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Research Article

THE INFLUENCE OF ANNEALING TEMPERATURE ON PHOTOLUMINESCENCE OF NANORODS OF ZINC OXIDE

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Abstract.

A research method of photoluminescence has shown that the annealing temperature of the nanorods of zinc oxide has a great influence on the luminescence, which is associated with exciton and recombination mechanisms.

The intensity of luminescence in the UV region increases with the increasing of treatment temperature to 400°C by reducing the concentration of surface and bulk point defects.

The dependence of the luminescence intensity on the annealing temperature in the visible region is more complicated due to the specific dependence of the concentration of defects and their complexes involved in the radiative and non radiative processes, because of the temperature of processing.

Key words: Photoluminescence, UV luminescence, electron microscopy, annealing temperature, bulk point defects.

Introduction

Zinc oxide is a well – known semiconductor material with wide (E = 3,37 eV) and direct gap. Such width of the gap makes it transparent for the visible wavelength range. Zinc oxide can be applied in optoelectronic devices in the ultraviolet range, but due to the large binding energy of the exciton (60 MeV) it is possible to generateradiation at temperatures upto 550 K[1].

Also it has high radiation resistance compared with other semiconductor materials. Nanostructures based on ZnO attracted great attention due to its unique electrical, optical and magnetic properties. The popularity of nanorods of zinc oxide is due to their ability to the self-organized growth not only in crystalline, but also on amorphous substrates. The nanorods on the *ZnO* film increase the sensitivity of its photoconductivity, which is useful for sensors of ultraviolet radiation [2]. Since they have a high surface area relative to volume, this leads to a large light absorption

and charge separation in converters of solar energy into electricity [3]. In addition, high specific surface allows using the *ZnO*nanorods in gas sensors and biosensors [4].

Methods of deposition of *ZnO*nanorods with pointed ends allow usingthemas highly efficient field emission cathodes [5].

The existing technologies of synthesis of nanorods allow growing structures of a rather high quality, however a large influence on the defective situation in them have a temperature and atmosphere of annealing. However, it is known that the best method of estimating structure of point defects, participating in radiative recombination, is the study of the photoluminescence spectra. These reasons formed the basis of the present study of luminescence at photoexcitation.

Sample preparation

Nanorods of zinc oxide were obtained by the sol-gel method on the substrate of glass according to the method proposed in [6]. In the first stage there was a cleaning of substrates from organic and inorganic contaminants. Organic contamination was removed in an ultrasonic bath with acetone. After washing in distilled water, the substrate was placed in a chromic mixture to remove inorganic contaminants. The remnants of the chromic mixture were washed with a large amount of distilled water. The final purification was carried out in an ultrasonic bath with deionized water.Drying of substrates was held at a temperature of 25 °C during the day.

For applying the seed layer was used a 0.005 molar solution of zinc acetate,$Zn(CH_3COO)_2 \cdot 2H_2O$, in the isopropyl alcohol.

The solution was applied by drops on the rotating substrate. At applying the seed layer the rotation speed of the substrate was 2000 rpm. After applying of five drops of solution, the substrates were dried at 200 °C. For each substrate was performed three cycles of applying the priming and drying.

To prepare the gel, in 0.2 molar solution of zinc acetate in the distilled water, with an active stirring and controlling the level of *pH*, was added ammonia, the pH was increased to 8.6. Further, on the substrate with the seed layer was applied a layer of gel. The growth process of *ZnO* nanorods was carried out for one hour at a temperature of 110 ºC.

Removal of the gel and washing of the samples was carried out a large amount of distilled water and the final washing was performed in an ultrasonic bath.

A heat treatment of samples was carried out in air at temperatures of 160, 200, 250, 300, 350, 400 and 450°C. The duration of treatment was 60 minutes.

Research methods

Electron microscopic images of the surface samples were obtained using scanning electron microscope TescanMira 3LM. Measurements of the spectra of x-ray diffraction were performed on x-ray diffractometer*PANalyticalEmpyrean*. Measurements of spectra were carried out on the spectrophotometer SF-56. Luminescence spectra under photoexcitation were obtained by the device for the study of the luminescent and photovoltaic properties according to the methods described in [7].Photoexcitation was carried out by lines of mercury with a wavelength of 313 nm and 365 nm.

