INVESTIGATION OF THE NANOSTRUCTURES USING OPTICAL AND SPECTROSCOPIC METHODS

(HULUMTIMI I NANOSTRUKTURAVE ME ANË TË METODAVE OPTIKE DHE SPEKTROSKOPIKE)

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ABSTRACT

Material structures and optical morphology of the grains, deposited on the surface of a film, using optical and spectroscopic techniques, are studied. Using scanning electron microscopy, structures of the grains deposited on the substrate are analyzed. Optical and electrical properties of aligned ZnO rods vertically grown on stainless steel (SS) foil are studied. Transparency, absorption is measured and band gap is determined. Spectroscopic and electrical techniques are used to study the microscopic and electric properties respectively.

Key Words*: nanostructures, fluorescent spectroscopy, absorption, thin films.

PËRMBLEDHJE

Me anë të metodave optike dhe spektroskopike janë analizuar strukturat materiale dhe pamjet morfologjike të disa grimcave filmike. Me anë të mikroskopit elektronik janë analizuar vetitë optike dhe elektrike të këtyre grimcave me përbërje ZnO të cilat kishin formë të shkopthave. Është matur transparenca, absorbimi dhe është përcaktuar gjerësia e brezit gjysmëpërçues. Me anë të metodave spektroskopike dhe elektrike janë hulumtuar vetitë mikroskopike dhe elektrike të grimcave në fjalë.

Fjalët kyçe*: nanostrukturat, spektroskopia fluoreshente, absorbimi, filmat e hollë.

INTRODUCTION

Aligned ZnO nanorods grown on polycrystalline substrates have promising optoelectronic applications. Novel samples with such structures were electrodeposited on stainless foil from a $ZnCl_2$ and other materials [1-2]. Well-aligned and free-standing hexagonal grains with 100-nm diameter and closely-packed could be grown normal to the substrate [2].

Zinc oxide is a remarkable multifunctional semiconductor with a unique set of properties suitable for applications in a wide range of emerging domains such as solid-state lighting, nanotechnology, transparent electronics and spintronics [2-4]. It has band gap energy of 3.37 eV (300 K) and large exciton energy of 60 meV. Electro deposition is a cost- effective method for the growth of calcogenide and oxide films and their nanostructures [5, 6]. There have been many reports on the synthesis of ZnO nanowires using various growth methods [7-12]. Some research

groups have studied the synthesis of ZnO nanowires on a Si substrate [11, 12].

Despite much progress in the synthesis of ZnO nanowires, there have been only rare reports on the synthesis of high quality ZnO nanowires without a catalyst on a Si substrate at low temperature. In addition, only few reports regarding the study of the growth behavior and the growth mechanism of ZnO nanowires have been explained. New research has been recently triggered by the availability of ZnO nanostructured materials that are characterized by exotic properties extremely interesting for electronics, optics and photonics devices. Applications of ZnO nanostructures in nanosensors , field effect transistors, optical switches, solar cells, etc., have been demonstrated [13, 16].

Since the demonstration of room temperature optically pumped lasing in ZnO microcrystallite thin films in 1997 [13, 14], efficient excitonic ultraviolet stimulated emission (SE) and lasing actions have been investigated in many forms of ZnO nanostructures. These studies can be mainly classified into two groups including the ultraviolet SE and lasing actions in microcrystallite thin films deposited on substrates and in ZnO powder [16]. However, for the fabrication of ZnO nanodevices, it is still a challenge to prepare ZnO products with a low SE pump threshold by a simple and effective synthesis method [17].

The large exciton binding energy, which is much greater than the thermal energy (26 meV, 300 K), inhibits thermal depopulation of the lowest, radiative transition, and then results in more efficient excitonic emission at room temperature [18]. These are highly advantageous to realize a nanolaser with a low and temperature- insensitive optical-gain threshold, a narrow emission line, and high-temperature stability. Since Yang et al demonstrated the room-temperature ultraviolet (UV) laser in a ZnO nanowire array grown on saphire substrates[17], optically pumped UV stimulated emission and lasing have been widely studied in nanopowder, nanowires, nanobelts and thin films at room temperature. Nanostructures have a higher surface to volume ratio than the bulk material. For ZnO nanowire, the deep-trap-type

emission (green emission) from surface state and near-band-edge emission (UV emission) always exist simultaneously [19].

In quantum-size nanowires, the surface-trap-state recombination may quench the near-band-edge emission entirely [18, 19]. However, the situation in realizing stimulated emission is quite different. The dependence of the ratio of the near-band-gap emission to the deep-level emission on the excitation energy from different ZnO samples was discussed [20].

