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HYDROGEN PASSIVATION EFFECT ON ZnO POWDER

BY

ELENA-VASILICA GAFTON[1,2,*], FRANCIA HAQUE[2], FRANCISCA HUŞANU[1], MARIUS MIHAI CAZACU[3,1], GEORGIANA BULAI[4] and SILVIU GURLUI[1]

[1]“Alexandru Ioan Cuza” University of Iași,
Faculty of Physics, Atmosphere Optics, Spectroscopy and Lasers Laboratory
[2]Institut des NanoSciences de Paris
[3]“Gheorghe Asachi” Technical University of Iași,
Department of Physics
[4]“Alexandru Ioan Cuza” University of Iași,
Integrated Centre for Environmental Science Studies in the
North-East Development Region - CERNESIM

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Abstract. The results of an experimental project concerning the optical properties of zinc oxide (ZnO) nanostructures are reported. The aim of the study is to find the origin of the yellow and the green emission bands of *n*-type ZnO sample by hydrogenation. A discussion about absorption spectra in UV-visible region was done by comparison with previous results. Parameters obtained from photoluminescence and UV absorption measurements of the ZnO powder in different stages of sample processing (in vacuum, hydrogenated before and after an annealing treatment) are discussed.

Keywords: *n*-type zinc oxide; wurtzite; photoluminescence; UV-VIS; powder hydrogenation.

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[*] Corresponding author; *e-mail*: gafton.vasilica@gmail.com

1. Introduction

Zinc oxide is a chemical compound found in nature as a mineral called zincite. Synthetic ZnO is obtained as a white powder. The synthesized crystalline ZnO has a hexagonal structure, also called wurtzite. ZnO is a promising semiconductor in materials science due to its wide band gap (3.24 eV at room temperature) which makes it a good material for photonic applications in the UV-visible spectral range (Djuristic and Leung, 2006; Pankove, 1971), or its piezoelectric property which makes it adapted for electromechanical sensor (Ramadan *et al*., 2014). In addition, the high exciton-binding energy (60 meV) allows an efficient excitonic emission even at room temperature. The biocompatibility of ZnO makes him suitable in biomedical applications or in daily life products, such as cosmetics, food or sunscreen and UV absorbers (Kim *et al*., 2011). ZnO presents an advantage compared to other metal oxides that can be used for sunscreen. TiO_2 particles have to be coated with silica or alumina to avoid the formation of carcinogenic radicals which can damage the skin (Jacobs, 2010).

A variety of ZnO nanostructured morphologies have been reported (*e.g.*: such as tetrapods, nanorods, nanowires, nanorings, nanobelts). The different shapes of particles are due to various fabrication methods (Roy *et al*., 2003). Indeed, while a hydrothermal method without any metal catalyst enables the synthesis of aligned nanorods, a combustion leads to tetrapods (Zhao *et al*., 2011).

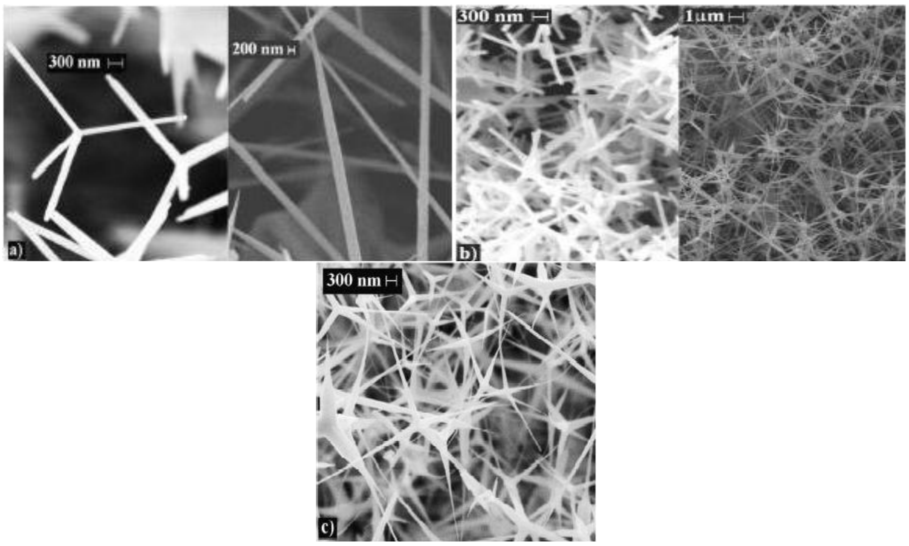

Fig. 1 – SEM images from ZnO nanostructures (Roy *et al*., 2003): (*a*) tetrapods (left) and rods (right) obtained in the air; (*b*) small tetrapods (left) and mixture of tetrapods and wires right obtained in dry argon flow; (*c*) mixture of tetrapods and wires obtained in humid argon flow.

