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Room-temperature deposition of crystalline patterned ZnO films by confined dewetting lithography

S. Sepulveda-Guzman [a,*], B. Reeja-Jayan [b], E. De la Rosa [c], U. Ortiz-Mendez [a], C. Reyes-Betanzo [d], R. Cruz-Silva [e], M. Jose-Yacaman [f]

[a] Centro de Innovación, Investigación y Desarrollo en Ingeniería y Tecnología. UANL, PIIT Monterrey, CP 66629, Apodaca NL, Mexico
[b] Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712, USA
[c] Centro de Investigación en Optica, Loma del Bosque #115 Col. Lomas del Campestre C.P. 37150 León, Gto. Mexico
[d] Instituto Nacional de Astrofísica Optica y Electrónica, Calle Luís Enrique Erro No. 1, Santa María Tonanzintla, Puebla. Apdo. Postal 51 y 216, C.P. 72000 Puebla, Mexico
[e] Centro de Investigación en Ingeniería y Ciencias Aplicadas, UAEM. Av. Universidad 1001, Col. Chamilpa, CP 62210 Cuernavaca, Mor., Mexico
[f] Physics and Astronomy Department University of Texas at San Antonio 1604 campus San Antonio, TX 78249, USA

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ABSTRACT

In this work patterned ZnO films were prepared at room-temperature by deposition of ~5 nm size ZnO nanoparticles using confined dewetting lithography, a process which induces their assembly, by drying a drop of ZnO colloidal dispersion between a floating template and the substrate. Crystalline ZnO nanoparticles exhibit a strong visible (525 nm) light emission upon UV excitation (λ = 350 nm). The resulting films were characterized by scanning electron microscopy (SEM) and atomic force microscope (AFM). The method described herein presents a simple and low cost method to prepare crystalline ZnO films with geometric patterns without additional annealing. Such transparent conducting films are attractive for applications like light emitting diodes (LEDs). As the process is carried out at room temperature, the patterned crystalline ZnO films can even be deposited on flexible substrates.

1. Introduction

In recent years, ZnO has attracted a great deal of scientific interest due to its optical and electronic properties. ZnO is a semiconductor with a large exciton binding energy (60 meV) and a wide band gap (3.37 eV) at room temperature. In addition the optical and catalytic properties of ZnO can be tuned by changing parameters like morphology and size [1,2]. For this reason, the control of the morphology of ZnO nanostructures, such as nanowires, nanobelts, nanosprings, and nanorings, plays a key role in obtaining specific optical properties. The use of films made by ZnO nanostructures and three-dimensional ZnO structures, has been proposed as next-generation gas sensors, piezoelectric devices, and as highly transparent conducting electrodes for solar cells and light emitting diodes (LEDs) [3–5]. So far, ZnO films have been prepared by different approaches, such as sputtering, sol–gel, spray pyrolysis, and chemical vapor deposition (CVD) [6–9]. However, the preparation of three-dimensional ZnO structures and electronic devices often demands patterned ZnO thin films. Conventional techniques such as photo or e-beam/ion beam lithography have been used to obtain patterned films but in spite of the resulting high-resolution patterns the complexity of the process and the expensive equipment make these techniques a complicated and costly method. In order to find a general method to pattern and modify ZnO thin films, alternative site-selective deposition techniques have been proposed. These techniques include the in situ growth of ZnO on patterned surfaces and the printing of ZnO precursor on modified flexible substrates [10,11]. Lipowsky et al. [12] reported the fabrication of patterned ZnO films by deposition of ZnO on self-assembled monolayers (SAM). Selective SAM removal using UV light and the oxidation of Zn^{+2} ions in a polyvinylpyrrolidone film placed on the remaining SAM, resulted in a patterned film. Kuan et al. [13] also prepared a patterned ZnO film by simply printing a pattern using a poly(dimethylsiloxane) (PDMS) mold on a sol–gel derived ZnO film. The sol–gel route has also been applied to obtain patterned films by micromolding in capillaries (MIMIC) [14]. In order to improve the crystallinity of the sol–gel ZnO films, post processing thermal treatments are usually required, limiting its use on flexible substrates like plastic sheets. However, it has been found that structural and some optical properties can be improved by applying thermal treatments [15]. For instance, as photoluminescence properties are strongly associated with the microstructure and composition of ZnO particles, several reports have attributed visible emission under UV excitation to structural defects, which can be removed by thermal treatments [16]. When this process is