Results and discussion

Figure 1 shows a typical electron microscopy image of nanorods of zinc oxide, obtained in this work. The length of nanorods made up of 1-3 microns, with a diameter of 250-350 nm. Of a hexagonal form, the predominant growth direction is close to normal.

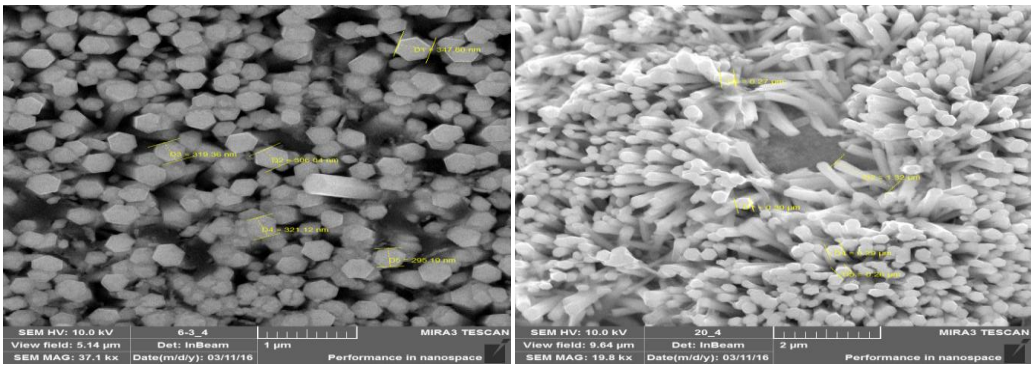

Figure 1:Electron microscopic image of zinc oxide at different magnifications.

High crystalline structure perfection of the obtained samples is confirmed by x-ray crystallography. On the radiograph shown in figure 2, we can see the visible peaks belonging exclusively to zinc oxide. So, we can conclude about the absence of foreign phases and reaction products in the resulting material. The predominance of crystalline orientation (002) in the manufactured samples and the presence of reflexes (100), (101), (102) and (103), according to the literature[8], indicates the lattice of awurtzite type, which is characteristic for nanocolumn of zinc oxide.

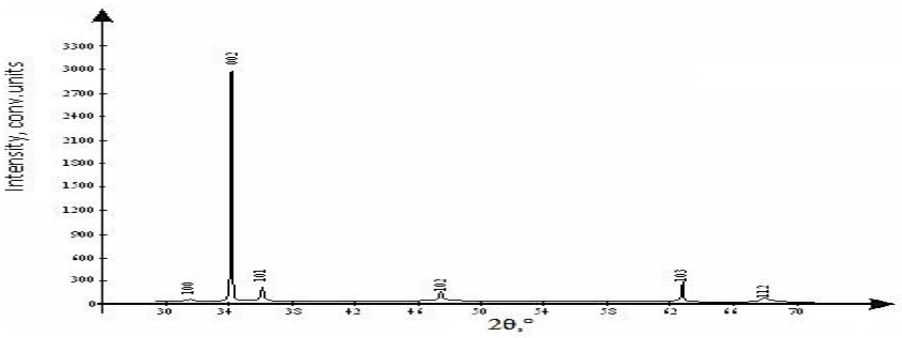

Figure 2: Radiograph of nanorods of zinc oxide.

As it was shown by the results of a study of the luminescence of the nanorods of zinc oxide in their emission spectrum (the measurements were carried out at a room temperature) is dominated by exciton (380 nm), green (510 nm) and red (652 nm) radiation. Figure 3 shows the luminescence spectra associated with exciton mechanism. An annealing conducting does not affect the shape of the spectrum of the exciton luminescence. Its maximum is almost coincides with the value of the energy obtained from the optical band gap of samples, obtained from the absorption spectra (figure 3, curve 2), constructed in the coordinates $(\alpha(v)\cdot hv)^2 - hv$ (where α is the absorption coefficient, it was determined according to the method described in [9]). The band gap of the samples before and after the heat treatment were changed slightly and amounted to about 3.2 eV. Low absorption in the visible wavelength range is confirming the high quality of the obtained structures.

