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Morphologic and optical characterization of ZnO:Co thin films grown by PLD

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Abstract. The morphological properties of the surface and optical characteristics of nanocomposite ZnO:Co structures grown on substrates of monocrystalline silicon and sapphire by pulsed laser deposition (PLD) method have been studied. The influence of thermal annealing on formation of characteristically developed surface of films has been analyzed. The experimental transmission and reflectance spectra in the visible region have been measured. In the framework of the dielectric function, the optical constants n and k and dispersion parameters of oscillators that provide the best fit with experimental data have been obtained. From the infrared reflectance spectra of ZnO:Co structures, the frequency positions of E_1(LO) and E_1(TO) optical phonons have been determined. It gives a possibility to suppose that the obtained films possess the wurtzite structure.

Keywords: pulsed laser deposition, ZnO thin films, optical spectroscopy.

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1. Introduction

Recently, much attention is focused on scientific studies of thin films ZnO, due to the prospects of its using as the basic elements for ultraviolet lasers, solar energy converters, gas sensitive sensors, transparent electrodes and others [1-3]. ZnO is a wide-band gap semiconductor that is non-absorbing over most of the solar spectrum. This material has the following attractive properties as a large band gap (3.1 – 3.4 eV in the bulk material), high electron mobility, strong luminescence, etc. With low cost, low temperature techniques, ZnO nanowires can be grown with a variety of morphologies. Theoretical studies suggest that layers with a suitable gradient-index of refraction can create both a broadband and directional anti-reflective coating [4].

Particular attention is focused on the study of thin film structures, doped by magnetic impurities, as these structures are promising to create devices for spintronics [5].

It is known that thermal annealing not only improves the crystalline properties of the films but leads to interaction between the film and impurities, especially at high temperatures [6, 7]. Effect of annealing on the optical and electrical properties of the erbium doped ZnO thin films was studied in [6].

In this work, morphological and optical properties of ZnO thin films doped by cobalt were studied. The comparative analysis of the above-mentioned properties of annealed and unannealed ZnO:Co thin films has been carried out.

One of the non-destructive methods for investigations of semiconductor thin films and nanostructures, which allow checking its quality and structural perfection, is transmittance and reflectance spectroscopy. The aim of this work consists in the growth of structurally perfect thin films ZnO:Co by using different technological conditions and studying their morphological and optical properties.

2. Experiments

ZnO:Co thin films were grown using the pulsed laser deposition (PLD) method. Some practical criteria make deposition by PLD method promising for manufacturing these thin films. The major advantages of this method are as follows: low substrate temperature, good adhesion and high deposition rate, a comparatively wide range of energies of particles (1…1000 eV). Simplicity and benefits of PLD method has been successfully used for deposition of semiconductor compounds A_2B_6.

The two types of ZnO:Co films with a different thickness were obtained: on Al_2O_3 and Si substrates in vacuum close to $1 \cdot 10^{-5}$ Torr by using PLD. The samples were grown at the substrate temperature 300…473 K. The thickness of films was within the range 0.5 to 1 µm depending on the number of laser pulses [8, 9].

After deposition of thin films, the samples were subjected to thermal annealing in air at 250 °C for optical activation of cobalt ions.

To study the morphology of the samples, the scanning probe microscope "FemtoScan" was used [10]. Measurements were carried out in the contact mode by using the silicon cantilevers. The nominal radius of curvature of the probe tip was 10 nm.

Optical investigations (transmittance and reflectance) were performed within the range 200 to 2600 nm by using two-beam spectrophotometer Shimadzu UV-3600 and within the range 2 to 25 µm by using the Fourier spectrometer "Perkin Elmer" Spectrum BXII. All the measurements were conducted at room temperature. Resolution of devices was better than 0.01 nm. For comparison, the reflection and transmission spectra of substrates, on which the films were grown, were recorded.

3. Results and discussion

In Fig. 1, the three-dimensional AFM image of the surface morphology of ZnO:Co thin films grown on single crystal silicon substrates before (Fig. 1a) and after (Fig. 1b) thermal annealing are shown. Three-dimensional AFM image of the surface morphology of ZnO:Co thin films grown on Al_2O_3 substrates before (Fig. 2a) and after (Fig. 2b) thermal annealing are shown in Fig. 2.