In this work we discuss the structure the optical properties of aligned ZnO rods vertically grown on stainless steel (SS) foil. The choice of SS foil is due to its low cost and mechanical flexibility and the fact that little is known about the properties of ZnO electrodeposited on SS [19,20]. Two techniques are applied for deposition of nanostructures on SS foil: Chemical deposition (CD) and electro deposition technique. Our study is concentrated mainly on the films obtained by ED technique. As gown and annealed cases of the films deposited by ED techniques are characterized by using optical and spectroscopic approaches.

Both fundamental research and progress in potential device applications have stimulated many efforts on ZnO materials. Despite extensive investigations, some fundamental luminescence properties of ZnO are still not fully understood, such as the origin of the room temperature photo luminescence PL [19, 20]. In this work we study PL of ZnO at room temperature. The optical transition energies (absorption and emission) of samples were determined by transmittance and photoluminescence spectroscopy.

Experimental procedure

Chemical deposition (CD) and Electro deposition (ED) technique are applied for deposition of the thin films on the SS foil. The experimental details of the procedure for the CD technique are given elsewhere [21-23], here we focus mainly on some relevant details for ED deposition of the thin film.

Electro deposition was performed from a 800-ml aqueous $ZnCl_2$ solutions (5-9 mM) containing

0.1 M KCl as the supporting electrolyte. The reference and the counter electrodes were Ag/AgCl (SSC) and Pt, respectively. The solution temperature was maintained constant in the range 60-80 °C for the preparation of different samples. The SS substrate (AISI302), used as a working electrode, was cleaned in an ultrasonic bath of ethanol just before the deposition process which was performed at a cathode potential of – 630 mV to – 1000 mV with respect to the reference electrode. The solution was continuously purged with pure oxygen during the deposition period which varied from 50 to 80 minutes. The samples were immersed in a boiling hydrogen peroxide solution for 3 to 10 minutes. The post-deposition thermal annealing of samples was performed in pure oxygen at atmospheric pressure (400 C°, 1h).

The film thickness was determined gravimetrically from its mass and using a density of 5670 kg/m³. For some samples thermal annealing was per-
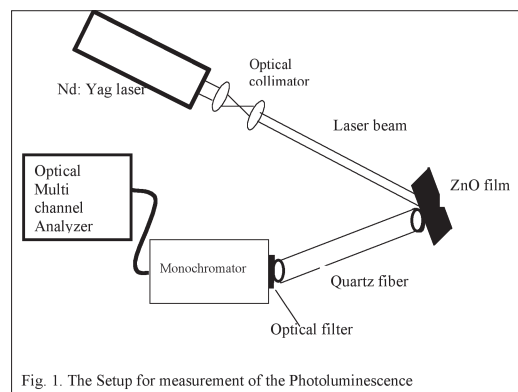

Fig. 1. The Setup for measurement of the Photoluminescence

formed in a tube furnace. In some cases films were lifted from their metallic substrate and transferred onto glass using transparent epoxy. Composition, morphology and structure of the films were studied using scanning electron microscopy, SEM (Jeol JSM-6300) and x-ray diffractin XRD (Siemens D500, Cu K_α: 0.154056 nm). Photoluminescence measurements were performed at room temperature using a setup consisting of Nd:YAG laser (excitation wavelength355 nm), optical multichannel analyzer (EG&G PAR 1689), 0.35-m monochromator (McPherson-270), optical waveguides and filters.

We used Photoluminescence phenomenon

to characterize the films and get insight into its microscopic and dynamic structure the photoluminescence to characterize the ZnO films. The experimental setup is shown in figure 1.

The laser beam used for excitation is collimated in order to control its size or to focus the light at the required place on the optical axis. In front of the beam ZnO film to be characterized is placed. The laser beam and the fiber collecting the florescent light are placed at the same side of the film, as shown in the Fig. 1. Perpendicular to the plane of the film is placed an optical fiber collecting the fluorescent signal and transmitting to the slit of a monochromator. In front of the slit the other end of the optical filter is placed. The output electrical signal from the monochromator is transmitted to an Optical Mulichannel Analyzer OMA. The intensity of the laser beam used for fluorescent excitation can be changed by changing the output laser power, or by focusing the light illuminating the film. The film is placed on a stage, with 5-degree of freedom, making possible to reach the optimal position for the maximum of the collected fluorescent signal by the fiber that could be seen on the screen of the OMA.

RESULTS

In this section the results obtained by chemical deposition and electro deposition technique, optical and spectroscopic analysis are presented. Since the experimental procedure is given in section 2, here only required comments and relevant points akin to the particular experiment and corresponding result will be elaborated.

