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Zinc oxide nanostructures prepared on glass substrates by thermal evaporation of zinc at atmospheric pressure

S. Kitova[*], I. Kalaglarski, R. Stoimenov, R. Kazakov and V. Mankov

Institute of Optical Materials and Technologies "Acad. J .Malinowski",
Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl.109, 1113 Sofia, Bulgaria

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In this work ZnO nanostructures were prepared on glass substrates without any ZnO seeds by a simple thermal evaporation of high purity metallic Zn powder. ZnO nanostructures with different morphologies and sizes were synthesized at atmospheric pressure at low temperature of glass substrates (390°C) by the oxidation of Zn vapour in a flow of Ar and O_2 gas mixture. The morphology, phase composition and crystallinity of the nanostructures were investigated by scanning electron microscopy and X-ray diffraction analysis. The electrical properties of ZnO/glass system were investigated via current-voltage (I-V) characteristics. XRD demonstrates that the wurtzite phase of ZnO with preferred c-axis orientation is formed predominantly. The results obtained reveal that the gas flow rate and oxygen content during the layer deposition influence strongly the morphology and electrical resistance of the produced ZnO nanostructures. The layers grown at low gas flow rates were built by ZnO nanotapes, while the other layers consisted of ZnO nanorods with tripod morphology. The increase in the resistivity of the nanostructures was observed with increasing amount of oxidizing agent in the currier gas. All structures exhibit a strong near-band-edge emission at 380 nm.

Keywords: ZnO nanostructures, thermal evaporation, SEM, XRD, electrical properties, photoluminescence

INTRODUCTION

In recent years, ZnO has gained much more interest because of its potential use in many applications, ranging from transparent conductive contacts, solar cells, sensors, laser diodes, ultraviolet lasers, thin film transistors, optoelectronic and piezoelectric applications to surface acoustic wave devices [1-5].The tendency of ZnO to grow in a variety of exotic morphologies such as nanowires, nanorods, nanostars, nanotubes, nanobelts, nanosprings, nanopropellers, etc has induced great interest to explore simple methodologies to grow such nanoarchitectures. Many methods have been developed to produce ZnO nanostructures such as vacuum thermal evaporation and condensation, metalorganic chemical vapor deposition, solution phase method, electrochemical deposition, etc. [1, 6-9]. Different types of ZnO nano- and microstructures were reported in the literature, synthesized by the thermal evaporation processes using metallic zinc powder as source materials for zinc. ZnO micro and nanorods were synthesized on silicon substrates in a horizontal quartz furnace by the thermal evaporation of metal zinc powder under oxygen ambient [10-13].

In the present paper, we report the synthesis of different kinds of ZnO nanostructures on glass substrates at relatively low temperature (390 °C) without use of any seeds, via a simple thermal evaporation of zinc powder at atmospheric pressure. The influence of the Ar flow rate and oxygen content in deposition atmosphere on the phase composition, morphology, electrical resistance and photoluminescence of the nanostructured layers obtained has been studied.

EXPERIMENTAL

ZnO nanostructures were grown on glass substrates using a metal vapour deposition method. The schematic diagram of the experimental setup for the fabrication of ZnO nanostructures is shown in Fig. 1. Zinc powder (99.9999 %) was placed in a quartz boat as the Zn source in the center of a quartz tube in a furnace. The quartz tube was kept at atmospheric pressure by flowing high purity Ar (99.99%) with a flow rate of 300 sccm and heated up to 710 °C. Ar carrier gas mixed with different O_2

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[*] To whom all correspondence should be sent:
E-mail: skitova@iomt.bas.bg

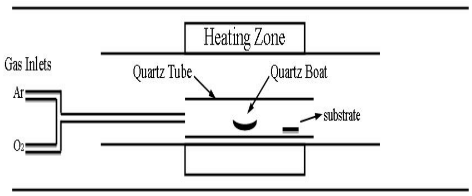

Fig. 1. Schematic diagram of the experimental setup for fabricating ZnO nanostructures by thermal evaporation of Zn.

content from 0.5 to 20 vol.% flew through the quartz tube at reaching the synthesis temperature. The flow rate, R, of gas mixture varied from 200 to 700 sccm. All gas flows were controlled by mass flow meters controllers. The substrates were placed horizontally at the downstream side of the Zn source at a distance of about 25 cm. The temperature of the substrate, controlled by a thermocouple, was 390 °C. The growth time was set to 30 min before terminating oxygen flow and cooling down to room temperature. The thicknesses of the layers were measured by a profilometer type Talystep. The thickness varied within the range 500 – 2500 nm in dependence of deposition conditions.

