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Morphological, structural and optical properties of ZnO thin solid films formed by nanoleafs or micron/submicron cauliflowers

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ABSTRACT

Thin films of ZnO formed by nano and microstructures with hexagonal crystal phase were successfully synthesized by using pyrolysis technique. At first glance the films resulted divided in 7 zones that were morphologically analyzed and showed the presence of three types of particles: nano-leafs, single microparticles, and particles formed by the addition of microparticles, “clusters”. The largest and therefore the main zone was formed by nanoleafs. Studies on morphology, structure and optical properties of these nanoleafs were obtained and correlated too. The knowledge acquired from these studies allowed the synthesis of nanostructured films entirely formed by nanoleafs with a width of 25 nm and a length 200 nm long regardless of the roughness of the substrate. Energy gap of 3.26 eV was invariant to changes in synthesis parameters. The studies on optical properties of nanoleafs and micro-cauliflower give an energy diagram that account for the location of the energy states introduced by native crystalline defects into the energy band gap and their radiative electronic transitions.

1. Introduction

Semiconductors in a nanometer size have been widely investigated in the past few years, there has been particular interest in correlating their optical properties with the size and shape of the nano-structures [1,2]. Recently, Zheng et al. reported the synthesis of ZnO nanocrystals with controlled size, aspect ratio, and oxygen defects via solvothermal and thermal treatment methods [3]. Their works show that the photocatalytic activity of ZnO nanocrystals is mainly dependent on the type and concentration of the oxygen defects. By other hand, obtaining ZnO as thin film significantly reduces the active surface area which is critical for the catalytic process. In order to counteract this disadvantage, many efforts have been made to produce films with convenient nanostructures that enhance the photocatalytic activity. The control of size, shape and the orientation of ZnO nano-microstructures, in particular the ability to order them into three dimensional arrays onto various types of substrates, as well as to clarify the origin of the visible emission of ZnO represent essential tasks to create functional ZnO.

Zinc oxide has always been considered one of the most important semiconductors due to its physical and/or chemical properties and the consequent multiple applications it has, which include: antireflection coatings, transparent conducting films (as electrodes in solar cells), gas sensors, varistors, surface acoustics wave devices, and electro- and photo-luminescent devices. Recently ZnO nanostructures have attracted much attention due to their potential applications in field emission displays [4,5] highly efficient optoelectronic devices [6–10], UV laser technology at room temperature [6,11] phosphors [12–14], photo-catalysis [15], electromechanical coupled sensors and transducers [16,17], spintronics [18,19], super-hydrophobicity and super-hydrophilicity sufaces [20,21], cosmetics [22], etc.

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Science has much further to do in the functional ZnO nanostructures direction, that is why detailed investigations of prepare methods, growth mechanisms and properties of ZnO nanostructures are needed. In the last decade, different ZnO nanostructures have been obtained by several synthesis methods [2–11,13,14,16–22]. In particular, shapes like: nanocombs, nanorings, nanohelixes/nanosprings, nanobows, nanobelts, nanowires, and nanocages have been obtained under specific conditions using only the solid-vapor phase thermal sublimation (VPTS) technique [23], which should be considered as an achievement and a proof of the well understanding of the VPTS technique by the research group involved in this investigation [23], following this idea and continuing in this direction we considered the use of spray pyrolysis (SP) technique for the synthesis of ZnO nanostructures, this considering that under certain parameter condition SP technique could involve a VPTS micro-process in every single droplet.

Using SP technique Oliviera Milosevic et al. [24] , Sang Duck Lee et. al. [25] and Nora S. Portillo-Vélez and Monserrat Bizarro [26] obtain nanoparticles of ZnO. Oliviera et. al. employ ultrasonic SP with furnace tube as reactor and zinc nitrate hexahydrate as precursor. They discuss the influence of the solution concentration, the synthesis temperature and the residence time of droplets on the particle morphology. They show submicrometric as well as nanosize (100–200 nm) ZnO spherical shaped particles supported on aluminum substrate that were exposed to temperatures of: 72, 230, 588 and 892 °C and solution concentrations of: 0.004 and 1.5 mol dm^{-3}. Both studies, reported by Sang Duck Lee et. al. and Nora S. Portillo-Vélez and Monserrat Bizarro, were oriented to the photocatalytic property of ZnO nanoparticles because it confers promising application into environmental remediation, comparable to TiO_2 [27]. Sang Duck and co-workers obtain a powder composed of nanoparticles with two-types shape (spherical and crushed sphere) through an ultrasonic spray pyrolysis system with furnace tube as reactor. They employ a synthesis temperature of 900 °C and solution concentrations of: = 0.01, 0.1 and 1.0 mol dm^{-3}. Nora S. Portillo-Vélez and Monserrat Bizarro obtain two-type of films, one formed by nanoflakes and other formed by nanorods, through pneumatic spray pyrolysis with a tin bath as reactor, synthesis temperature of 450 °C, zinc acetate and zinc chloride as precursors, desionized-water and desionized-water/methanol ratio mixtures of: 100/0, 75/25, 50/50, 25/75 and 0/100 as solvents and solution concentrations of: 0.05, 0.1 and 0.2 mol dm^{-3}. Both studies, reported by Sang Duck Lee et. al. and Nora S. Portillo-Vélez and Monserrat Bizarro, show ZnO with high photocatalytic performance, but only the second one has the ZnO anchored onto a substrate, which is desirable for water treatment applications.