* Corresponding author. Tel.: +52 81 1340 4020; fax: +52 81 1052 3321.
E-mail address: selene.sepulvedagz@uanl.edu.mx (S. Sepulveda-Guzman).

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carried out under a controlled atmosphere, the visible emission is quenched. For this reason, in spite of intense research focused on implementation of ZnO in electronic devices, the preparation of patterned ZnO films, with good quality and visible-light emission under UV excitation, through simple, low cost methods still remains a challenge. In this study, ZnO nanoparticles were synthesized by precipitation in ethanol solution using Zinc Acetate (Zn(Ac)), and sodium hydroxide (NaOH). The nanoparticles were characterized by photoluminiscence (PL) spectroscopy and transmission electron microscopy (TEM). These particles show visible-light emission upon excitation in UV. They are also dispersible in ethanol and can be used as ink for confined dewetting lithography (CDL). This technique facilitates the assembly of nanopartilces using a PDMS mold as floating template. The resulting films were characterized by scanning electron microscopy (SEM) and atomic force microscope (AFM). The method described here presents a relatively simple, room temperature and low cost method to assemble geometric patterns using ZnO nanoparticles from ethanol dispersion.

2. Experimental section

All reagents and solvents including Zn(Ac), NaOH and ethanol were purchased from Aldrich, and used without any purification. In a typical process, 25 ml of 0.02 M Zn(Ac) solution was added dropwise to 25 ml of 0.04 M NaOH solution, over a 25 min period at 70 °C. After the complete addition, the mixture was continuously stirred and heated for 2 h. The resulting white powder was separated by centrifugation and washed with ethanol. The ZnO nanoparticles were analyzed by transmission electron microscopy on a Philips Tecnai F20 and JEOL 2010F at 200 kV. Samples were dispersed in ethanol at room temperature and sonicated. Aliquots were dropped on 3 mm diameter carbon film copper grids. The photoluminescence characterization was performed at room temperature on a Jovin Yvon fluorometer under 350 nm excitation from a 75 W UV Xe lamp. The spectra were acquired from ZnO powder dispersed in ethanol in a quartz cuvette and all spectra were normalized to maximum value. Patterned ZnO films were prepared by placing the PDMS mold on a silicon wafer substrate. For best results, the substrates were first cleaned with a piranha solution (3:1, v/v, H_2SO_4:H_2O_2). A drop of the colloidal solution containing ZnO was dropped on one side of the mold. The mold was carefully removed after 24 h. The morphology of the resulting patterned films was analyzed by scanning electron microscopy (SEM) using a Hitachi S-4500II operating at 10 kV. The patterned films were also analyzed by atomic force microscopy using a Digital Instrument Dimension 3100 in tapping mode and the images were analyzed using Gwydion image analysis software.

3. Results and discussions

3.1. Synthesis and characterization of ZnO nanoparticles

The ZnO nanoparticles were synthesized by precipitation method using Zn(Ac) in alcoholic solution under basic conditions. TEM image of the resulting nanoparticles (Fig. 1) clearly indicates a particle size of about 5 nm. HRTEM image of the ZnO nanoparticles shows lattice fringes of 0.26 nm and 0.28 nm attributed to the (0 0 2) and (1 0 0) planes, respectively in wurzite ZnO crystal structure. Both synthesis and growth mechanism of ZnO nanoparticles in alcoholic solution have been widely investigated [17]. It has also been observed that the quasi-spherical nanoparticles aggregate like a chain of pearls by attaching in directions perpendicular and parallel to [0 0 0 1] (*c*-axis). However, as seen in Fig. 1, this is not always an oriented attachment process. In addition, although the particles initially tend to remain well