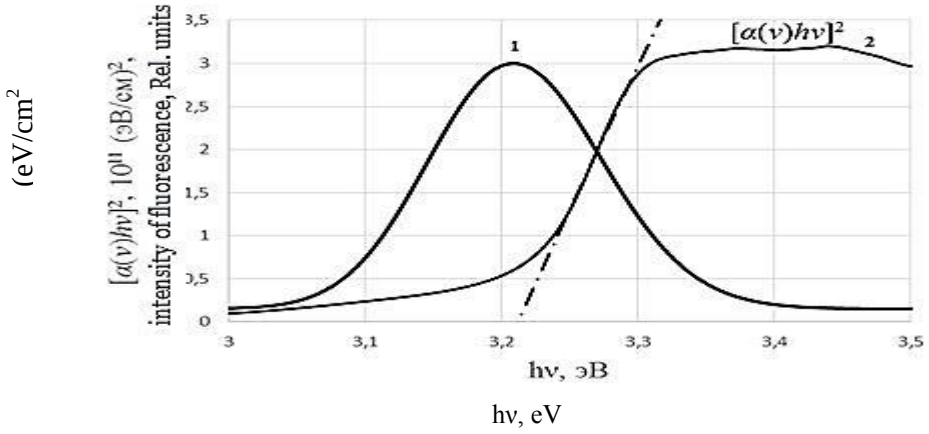

Figure 3: Spectrum of the exciton luminescence

(1)and the absorption (2) of nanorods of zinc oxide

Figure 4 shows the luminescence spectra of the nanorods of zincoxide of the visible region obtained for samples that were subjected to the heat treatment.

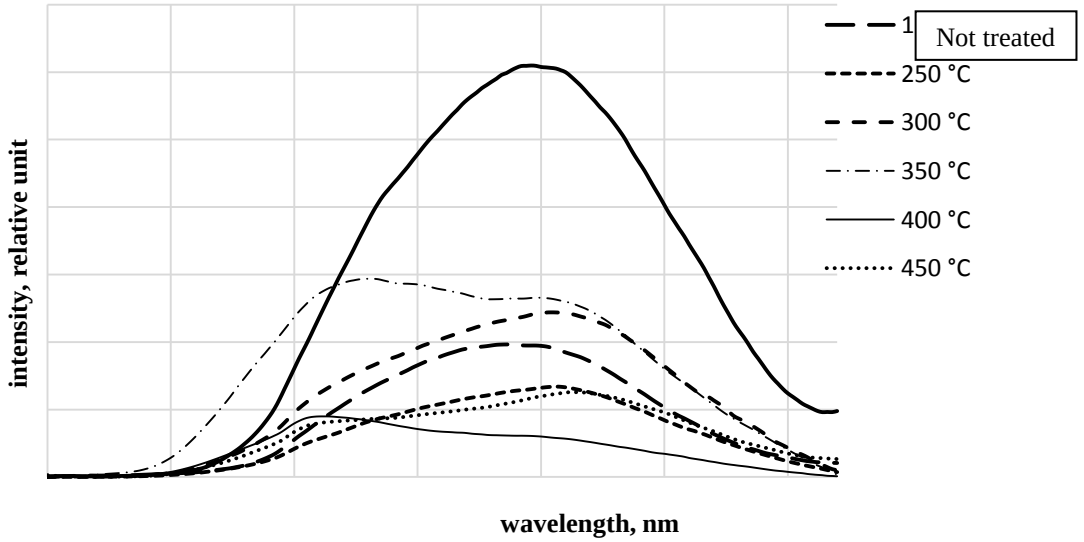

Figure 4: Effect of annealing temperature on the PL spectra of the nanorods of zinc oxide

As can be seen from figure 4, the highest intensity of luminescence has the untreated sample. The increase of annealing temperature leads to a preferential decrease in the integral photoluminescence. It is worth noting that the shape of luminescence spectra is not elementary, apparently, associated with multiple bands. Different recombination transitions of photoexcited carriers in *ZnO* are responsible for these bands. To identify the contribution of radiative transitions in the emission spectrum was conducted of its decomposition into Gaussian components. The obtained results indicate the existence of two luminescence bands with maxima at wavelengths of about 520 and 600 nm.

