Pulsed laser deposition and investigation of antimony-doped ZnO films

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Abstract. We have investigated the influence of oxygen partial pressure, temperature of synthesis and annealing conditions on nanocrystalline Sb-doped thin films, grown by pulsed laser deposition. It is shown that the minimum resistivity (~8•10^{-3}Ω•cm) and the maximum carriers density (~2•10^{19} cm^{-3}) corresponds to the pressure range 5•10^{-3}–7•10^{-3} mbar, to the temperature 550 °C and in situ annealing at 700 °C. Also we show the features of the crystal lattice’s dynamics, which are found in the Raman research.

1. Introduction

Owing to a wide band gap of ~3.3 eV at room temperature and a large exciton binding energy of 60 meV, ZnO holds great promise for various applications in electronic and optoelectronic devices. The absence of reliable p-type doping is the major challenge limiting the development of various types of bipolar ZnO-based devices, including light emitting and laser diodes. Antimony-doped p-type ZnO thin films grown by PLD, MBE, and thermal oxidation have been investigated by different groups however, films exhibits diverse characteristics and properties with poor stability [1, 2, 3]. In this work, we undertook an experimental investigation of the structural, electrical and optical properties of ZnO:Sb films.

2. Objects and methods of research

The samples were obtained on the sapphire (Al₂O₃) substrates by means of pulsed laser deposition. KrF laser (\( \lambda = 248 \text{ nm}, E = 300 \text{ mJ} \)) was used for ablation of ZnO and ZnO:SbO3 ceramic targets with Sb concentration 1 – 5 at. %. The scheme of the synthesis chamber is presented in figure 1. The distance between targets and substrates was 50 mm. The synthesis was carried out in oxygen atmosphere.

![Figure 1. The scheme of the synthesis chamber for pulsed laser deposition.](image-url)
The ZnO sublayers were deposited before ZnO : Sb. ZnO:Sb films have been grown at the range of pressure $2 \times 10^{-3} – 5 \times 10^{-2}$ mbar; the growth temperature was varied from 500 to 650 $^\circ$C. The influence of the growth temperature, oxygen pressure and annealing conditions on the resistivity, carriers concentration and mobility was investigated.

An X-ray diffraction apparatus (XRD DRON-7) with Co $K_\alpha$, $K_\alpha_1$, $K_\beta$ incident radiation was used to identify the phase structure of the films. The surface morphology and roughness were investigated by a scanning electron microscope (SEM; Zeiss SUPRA 25). Raman backscattering spectra were measured by Renishaw inVia spectrograph at room temperature using the 514.5 nm line of an Ar+ ion laser for the excitation. The Hall effect and the resistivity measurements at room temperature were performed under Van der Pauw configuration.

3. Experimental results and discussion

It was found by using scanning electron microscopy that the uniformity of the surface is improved by decreasing the concentration of antimony in samples.

One of X-ray diffraction spectra is shown in figure 2.

![Figure 2. XRD pattern of as grown and annealed ZnO : Sb thin film deposited at $2 \times 10^{-3}$ mbar and 550 $^\circ$C.](image)

Diffraction patterns contain intensive reflections corresponding to the family of $\{001\}$ planes of ZnO. Besides ZnO peaks, reflection of the $Al_2O_3 (110)$ were found, because films’ thickness (about 400 nm) is not sufficient to fully absorb the incident X-ray beam. The presence of such a set of peaks leads to the conclusion that in the normal direction mutual crystallographic orientation $(001)_{ZnO} \parallel (110)_{Al_2O_3}$ is observed. This fact suggests the possibility of an epitaxial film growth, or at least the presence of an axial texture, but is not blocked rigorous proof. However, Sb-related secondary phase was detected in the films (wide band around 22$^\circ$).

In Raman spectra of the films the broad band between 500 and 600 cm$^{-1}$ was detected (see figures 3a, 3b), which is in good agreement with reports of other authors. Most likely, this band appears due to Sb-related in-band modes which coupling to the LO phonon modes of the host lattice [4]. Also the additional phonon mode was detected around 277 cm$^{-1}$ (marked ‘*’ in the figures). It is due to the fact of doping ZnO with antimony, such mode was detected by different researchers in the films of ZnO doped with gallium, aluminum and iron [5]. The intensity of the $E_2^{high}$ phonon mode decreases with increasing of antimony concentration. It indicates an increase in the compressive strain in the ZnO:Sb
layers. In addition, a broad phonon mode appears at \(\sim 700 \text{ cm}^{-1}\) that is attributed to Sb–O–Sb vibrations \([6, 7, 8]\).