CHEMICAL DEPOSITION TECHNIQUE

Here are presented results of chemical deposition (CD) technique. Two different cases were studied. In the first case the film was deposited by using the solution $ZnCl_2$ + NaOH. In second case a new film was
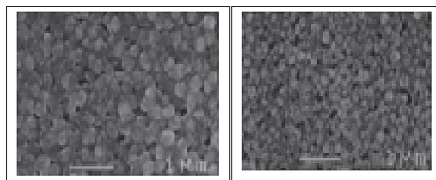

Fig. 2.Image surface of the films obtained by CD for two different solutions. 2. a. The case of Zn Cl₂ solution, 2. b. The case for the ZnSO₄ solution
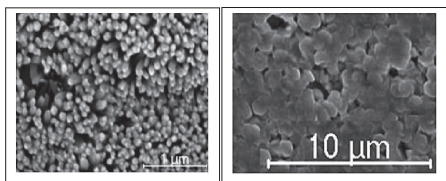
Fig. 3.a   Fig. 3.b

Fig. 3. Images of surface of the thin films obtained by electro deposition
3. a) the case of lower concentration, 3. b) the case of higher

deposited by using the solution $ZnSO_4$ + NaOH.

ZnO films were deposited on a glass substrate by immersion of the substrate in zincate solution kept at room temperature and hot water at relatively low temperature (100^0C).

The detailed procedure for the deposition is similar to the one given in [19], where a steel substrate was used instead of a glass substrate.

Two different cases of CD for different solutions are presented in Figures 2.a,b. While in Figure 2.a is shown the image for the deposition of $ZnCl_2$, in Figure 2. b the case of $ZnSO_4$ solution is shown. In the first case the round shaped grains composed in a random structure can be seen. In the second case the more compact grains forming a relative smooth surface is shown. In both cases the features such as the shape of the grains can not be seen. The rod shaped grains perpendicular to the surface of the SS foil can be obtained by using ED technique. The shape of the grains, their sizes and position of their axis are some of factors that determine the band gap structure of the film. For this reason we study the ED-based film.

Electro deposition technique

ZnO thin rods are synthesized by electro deposition technique. The film containing the rods is annealed at a temperature of 400 ^0C. Results of scanning electron microscopy of the film before (as grown) and after annealing in the figure 3 are shown. The case of the as grown film is shown in figure 3.a. The isolated rods forming a random pattern can be seen. It is expected that incident light on this film will be scattered randomly generating wavelets and leading to a speckle pattern. Therefore this kind of film can not be used for information processing using the coherent laser source.

Figure 3.b shows the plane view of the sample after the annealing process is performed. A close
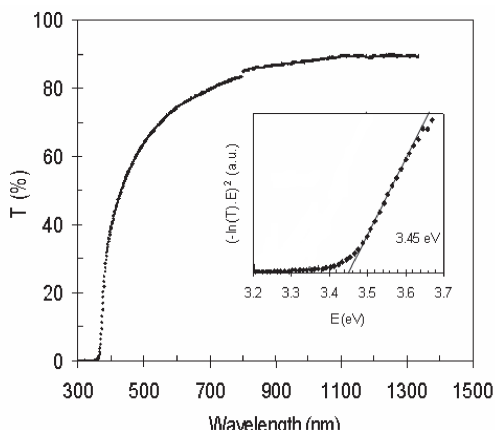

Fig. 4. The optical transmittance spectrum for sample 3.b.

examination of this image reveals that it is formed from the closely-packed hexagonal rods covered with a thin ZnO film. This kind of deposition and annealing process would yield a continuous film which can be used as a contact to one end of the arrayed rods, suitable for device applications. The incident light on this film will be reflected in a regular fashion leading to a pattern similar to a mirror reflection.

Optical transmittance

A double-beam spectrophotometer (Cary 5E) was used to measure the optical transmittance of the film (Figure. 2.b). The procedure of measurement is given elsewhere [21, 23]. The experimental results of the transmittance are shown in Figure 4. Data used of the same graph are used to calculate absorption and band-gap structure, results are shown inset the same figure.

The optical transmittance (T) versus wavelengths is shown in figure. 4. The transmittance increases when the wavelength is higher. The maximum and saturated value of transparence corresponds to the wavelengths 800-1300 nm. E represents the photon energy.

The band gap is determined graphically by interpolation based on our experimental data and on calculation performed by a computer. The plot shown in the inset figure shows the band gap value 3.34 eV. This number is the numerical value of the graph obtained by computer calculation. The variation of ZnO band gap with deposition pa-
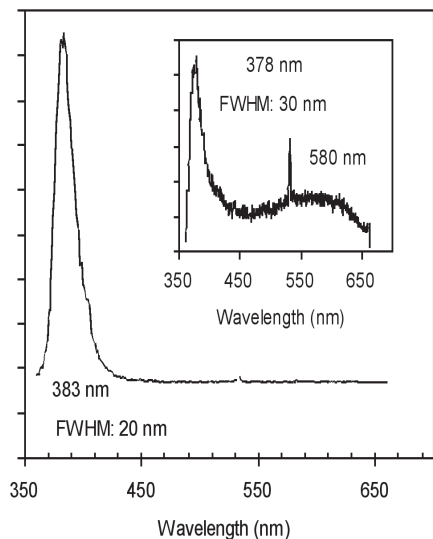
Figure 5. The room-temperature photoluminescence of sample 1, before (inset) and after being annealed in air for 1 h at 400 °C. The sharp peak at 532 nm is the second harmonic of the excitation source.

rameters is reported to be in the range 3.27-3.55 eV [11, 14, 21]. Our result is within this range.