The influence of factors such as the synthesis medium, temperature, vapor-phase or solution-phase deposition on ZnO morphology has been widely studied, but there are still several unanswered questions concerning the relationship between fabrication conditions and optical properties. Fig. 1 shows Scanning Electron Microscopy (SEM) images found in previous articles while Fig. 2 presents Tunneling Electron Microscopy (TEM) image of tetrapodal shape of ZnO particles, as reported by Roy *et al.*

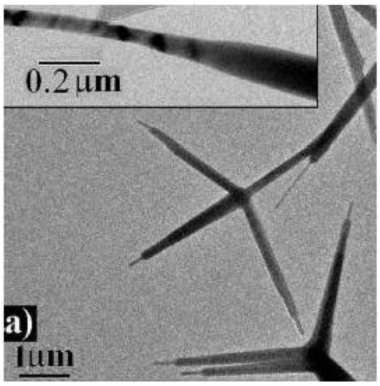

Fig. 2 – TEM images of nanowires (Roy *et al*., 2003) growing out of a tetrapod leg, inset shows a magnified image of the nanowire – tetrapod leg.

Considering that the surfaces of oxide powder particles contains a large number of defects such as steps, edges, and vacancies, which are not present on the perfect single crystal surfaces, it was interesting to study the effect of exposure to H_2 molecules at room temperature. According to literature, it is expected that the hydrogenation of the ZnO powder leads to the presence into the bulk of H atoms located at interstitial sites (Scarano *et al*., 2006; Noei *et al*., 2010; Kim *et al*., 2011).

In the present study, we focus on the hydrogenation effect on the optical properties of a sample of ZnO powder, consisting of tetrapodal particles.

2. Experimental Details

ZnO powder was synthesized by combustion method in air atmosphere. This method offers a higher purity of the final product in comparison with other synthesis techniques. The ZnO powder was prepared from the evaporation of metallic zinc pieces attached to a wire of nickel-chrome. The wire was placed in a closed chamber full of air, at room temperature and atmospheric pressure, connected to a generator. Once the wire was put in touch to the two electrodes, the zinc was brought to evaporation state by passing current through the wire; thus, the product was collected on a glass plate placed just above the zinc sample. The ZnO product obtained as gas phase is then condensed as a white powder and transferred into a tube that will allow the removal of the moisture by pumping it into vacuum, until the pressure inside the tube reaches 10^{-4} mbar.

The sample was annealed for 1h under a dynamic vacuum of 10^{-4} mbar (Noack and Eychmuller, 2002) and activated by outgassing at 580°C, in order to remove all the impurities such as CO, CO_2 or HO^- groups which could have been adsorbed during the synthesis. In order to compensate for the oxygen loss during annealing treatment, at the end of the activation period, 120 mbar of oxygen was dosed to the sample (still kept at 580°C). After 30 min the sample was cooled and the oxygen removed by outgassing at room temperature to a final pressure of 10^{-5} mbar. The sample obtained consists of a clean *n*-type ZnO, a white powder which most probably has defects in its wurtzite crystal structure.

After the annealing process, 40 mbar of H_2 molecules were added into the tube, at room temperature. The hydrogenation of zinc oxide has been currently studied by transmission in infrared range, whose results demonstrated that exposure of mixed-terminated ZnO to atomic hydrogen leads to the metallization of the surface, whereas the exposure of the oxygen-terminated O- ZnO surface leads to the occupation of bulk interstitial sites. It was found that after exposure to H_2 molecules, there is a reversible dissociative adsorption of H_2 on both surface O and Zn sites. The H atoms are then diffusing into the bulk, and occupy interstitial sites (Noei *et al.*, 2010).