In this work, ZnO micro and nanoarrrays as a function of solution concentration (molarity) and synthesis temperature were synthesized by using SP technique. Low synthesis temperature values (300–450) °C without any additional treatments were employed. This in order to have nanostructured ZnO films with high active surface area and appropriated optical properties for potential applications in photocatalysis. Properties on crystalline structure, microstructure, low and room temperature photoluminescence (PL), cathodo-luminescence (CL), diffuse reflectance (DR) and Transmittance, were investigated.

2. Experimental procedure

Zinc oxide nano-/microstructures were synthesized using SP technique, which is a low cost and relatively easy scalable technique compared with other techniques that employ vacuum systems. The Fig. 1 shows the configuration of the system and the way the substrate was placed into the tubular furnace. The substrate was placed so that both sides were covered by the synthesized zinc oxide. Several samples were prepared as a function of solution concentration (M_s) and reactor temperature (T_r). The M_s values were in ranges of (0.002–0.064) mol dm^{-3}. T_r was varied from 300 to 450 °C, in 50 °C steps. The samples were labeled as Al-M_s-T_r or Si-M_s-T_r, for ZnO synthesized on aluminum or silicon substrate, respectively. The deposition time was of 5 hours and 30 min for all the samples. Precursor solution was composed of zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] in de-ionized water (resistivity = 18 MΩ). This solution was nebulized using an ultrasonic generator working at 800 kHz and then carried to the substrate by using compressed and filtered air in a flux rate of 8 Liters / min as a carrier gas. The flow rate value in precursor solution was 0.5 ml/min. The substrates were square pieces of silicon and aluminum with 1.5 cm × 1.5 cm dimensions. The aluminum and silicon substrates were obtained from commercial aluminum and silicon wafer with (100) preferred orientation, respectively. The aluminum substrates were sanded previous to zinc oxide deposition in order to clean and scratch theirs surfaces. One of the two surfaces of the silicon substrate came etched from factory; this surface shows a square tessellate.

In order to investigate about the origin of the visible emission, the Si-032-450-O25-N75 sample was synthesized changing the carrier gas of filtered air with a mixture of 75 % nitrogen and 25 % oxygen; using silicon as substrate, Ms = 0.032 mol dm^{-3} and Tr = 450 °C. Nitrogen and oxygen gases were from Praxair Co. Once the film was analyzed by PL spectroscopy, it was subjected to the following high temperature heat treatment: room temperature (T_{room}) – 500 °C in 6 h, remains at 500 °C for 1 h, 500–700 °C in

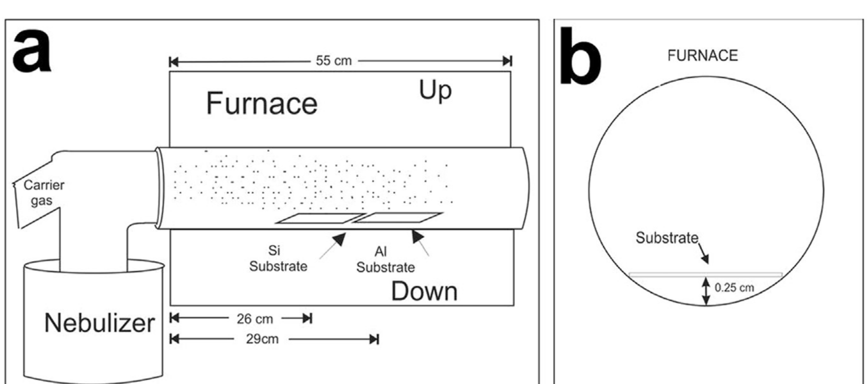

Fig. 1. a) Configuration of the system employed for the synthesis of the ZnO films. b) Diagram of the transversal section that indicate how the substrates were placed into the tubular furnace.