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Investigation of structural properties of electron-beam deposition of zinc oxide coatings doped with copper

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ABSTRACT

A new method of vacuum formation of doped ZnO coatings is proposed. ZnO thin films doped with copper were coated in silicon substrate by low-energy electron beam deposition method. The authors investigated the effect of deposition parameters on the structural properties of the ZnO thin films. The orientation of the ZnO thin films were investigated by X-ray diffraction (XRD) patterns. The doping of zinc oxide coatings with copper led to a disorienting effect. It has been shown that copper has a non-monotonic effect on the bandgap value, which is changing from 2.67 to 3.33 eV. The increase in E_g is determined due to the changes in structure of ZnO matrix layer with low concentration of Cu, whereas with high concentration of copper, E_g decreases due to the presence of copper oxide as a separate phase. UV–Vis and IR spectra demonstrate the significant change in structure of ZnO in presence of Cu.

1. Introduction

The zinc oxide thin layer system exhibits a combination of interesting piezoelectric, electrical, optical, and thermal properties already applied in the fabrication of devices, such as gas sensors, ultrasonic oscillators and transparent electrodes in solar cells [1–5].

The efficient way to improve the properties of ZnO films is by adding suitable dopants. Transition-metal elements, such as V, Ni, Mn, and Cu, have been successfully employed as dopants in ZnO. Cu-doped ZnO shown significant improvement in relevant properties such as optical, electrical, magnetic, photocatalytic performance and gas sensing [6,7]. ZnO film systems can be formed by using pulsed laser deposition [8–11], the sol-gel method [12,13], thermal evaporation, [8,14], ion sputtering systems [8,15,16], solution methods [17], electron beam evaporation [18], etc., as well as their various combinations.

Each method is characterized by its advantages and disadvantages. The disadvantages of the mentioned methods of forming doped ZnO coatings are the need to use liquid media, the inability to deposit the layers of equal thickness on finished products and products of complex shape, low deposition rate, the multi-stage process of forming doped layers, the complexity of the equipment and the control systems for the deposition process.

The paper proposes a new method of depositing doped ZnO layers. The coatings are proposed to be formed by electron-beam deposition using low-energy electron flow (EBD) [19]. Unlike the classical method of electron-beam evaporation, this method is not applicable to coatings based on metals and metal compounds (oxides, nitrides, etc.). This is explained by the fact that the exposure of the low-energy electron flow does not result in melting of the metal or its significant heating. Despite that, we had previously demonstrated the possibility to use the method in the formation of ZnS coatings [19]. The electron-beam exposure is able to initiate intense exothermic chemical interactions between the components of the targets. The released energy may be sufficient for both further initiation of chemical interactions and transferring the chemical compounds into the gas phase. This eliminates the need for multi-step manufacturing of the targets and for the use of process gases. In this case, not finished high-melting substances, but the chemical compounds whose exothermic interaction is accompanied by the formation of the desired compound (metal salts, in particular) are used as the target. When implementing this deposition scheme, the growing layer will not be affected by elastically

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reflected electrons of high energy and soft X-ray bremsstrahlung, which is inevitable when using powerful electron-beam evaporators. This unwanted energy exposure initiates the formation of defects in the formed thin layer. It should be noted that the major part of vacuum deposition methods are characterized by low reproducibility of the properties of the deposited coatings. The novelty of the proposed method also lies in the fact that chemical reactions in the electron flow impact zone are able to determine high reproducibility of the structure and properties, as shown previously in [19]. This approach may further help to define the technological conditions for the development of the most simple thermal method of formal doped ZnO layers, which would be devoid of its currently inherent disadvantages. In other words, to significantly simplify the technology of their forming without loss of quality of the deposited layers. This, together with the study of the structure and properties of the coatings deposited with the proposed method, is the main objective of the given paper.

The paper discusses the features of doping of ZnO coating with copper. As the source of the doping element, copper nitrate is proposed to use. This choice is caused by the fact that copper nitrate is easily vaporized in a vacuum when heated. If a high-melting compound is formed under the influence of electron flow, then the magnitude of the thermal effect of the primary reaction may be insufficient to transfer the doping metal into the gas phase. This is considered in detail in [19]. It should be noted that other compounds can also be used for doping, in particular, europium nitrate.

2. Experimental

2.1. Methodology of coatings forming

The films were deposited from the gas phase generated by the exposure of the initial target to electron flow with 800–1600 eV energy with current density of 0.01–0.03 A/cm^2. The film preparation is reported in details in our earlier work [19]. Low-energy electron guns are used while obtained polymer-based coatings in vacuum.