Two types of measurements were done on the obtained samples: UV-visible absorption and photoluminescence. These two complementary techniques were chosen for investigation because UV absorption gives information about the electronic transition from the ground state to an excited state, while the photoluminescence focuses on the electronic transition from an excited state to the ground state. In our case, UV absorption measurement was first done in order to have an overlook on the band gap energy of the semiconductor which was necessary in order to choose the proper excitation energy in photoluminescence measurements.

UV absorption measurements were done on a Varian Cary spectrometer. The background was measured with a pellet of barium sulphate ($BaSO_4$) by recording the reflectance intensity versus the wavelength in UV-visible range, 200-800 nm. On the surface of finally powdered sample the incident beam was diffusely scattered. The diffusely scattered beam is concentrated in the reflectance sphere. The results of reflectance were converted into absorbance using the Kubelka-Munk equation (Kubelka and Munk, 1931), Eq. (1):

$$\frac{K}{S}=\frac{[1-0.01\,R]^2}{2.[0.01\,R]} \tag{1}$$

where: K is the absorption coefficient, S the scattering coefficient, and R the reflectance. The energy gap was then evaluated from the UV spectra.

Photoluminescence (PL) measurements explored the effects of hydrogenation on the annealed *n*-type ZnO bulk sample. The PL spectra were obtained using a series of monochromators and a CCD camera connected to the computer. The excitation source was the 360 nm line of a Xenon laser, with a power of 450 W. The value of the excitation energy was chosen to be higher than the energy gap observed in the UV absorption measurement, in order to be able to excite electrons from the valence band to the conduction band. As a result of these transitions, the corresponding excitonic peak at 378 nm (3.28 eV) will be observed in PL spectra. A 375 nm filter was used in order to get only the photoluminescence signal. All measurements were carried at room temperature in a dark room since the photoluminescence technique is sensitive to light.

3. Results and Discussion

From the spectra shown in Fig. 3 the energy gap of the semiconductor was extracted. For the higher wavelength (low energy), the absorbance is minimum since the incident energy was not sufficient to excite the electrons. By decreasing the wavelength, the energy is enough to make electrons cross the gap, escaping from the valence band into the conduction band. So the maximum value observed for lower wavelength corresponds to the electrons absorbed in conduction band.

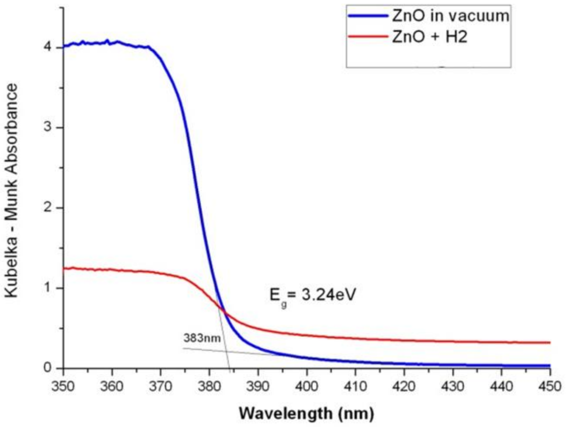

Fig. 3 – UV spectra for the ZnO particles in vacuum and hydrogenated samples.

Charge carriers are donated to the conduction band, thus providing strong evidence that H atoms diffuse into the bulk and occupy interstitial sites in a manner similar to that observed after exposure to atomic hydrogen. Absorption probes the conduction band tail of states in a *n*-type semiconductor. The tail of the valence band has been omitted since, being empty, it does not participate in the absorption process.

The results of the PL measurements of ZnO sample after synthesis, and after hydrogenation, in vacuum with a pressure of 10^{-4} mbar, at room temperature are shown in Fig. 4. For each measurement, two dominant emission peaks are observed: a near band edge ultraviolet emission peak centred around 380 nm arising from the existence of excitons, accompanied by a broad deep-level luminescence, centred on 440 nm (green) and 530 nm (yellow), and related to presence of defects as impurities or oxygen vacancies.

Both spectra were measured in the same conditions, so a comparison between the intensities may be done and the effect of hydrogenation on the sample can be observed and interpreted. It is obvious that the only effect of the hydrogenation on the as-grown sample without thermal treatment is increasing four times the intensities of the peaks due to interaction of the hydrogen with the powder.