Currently there are many models describing the visible luminescence in the self-activated zinc oxide.

In the general case, their essence is reduced to the recombination of nonequilibrium charge carriers at the levels of native defects - of oxygen vacancies, zinc vacancies or centers associated with their participation. Established in the theoretical study [10] the depth of the complex centers of$V_{Zn} - V_{O\ of}$ two types gives a good agreement with the maxima of the bands obtained during the decomposition into Gaussian components in the present work, this suggests the presence of recombination on the levels that were formed by these associates, as in our case.

Figure 5 shows the effect of annealing temperature on the intensity of the bands obtained by decomposition into Gaussian components, and the exciton luminescence. As can be seen from this figure, the unannealednanorods of zinc oxide do not possess the exciton luminescence. The intensity of the UV luminescence increases with the increasing of annealing temperature and has a maximum at 400 °C. A further increase in temperature of heat treatment leads to a sharp drop in the intensity of UV light. A structural improvement of zinc is greatly influence for the excitonic luminescence.This is confirmed by the results of the studies. So from figure 5, it follows that the most intensive UV luminescence is observed at the annealing temperature of 400°C, when the intensity of the visible glow, that is associated with the own defects, is minimal.

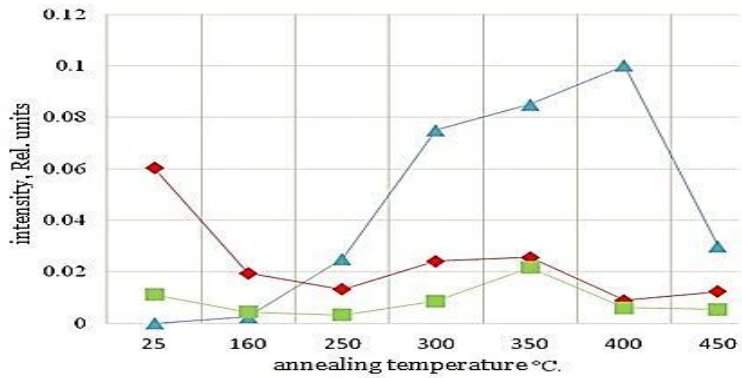

Figure 5: The effect of annealing temperature on the photoluminescence intensity of nanorods of zinc oxide: blue color shows the exciton luminescence (max 380 nm), green emission band with maximum of 520 nm and red with a maximum of 600 nm.

The most intense visible luminescence is observed in the untreated sample at 25 °C. In this case, a concentration of vacancies of zinc and oxygen is high, and therefore increases the likelihood of formation of associated centers of two types. The presence of these types was indicated in [10]. The decrease in the intensity of the visible luminescence with annealing temperature of 250 °C may be due to a decrease in the concentration of surface defects due to the desorption of hydroxycomplexes and aquacomplexes of zinc on the surface of the nanorods. A further increase of luminescence intensity at annealing of up to 350 °C is associated with an increase in the concentration of the associated luminescence centers due to the increase of the concentration of zinc vacancies in the volume of rods.The decrease in intensity both excitonic and visible photoluminescence at annealing temperatures of over 400 °C, apparently, is the result of the formation of a large number of centers ofnon radiative recombination, as a result of the increased concentration of vacancies and interstices of the zinc, of oxygen defects with high activation energy of the complexes with their participation. The increase in the concentration of defects in the sublattice of zinc is confirmed by measurements of the transmittance of the obtained structures, on which is observed a monotonic drop of the transmittance in the region from 400 to 1.1 nm that is probably associated with the release of zinc to the surface of nanostrip.

Conclusion

With a help of sol-gel method on glass substrates are synthesized the arrays ofzinc oxide nanorods, that are having a hexagonal shape and the diameter of 250-350 nm and length of 1-2 μm. Preferential growth direction is close to normal.

It is shown that annealing temperature has a great influence on the luminescence associated with exciton and recombination mechanism. The intensity of luminescence in the UV region increases with the increasing of temperature treatment up to 400°C by reducing the concentration of surface defects and bulk point defects.

Gratitude

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