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Research Article

Nanostructured ZnO Arrays with Self-ZnO Layer Created Using Simple Electrostatic Layer-by-Layer Assembly

PilHo Huh[1] and Seong-Cheol Kim[2]

[1] *Samsung Electronics Co., Ltd., Solar Energy R&D Center, San #24 Nongseo-Dong, Giheung-Gu, Yongin-City, Gyeonggi-Do 446-711, Republic of Korea*
[2] *Department of Nano, Medical and Polymer Materials, Yeungnam University, 280 Daehak-Ro, Gyeongsan, Gyeongbuk 712-749, Republic of Korea*

Correspondence should be addressed to Seong-Cheol Kim, sckim07@ynu.ac.kr

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Formation of unique ZnO nanoarrays utilizing photodynamic polymer, surface-relief grating structures, and unique electrostatic layer-by-layer assembly as a simple and economical methodology was demonstrated. Atomic force microscope (AFM), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDAX) analysis were employed to characterize elemental composition and morphology of the resulting ZnO nanostructures with self-ZnO layer. Optical behavior of the final product was studied by UV-vis-NIR absorption and photoluminescence (PL) spectra.

1. Introduction

Since the large exciton binding energy of 60 mV and quantum confinement effects [1] of low-dimensional nanostructures, zinc oxide (ZnO) has become an attractive candidate for potential electronic, optoelectronic, electrochemical, and electromechanical devices, such as ultraviolet (UV) lasers, [2] light-emitting diodes (LED), [3] field emission devices, [4, 5] solar cells, [6] and piezo-nanogenerators [7, 8]. With changes in size and shape, unique electrical, mechanical, chemical, and optical properties may be freshly introduced, which are extensively believed to be the result of surface and quantum confinement effects [1]. To further improve its physical properties, substantial efforts have been devoted to develop various methodologies to create uniform and continuous one- (1D) or two-dimensional (2D) ZnO nanostructures. In an effort to integrate the resulting ZnO arrays into a more ordered fashion to enhance the performance of the nanodevices, a variety of techniques, including nanolithographic techniques (e.g., electron beam lithography, proximal probe patterning, and X-ray patterning) [9] and several chemical methods (e.g., vapor-solid, vapor-liquid-solid, and solution-solid) [10], have been employed. All these methods are not suitable for large fabrication process due to their exorbitant cost and complicated procedure. In contrast, an unconventional method used in this study may be much easier and economically more favorable, considering it can offer a much higher throughput in practice for solar energy conversion, light emission, and other promising areas. Periodic 1D and 2D ZnO nanostructures that were created simultaneously by self-assembly of the ZnO layers were prepared easily using the electrostatic layer-by-layer (ELbL) method by spin-coating, surface-relief grating (SRG) on the deposited photodynamic polymer film, and finally simple heat treatment. The alternating depositions of aqueous zinc acetate solution utilizing ELbL and polyanions assembly gave a good opportunity for facile fabrication of novel 1D and 2D ZnO nanostructures with self ZnO layer within a few hours.

2. Experimental Procedure

The indium doped tin oxide- (ITO-) coated glass and quartz substrates were used after cleaning by ultrasonication with isopropanol. A photodynamic polymer, poly orange 3 (PDO3), was synthesized from the diglycidyl ether of

