Well-aligned ZnO nanoneedle arrays grown on polycarbonate substrates via electric field-assisted chemical method

Ramazanali Dalvand a,*, Shahrom Mahmud a, Jalal Rouhi b, C.H. Raymond Ooi c

a Nano-Optoelectronic Research (NOR) Lab, School of Physics, Universiti Sains Malaysia, 11800 Gelugor, Pulau Pinang, Malaysia
b Centre of Nanoscience and Nanotechnology (NANO-SciTech Centre), Institute of Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
c Department of Physics, University of Malaya, 50603 Kuala Lumpur, Malaysia

ABSTRACT

Well-aligned ZnO nanoneedle arrays were prepared for the first time on polycarbonate (PC) substrates via an electric field-assisted chemical method. The surface morphologies of ZnO nanoneedles at different current densities were studied using field emission scanning electron microscopy. The X-ray diffraction pattern of the ZnO nanoneedle arrays showed strong c-axis oriented crystal structure with preferred (0 0 2) orientation. Room-temperature photoluminescence measurement of the ZnO nanoneedles revealed an ultraviolet peak at 380 nm, which is comparable with those found in high-quality ZnO films. UV-visible spectroscopy was also conducted to study further the optical properties of ZnO nanoneedles. The growth of ZnO nanoneedles on PC substrate exhibited the greatest absorption enhancement and the best antireflective property, which indicated that this product has great potential for the applications in energy-harvesting devices and flexible solar cell applications.

1. Introduction

Zinc oxide (ZnO), with its unique chemical and physical properties, has vast device applications, such as light-emitting diodes, optical waveguides, solar cells, and many other promising applications in gas sensors. Various ZnO nanostructures, such as nanowire [1], nanorod [2], and nanoflower [3], have been fabricated, and their photoluminescence has been studied by many researchers. Recent techniques in controlling growth directions and structures of ZnO nanostructures, such as thermal evaporation condensation [4], vapor-liquid solid, and metalorganic chemical-vapor deposition [5], still requires growth temperatures of above 400°C. Given that the electric field-assisted chemical (EFAC) method is of significant interest in fabricating ZnO nanostructures directly on polymer substrates, this method can lead to a new approach to fabricate semiconductor nanostructures selectively on any substrate, particularly on temperature-sensitive substrates which may find applications in flexible dye-sensitize solar cells and emerging plastic electronic devices. We believe that this study is the first to report the growth of aligned ZnO nanoneedles on polycarbonate (PC) substrates via a simple and low-cost EFAC technique.

2. Material and methods

A ZnO seed layer was deposited on PC substrates by using a radio frequency magnetron sputtering system (Auto HHV500 Sputter Coater). The deposition of seed layer was performed at a low sputtering power of 100 W for 1 h at 100°C with a sintered oxide ceramic target composed of ZnO with 99.99% purity.

Zinc nitrate hexahydrate (Zn(NO3)2·6H2O) and hexamethylenetetramine (C6H12N4) were individually dissolved in deionized (DI) water at equal molar concentrations at room temperature. After mixing and uniform stirring, the aqueous solution (10 mM) was transferred into an electrochemical cell. The seed layer-coated ZnO/PC film (cathode) and platinum electrode (anode) were immersed into the aqueous solution.

The growth temperature and time were maintained at 110°C and 1 h, respectively. After the synthesis of ZnO nanorod arrays, the sample was rinsed with DI water and dried in a nitrogen gas flow. The samples were characterized via field emission scanning electron microscopy (FESEM; FEI/Nova NanoSEM 450). The crystal structure of the ZnO nanostructures was characterized using X-ray diffraction (XRD) (PANalytical X’Pert PRO MRD PW3040) with Cu Kα radiation (λ=1.54 Å). The optical properties were studied at room temperature PL spectroscopy (Jobin Yvon HR 800 UV, Edison, NJ, USA) by using a He–Cd laser 325 as a source. The optical absorption and reflectance characterizations were performed using a UV–vis spectrophotometer (Perkin Elmer Lambda 750).

* Corresponding author.
E-mail address: ramazan.dalvand@gmail.com (R. Dalvand).

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3. Results and discussion

In the EFAC process, the growth of the ZnO nanostructures typically happens based on the generation of hydroxide (OH\(^-\)) ions under a current density. The Zn\(^{2+}\) ions then react with OH\(^-\) ions, thereby forming zinc hydroxide. Finally, ZnO is formed on the substrate through a dehydration reaction of Zn(OH)\(_2\) [6]. The formation of OH\(^-\) ions is affected by the current density. The reactions in the solution can be simplified as described by the following formulae:

\[
(\text{CH}_2)_6\text{N}_4^+ + 6\text{H}_2\text{O} \rightarrow 6\text{HCHO} + 4\text{NH}_3 \quad (1)
\]

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \quad (2)
\]

\[
\text{Zn}^{2+} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} \quad (3)
\]

\[
\text{Zn(OH)}_4^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (4)
\]