The layers were deposited on carefully cleaned glass substrates. The cleaning procedure first involved washing with a 1% detergent solution and then with deionized water in an ultrasonic cleaner.

The crystal structure of the layers was characterized by XRD diffraction (XRD), using a Philips (PW 1710) apparatus with Cu-Kα radiation, separated by a graphite focusing monochromator. The 2θ range used in XRD measurements was from 20° to 80° in step of 0.05° s^{-1} and fixed counting time of 5 s per step. The surface morphology of the layers was examined by a scanning electron microscope (SEM Philips 515).

The measurement of resistivity was provided with 2 mm planar narrow strip Al electrodes, 200 nm thick, with a distance of 2.9 mm between each other. Al was vacuum deposited through a precise stainless steel mask on the ZnO surface. Current – voltage (I-V) measurements were performed in dark at 25 °C with Keithley 230 voltage source and Keithley 617 electrometer.

The optical properties of these layers were studied by means of room-temperature photoluminescence (PL) spectroscopy using pulsed Nd:YAG laser (third harmonic at 355 nm) as the excitation source and Ocean Optics HR2000+ spectrophotometer as a detection system.

RESULTS AND DISCUSSION

All deposited layers were white in color. The phase of the layers and their crystallographic orientation were determined by XRD spectra. Fig. 2 shows XRD patterns of the layers deposited on glass plates at different flow rates of Ar gas mixed with 1 vol. % O_2 during their deposition. The XRD results show that the ZnO layers consist of ZnO crystalline phase. Five peaks observed at 31.55, 34.2, 36.0, 47.30, 56.4, 62.69 and 72.5° match the values given in powder diffraction file 80-0074 [14] while the relative intensities of these peaks are

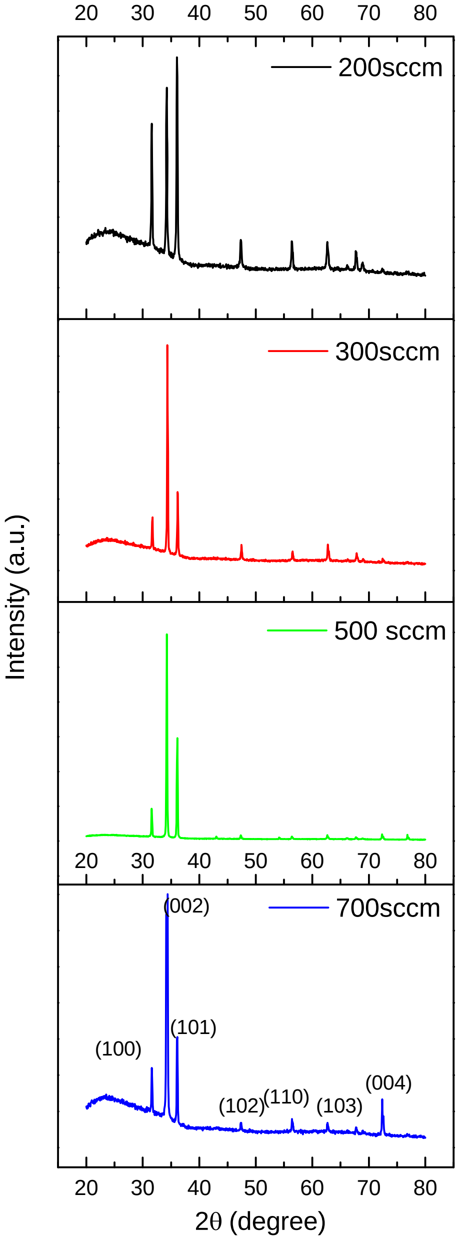

Fig. 2. XRD spectra of ZnO layers deposited at indicated flow rate of Ar gas mixed with 1vol. % O_2 gas.

distinct from those of ZnO powder. These peaks can be indexed to (100), (002), (101), (102), (110), (103) and (004) planes of the hexagonal wurtzite structure of ZnO crystal. The analysis of spectra indicate that the increasing of gas flow rated leads to deposition of ZnO layers with predominant c-axis phase, while the layers grown at low flow rate of 200 sccm exhibit more random orientation with formation of a-axis phase. No peaks of metallic Zn is observed which means that 1% O_2 in gas mixture is sufficient for complete oxidation of Zn independently of gas flow rate and no additional thermal annealing in oxidation atmosphere is needed.