Absorption vs. energy analysis is given in the appendix of this work*.

PHOTOLUMINESCENCE ANALYSIS

Photoluminescence of the film shown in Figure 3. b is studied and results are shown in Figure 5. Figure 5 shows the room temperature PL spectra of the same film: as-grown (before) and after the film is annealed. In case of as grown film a high and relatively narrow peak is shown to be at 387 nm wavelength. A broader PL peak is at wavelength of 580 nm. The sharp peak at 532 nm is not associated with PL effect. This peak is e very narrow indicating that it comes from a coherent source. This is the light coming from Nd-Yag laser we used for excitation and for generating the PL.

After the film was annealed the PL spectra is measured and shown in figure 5. Its peak appears to be at 383nm. Actually this is the red shifted peak which is at wavelength of 378 nm of the inset spectra. The broader peak (at 580 nm) shown in as grown case is suppressed completely after the film is annealed.

CONCLUSIONS

ZnO films grown on SS substrates, with different techniques show different surface textures. The SEM images representing the films obtained by CD technique show that randomly shaped grains are distributed on the surface of the substrates. In this work the study is focused is in case of ED technique where the individual rods can be distinguished. Here, the grains or rods grow preferentially along the c-axis normal to the substrate.

The optical and the spectroscopic investigation have revealed useful properties of the films deposited by ED technique. The optical transmittance of the film is 90%. The band gap value is 3. 34eV. Therefore this film can be used for optoelectronic devices. The application of this film for making a Schottky diode will be reported in the future.

PL results are shown for the as grown and when annealing process is performed on the same film. In case of the as grown film the UV emission band at 378 nm and broad band emission at 580 nm are obtained. The latest peak value emission appeared because of the radiative recombination of photogenerated holes with electrons with the single ionized oxygen vacancies of the surface.

The red shift of spectra with a peak value at 383 nm is measured for the same film after the annealing process is performed. This peak value is part of UV spectra and originates from the recombination of free excitons through an exciton-exciton collision corresponding to near band edge emission of wide band gap. PL spectra obtained after annealing is performed, show a complete suppression of the broad band emission at 580 nm. Disappearance of this band emission and red shift of the peak from 578 nm to 378 nm will be studied in our future work. However, we report here that due to the intense room temperature UV emission rod-shaped nanostructures grown by ED on the SS substrates open the way to valuable applications in optical devices and may be applicable in fabrication of electronic devices.

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APPENDIX

1) ENERGY AND WAVELENGTH OF LIGHT

In 1900 Max Plack discovered that all natural oscillating systems of natural frequency ν, have discrete energies E = n hν (where n is a natural number, h is Planck's constant h=6.63 x 10^{-34} J.s, ν is the frequency of oscillating system). Einstein in 1905 introduced the concept that light consists of pointlike quanta of energy E= hν.

By using formula ν = c/λ, the expression for energy becomes E= ch/λ. Therefore E can be replaced by λ and vise versa.

2) TRANSPARENCY AND ABSORPTION

The band gap transitions in a semiconductor film are normally evaluated from the measurement of the film absorption coefficient α as a function of the incident photon energy, E. From the linear part of a plot of $(\alpha E)^2$ against E, the direct transition energy and from a $(\alpha E)^{1/2}$ versus E plot the indirect transition energy can be measured.

$$\alpha = \alpha_0 \, exp(\frac{E - E_0}{E_u})$$

where α_o and E_o are two constants. E_o coincides, roughly, with the energy of the lowest free exciton at zero lattice temperature.

Instead of the α one can introduce (–lnT). This is based on the experimental observation on the transmutation in homogeneous absorbing medium [See the books: R.W. Dichburn, *Light, Transmission of light in an absorbing medium*, pg. 440-444, Interscience Publisher, Inc, New York (1991), or F.G. Smith and T.A King, *Optics and Photons*, pg. 103-107, John Wiley & Songs, Ltd. Chinchester, West Sussex PO19 8SQ, England (2004)].

By performing ln in both sides, and assuming that I_0 is 1, for a very thin film (this condition is satisfied in our case) α is replaced by (-ln T)

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