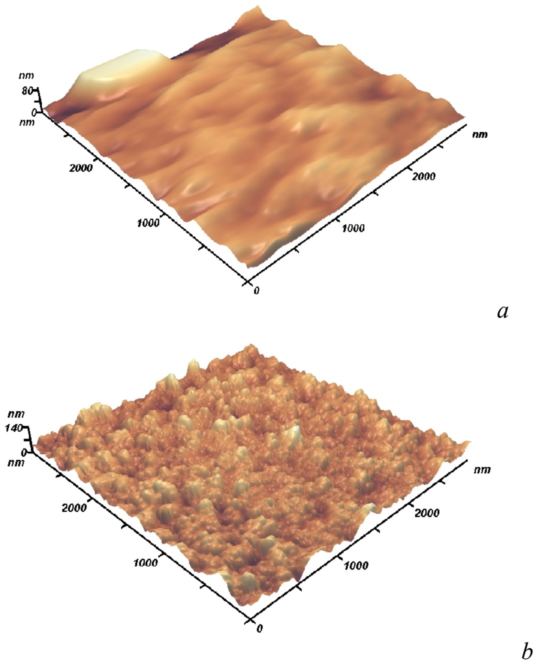

Fig. 1. Three-dimensional AFM image of surface morphology of ZnO:Co thin films grown on monocrystalline silicon substrates, before (a) and after (b) thermal annealing.

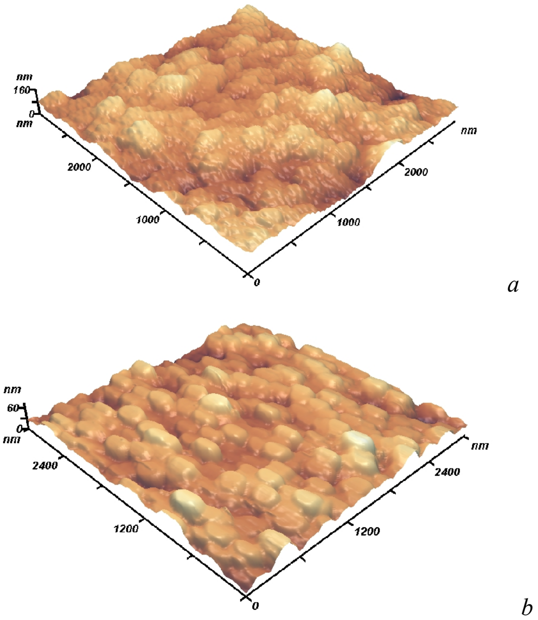

Fig. 2. Three-dimensional AFM image of surface morphology of ZnO:Co thin films grown on Al_2O_3 substrates, before (a) and after (b) thermal annealing.

As it can be seen from the images, the surface of unannealed ZnO:Co films on different substrates has no clearly pronounced structure, the roughness of surface is practically the same all-over the films. Annealing of the films at 250 °C cardinally changes morphology of the surface (Figs 1b and 2b), and in different ways on various substrates. So, ZnO:Co thin films grown on monocrystalline Si substrates after annealing are characterized by uniform nanostructure with the grain size 50 to 70 nm, and their height is 10…50 nm. All grains have clearly pronounced tapered shape. In the case of ZnO:Co films grown on Al_2O_3 substrates, annealing leads to creation of homogeneous nanorelief with grains of a spherical shape. The lateral size of such grains varies from 250 to 300 nm, and their height is 10…20 nm. In both cases, annealing increases the surface roughness.

In order to determine the optical parameters of ZnO:Co thin films, transmission and reflection spectra near the fundamental absorption edge were measured (Figs 3 and 4).

Comparing the transmission and reflection spectra of annealed samples and samples without annealing, one can see some differences in these spectra. These differences can be explained by that annealing leads to an improved crystalline structure of the films.

Thus, there is a shift of the fundamental absorption edge of the thin films. Both annealing and material of substrate effect on the magnitude of the shift. As it was mentioned above, annealing leads not only to improving of the crystalline structure of the films, but also strengthens the interaction between the film and impurities.

Band-gap can be estimated using the assumption of direct gap semiconductor transitions between the valence and conduction bands [11]. The dependence of the absorption coefficient α on the photon energy can be expressed as

$$(\alpha h\nu)^2 = A(h\nu - E_g)\,,$$

where A is some constant. The value of band-gap is obtained by extrapolation of the linear part of the curves as functions of photon energy of the incident radiation to the intersection with the energy axis (at $\alpha = 0$).