2.2. The material of coatings and substrates

Zinc dust, (<10 μm, ≥98%, Sigma Aldrich), zinc nitrate hexahydrate (reagent grade, 98%, Sigma Aldrich) and copper (II) nitrate trihydrate (Sigma Aldrich) were used. The coatings were formed with the same effective thickness, which was controlled by using a quartz crystal microbalance (QCM) placed close to the substrates. The coatings deposition process was executed at ≈$4{\cdot}10^{-3}$ Pa initial pressure of residual gases in a vacuum chamber.

The powders had not been preliminary dried. The targets were obtained by thorough mixing different powders in a vibrating ball mill.

The mixture of zinc dust and zinc nitrate powders was used with optimal weight ratio of 1:1 for ZnO film deposition. The melting and spreading of the target material under the influence of the electron flow did not take place, which ensured the high stability of the structure and composition of the layers formed. The mixture of zinc, zinc nitrate and copper nitrate powders were used with the weight ratio of 1:0.25, 1:0.5, 1:1, 1:2.

At the layers deposition, quartz plates (in spectroscopic measurements in the ultraviolet and visible regions), NaCl plates (in IR spectroscopic studies), silicon single crystal plates (in XRD, XPS and SEM), special carbon-coated copper grids (i.e. for TEM) were used as substrates. The substrates temperature during deposition was 25 °C and 250 °C, respectively, below and above the decomposition temperature of zinc nitrate thin films [20]. The substrates were placed in immediate proximity to each other, which allowed depositing the coatings in the same technological cycle. The depressurization of the vacuum chamber was made only after decreasing the substrate temperature below 50 °C. For comparison, in some cases, the coating was annealed in air at the temperature of 250 °C for 30 mi.

2.3. Spectroscopic and morphological analysis

The IR spectroscopic studies were carried out using the FTIR spectrophotometer (Vertex-70, Bruker). UV–Vis spectroscopic studies were performed using a Cary-50 spectrophotometer (Varian). The band gap (E_g) values were determined with the method reported in literature [21].

The studies of the cross-section morphology and the depth distribution of chemical elements of thin coating were performed by using an electron microscope (SEM, Quanta 200F) with EDAX microanalysis, along with the Auger electron spectroscopy (AES, PerkinElmerPHI-660) with 3 kV argon ion energy. Since the simultaneous analysis on O, Zn, and Cu is technically complex and associated with a high error in determining the Zn/Cu ratio, this paper only analyzes the distribution of oxygen and zinc throughout the thickness of the deposited layer.

The transmission electron microscopy studies were carried out using JEOL JEM-2100 electron microscope. For TEM-studies of the coatings formed by the electron-beam dispersion of the composite targets, a special sample preparation was used. The coatings were doped on a NaCl plate. Then the substrate with the coating was placed into warm distilled water. In the dissolution process of the salt, the thin layer separated from the substrate and was easily carried on special carbon-coated copper grids. In most cases, a partial destruction of the continuous layer was observed. This sample preparation, as a rule, allows to study the coatings, which are impossible to research at direct deposition on carbon-coated copper grids. What is concerning the initial stages of depositing the thin layers with TEM, their study is only possible in the case of high degree of stationarity of the deposition process. This was not the objective of the studies conducted and required a complex sample preparation. It should be noted that the heating of carbon-coated copper grids may be followed by its deformation, which additionally prevents the studies.

2.4. X-ray diffraction and X-ray spectral analysis

The X-ray diffraction analysis was performed on Bruker D8 X-ray diffractometer using CuKα ($\lambda = 1.54056$ Å), 40 kV, 40 mA radiation source. The constant of crystal lattice, the internal stresses of ZnO thin layers, and the size of crystalline regions were calculated under the methodology given in [22].

The X-ray photoelectron spectroscopy was implemented with the use of photo-electron spectrometer (XPS, PHI Quantera II), with the base pressure of 1×10^{-10} Torr and Al (Kα) X-rays (1486.6 eV).

3. Results and discussion

3.1. Features of chemical interactions between the mixed target components

The kinetics of electron-beam dispersing composite targets is determined by chemical interactions between their components. The chemical reactions take place not only by the electron beam exposure, but also at the stage of targets making. In the process of mixing powders of zinc nitrate and zinc dust, the intensive mixture heating was observed by release of red-brown gas. The reaction may be written as follows:

$$Zn(NO_3)_2{\cdot}6H_2O + 5Zn = Zn(NO_2)_2 + 2ZnO + 3Zn\ (\text{residue}) + 6H_2O\uparrow + Q,$$