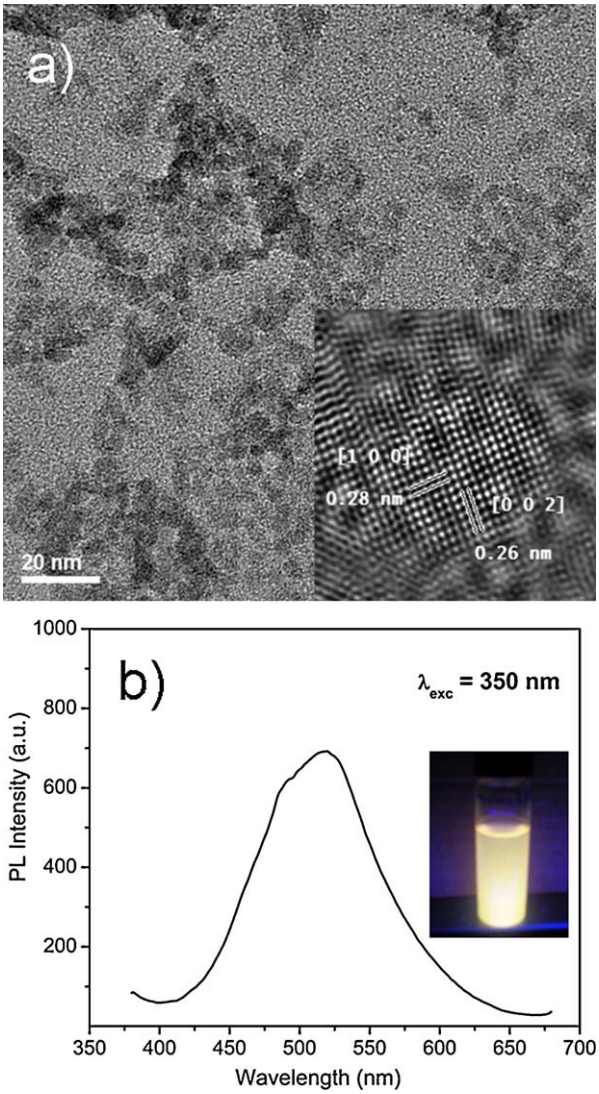

Fig. 1. (a) Transmission electron microscopy image of as-synthesized ZnO nanoparticles. Inset: HRTEM image of ZnO nanoparticle. (b) Photoluminescence spectrum of the ZnO colloidal dispersion in ethanol (λ_{exc} = 350 nm). Inset: Picture of colloidal dispersion of ZnO under the UV lamp.

dispersed in alcoholic solution on account of their small size, aggregation occurs after several days of storage leading to a white precipitate.

The optical properties of the ZnO nanoparticles were analyzed by using photoluminescence spectroscopy. The room-temperature PL spectrum shows a dominant and broad visible emission band from 425 nm to 600 nm, centered at 525 nm (Fig. 1b), when the sample was excited with UV light at 350 nm. The characteristic UV emission of ZnO at 390 nm, which is associated with the near band gap emission (NBG) due to the free recombinations of excitons, is weak and almost illegible in the PL spectrum. The visible emission observed in a wide variety of nanostructured ZnO is receiving great attention, but still has not been fully understood. It has been frequently attributed to structural defects such as oxygen vacancies and Zinc interstitial defects produced during ZnO synthesis [18–20]. For example, ZnO nanoparticles are usually coated with a thin layer of Zinc oxyhydroxides because of its surface energy and the reaction conditions. This layer in turn modifies their optical properties resulting in a weak exciton transition in ZnO that increases the visible emission [20]. The unusual yellow emission observed in this case, is explained by the presence of defect centers. These results are in agreement with

observations reported by Patra et al. [21], wherein yellow emission is attributed to the transition of a photo-generated electron from the conduction band to a deeply trapped hole. According to this report, the defect center is produced by a very fast process that involves trapping of the photo-generated hole at the surface site followed by tunneling of the surface-trapped hole back into the particle, where it recombines with an electron in an oxygen vacancy. These defect centers are present in particles with diameter size about 5 nm like in this case.