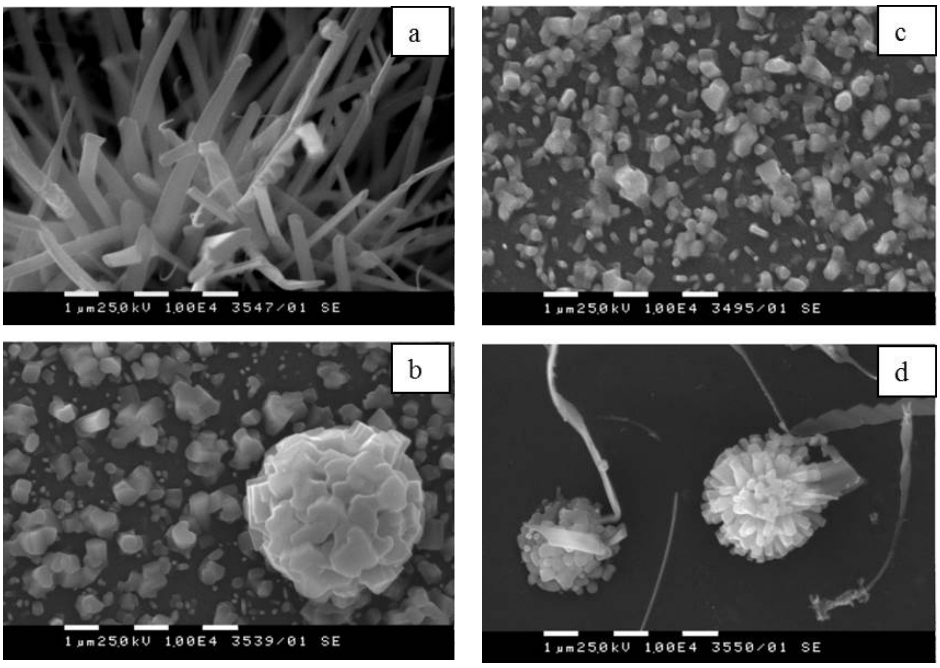

Fig. 3. Top-view SEM images of ZnO layers deposited at Ar/O_2 (1 %)gas flow rates of: a) 200 sccm; b) 300 sccm; c) 500 sccm; d) 700 sccm.

Fig. 3 shows top-view SEM images of the same layers. It is seen that the layers have different morphology which depend strongly on gas flow rate. The layers grown at low flow rate of 200 sccm are built by ZnO nanotapes, while the other layers consist of ZnO nanorods. At middle flow rate of 300 and 500 sccm all the observed nanorods are produced regularly on a whole substrate (30 mm x 20 mm) and they exhibit hexagonal surfaces throughout their length with hexagonal facets. Further increasing of gas flow rate however leads to destroying the uniformity of the layer and the substrate is covered with small drops consisting of randomly distributed ZnO nanorods.

SEM images presented in Fig. 4 illustrates the influence of the oxygen content in deposition atmosphere on the morphology of the obtained ZnO layers. It is seen that the layers deposited at O_2 content up to 10 % in the gas mixture consist of ZnO nanorods grown perpendicular to the substrate surface. It is seen that layers exhibit tripod morphology with feet in different lengths and diameters depending on O_2 content. A further increase in the amount of oxidizing agent up to 20 % in the carrier gas destroys the uniformity of the layer. The substrate is covered with small drops consisting of randomly distributed ZnO nanowires shown in the Fig. 4f.

The XRD and SEM analysis shed some light on the growth mechanism. The formation of ZnO nanostructures with different morphologies is obviously due to the different Zn and O vapour pressure since the morphologies of ZnO layers are influenced by the gas flow rate and concentration of oxygen gas. Most probably on pure glass plates the growth of ZnO nanorods followed a self-seeding vapor–solid (VS) growth mechanism [15]. In the initial growth stage, the self-seeding occurred on the glass substrate and then the ZnO nanorods grew on the seeds by feeding with the evaporated zinc and oxygen elements. ZnO will grow preferentially on the ZnO nuclei that have been formed during the

