Effect of tin doping on optical properties of ZnO thin films grown on glass substrate

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Abstract. The optical properties of synthesized zinc oxide films doped with tin in different concentrations (0-5 mol.%) were studied. X-ray diffraction revealed that the main phase of the obtained films is ZnO (wurzite). According to SEM data, the film consists of nanocrystallites, which are 10-20 nm in size. It was shown that the introduction of 0.5 mol.% tin ions leads to an increasing in the absorption of wavelengths (in the range of 300-370 nm) and a slight narrowing of the band gap.

1. Introduction

Multifunctional thin film materials based on metal oxides have unique optical, electrical, gas-sensitive properties and have great opportunities for application. One of the widely used n-type semiconductor materials is zinc oxide (ZnO) due to its unique physical and chemical properties, cheapness and ease of production. Nanoscale ZnO films possess transparency in the visible range and good optical properties, what can be explained by the wide band gap. In addition, ZnO-based films have low resistance, and are highly sensitive to different toxic gases, such as ammonia, hydrogen sulfide, and organic compounds [1, 2].

To improve the materials properties, doping with different atoms and ions is used. For example, doping of ZnO with fluorine ions leads to decreasing of the band gap; when the concentration of modifying agents is equal to 6%, materials showed a minimum resistance and maximum carrier concentration [3]. When zinc oxide is doped with tin, the temperature dependence of resistance changes in comparison with pure ZnO [4]. The introduction of aluminum and tin ions into the ZnO structure also led to changes in the material properties: the films transparency increased from 65% to 81%, and the electrical conductivity of the samples reached 0.335 (Ω.cm)−1, the band gap increased to 3.3 eV [5].

The ZnO-SnO2 binary system (ZTO films) is widely studied by different researches, since these metals have symmetrical s-orbitals, which may explain the unique properties of composite materials based on them, such as high resistance, unique optical properties, gas sensitivity, etc. [6]. As ZnO and SnO2 are n-type semiconductors, simultaneously using of these oxides could increase the charge separation, which is important for optoelectronic applications [7]. Except above mentioned, both ZnO and SnO2 have wide band gap and transparency in visible light range, which allows to expect similar properties and high stability for ZTO system. Recently ZTO films are widely researched for...
application in different elements of “transparent electronics” [8]. However, in most cases, ZTO films with high concentrations of both tin and zinc ions are studied. At the same time, it is known that low concentrations of the modifying component can significantly change electrophysical properties of the resulting material. For example, authors [9] showed that optimal structural, optical and other properties were shown for ZnO films doped with 4% tin ions. With an increasing in modifying additives to 6%, the band gap increased; when tin concentration increased up to 10%, the band gap decreasing was observed. Similarly, in [10] film materials based on zinc oxide doped with small concentration of tin ions (from 0.5 to 2%) were studied. It was found that the best optical properties were shown for zinc oxide doped with 0.5% Sn$^{4+}$.

In this paper, the optical properties of synthesized zinc oxide films doped with tin ions in low concentrations are studied. As substrate for films materials the glass was chosen.

2. Experiment

As precursors, SnCl$_4$·5H$_2$O, Zn(CH$_3$COO)$_2$·2H$_2$O and organic acid were used. The molar ratios of tin and zinc were 0:100, 0:5:99:5, 1:99 and 5:95 for materials 1, 2, 3, and 4, respectively. Synthesis was carried out through the formation stage of organic Zn$^{2+}$ and Sn$^{4+}$ salts, which were dissolved in an organic solvent. The solution was applied to pre-prepared glass substrates and dried at room temperature. In this way 3 layers of the precursor solution were applied. Then the materials were heat-treated at 500 °C for 1 h. The obtained samples were studied using the X-ray powder diffraction analysis (powder diffractometer Thermo ARL) in CuKα radiation, electron microscopy (SEM, EMXplus 10/12 Bruker). The crystallite particles size (D) was calculated using the Scherrer equation $D = \frac{k \lambda}{\beta \cos \Theta}$, where k is the shape factor ($k = 0.9$), $\lambda$ is the X-ray wavelength ($\lambda = 0.1540562$ nm), $\beta$ is the full width at the half maximum of the diffraction line and $\Theta$ is the diffraction angle. The values of $\beta$ and $\Theta$ are taken for crystal plane (101) of the ZnO wurtzite phase.

Optical properties were studied using optical absorption spectra obtained on the Varian Cary-100 spectrophotometer in the wavelength range of 300 – 1100 nm. The band gap energy was find according to absorption edge analysis [11] using the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$, where $h$ is Planck’s constant; $A$ is a constant and $E_g$ is the optical band gap.

3. Results and discussion

The main phase of obtained films is the typical wurtzite crystal structure for zinc oxide that was confirmed with X-ray diffraction analysis (Figure 1a). All the material’s diffraction peaks: (100), (002), (101), (102), (110), (103), (200), (112) and (201) can be indexed as single-phase, hexagonal wurtzite structure ZnO according to Crystallography Open Database, COD ID 2300113 [12]. The presence of diffraction peaks along different planes indicates that the films nanocrystalline structure is growing in a multidirectional manner. It was found that signals on the XRD patterns are expanded, which is typical for nanocrystalline materials. According to Sherrer’s equation, the particle size is about 10-17 nm. According to SEM data, film consists of nanocrystallites, which are 10-20 nm in size. Obtained films form dense and uniform coating on the substrates. The average thickness of three-layer films is about 180-200 nm (figure 1b).
Analysis of optical absorption spectra (Figure 2) showed that the maximum absorption coefficient in the wavelength range up to 370 nm was observed for films obtained in the Sn:Zn ratio equal to 0.5:99.5 and the minimum for films with the Sn:Zn ratio equal to 5:95. Above 380 nm, the absorption coefficient for all synthesized materials was close to zero.

The results of optical transmission spectra analysis demonstrated high transparency (above 99%) for all obtained film's materials. Since concentration of Sn⁴⁺ wasn't high, transparency of pure zinc oxide was saved.

The band gap ($E_g$) estimation of the Sn-doped ZnO films was performed based on the material's absorption edge analysis [8] and showed in table 1 and figure 3. Graphs of the optical band gap energy determination are shown in figure 3 for material 1 (Figure 3a) and 2 (Figure 3b), respectively. The $E_g$ values were derived by extrapolating the linear part of the curves to the zero X axis. The obtained values of $E_g$ are close to the band gap of crystalline ZnO, equal to 3.37 eV.
Figure 3. Plot of energy band gap determination for materials 1 (a) and 2 (b).

Table 1. Band gap of synthesized materials.

| Materials | $E_g$(eV) | Concentration of Sn$^{4+}$, % |
|-----------|-----------|------------------------------|
| 1         | 3.31      | 0                            |
| 2         | 3.28      | 0.5                          |
| 3         | 3.30      | 1                            |
| 4         | 3.31      | 5                            |

The decreasing of the obtained films band gap in comparison with their single crystals is a consequence of their nanoscale structure and tin doping. On the one hand, the presence of nanocrystallites leads to a significant increasing in the material's surface area, which has a high defect. On the other hand, it leads to the "blurring" effect of the band gap border. It is also seen that the tin introduction into the ZnO structure with a concentration of 0.5 % leads to a certain narrowing of the band gap from 3.31 to 3.28 eV.

4. Conclusion

Based on the obtained results, it is possible to create transparent nanostructured films with controlled optical properties, which are of great interest for solving various problems of modern optoelectronics and photovoltaic energy. The high transparency of all film materials allows us to recommend obtained materials for further study of electrophysical properties and possible using in optical and electronic devices.

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