DETERMINATION OF STRUCTURAL AND PHOTOELECTRIC CHARACTERISTICS OF ZnO POLYCRYSTALLINE THIN FILMS AND ZnO NANOROD ARRAYS OBTAINED BY SPRAY PYROLYSIS

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Abstract. ZnO polycrystalline thin films and ZnO nanorod arrays were obtained by the spray pyrolysis method at a substrate temperature of 450 °C. By analyzing the XRD diffractograms, the hexagonal crystal structure of the ZnO films and ZnO nanorods was determined. On the other hand, the grain size of the films and nanorods was determined using the Debye-Scherrer equation. The optical properties of the films and nanorods were determined by measuring the dependence of the transmission on the wavelength of the light. Also, the optical band gap of 3.28 eV for the ZnO films and 3.21 eV for the ZnO nanorods was estimated. The photoconductivity spectrum of thin films and nanorods was recorded in the visible light range and their photoconductivity was studied when they were illuminated by X-rays, where the incident X-rays increase the conductivity of thin films of nanorods. The surface morphologies of the ZnO films and the ZnO nanorods, as well as the grain size of the film and the dimensions of the nanorods, were studied by a scanning electron microscope.

Key words: Zinc oxide, optical band gap, photoconductivity, surface morphology

1. INTRODUCTION

Zinc oxide is a semiconductor with a band gap of 3.3 eV which is used as a transparent conductive film in solar cells and flat screens, gas sensor, ultraviolet light laser, transistors for various applications, photoconductive devices and radiation detectors [1]. The photoconductivity of ZnO leads to an increase in the number of charge carriers but, under certain conditions, chemical absorption and desorption of molecules may also occur [2]. However, the morphology of ZnO thin films could be different. Namely, the ZnO film could be found in polycrystalline form [3] with different grain sizes, in the form of nanowires [1] or in the form of nanorods [4]. In addition, the nanocrystals in the form of assembled nanorods are of particular importance due to the charge transfer in a designated direction, and the reduction of charge carrier recombination [5].

The semiconductor X-radiation detectors are used in material characterization devices, monitoring of nuclear reactions, determining the radiation from medical nuclear devices and radiation detectors [6]. Therefore, semiconductors with a wide forbidden zone are used, such as GaN [7] and ZnO [6, 8], which change the conductivity depending on the intensity and the wavelength of X-radiation.

Zinc oxide thin films are obtained by various methods such as chemical deposition [9, 10], magnetron sputtering [11], electrodeposition [12], spray pyrolysis [4, 13], metal organic chemical vapor deposition [1] and other [6]. For making ZnO thin films and ZnO nanorod array films, the method of spray pyrolysis of aqueous solution with various precursors is being used, since the method is simple and economical [4, 13]. In this paper, we study the spectral photoconductivity of ZnO thin films and ZnO films of nanorods arrays, as well as the conductivity of films while being irradiated with X-rays.

2. MATERIALS AND METHODS

Thin films of ZnO were obtained by the spray pyrolysis method of 0.2 M $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution, on glass substrates heated at temperature of 450 °C, whereas the films were polycrystalline. In addition, the thin film of ZnO nanorods array was obtained by spray pyrolysis of 0.2 M ZnCl_2 aqueous solution on glass substrates, which were heated to the same temperature. The air was used as the carrier gas, and the spraying was continuous. To measure the conductivity of the ZnO thin films, they were deposited on glass slides previously covered with a transparent and conductive SnO_2 thin film with a resistance of 10 Ω/cm^2 [14]. The SnO_2 thin film was scratched from

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the glass substrates in a form of a narrow line with a diamond blade. A ZnO thin film was deposited on that line and, because of its small width, its resistance was reduced.

The crystalline structure of the ZnO films was determined by the X-ray diffraction pattern obtained using the Rigaku Ultima IV powder X-ray diffractometer when measuring the intensity of X-ray diffraction for 2θ in the range of 20° – 70° . Cu-K α source of X-ray radiation with $\lambda = 0.15418$ nm was used, operating at 40 kV anode voltage, current of 40 mA and a scan rate of $2^\circ/\text{min}$. The optical properties of ZnO films were studied by measuring the dependence of transmission on wavelength in the range of 350–900 nm using the Varian Cary 50 spectrophotometer. Also, the structure and morphology of ZnO films was studied by scanning electron microscope VEGA3 LMU. For this purpose, the samples were cut and fastened to the carrier using double-sided adhesive carbon tape. Then, gold was deposited on them with magnetron sputtering on the side of the film. The samples were analyzed with a SE detector at a voltage of 20 kV and a vacuum of 0.018 Pa.