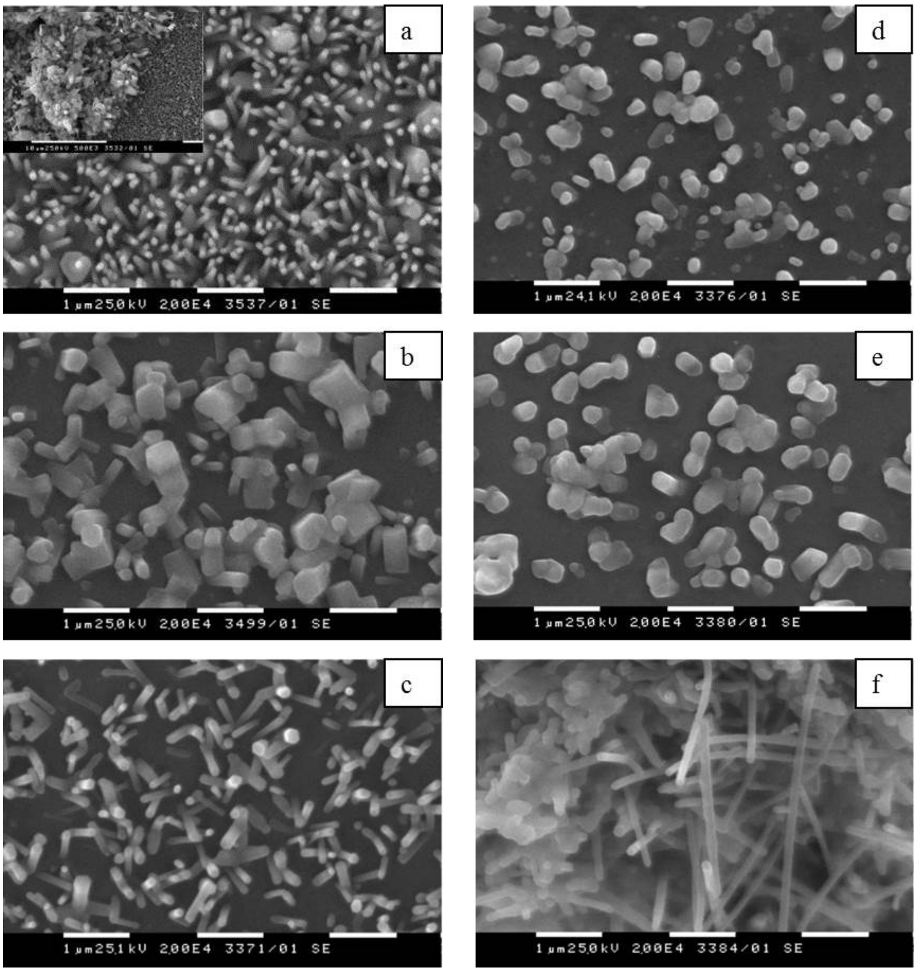

Fig. 4. Top-view SEM images of the layers grown at constant gas flow rate of 500 sccm and different O_2 content in gas mixture: a) 0.5 %; b) 1%; c) 2.5%; d) 5%; e) 10%; f) 20%.

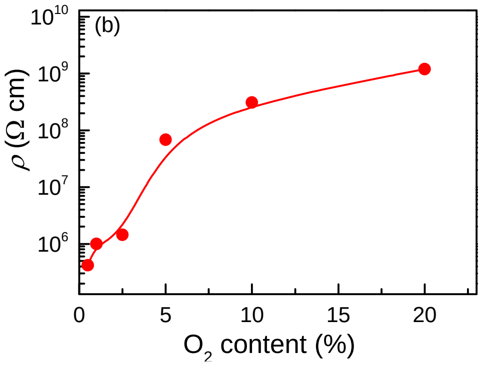

Fig. 5. Resistivity (ρ) of the ZnO layers grown at constant gas flow rate of 500 sccm in function of O_2 content in the gas mixture.

beginning of the layer growth. Growth of tripod structures on pure plates can be explained by the formation of a zinc blende nucleus, out of which wurtzite legs grow [16]. The formation of such highly anisotropic shapes as tripods requires a kinetic growth regime, where the rate of the monomer arrival is greater than its diffusion on the surface [16].

Fig. 5 depicts the resistivity of layers in dependence of the O_2 content in the gas mixture. It is seen that the resistivity of ZnO nanostructures increases from 4.2×10^5 Ω cm to 1.2×10^9 Ω cm as the oxygen content in carrier gas increases from 0.5 to 20 %. This result is in correspondence with the data of other authors published in the literature [17]. As it was well known undoped ZnO thin films have n-type conduction which is caused by a deviation from stoichiometry due to native defects. Various kind of native point defects are present in ZnO layers [18]. They include oxygen vacancies (V_O), zinc vacancies (V_{Zn}), Zn interstitials (Zn_i), oxygen interstitials (O_i), Zn atoms at oxygen anti-sites (ZnO), and oxygen atoms at Zn anti-sites (O_{Zn}). Previously, (V_O) and Zn_i have been assumed to be the main sites of donors in ZnO crystals. However, recent first principles calculations verified that V_O is a deep donor and it cannot be the origin of n-type conduction [18]. In contrast, Zn_i can act as a shallow donor. The high value of ρ obtained for ZnO layers deposited at high O_2 content in gas mixture indicates that the number of defects in ZnO layers have diminished. More probably in our case with the increase in oxygen content in the gas mixture during the deposition some oxygen vacancies and especially interstitial Zn disappear thus causing the increase in film resistivity.

