Effect of substrate temperature on morphology and properties of ZnO:In nanocrystalline films grown by PLD

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Abstract. The purpose of this work is to study the formation regularities of ZnO:In nanocrystalline films grown by pulsed laser deposition (PLD) for application as contact layers of photosensitive elements. It was found that increasing in the substrate temperature from 300 °C to 400 °C the films have a continuous granular structure with a grain size of 9±2 nm and 13.5±4.5 nm, respectively. The sample obtained at the substrate temperature of 150 °C is characterized by the presence of whisker-like structures with 200±47 nm long and 12±8 nm wide on the film’s surface. With increasing substrate temperature from 150 °C to 400 °C, the value of resistivity decreases from 9.3·10^-1 Ω·cm to 2.9·10^-2 Ω·cm, the concentration of current carriers increases from 2.12·10^{18} cm^-3 to 3.5·10^{19} cm^-3, and the mobility of current carriers also increases from 2.51 cm^2/(V·s) to 6.17 cm^2/(V·s). The results obtained can be used in the development and manufacture of highly efficient photoelectric converters based on hybrid nanostructures.

1. Introduction

Conducted transparent films are widely used in electronic devices, such as solar panels, LEDs, and other types of electronic devices [1]. The characteristics of the devices depend on the optical and electrical parameters of the films. Currently, the issue of transparent conductive layers fabrication is urgent since requirements for the efficiency of alternative energy sources are growing from year by year [2]. Of particular interest is the fabrication of flexible photosensitive structures [3]. However, not all materials of conducted films can be used in flexible photosensitive structures. For example, one of the most common materials of transparent contacts is ITO [4].

Frequently, the transparent conductive layers formed from metal oxides [5]. ZnO: In is a transparent (at small film thickness) semiconductor material. The conductivity and optical properties of such materials are primarily affected by their nature (the quantity and atomic arrangement of metal cations in the oxide structure), as well as the presence of intrinsic or introduced defects in the crystal structure [6]. So, the electrical conductivity determined by doping, oxygen vacancies, or introduced impurities [7]. Since doping of zinc oxide with indium enhances the generation of free current carriers in ZnO: In films and the films can act as an alternative to transparent thin conductive ITO films, which have limitations of optical tuning and poor mechanical flexibility.

An urgent task under the formation of thin transparent conductive films is controlling technological parameters that directly affect the morphology of the films (thickness, grain size), electro-physical parameters (resistivity, carrier concentration, and mobility), as well as optical properties (refractive index and transmittance) [8-10]. All these parameters depend not only on the technological modes but
also on the fabrication methods [11, 12]. Pulse laser deposition (PLD) is one of the most promising methods of nanocrystalline oxide film fabrication by condensation of the products of the interaction of laser radiation with the target material on the substrate surface. This method allows to obtain thin ZnO:In films with various parameters, since you can control many technological parameters, such as energy and number of laser pulses, energy density on the target surface, as well as background gas pressure and substrate temperature [13, 14]. The main advantage of PLD is a high degree of stoichiometry compliance of the formed films with the target material. In addition, a high degree of supersaturation during condensation of ablation products leads to intensive nucleation on all surfaces of the substrate and high morphological homogeneity of the formed film, which is important in the formation of transparent thin films. Thus, the purpose of this work is to study the effect of a substrate temperature of ZnO:In films growth by PLD on morphological and electro-physical parameters.

2. Experiment

ZnO:In nanocrystalline films were obtained using a Pioneer 180 PLD module (Neocera Inc., USA), which is part of the NANOFAB NTK-9 nanotechnological complex (NT-MDT, Russia). Sitall and p-Si (111) with a concentration of the main current carriers of ~ 10^{15} cm^{-3} were used as the substrates for the formation of ZnO:In nanocrystalline films. Before the formation of the films, the substrates were chemically cleaned of contaminants and oxides. ZnO:In films with a thickness of 150-300 nm were obtained at a pulse repetition rate of 10 Hz with an energy of 170 mJ, the number of pulses was constant and amounted to 50,000. The background pressure of argon was 1·10^{-4} Torr. The substrate temperature ranged from 150 °C to 400 °C. The choice of the temperature range for the formation of films is largely determined by the results of past experimental studies [15]. The morphology of the obtained films was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM) in semi-contact mode using Nova Nanolab 600 scanning electron microscope (FEI.Co, Netherlands) and Ntegra probe nanolaboratory (NT-MDT, Russia), respectively. The electro-physical parameters were determined by measuring the EMF of the Hall using an Ecopia HMS-3000 setup (Ecopia Co., Southern Korea).