The photoconductivity spectrum of the films was recorded using the HP 34401A multimeter, also the monochromatic light of a Beckman DU-2 spectrophotometer was used as a light source with a precisely determined wavelength. Further, the film resistance was measured during darkness and ten seconds after its irradiation with polychromatic X-ray radiation, obtained from the Fe-anode of the JEOL JDX 7E X-ray diffractometer, at voltages of 30 kV and 40 kV and constant current of 30 mA. The absorbed dose of polychromatic X-ray radiation was measured with the AT1117M Radiation Monitor PU.

3. RESULTS AND DISCUSSION

Figure 1. X-ray diffraction pattern of: a) ZnO films obtained by spray pyrolysis of $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution and b) ZnO films obtained by spray pyrolysis of ZnCl_2 aqueous solution

The XRD patterns of ZnO films obtained by spray pyrolysis of $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution showed a hexagonal wurtzite structure with an expressive peak due to reflection from plane (002), with c-axis preferred orientation, and smaller peaks that refer to planes (100) and (101) (Figure 1) [15, 16].

The sharp peaks show the polycrystalline structure of the ZnO film, but an observed hump in the X-ray diffraction pattern may indicate the presence of an amorphous phase in the ZnO film. On the other hand, films obtained by spray pyrolysis of ZnCl_2 aqueous solution showed a much larger peak at $2\theta = 34.38^\circ$, relative to films obtained by spray pyrolysis of $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution, because of the reflection from plane (002) (Figure 1) [1]. This means that the films had different morphologies, despite the fact that they had the same crystal structure. The average grain size was determined from the Debye-Scherrer equation [2]:

$$D = \frac{0.9 \cdot \lambda}{\beta \cdot \cos \theta} \quad (1)$$

where λ is the wavelength of the X-ray source, β is the full-width at half-maximum (FWHM) of the diffraction peaks and θ is the Bragg's angle. By applying the Debye-Scherrer equation, the grain size was calculated to be 40 nm for ZnO films obtained by spray pyrolysis of $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution. However, for ZnO films obtained by spray pyrolysis of ZnCl_2 aqueous solution, the grain size was calculated to be 56 nm.

Figure 2. SEM image of the ZnO polycrystalline films

The morphology of films obtained by spray pyrolysis of $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution shows (Figure 2) that the films are polycrystalline [17]–[19], without the presence of holes. However, the films obtained by spray pyrolysis of ZnCl_2 aqueous solution demonstrate (Figure 3) strong-oriented ZnO nanorods with a maximum diameter of 500 nm and length of 1 μm . ZnO nanorod arrays are grown in the form of vertical columns relative to the surface of the

substrates, and are oriented in the direction of the *c*-axis. The interface includes nanorod arrays with a diameter of 500 nm or it is filled with nanorods with a smaller diameter and, in some places, there are none. However, the density of the nanorods depends on the density of ZnO seeds and the temperature of the substrates [10].

It is obvious that the differences of grain size determined by the Debye-Scherrer equation and SEM image are due to the limited Debye-Scherrer equation. Namely, Debye-Scherrer equation exists for nano-scale particles, and cannot be used for large grains [20]. This means that many factors could contribute to the width of a diffraction peak, such as crystallite size, micro-strain and instrumental broadening [21].

The optical properties of the ZnO polycrystalline thin film and the thin film of ZnO nanorod array were studied by recording the spectrum of transmission (Figure 4). The ZnO polycrystalline films show a change in the light transmission for wavelength of 380 nm, indicating that the film has a defined crystal structure. However, the transmission of the ZnO nanorod array thin films begins to gradually increase for wavelength of the light of 380 nm, which could be attributed to the light scattering from the nanorods. In order to determine the bandwidth of the forbidden zone, the absorption coefficient is calculated from the following equation [3]:

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right) \quad (2)$$

where T is the transmittance and d is the thickness of the film.

Figure 3. SEM image of the ZnO nanorod array films

In addition, the bandwidth of the forbidden zone and the character of the electronic transitions are determined by the graphical presentation of $(ah\nu)^2 = f(h\nu)$, from the cross-section of the linear part of the curve and the x-axis (Figure 5). From the graphs given in Figure 5, the band gap is valued to be 3.21 eV for

polycrystalline ZnO films and 3.28 eV for ZnO nanorod array film.