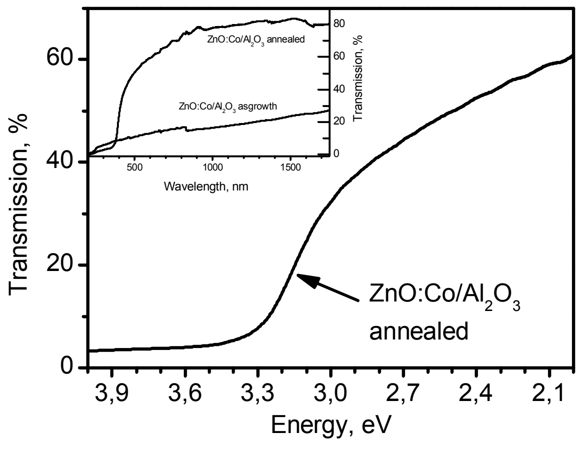

Fig. 3. Transmission spectrum of ZnO:Co thin film grown on Al_2O_3 substrate, after annealing. Transmission spectra of annealed and unannealed ZnO:Co/Al_2O_3 thin films in dependence on the wavelength are shown in the inset.

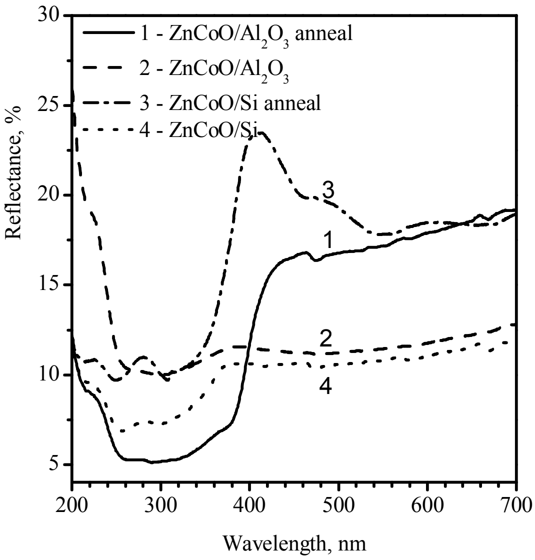

Fig. 4. Reflectance spectra of ZnO:Co thin films grown on different substrates, before and after annealing.

Calculation of the band-gap for the annealed sample grown on Al_2O_3 substrate gives the value 3.32 eV that corresponds to the band-gap of bulk ZnO. The calculated value of band-gap for annealed ZnO:Co thin films grown on Si is 3.10 eV. This value differs a little from the value of bulk ZnO. Calculation of the band-gap of samples without annealing by this method has some difficulties. In zinc oxide films, especially as-grown, there is zinc excess and annealing of the structure leads to the decrease in the concentration of intrinsic defects. In [8], it was explained by the resorption of fluctuation clusters of inhomogeneity.

The shift of the absorption edge towards the high-energy side (Burstein-Moss shift) with increasing the band-gap is associated with increasing the carrier concentration. That is, these results indicate that annealing of structures increases the concentration of electrons in the conduction band. On the other hand, the mechanical stresses, appearing because of the lattice mismatching parameters on the film-substrate interface, effect on the shift of the absorption edge. In these films, this effect occurs because of different values of the shift of the absorption edge for the films grown on Al_2O_3 and Si substrates.

Analysis of experimental results obtained from the reflection spectra was carried out in the framework of the dielectric function model [12]. The dielectric function $\varepsilon(\lambda)$ within application of the method of dispersive analysis of reflectance spectra of thin films in the region of interband transitions is described by a set of Lorentz oscillators:

$$\varepsilon(\nu) = \varepsilon_1(\lambda) + i\varepsilon_2(\lambda) = n^2 - k^2 + 2ink =$$
$$= \varepsilon_\infty + \sum_{n=1}^{N} \frac{S_j \lambda^2}{\lambda^2 - \lambda_{0,j}^2 - i\gamma_j \lambda}\,.$$

Here, ε_∞ is the high-frequency dielectric constant of the material, λ_{0j}, S_j and γ_j are the resonance wavelength, oscillator strength and width of the *j*-bands, respectively, all of which are treated as an adjustable parameters. Then, using the found parameters, the reflection spectrum of a thin film is reconstructed and compared to the experimental data with following optimization of the dispersion parameters.

Thus, after processing the spectra we have optical constants *n* and *k*, the experimental and model spectra and dispersion parameters of oscillators that provide the best fit. Table shows the optical constants of ZnO:Co films grown on different substrates before and after annealing.