In literature, the remarkable increase in the intensity of the bound exciton peak after hydrogenation is explained as follows: when a hydrogen atom enters ZnO, it either interacts with an impurity, such as an H donor or a carrier bound of a complex in the ZnO crystal, or it passivates a non radiative recombination centred at deep level (Khan *et al.*, 2006).

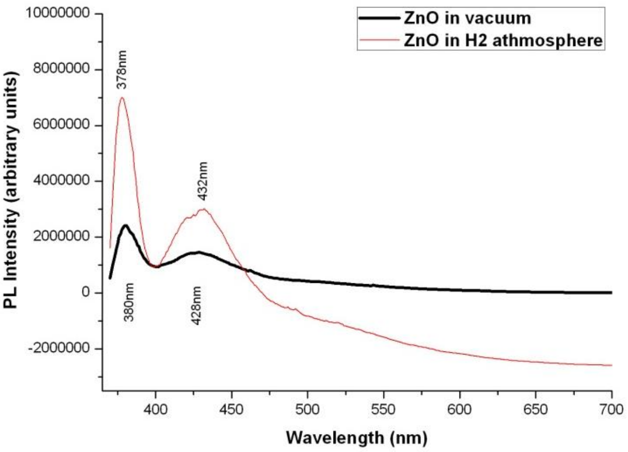

Fig. 4 – Photoluminescence spectra at room temperature of the as-grown and the hydrogenated ZnO bulk samples.

However, these results are not in totally accordance with previous ones. Kim *et al.* (2011) observed that the peak position corresponding to the defect-related wide-band emissions changes remarkably (Fig. 5). The yellow band emission peak around 2.1 eV was not present for hydrogenated ZnO, and the intensity of the green band emission peak at 2.43 eV was almost unchanged. It was concluded that the emission is related to vacancies, such as oxygen, since the yellow band is strongly passivated by hydrogen atoms after hydrogenation.

These results indicated that the yellow band emission (peak at 2.1 eV) is due to oxygen vacancies and disappears with the addition of hydrogen atoms. At the same time, it was concluded that the 2.43 eV emission peak is not related to oxygen vacancies because it remained after passivation by hydrogen atoms. Therefore, the wide defect emission was reported as due to complex vacancies and impurities or native defects.

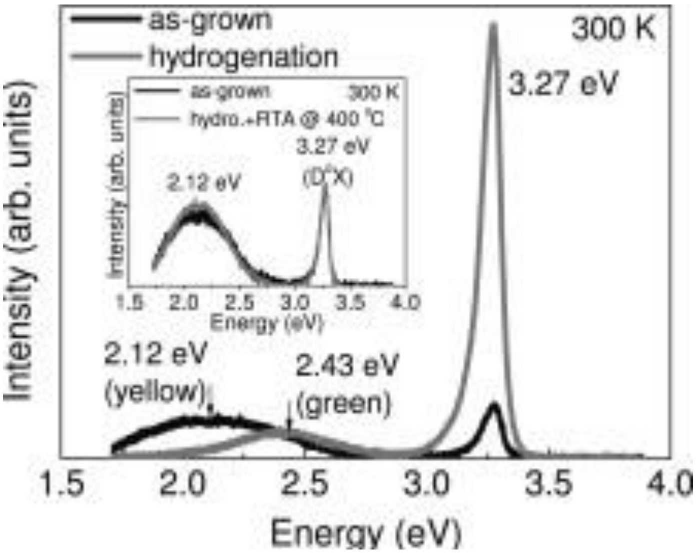

Fig. 5 – Photoluminescence spectra at room temperature of the as-grown and the hydrogenated *n*-ZnO bulk samples reported in (Kim *et al.*, 2011). The inset shows the PL spectra for annealing at 400ºC of the hydrogenated sample.

The same remark as reported by Kim *et al.* (2011) can be observed in present measurements when the annealed and hydrogenated sample is taken into discussion. In Fig. 6 the PL spectra of the annealed sample at 580ºC in O_2 atmosphere, in presence of and after the H_2 outgassing is reported. An immediate observation is the increase of the peak intensities corresponding to the hydrogenated sample compared to the as-synthesized one, which is due to the interaction of the hydrogen atoms with the crystal defects.