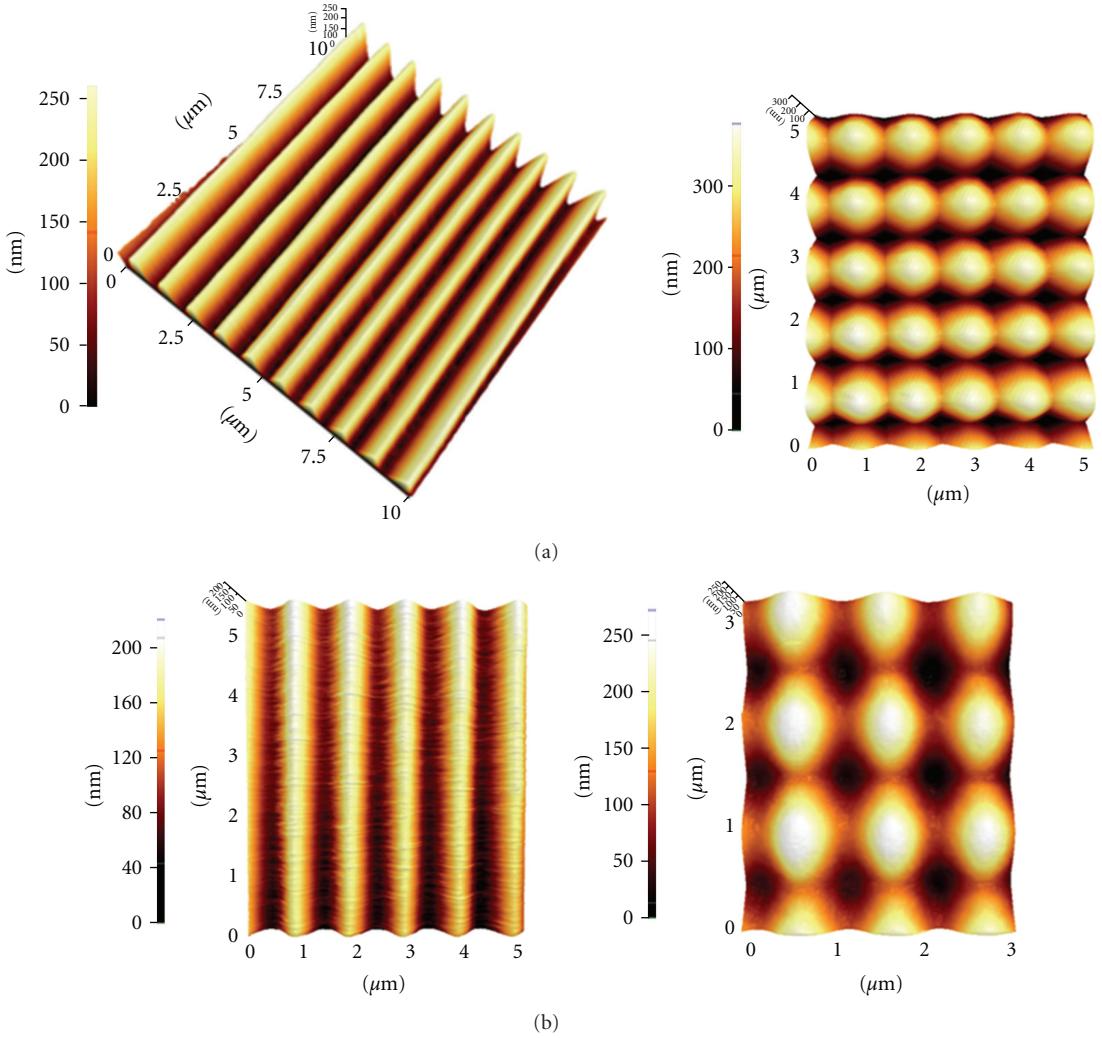


Figure 1: (a) 3D AFM views of submicrostructured 1D and 2D SRGs fabricated by exposing PDO3 to Ar^+ ion laser interference pattern and (b) 3D views of three bilayers of SPS/zinc acetate assembled in depressions on 1D and 2D SRG polymeric templates.