Fig. 5 shows the reflection spectra in the far-infrared region of ZnO:Co thin films grown on Al_2O_3 substrates. The spectra were recorded at room temperature with the resolution 2 cm^{-1}. Reflection spectra of the film before annealing (curve 2) are similar to the reflection spectrum of the substrate.

Analyzing the reflection spectra of ZnO:Co films, it is necessary to keep in mind that the structure of wurtzite belongs to space group $P6_3mc$. The groups theory implies the existence of the nine branches of optical phonons $A_1 + 2B_1 + E_1 + 2E_2$, some of which are doubly degenerated branch E_1 and totally symmetrical branch A_1 that are active in both Raman and infrared spectra. The optical modes E_2 are active only in Raman scattering, modes B_1 are not registered. Therefore, the following optical modes can be registered in the infrared spectra: A_1(LO) = 579 cm^{-1}, A_1(TO) = 380 cm^{-1}, E_1(LO) = 591 cm^{-1}, E_1(TO) = 413 cm^{-1}. Sphalerite structure contains one formular unit and at the point Γ of Brillouin zone of sphalerite the optical branch is triply degenerated with frequencies: TO = 403 cm^{-1} and LO = 558 cm^{-1} [9, 13].

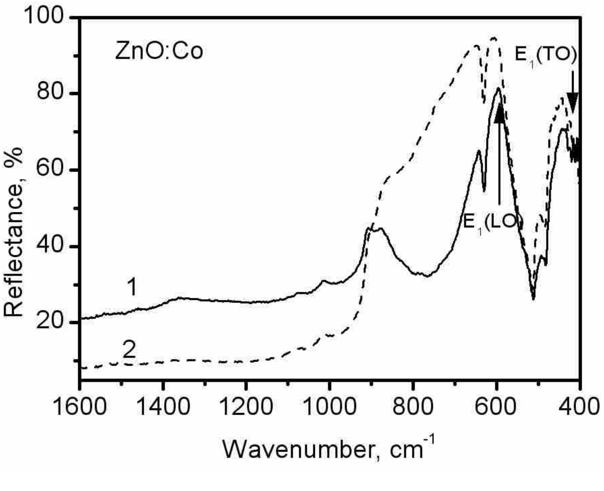

Fig. 5. Reflectance spectra of ZnO:Co thin films grown on Al_2O_3 substrates, before (*2*) and after (*1*) annealing.

Table. Optical parameters of ZnO:Co thin films grown on different substrates, before and after annealing.

Sample	Annealing	*n*	*k*
ZnO:Co/Al_2O_3	–	2.45	0.88
ZnO:Co/Al_2O_3	+	2.29	0.23
ZnO:Co/Si	–	3.11	0.62
ZnO:Co/Si	+	2.97	0.95

Fig. 5 shows the spectral diapason that contains almost all the active optical phonons, which gives information about the degree of perfection inherent to the crystal structure in the investigated films. Dominating in this range oscillatory modes of substrate prevent the analysis of optical phonons. In order to avoid the influence of the substrate, the reflectance spectrum of substrate was recorded in the same range. Subtraction of reflection spectrum of the substrate from reflectance spectra of the film-substrate system allows an assumption that thin films have the wurtzite type crystal structure. However, it should be noted that the frequency position of the optical phonons E_1(LO) = 588 cm^{-1} and E_1(TO) = 411 cm^{-1} are slightly shifted relative to the theoretical values. The reasons for this could be either the presence of mechanical stress in the films, which are determined by the lattice parameter mismatching of the film and substrate, or the effect of cobalt (formation of solid solution $Zn_{1-x}Co_xO$). To accurately answer these questions, it is necessary to perform additional structural studies of these thin films.

4. Conclusions

The morphological surface properties and optical characteristics of nanocomposite structures ZnO:Co grown on different substrates have been studied. The value of the band-gap for these structures has been calculated. It has been shown that thermal annealing leads to a decrease in the concentration of intrinsic defects, and the band-gap value is close to the value of bulk crystals. Through the comparative analysis of experimental and model data within the model of dielectric function, optical constants *n* and *k*, the experimental and model spectra in the visible region of the spectrum and dispersion parameters of oscillators that provide the best fit have been obtained. From the reflectance spectra in the infrared region, the frequency positions of optical phonons E_1(LO) and E_1(TO) have been defined, which allows to assume the wurtzite structure of the obtained films.

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