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Researching Influence of IBAD PLD Parameters on Properties of Nanocrystalline ZnO Thin Films

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Abstract. Nanocrystalline ZnO thin films were manufactured by Ion Beam Assisted Pulsed Laser Deposition (IBAD PLD). The influence of technological parameters and parameters of ion assisted deposition on structural, morphological and electrical parameters of ZnO thin films were researched in the experiments. As a result it was determined that changes in the basic technological parameters of IBAD PLD (target-substrate distance, substrate temperature, energy density of the laser pulses, annealing temperature, Ar flow) are able to change properties of the thin films significant, including surface roughness in the range from 0.75±0.20 nm to 7.8±2.2 nm, resistivity in the range from 10^{-3} Ohm · cm to 10^4 Ohm · cm. The possibility of controlling the morphological and physical properties of ZnO nanocrystalline films obtained in the experiments has been shown.

Introduction

Nanocrystalline films of ZnO, have an interesting combination of optical, chemical and electrical properties. Nowadays the nanocrystalline ZnO are applied as gas sensors, UV and pressure detectors, solar cells, optic gates and elements of non-linear optics [1]. In each case the properties of ZnO films must meet specific requirements. The widespread implementation of these devices is limited by difficulties in manufacturing films with the desired morphology and physical properties. Therefore solving the task of manufacturing nanocrystalline ZnO films with wide ranging controlled electro-physical and morphological parameters is very important for the creation of nanoelectronic devices and microsystems technology.

Nanocrystalline ZnO films can be manufactured by using various techniques like molecular-beam epitaxy [2], sol-gel method [3], chemical vapor deposition [4], RF-sputtering [5], pulsed laser deposition (PLD) [7]. One of the most promising methods of manufacturing nanocrystalline oxide films is ion beam assisted pulsed laser deposition (IBAD PLD) [6-8]. PLD was used to grow the crystalline ZnO thin films. During the process a target is evaporized in vacuum by laser pulses and creates plasma plume. Vaporized material is deposited on a substrate. In order to provide the ionic stimulation of nanocrystalline ZnO thin films formation, Kaufman-type ion source can be used. This ion source generates an Ar ion beam falling on the substrate holder. Due to the variable number of controlled process parameters, affecting each other, IBAD PLD allows to obtain a wide range of film properties. Advantages of the method is the high adhesion and crystal perfection applied at relatively low temperatures of the substrate, the possibility of deposition of films with complex stoichiometry by ion assisted evaporation particles from the target surface (congruent ablation), and the ability to create multilayer structures. Basic technological parameters of IBAD PLD are: target-substrate distance, substrate temperature, energy density of the laser pulses, annealing temperature, and as well Ar flow in case of ion assisted [9].

The purpose of the research is to study the influence of basic process parameters IBAD PLD on the electrical properties of nanocrystalline films of ZnO.

Experiment

Experimental studies of the effect of the IBAD PLD process were held in the modular ion assisted pulsed laser deposition system (Neocera Co., USA) at Nanotechnology multi-functional complex UHV NANOFAB NTK-9 (NT – MDT, Russia). The PLD module includes of the ion source KDC 10 DC (Kaufman & Robinson Inc., USA). Surface morphology of ZnO thin films was studied by Atomic Force Microscopy (AFM) Probe Nanolaboratory NTEGRA (NT - MDT, Russia). AFM images obtained were processed using the Image Analysis (NT – MDT, Russia). Electrical measurements were performed using Hall Effect measurement system HMS-3000 (EcopiaCorp., Korea).

In experimental studies, several series of samples were obtained at different target-substrate distances, background gas pressures, energy densities of the laser pulses, substrate temperatures and flows of ionizable gas.

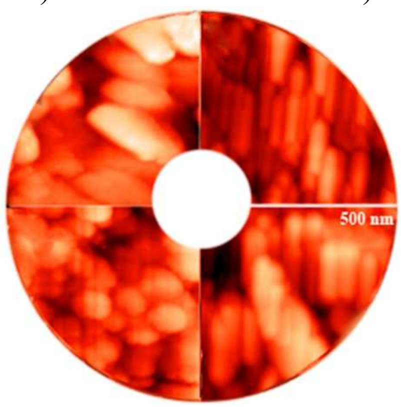
ZnO films were formed at substrate temperatures ranging from 100 ° C to 500 ° C, the gas pressure in the growth chamber varied from $1 \cdot 10^{-5}$ Torr to 1 Torr, the target-substrate distance varied from 20 mm to 135 mm, the energy density laser pulses - from 2 J/cm^2 to 3.5 J/cm^2. Stimulation was applied to the ion source KDC 10 DC (Kaufman & Robinson Inc., USA) directed at an angle of 45 ° to the substrate. The growing film was bombarded with Ar + ions with energy of 300 eV for different values of the flow from 0 cm^3/min to 5 cm^3/min.