The photoconductivity of ZnO films was examined in the presence of UV light illumination, due to the chemisorption/desorption of oxygen on the surface of the ZnO film [1]. Namely, in dark conditions, the oxygen is absorbed on the surface of the ZnO film by capturing the electrons from the films, decreasing the conductivity of the ZnO film. While being illuminated by light, pairs of electron-holes are generated, where the holes interact with the oxygen which is then released from the surface of the film, given by the equation:

Figure 4. Transmission optical spectra of: a) ZnO polycrystalline films and b) ZnO nanorod array films

Figure 5. Plot of $(ah\nu)^2$ versus photon energy of: a) ZnO polycrystalline films and b) ZnO nanorod array films

On the other hand, photogenerated electrons remain in the film and lead to increasing conductivity of the ZnO film. Figure 6 shows the dependence of the photoconductivity of the polycrystalline ZnO film on the energy of photons, where the maximum photoconductivity matches the photon energy of 3.36 eV, and 3.27 eV for the ZnO nanorod array film. If they are considered to be a direct semiconductor according to the electron transfer, then the band gap could be determined from the photon energy values at maximum photoconductivity. The band gap of a polycrystalline ZnO film determined from the photoconductivity differs from the band gap determined by the transmission spectrum. This may be as a result of a change in the conductivity of the film due to the effect of chemical adsorption and desorption of oxygen by the polycrystalline ZnO film.

In addition, the electrical resistance of the films was studied during their irradiation with polychromatic X-ray radiation produced in the X-ray tube with Fe-anode. The absorbed dose of 5.9 $\mu\text{R/h}$ was measured for polychromatic X-ray radiation at 30 kV voltage, as well as the absorbed dose of 48 mR/h at 40 kV voltage. The intensity and the energy spectrum of X-ray radiation depends on the applied voltage and current, where the energy of X-ray radiation increases with the voltage of X-ray tube. Additionally, the X-ray absorption spectrum of ZnO depends on their mass attenuation coefficient and the energy of X-ray radiation [22].

The $R = 444 \text{ k}\Omega$ resistance of the polycrystalline ZnO film in dark conditions was determined. While, the resistance $R = 1.096 \text{ M}\Omega$ under X-ray irradiation was measured at 30 kV anode voltage of the X-ray tube; at the anode voltage of 40 kV, the resistance had the value of $R = 1.160 \text{ M}\Omega$. Also, the resistance $R = 300 \text{ k}\Omega$ for the ZnO nanorod array film was measured in dark conditions, whereas $R = 279 \text{ k}\Omega$ and $R = 250 \text{ k}\Omega$ under X-ray irradiation were obtained at 30 kV and 40 kV anode voltage, respectively.

Figure 6. Photoconductivity spectra versus photon energy of: a) ZnO polycrystalline films and b) ZnO nanorod array films

The X-ray irradiation of the polycrystalline ZnO film contributes to the reduction of its conductivity, while the conductivity of the ZnO nanorod array film increases. This could be due to the difference in the adsorption/desorption rate of the oxygen and the number of generated electron-holes pairs, in the polycrystalline ZnO film and on the ZnO nanorod array film during their irradiation with X-rays.

The performed X-ray irradiation on the ZnO polycrystalline film helps the release of oxygen from grains, as well as the adsorption of oxygen at the grain boundaries. By taking into account the presence of an amorphous phase in the polycrystalline film, shown in the X-ray diffraction pattern, the conductivity would reduce due to the released oxygen which is then captured at the grain boundaries [23] and decreases over time. On the other hand, the X-ray irradiation on ZnO nanorod array film promotes the release of oxygen, thus creating Zn atoms with dangling bonds [24] which would, in this case, increase the conductivity over time [1].

4. CONCLUSION

Zinc oxide thin polycrystalline films and ZnO nanorod array films were obtained by spray pyrolysis of $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution and by spray pyrolysis of ZnCl_2 aqueous solution, respectively. The ZnO films show hexagonal wurtzite structure with an expressive peak that is due to reflection from the lattice plane (002). The optical band gap of 3.21 eV of polycrystalline ZnO films and 3.28 eV of ZnO nanorod array films were determined. Further, by using the photoconductivity, the bandwidth of the forbidden zone of polycrystalline ZnO films valued 3.36 eV and 3.27 eV for ZnO nanorod array films were determined. In addition, the conductivity of the films was studied under polychromatic X-radiation, at 30 kV and 40 kV anode voltage of the X-ray tube. The X-ray irradiation of the polycrystalline ZnO film contributes to the reduction of its conductivity, while the conductivity of the ZnO nanorod array film increases. Likely, there is a difference in the mechanism of conductivity of the ZnO polycrystalline film and the ZnO nanorod array film in case of UV light illumination and X-ray irradiation, as well as in the effect of the generated electron-hole pairs in the conductivity mechanism.

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