3. Results and discussion

The results of the films’ morphology study are presented in Figure 1.

![Figure 1 (a, b, c). SEM images of the surface of ZnO:In nanocrystalline films fabricated at various substrate temperatures: (a) 150 °C; (b) 300 °C; (c) 400 °C.](image-url)
temperature from 300 °C to 400 °C, the grain size increases from 9±1 nm to 13±1.5 nm. The process of grain growth on the surface of the substrate is controlled by its temperature, which, in turn, determines the diffusion ability of the deposited atoms. At relatively low substrate temperatures (≥150 °C), grain growth along the surface of the substrate is limited, and the increase in grain height is preferable, which leads to the formation of whisker-like structures on the film surface. When the temperature of the substrate increases above 300 °C, the higher temperature of the substrate increases the mobility of the deposited particles on the surface of the substrate, which leads to a decrease in grain height and its growth in the lateral direction. Figure 2 shows focused ion beam (FIB) cuts of the formed ZnO: In nanocrystalline films.

![Figure 2](image)

**Figure 2 (a, b, c).** FIB cuts of ZnO:In nanocrystalline films fabricated at different substrate temperatures: (a) 150 °C; (b) 300 °C; (c) 400 °C.

It was found that with an increase in the substrate temperature from 150 °C to 400 °C, the film thickness decreasing from 197.6±17 nm to 62±5.4 nm. Figure 3 shows the results of the electro-physical parameters study of the obtained ZnO:In films by the Hall EMF method.

![Figure 3](image)

**Figure 3 (a, b, c).** Dependences of the electro-physical parameters of ZnO:In nanocrystalline films on the substrate temperature: (a) carrier concentration; (b) carrier mobility; (c) resistivity.

With increasing substrate temperature from 150 °C to 400 °C, the value of resistivity decreased from 9.3·10¹² Ω·cm to 2.9·10¹⁲ Ω·cm, the concentration of current carriers increased from 2.12·10¹⁸ cm⁻³ to 3.5·10¹⁹ cm⁻³, and the mobility of current carriers also increased from 2.51 cm²/(V·s) to 6.17 cm²/(V·s). To reduce the electrical resistivity, additional thermal annealing of the films or doping is necessary.
4. Conclusion
As a result of the work, the influence of the substrate temperature during the formation of ZnO:In nanocrystalline films by the PLD method on their morphology and electrophysical parameters was investigated. Conducting nanocrystalline films with a thickness of 62±5.4 - 197.6±17 nm was obtained. Morphological studies showed that with increasing substrate temperature, the grain size increased, due to an increase in the diffusion ability of the deposited particles. So, at a relatively low substrate temperature, whisker-like structures formed on the surface of the films. An increase in the substrate temperature increases the mobility of the deposited particles on the surface of the substrate, which leads to a decrease in the height of the grain and its growth in the lateral direction. As a result of the electrical parameters study the dependencies of concentration and mobility of current carriers and resistivity on substrate temperature are obtained. It was found that increasing substrate temperature from 150 °C to 400 °C, the resistivity goes down from 9.3·10^2 Ω·cm to 2.9·10^2 Ω·cm, the concentration of current carriers increasing from 2.12·10^18 cm^-3 to 3.5·10^19 cm^-3, and the mobility of current carriers also increasing from 2.51 cm^2/(V·s) to 6.17 cm^2/(V·s). The obtained results can be used in the development and manufacture of highly efficient photoelectric converters based on hybrid nanostructures.

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