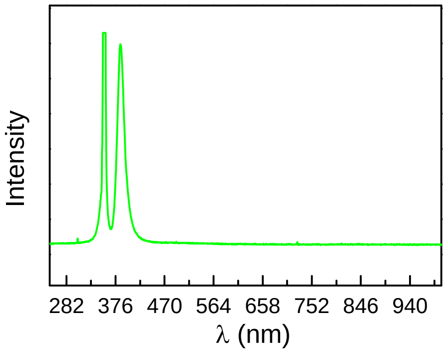

Fig. 6. PL spectrum of ZnO layer grown at 500 sccm flow rate of gas mixture of Ar with 2.5% O_2.

The optical properties of ZnO layers were studied by means of room-temperature photoluminescence (PL) spectroscopy. The spectra of all samples showed a single strong, dominated and high intensity peak in the UV region at 382–388 nm as illustrated in Fig. 6. In addition of these peaks, no emission in the visible range was observed. The peak at 355 nm is due to emission of the excitation source. The UV emission is also referred to as the ‘‘near band edge’’ emission, generated by the recombination of the free excitons between the conduction and valence bands through an exciton–exciton collision process, while the visible light emission is ascribed to the structural defects such as zinc vacancy, oxygen vacancy, interstitials of zinc and oxygen and antisite oxygen [2]. Disappearance of visible emission implies that the as prepared ZnO nanostructures have very low defects density and good optical quality.

CONCLUSION

The polycrystalline nanostructured ZnO layers with different morphology were obtained at low temperature of glass substrates without the use of any seeds at atmospheric pressure. The XRD data indicated that all layers exhibit the hexagonal wurtzite structure. It was found that c-axis phase was most predominant in layers deposited at higher flow rates.

Scanning electron microscopic observations revealed that the morphology of layers strongly depended of gas flow rate and O_2 content in gas mixture. The layers grown at low flow rate were built by ZnO nanotapes, while the other layers consisted of ZnO nanorods. The layers exhibit tripod morphology with feet in different lengths and diameters depending on O_2 content. The further increase in amount of oxidizing agent up to 20 % in the carrier gas destroyed the uniformity of layer.

The results by I-V measurements showed that the resistivity of the nanostructures increased with increasing O_2 content in the gas. The room-temperature photoluminescence spectra of all the deposited structures displayed a strong near-band-edge emission without visible light emission implying the formation of ZnO nanostructures with very low defects density and good optical quality.

It can be expected that due to their characteristics these nanostructured layers may be used as building blocks for preparing chemical and biosensors as well as photocatalysts where inherently large surface to volume ratio of structured materials are important prerequisite for enhanced sensitivity.

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ZnO НАНОСТРУКТУРИ ПОЛУЧЕНИ ВЪРХУ СТЪКЛЕНИ ПОДЛОЖКИ ЧРЕЗ ТЕРМИЧНО ИЗПАРЕНИЕ НА ЦИНК ПРИ АТМОСФЕРНО НАЛЯГАНЕ

Сн. Китова, И. Калагларски, Р. Стоименов, Р. Казаков и В. Манков

Институт по оптически материали и технологии "Акад. Й . Малиновски",
Българската академия на науките, ул. „Акад. Г. Бончев“, бл.109, 1113 София, България

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(Резюме)

В тази работа е изследвано отлагането на наноструктурирани ZnO слоеве върху стъклени подложки, без предварително нанасяне на зародиши върху тях, чрез обикновено термично изпарение на цинков прах. ZnO наноструктури с различни морфология и размери са израснати при атмосферно налягане при ниска температура на стъклени подложки (390 °C) чрез окисление на Zn пари в газов поток от аргон и кислород. Морфологията, фазовия състав и кристалността на получените наноструктури са изследвани чрез сканираща електронна микроскопия и рентгенов дифракционен анализ. Електрическите свойства на системата ZnO/стъкло са изследвани чрез снемане на ток - напрежение характеристики. Получените резулатати показват, че се формира предимно вюрцитната фаза на ZnO с предпочитана ориентация по c-оста. Установено е, че скоростта на газовия поток и съдържание на кислород по време на отлагането влият силно на морфологията и електрическо съпротивление на получените ZnO наноструктури. Слоевете, израснати при ниски скорости на газовия поток са изградени от наноленти, докато останалите са изградени от ZnO нанопръчки с три рамена. Показано е, че съпротивлението на получените наноструктури нараства с увеличаване количеството на окисляващия агент в газовия поток. Всички наноструктури имат силна фотолуминесцентна емисия при 380 нм.