bisphenol A and disperse orange 3 as reported previously [11, 12]. 5 wt% PDO3 was dissolved in 1,4-dioxane and filtered through a 0.45 μm membrane to obtain a film with uniform thickness. The spin-coated PDO3 films on ITO substrates were then dried in a vacuum oven overnight at 60°C. 1D and 2D Surface-Relief Gratings (SRGs) were formed on the PDO3 films using an interference pattern of an argon ion^+ laser beam at 514.5 nm with an intensity of 100 mW/cm^2. 7 wt% of $Zn{\cdot}(CH_3COO)_2{\cdot}2H_2O$ purchased from Aldrich was stirred vigorously in 20 mL of H_2O for 2 hours to obtain the zinc acetate solution. The concentration of the used poly (4-styrene sulfonate) (SPS) solution was 0.1 wt% with pH 1.0 for all subsequent polyanion layers. In the assembly process, the SRG templates were quickly modified as sulfonyl groups by spin-coating the pH 1.0 SPS solution. 7 wt% zinc acetate solution was subsequently spin-coated on the SPS surface-modified SRGs. This completed one cycle. A deposition of one-bilayer assembly of the SPS/zinc acetate was progressed in short time without additional drying and rising steps. Thereafter, the process was repeated by alternating the deposition of pH 1.0 SPS solution and 7 wt% zinc acetate solution until the desired amount of zinc acetate was deposited in the assembly. Three bilayer assembly of the deposited SPS/zinc acetate was heat-treated at 500°C for 2 hours to burn off the polymeric template and to create well-defined ZnO nanostructures with self-ZnO layer. Scheme 1 illustrates the stepwise procedure used to prepare the nanostructured ZnO arrays with self-layer.

The samples were characterized by atomic force microscopy (AFM), scanning electron microscope (SEM), and an energy-dispersive X-ray (EDAX) analysis to study their morphologies and elemental compositions. The UV-vis-NIR spectrum was recorded at a scan rate of 240 nm/min. Photoluminescence (PL) spectrum was measured at the exciting wavelength of 345 nm.

3. Results/Discussion

Figure 1(a) shows 3D views of (a) 1D and 2D SRGs formed on the photodynamic polymer films. 1D and 2D SRGs were