3.2. Patterned ZnO films

The patterned ZnO films were prepared by using a confined dewetting lithography (CDL) method [22]. Fig. 2 shows a schematic representation of the process that involves the assembly of nanoparticles by drying a small amount of colloidal ZnO nanoparticles suspension between a floating template (PDMS mold) and the substrate (silicon wafer). The solvent evaporation starts in the voids of the patterned mold and during drying the nanoparticles are transported by the remaining solvent under the mold. This movement results from a combination of Brownian motion and Van der Waals interactions in the solvent at room temperature [23]. After complete evaporation the mold is removed, and due to the low surface energy of the PDMS mold, the particles are preferentially attached to the substrate, resulting in a geometric pattern defined by the mold. The resulting ZnO films were analyzed using SEM (Fig. 3). Complex patterns of assembled ZnO nanoparticles with good homogeneity can be reproduced in this way. In this case, as the meniscus is formed into the mold channels there is a lack of concentricity and the ZnO nanoparticles are pulled under the mold by the capillary-bridge forces originating between the substrate and the mold resulting in very well defined lines. Fig. 4a shows the atomic force microscope image of the resulting film, which reveals an array pattern formed by the assembly of ZnO nanoparticles into circles of about 15 μm diameter. A height profile extracted from the AFM image (Fig. 4b) indicates that the array pattern has a thickness of about 10 nm corresponding to approximately three layers of ZnO nanoparticles. The analysis also shows that the ZnO nanoparticles were arranged

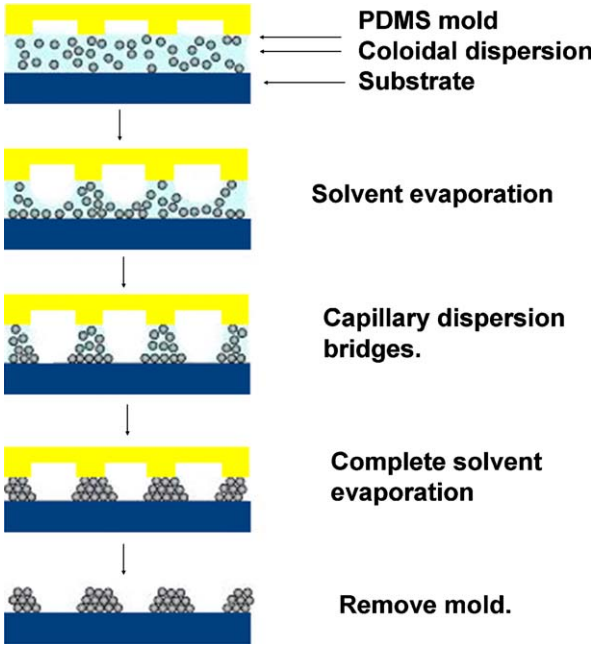

Fig. 2. Scheme of the confinated dewetting lithography process adapted from Ref. [22].