Results and discussion

It was determined that increasing the target-substrate distance in the range between 20 mm and 135 mm surface roughness of nanocrystalline films decreases from 3.6±0.2 nm 2.7±0.2 nm, and grain size goes down from 600±50 nm to 90±8 nm. With the increase of oxygen pressure in the growth chamber from 10^{-5} Torr to 10^{-2} Torr surface roughness increases from 1.5±0.1 to 3.5±0.3 nm. The roughness of the ZnO films obtained with the laser energy density ranging from 2.2 J/cm^2 to 3.4 J/cm^2 varied from 7.8±0.7 nm to 1.5±0.1 nm. With the increase of the substrate temperature from 100 ° C to 500 ° C surface roughness of the films rises from 0.75±0.7 nm to 1.6±0.1 nm. With the change in the flow of the Ar from 2 cm^3/min to 5 cm^3/min for the ion assisted deposition surface roughness was in the range from 1.67±0.10 nm to 2.01±0.20 nm.

Figures 1 and 2 represent AFM and SEM images showing the effect of oxygen annealing parameters on the morphology properties of ZnO nanocrystal films.

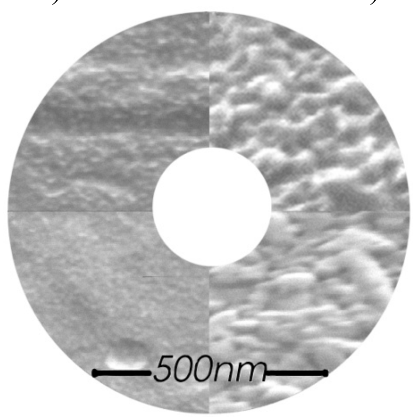
a) b)



d) c)

Fig. 1 AFM images nanocrystalline ZnO films annealed at various temperatures and oxygen pressure: 10^{-3} Torr, 300 °C (a), 10^{-1} Torr, 300 °C (b), 10^{-3} Torr, 800 °C (c), 10^{-1} Torr, 800 °C (d)

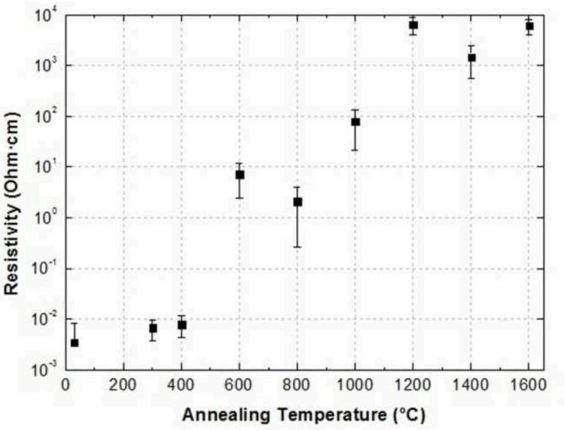
a) b)



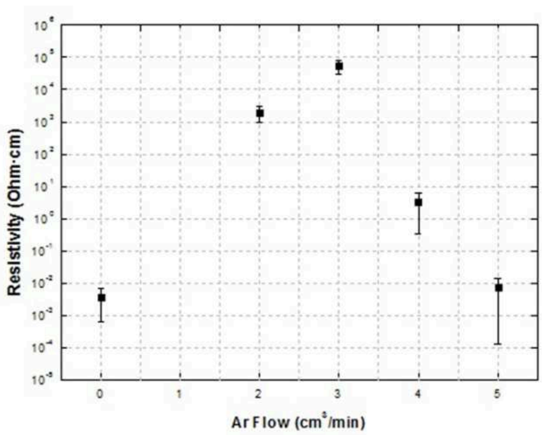
d) c)

Fig. 2 SEM images of nanocrystalline ZnO films annealed at different temperatures and oxygen pressure: 10^{-3} Torr, 300 °C (a), 10^{-1} Torr, 300 °C (b), 10^{-3} Torr, 800 °C (c), 10^{-1} Torr, 800 °C (d)