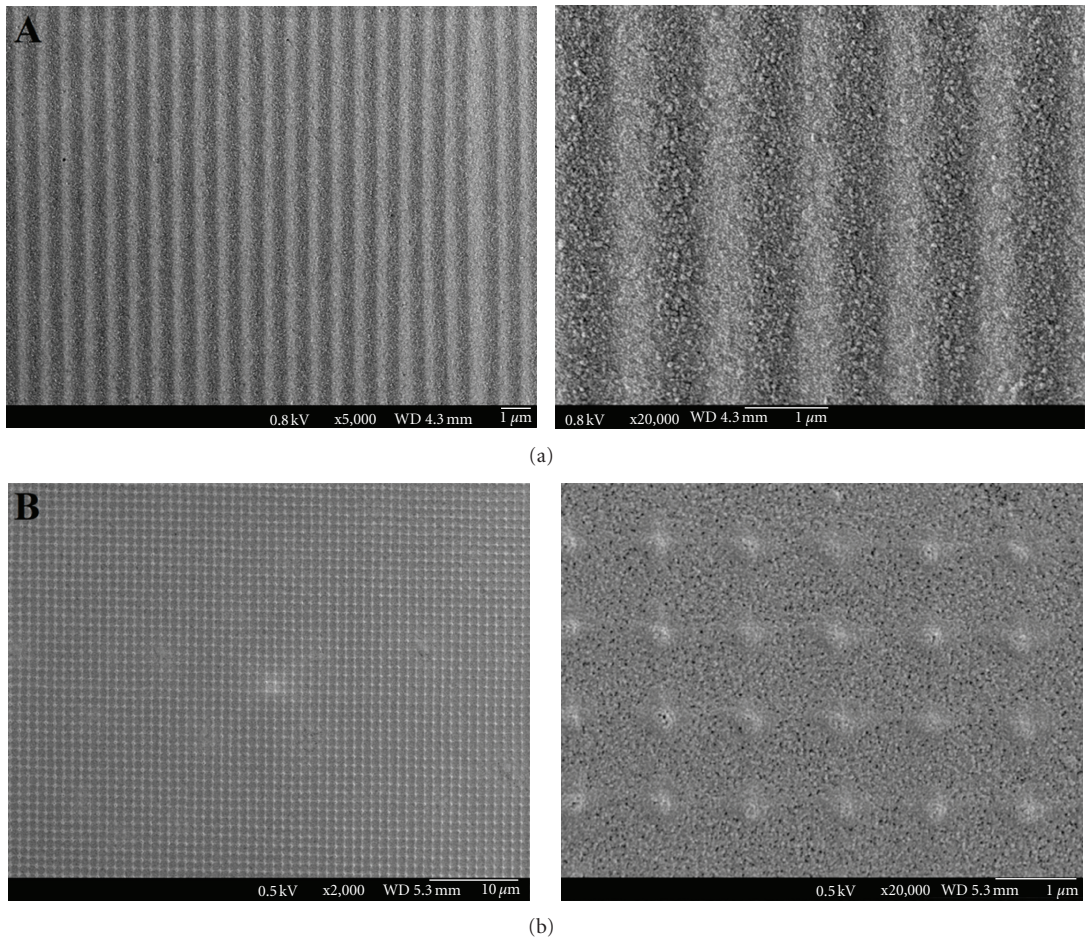


Figure 2: SEM views of nanostructured 1D (a) and 2D (b) ZnO arrays created on self-ZnO layer by simple electrostatic Layer-by-Layer spin-coating technique and pyrolyzing a three-bilayer assembly of SPS/zinc acetate on the individual 1D and 2D SRG templates.

used as polymeric templates to generate well-ordered ZnO nanostructures. The sinusoidally modulated gratings were used to fabricate a periodic array of 1D ZnO lines, while the egg-crate-like SRG structures were used to fabricate periodic arrays of 2D ZnO dots as shown in Figure 1(a). AFM height profiles of both SRG patterns showed an average modulation amplitude of about 210 and 200 nm, respectively. The periodicities of both gratings are approximately 1 μm. AFM images in Figure 1(b) show 3D views of an individual three-bilayer assembly of SPS/zinc acetate on both SRGs prepared using sequential ELbL by a spin-coating. The thickness of SPS/zinc acetate assembly can be controlled easily by adjusting rpm of spin-coater. Figure 1(b) indicated that the average thickness of SPS/zinc acetates ELbL on 1D SRG for a three-bilayer assembly was decreased by 10% to about 120 nm and that for 2D arrays was also reduced nearly by 40% to about 150 nm, respectively. Each cycle of a SPS/zinc acetate deposition by ELbL spin-coating was successively progressed for a three-bilayer assembly without additional washing and drying. Finally, a three-bilayer assembly of SPS/zinc acetate was dried at room temperature for an hour. Dried assembly was then heated for 2 hours through several steps (room temperature → 100°C → 300°C → 500°C) to remove the SRG polymeric template and to crystallize Zinc oxide.

Figure 2 summarizes typical SEM images of nanostructured 1D (a) and 2D (b) ZnO arrays created on ZnO self-layer on the ITO substrate. Well-ordered 1D and 2D ZnO arrays were formed as results of the sintering at 500°C for 2 hours in air condition as shown in Figure 2. The line and dot arrays created from collection of ZnO nanoparticles on self-layer show two distinctive shapes such as long sand ridges (a) and sand dunes (b) contrasted with various patterns fabricated by numerous techniques [13–17]. They also exhibit good uniformity and continuity within nanostructured patterns after sintering, although used SRG substrate is a microstructured polymeric template. Unique ZnO sand ridges and dunes created on self-ZnO layers may result from the difference of isoelectrical points between SPS polyelectrolyte and zinc acetate layer stacked alternatively. It is quite intriguing to note that zinc acetate layer was stacked selectively and quickly into grooves or hollows without buffer layer, SPS. However, when the buffer layer is present on top of hydrophobic SRG, ZnO-self layer appeared after the sintering process possibly due to adsorption of zinc acetate on the slope. The deposited SPS (or zinc acetate) to the SRG (or