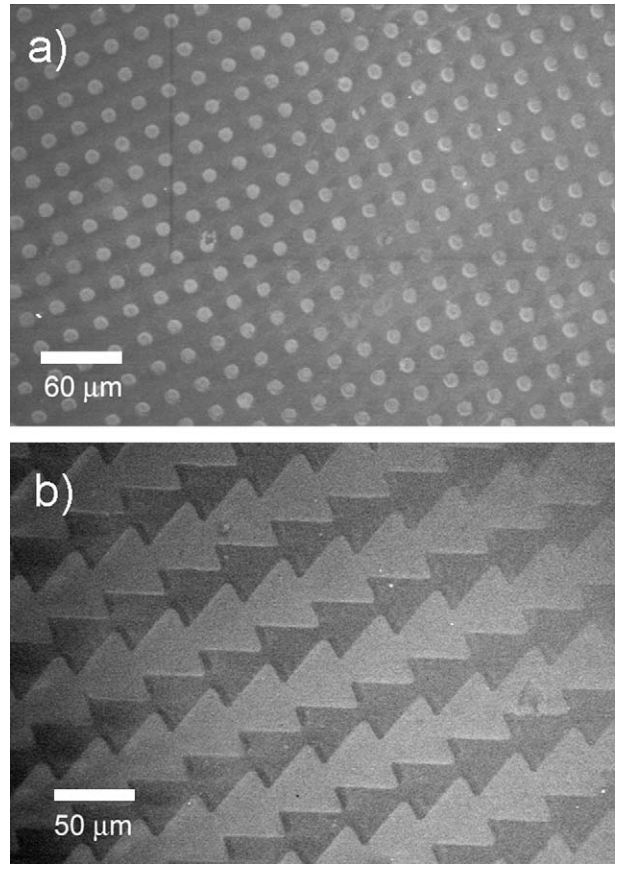

Fig. 3. Scanning electron microscopy images of the patterned ZnO film, area with (a) array pattern and (b) line pattern.

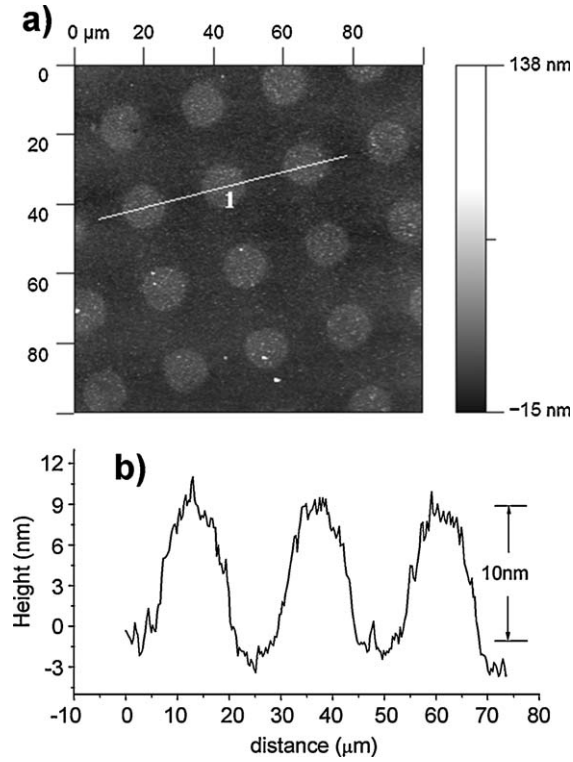

Fig. 4. (a) AFM topographic image of ZnO film with array pattern and (b) height profile of the patterned film.

without a flat surface on the patterned circle. This could be associated with the self-assembly of the confined nanoparticles by inter-particle attraction in the capillary bridges. In conclusion, we have demonstrated here a technique useful in the preparation of a geometric patterned thin film by assembling nanoparticles. Unlike sol–gel method that requires thermal treatments, CDL of ZnO nanoparticle dispersions does not need thermal annealing in order to obtain highly crystalline material, and is therefore, ideal for use on substrates with low-temperature resistance.

4. Conclusions

An ethanolic dispersion of ZnO nanoparticles exhibiting visible emission under UV excitation (350 nm) was obtained by a very simple precipitation method using ethanol as solvent. This dispersion can be used as ink in confined dewetting lithography to obtain uniform, patterned ZnO nanoparticle films with thickness of about 10 nm. The low-temperature processing conditions involved in this process are ideal for depositing patterned crystalline ZnO films on flexible substrates.

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