The investigation of electrical properties of films showed (see figures 4a, 4b, table 1) that the minimum resistivity \((\sim 8 \times 10^{-3} \Omega \text{cm})\) and the maximum carriers density \((\sim 2 \times 10^{19} \text{ cm}^{-3})\) corresponds to the pressure range \(5 \times 10^{-3}–7 \times 10^{-3} \text{ mbar}\).

**Figure 3.** Raman spectra of Sb-doped ZnO films: a.1, b.1 – spectrum of the pure ZnO film; a.2 – 1 at. % of Sb, synthesis temperature 550˚C, annealing at 750˚C, \(O_2\) pressure \(5 \times 10^{-3} \text{ mbar}\); a.3 – 1 at. % of Sb, synthesis temperature 550˚C, annealing at 650˚C, \(O_2\) pressure \(5 \times 10^{-3} \text{ mbar}\); b.2 – 2 at. % of Sb, synthesis temperature 550˚C, annealing at 750˚C, \(O_2\) pressure \(5 \times 10^{-3} \text{ mbar}\); b.3 – 2 at. % of Sb, synthesis temperature 550˚C, annealing at 650˚C, \(O_2\) pressure \(5 \times 10^{-3} \text{ mbar}\).

**Figure 4.** Electrical properties of Sb-doped ZnO films.
(a) – electron concentration versus oxygen pressure, (b) – resistivity versus oxygen pressure.

The figure shows graphs for the films with 1 at. % antimony concentration.

Significant differences in the photoluminescence spectra of samples obtained under different conditions were demonstrated (figure 5). The conditions under which there is no band in the region 500 - 600 nm the PL spectra were found: 1 at. % of Sb, synthesis temperature 550˚C, annealing at 650˚C, \(O_2\) pressure \(2 \times 10^{-3} \text{ mbar}\). The absence of this band can indicate low concentrations of point defects related with oxygen vacancies in films. It was also found that the peak corresponding to exciton transitions is red-shifted compared with such peak for pure zinc oxide.
### Table 1. Electrical properties at room temperature of ZnO : Sb films.

All obtained samples show n-type of conductivity.

| Concentration of Sb, at. % | O₂ pressure, mbar | Resistivity, Ω·cm | Mobility, cm²/V·s | Electron concentration, cm⁻³ |
|----------------------------|--------------------|-------------------|-------------------|-------------------------------|
| 1                          |                    |                   |                   |                               |
| 5·10⁻³                      | 8.072·10⁻³         | 38.08             | 2.031·10⁻¹         |
| 7·10⁻²                      | 8.859·10⁻³         | 38.98             | 1.808·10⁻¹         |
| 1.5·10⁻²                    | 5.609·10⁻³         | 49.04             | 2.269·10⁻¹         |
| 3·10⁻²                      | 1.180·10⁻²         | 35.97             | 1.471·10⁻¹         |
| 5·10⁻²                      | 3.253·10⁻²         | 20.94             | 9.162·10⁻¹         |
| 5·10⁻³                      | 2.925·10⁻¹         | 12.48             | 1.709·10⁻¹         |
| 2                          |                    |                   |                   |                               |
| 7·10⁻²                      | 5.815·10⁻¹         | 42.30             | 2.538·10⁻¹         |
| 10⁻²                        | 9.955·10⁻¹         | 13.08             | 4.792·10⁻¹         |
| 3·10⁻³                      | 1.295              | 5.881             | 8.199·10⁻¹         |

### Figure 5. Room-temperature PL spectra of ZnO:Sb films (1 at. %): (1) – synthesis temperature 550°C, annealing at 750 °C, O₂ pressure 2·10⁻³ mbar; (2) – synthesis temperature 550°C, not-annealed, O₂ pressure 2·10⁻³ mbar; (3) – synthesis temperature 550°C, annealing at 650 °C, O₂ pressure 2·10⁻³ mbar.

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