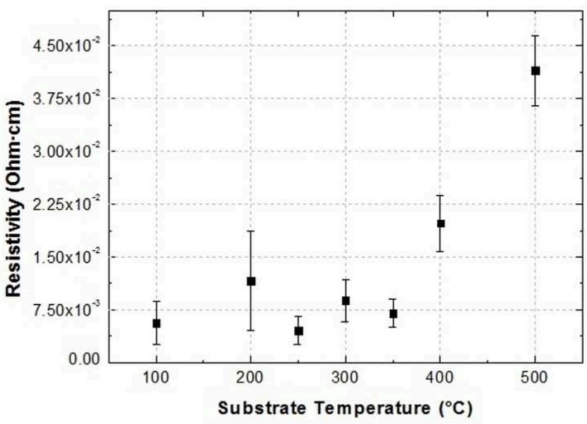
The results obtained in the experiments applying Hall measurement method show that all the films possess n-type conductivity. Figure 3 shows the dependence of the resistivity of nanocrystalline ZnO films on the main technological parameters of IBAD PLD.



a)



b)



c)

Fig. 3 Resistivity dependence on annealing temperature (a), Ar flow (b), and the substrate temperature (c)

The resistivity of the films obtained at different energy density of the laser pulses varies between from 4.27±1.01 Ohm·cm to 12.29±3.37 Ohm·cm. The resistivity of the film obtained without ion assisted deposition stood at $(3.65\pm0.30)\cdot10^{-3}$ Ohm·cm. With the increase of Ar flow to 3 cm^3/min resistivity increases to $(5.5\pm0.5)\cdot10^4$ Ohm·cm. In case of further increasing the flow, resistivity decreases to $7.13\cdot10^{-3}$ Ohm·cm. Thus, the change in the Ar flow ranging from 2 to 5 cm^3/min leads to significant changes in the structure and physical properties of the nanocrystalline ZnO films.

With the increase in the substrate temperature from 100 ° C to 500 ° C the resistivity of the films increases from $(4.0\pm0.4)\cdot10^{-3}$ Ohm·cm to $(4.0\pm0.4)\cdot10^{-2}$ Ohm·cm depending on the film structure. Since the films have a nanocrystalline structure, carriers are concentrated in areas near the grain boundaries. With increasing temperature of the substrate, a small grain structure is formed, and grain boundaries increase, leading to an increase in resistivity. The experiments also show the possibility of formation of nanocrystalline films with surface roughness below 1.6±0.4 nm.

With annealing temperatures increasing from 300 ° C to 1600 ° C, resistivity of the films increases from $(5.0\pm0.5)\cdot10^{-3}$ Ohm·cm to $(7.0\pm0.7)\cdot10^{3}$ Ohm·cm which is likely to be linked to a decrease in concentration of oxygen vacancies in the film leading to the formation of a stoichiometric films, thus proving the dependence of the electrical and morphological properties of nanocrystalline ZnO films on the basic parameters of IBAD PLD.

Summary

The experimental research of the influence of basic IBAD PLD parameters, including the target-substrate distance, background gas pressure in the growth chamber, the annealing temperature, the density of laser pulse energy, substrate temperature, and Ar flow with ion assisted deposition, on morphological and electrical parameters of nanocrystalline ZnO films.

The research shows the possibility of controlling the concentration and mobility of charge carriers, grain size and surface roughness of the films in a wide range of parameters by changing the process conditions nanocrystalline ZnO films by IBAD PLD.

It is possible to manufacture nanocrystalline ZnO films with controlled resistivity from $(3.65\pm0.30)\cdot10^{-3}$ Ohm·cm to$(7.01\pm0.30)\cdot10^{4}$ Ohm·cm , and surface roughness from 0.75±2.20 nm to 7.80±2.20 nm by changing target-substrate distance, energy density of the laser beam, substrate temperature, and annealing temperature.

The results can be used when developing of math model which might be fairly clear subscribe all of the process of IBAD PLD. It will allow understanding of the link of technological parameters of the method and allows expanding the range of electrical properties of nanocrystalline films. Moreover, the experiment results can be used when designing and manufacturing of CO2 high sensitivity gas sensor working without heater.

Also, the results obtained in the experiments can have many useful industrial applications, i.e. in the design and manufacturing of sensor devices based on nanocrystalline ZnO films (UV detectors, piezoelectric elements, functional elements nanosystem equipment).

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