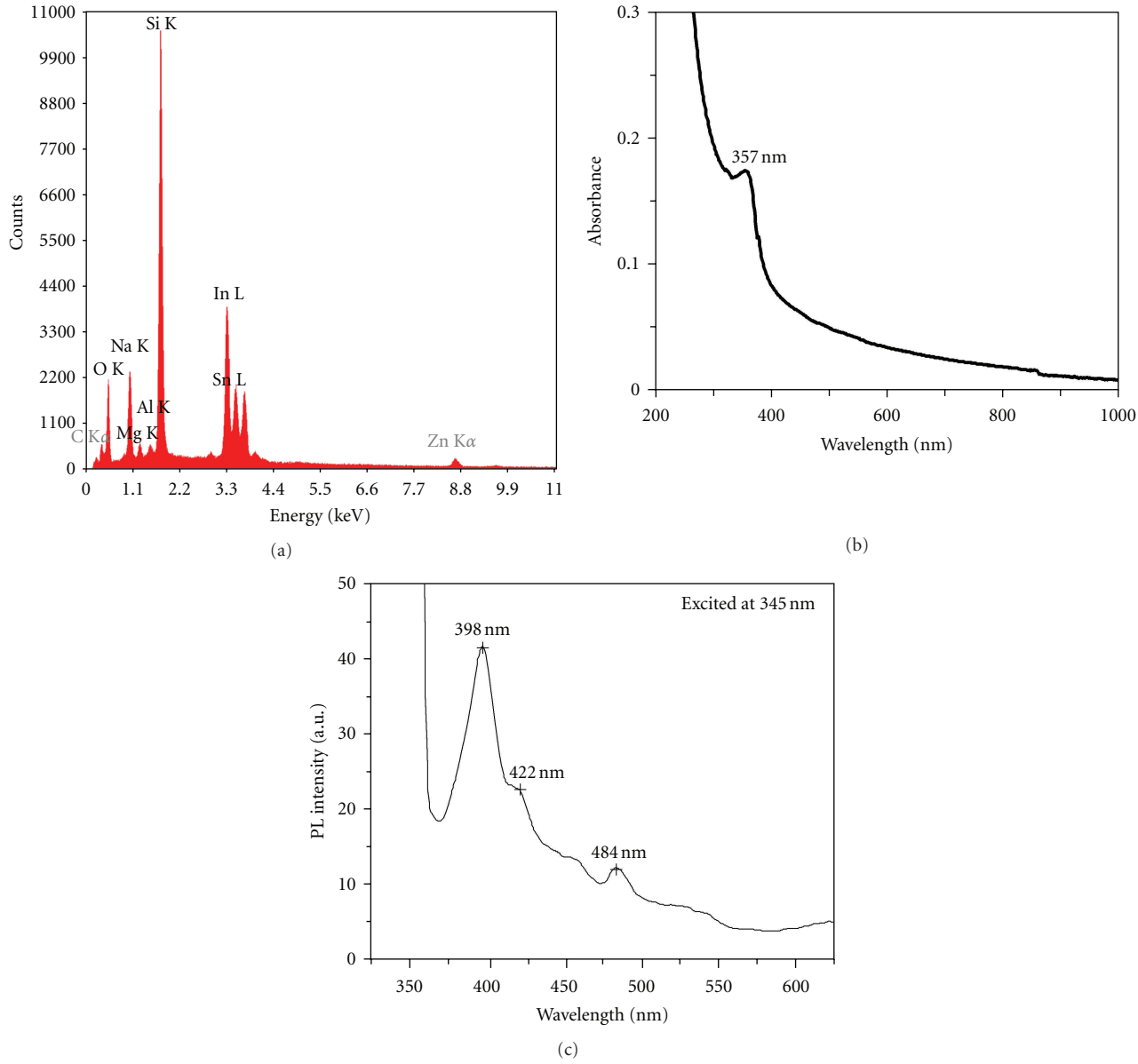
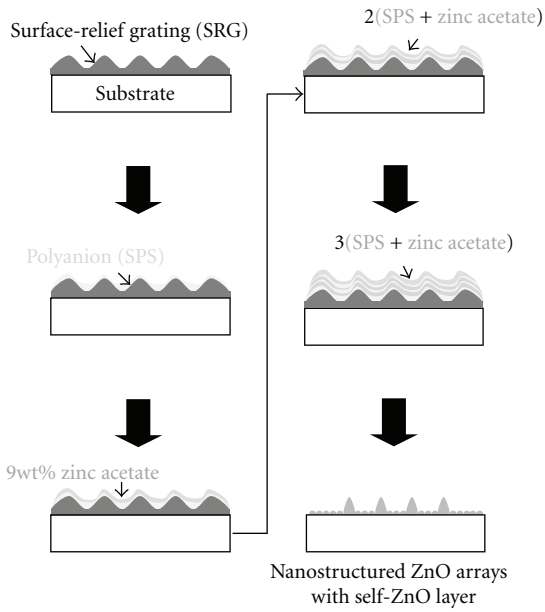


