ρ of the AZO thin films on the Al content in the target.

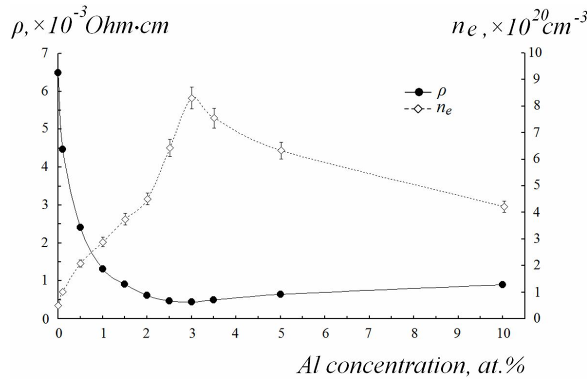

Fig. 2. The dependences of the resistivity ρ and the concentration of charge carriers n_e in the AZO thin films on the Al content in the target.

It was found that the resistivity and carrier density in the AZO thin films show the nonmonotonic dependence on the Al concentration in the target. The resistivity of the AZO films decreases and the carrier concentration grows as the dopant concentration builds up to 3%. This effect is caused by the Zn^{2+} ion substitution for the ion Al^{3+} that results in a conduction electron creation [24]. The minimum value of the resistivity (4.3×10^{-4} Ohm cm) and the maximum concentration of charge carriers (8.31×10^{20} cm^{-3}) in the AZO films were achieved with Al concentrations of 3 at.%. A further increase in the Al content causes the increase of the resistivity and the reduction of the charge carriers concentration is due to disorder rising in the lattice of ZnO. In addition, excessive Al doping leads to formation of nonconductive Al_2O_3 clusters in the films, acting as traps for charge carriers [22].

The study of resistivity and carrier concentration dependencies on the oxygen pressure showed that the AZO films obtained in anoxic deposition have the high density of oxygen vacancies and therefore high resistivity (Fig. 3).

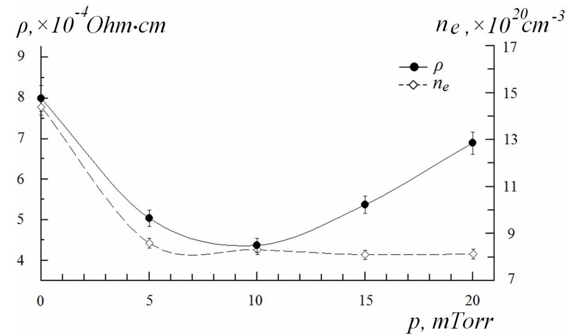

Fig. 3. The dependence of the resistivity ρ and the concentration of charge carriers n_e on the oxygen pressure in the chamber.

The metal oxides are a group of the non-stoichiometric composition materials [23]. The deviation from the stoichiometric composition is caused by the appearance of point defects related with the presence a certain degree of disorder in the crystal. So undoped ZnO exhibits the electronic conductivity because of the violation of the stoichiometric composition, associated with oxygen vacancies. The AZO thin films obtained in a vacuum have the high density of oxygen vacancies scattering of the charge carriers. The monotonic decrease in the charge carriers concentration from 1.44×10^{21} cm^{-3} to 8.13×10^{20} cm^{-3} is observed with buildup of oxygen pressure in the vacuum chamber. The resistivity of AZO films reaches a minimum at the oxygen pressure of $p = 10$ mTorr. A further increase in the oxygen pressure leads to a deviation from the stoichiometric composition of the films and to an increase in the films resistivity.

3. *Optical properties of the AZO thin films*

The transmittance spectra of the samples are presented on Fig. 4.

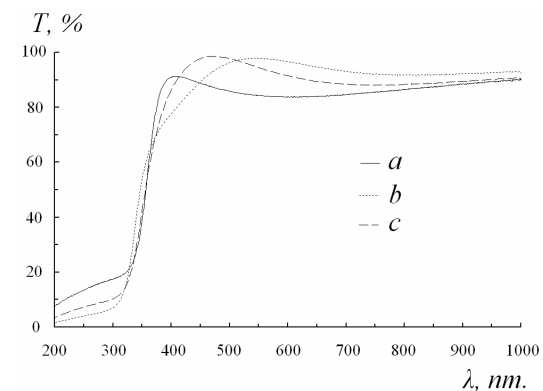

Fig. 4. The transmittance spectra of the AZO thin films with the Al concentration of: *a* – 1%, *b* – 3%, *c* – 5 %.

The transparency of the films exceeds 85% in the visible spectral region (400-700 nm). The growth in the Al concentration leads to the absorption edge shift towards the short wave region of the spectra, which can be explained by the Burstein-Moss effect [25].

Conclusions

We have demonstrated a possibility of the high quality AZO thin films fabrication using the second harmonic of the Q-switched YAG:Nd^{3+} laser. The dependence of the electrical and optical properties of the ZnO:Al thin films grown on the experimental conditions (concentration of Al in the target and buffer gas pressure) has been determined. The optimum conditions of the ZnO:Al thin films deposition have been defined. The surface roughness of the fabricated films is less than 5 nm. The lowest value of resistivity ($4\cdot10^{-4}$ Ohm cm) in the ZnO:Al thin films has been found at 3 at% Al. The films with high transparency in the visible region (>85%) have been fabricated. So the experiments conducted let us govern the electrical properties of the ZnO:Al thin films in the wide range.

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