The PL spectra of the annealed sample presents a wider peak centred at ~ 559 nm compared to the one found in Fig. 4 for the as-grown sample. This broadening is related to the emission due to transition of deep donors (as O vacancies and unknown acceptors). The peak width is due to the effect of annealing processed that created a large number of oxygen vacancies, despite the following addition of O_2 that supposed to compensate the loss of oxygen from the bulk. The intensity of the wide band emission is stronger than that of the emission peak at 380 nm.

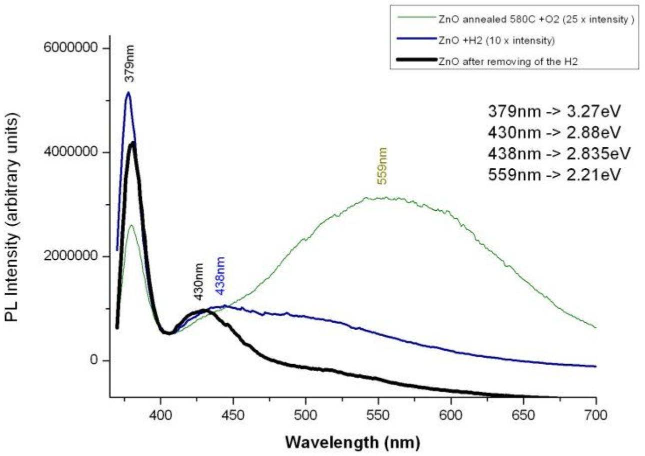

Fig. 6 – Photoluminescence spectra for annealing at 580°C and activated in O_2 sample, in presence of and after outgassing the H_2 samples.

The intensity of the emission peak of the hydrogenated sample (blue curve) at 380 nm (3.26 eV) is significantly increased and is related to shallow donor impurities due to hydrogen addition. The emission peak at 438 nm (2.83 eV) originates from complexes between oxygen vacancies and other crystal defects. The emission peak around 550 nm is no longer present. The yellow band is strongly passivated by hydrogen atoms after hydrogenation as indicated by the enhanced optical absorption and the presence surface defect states of zinc interstitials.

The hydrogen desorption from the ZnO powder causes a 10 times decrease of the emission intensity that is clearly related to the removal of the hydrogen atoms from both interstitial and surface sites. However, the hydrogen atoms are not completely removed since the yellow band emission does not reappear (Scarano *et al.*, 2006). Thus, outgassing the hydrogenated powder is not enough to remove the impurities.

The reported results indicate that i) the oxygen vacancies in ZnO are easily passivated by hydrogen atoms, ii) ionized hydrogen atoms act as shallow donors and neutralize defects and iii) a high temperature is required for hydrogen dissociation in *n*-type ZnO.

4. Conclusions

Photoluminescence measurements on synthesized, annealed and hydrogenated n-type ZnO samples were done in order to investigate the origins of the yellow and the green emission bands and the excitonic peak. After annealing, more oxygen vacancies are created, in spite of the oxygen addition, indicated by the increase of the yellow band emission in the PL spectra. After hydrogenation, the yellow band emission does not appear anymore, due to the passivation of hydrogen atoms on the ZnO powders. This result indicates that the yellow band emission is related to the oxygen vacancies. On the other hand, the green band peak is unchanged after hydrogen passivation and is assumed to originate from complexes between oxygen or zinc vacancies and other crystal defects. Finally, the sharp peak at 3.37 eV which is the signal of the exciton is related to the shallow donor impurities due to hydrogen donors, since its intensity increases significantly after the addition of hydrogen.

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EFECTUL DE PASIVARE A HIDROGENULUI ASUPRA PULBERII DE ZnO

(Rezumat)

Sunt raportate rezultatele unui proiect experimental privind proprietățile optice ale nanostructurilor de oxid de zinc (ZnO). Scopul acestui studiu este de a investiga natura benzilor de emisie galbenă şi verde ale oxidului de zinc de tip *n* cauzate de procesul de hidrogenare. Vor fi introduse pe scurt mai multe aplicații ale ZnO și diferite condiții de sinteză care conduc la diverse morfologii. O discuție despre absorbția în regiunea UV-VIS se va face prin comparație cu rezultate anterioare ale altor grupuri de cercetare. Sunt descrişi parametrii obţinuţi din măsurătorile de fotoluminiscenţă şi spectrosocopie UV-VIS ale pudrei de ZnO menţinută în vid, după hidrogenare, înainte și după procesul de calcinare.