FIGURE 3: (a) The EDAX spectrum of the 2D ZnO nanostructures shown in Figure 2 for element analysis, (b) UV-vis-NIR and (c) photoluminescence (PL) spectra of nanostructured 2D ZnO arrays with self ZnO layer created on a quartz substrate; Exciting wavelength for PL is 345 nm.

SPS) may provide more adhesive strength for complexation (or charge interaction) with zinc acetate (or SPS) layer. The resulting ZnO nanostructures have innumerable porous structures over large area, which can provide a potential advantage for solar cell and sensor applications.

Elemental composition and crystalline structure of ZnO nanostructures well-patterned on self-layer were determined by energy-dispersive X-ray (EDAX) analysis and X-ray diffraction (XRD). The EDAX spectrum of the ZnO nanopatterns with self-layer in Figure 3(a) clearly shows the Zn Kα X-ray line at 8.65 keV and O Kα X-ray line at 0.52 keV. A very weak C Kα (0.282 keV) line compared with that of the non-heat-treated sample is obtained from EDAX spectrum. The crystallinity of the ZnO nanostructures was confirmed by X-ray diffraction (XRD). In the small sample quantity, three XRD patterns observed at around $2\theta = 31.80°$, $34.60°$, and $36.12°$ correspond well to the diffractions from the (100), (002), and (101) planes, respectively [18, 19]. The results from EDAX and XRD indicated that the produced patterns are composed of crystallized ZnO nanoparticles and that no significant traces of the SRG polymeric template remained after the sintering process. Other peaks revealed that the existence of Na, Mg, Si, Sn, and Al come from ITO substrate. UV-vis-NIR spectrum in Figure 3(b) shows the abrupt absorption band or edge characteristic of nanostructured ZnO arrays with self-ZnO layer centered at around 357 nm, which is in good corresponding with our previously work [17].



Scheme 1: Schematic procedure for creating nanostructured ZnO arrays with self-ZnO layer using electrostatic Layer-by-Layer Technique by spin-coating.

The photoluminescence (PL) spectrum of ZnO nanostructures after sintering at 500°C is shown in Figure 3(c). The three emission peaks at 398, 422, and 484 nm in wavelength were obtained from PL spectrum when excited at wavelength of 345 nm. The emission band occurred at around 398 nm can be assigned to the near band-edge transition, which is, namely, the recombination of free excitons through an exciton-exciton collision process, of wide band gap ZnO nanoparticles composed of the nanostructured ZnO arrays [20], while the two emission bands observed at around 422 and 484 nm result from the radial recombination of a photogenerated hole with an electron that belongs to a singly ionized oxygen vacancy [21] and the defect-induced emission from ZnO [22–24].

4. Conclusion

A simple, cost- and time-effective approach to create periodic nanostructured ZnO arrays onto self-layer over large areas has been described. The unconventional method was carried out using periodic microstructured polymeric templates, modified ELbL spin-coating technique, and heat-treatment. ZnO nanoarrays with self-layer are expected to have a wide range of applications such as sensors, energy storages, and solar cells. For instance, various fluorescence dyes may be incorporated in the functionalized ZnO surface, and ZnO nanoarrays with self-layer may be also used as a laser pumping due to its attractive optical property. This methodology can be readily applicable for creating nanopatterns with self-layer in other metal oxides, metals, or novel organic materials using common lithographic fabrication methods.

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