Fig. 1(a) and (b) indicates that at an extremely low current density, well-faceted hexagonal nanorod arrays grew on the substrate that can be attributed to the hydrothermal growth treatment of ZnO at low current densities. When the current density was increased, the growth rate also increased. At high current densities, the growth rate of polar surfaces can be significantly higher than that of nonpolar surfaces. The fastest growing planes easily disappeared and finally resulted in a crystal shape caused by slow growth rate facets. At 0.5 mA, the individual ZnO nanoneedles were agglomerated together near the substrate because of the fast lateral growth rate. When the height of the ZnO nanorods was increased, the electric field intensity became weak because of the high resistivity of the ZnO nanorods, and the adsorption of the Zn\(^{2+}\) ions was limited at the end of the ZnO nanorods. The FESEM results indicated that the current density at the initial stage assisted shape transitions from hexagonal-shaped to needle-shaped nanorods and that the current density at the subsequent stage contributed to the increase in nanoneedle length (Fig. 1(c) and (d)). The aspect ratio (defined as their height divided by tip radius) of the ZnO nanostructures measured by FESEM were ranged from 12.3 to 56.4 when the current density was increased.

The XRD pattern of the sample demonstrates that all diffraction peaks matched well with a wurtzite hexagonal crystal structure (ICSD 01-080-0074, space group: C\(_{6\text{mc}}\), lattice parameters: \(c=0.52\) nm, \(a=0.32\) nm) (Fig. 2(a)). The strongest peak appears at 34.3°, which corresponds to the (0 0 0 2) plane of the wurtzite structural ZnO. This peak indicates a good crystal quality of the products. The wurtzite-structured ZnO has three fastest growth directions, namely, (1 1 2 0), (0 0 0 1), and (1 0 1 0), which respectively correspond to the diagonal, axial, and side directions of the hexagonal prism. The growth velocity along the [0 0 0 1] direction is commonly much faster than that along other two directions because of the lowest surface energy of the (0 0 0 2) facet, indicating a rodlike configuration.

No other peaks of impurities, such as those of hexamethylenetramine and zinc nitrate hexahydrate, appeared in the spectra. ZnO nanoneedles have preferential growth at the (0 0 2) orientation, indicating a high degree of orientation with the c-axis vertical to the substrate surface [7]. The average crystalline size was calculated using Scherrer’s formula:

\[
D = \frac{0.9\lambda}{B \cos \theta}
\]

where \(D\) is the crystalline size, \(\lambda\) is the X-ray wavelength, \(\theta\) is the Bragg diffraction angle, and \(B\) is the full width at half maximum after correcting the instrument peak broadening. The calculated crystallite size value was 36.4 nm.

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**Fig. 1.** FESEM images of the ZnO nanostructures growth at different current densities. (a) 0.05 mA/cm\(^2\), (b) 0.1 mA/cm\(^2\), (c) 0.5 mA/cm\(^2\), and (d) 1 mA/cm\(^2\). The insets show higher-magnification image of the samples.
obtained via chemical methods \cite{9}. This enhancement can be far have the highest relative PL intensity ratio among those a value of approximately 5. The ZnO nanoneedles fabricated thus emission was also calculated from the ZnO PL spectrum, which has intensity ratio of the band edge emission peak to the deep level emission results from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy. The emission associated with singly ionized oxygen vacancies in ZnO and the emission from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy. The intensity ratio of the band edge emission peak to the deep level emission was also calculated from the ZnO PL spectrum, which has a value of approximately 5. The ZnO nanoneedles fabricated thus far have the highest relative PL intensity ratio among those obtained via chemical methods \cite{8}. This enhancement can be mainly attributed to the size and density of the ZnO nanostructures. Once the size and diameters of the ZnO nanorods decreased, the surface area for nanorod configuration increased. Therefore, both incidents, namely, photon-to-electron conversion efficiency and PL property, were improved. The second-order UV peak at 760 nm was caused by the high-intensity primary UV peak.

Fig. 3 shows the room temperature optical absorbance and reflectance spectra of the ZnO nanostructure produced at 0.1 and 1 mA/cm² current density. Comparatively, the absorption intensity of the nanoneedle arrays was significantly higher than that of the highly ordered ZnO nanorod templates. This condition occurred because the nanoneedle arrays may exhibit a strong light trapping ability, which has been observed in well-aligned ZnO nanorods or nanocones. Furthermore, Fig. 3 shows the measured reflection spectra for the ZnO nanoneedle and nanorod arrays. By comparison, the ZnO nanoneedles and nanorods exhibit a broad reflectance of approximately 9% and 14% of the entire wavelength range, respectively.

Thus, the ZnO nanoneedle arrays indicate greatly enhanced absorption compared with nanorod structures. The best antireflective properties and the greatest absorption enhancement can be attributed to the gradual decrease in the diameter of ZnO nanocones from the root to the top, thereby resulting in a graded transition of the effective refractive index \cite{10}. The efficient antireflective effect of ZnO nanoneedle suggests that their effective refractive index could be significant, whereas their highly tapered shape might generate a gradual decrease in the effective refractive index through the region. Thus, ZnO nanoneedle arrays show excellent antireflection properties that can enhance the conversion efficiency of dye-sensitized solar cells through increased light coupling.

4. Conclusions

Well-aligned ZnO nanoneedles were successfully synthesized on PC substrates via a low-temperature EFAC process. The FESEM images show that the products have a needlelike morphology when the current densities were increased. The XRD and PL spectra revealed good crystallinity and orientation of the synthesized ZnO nanoneedles. The UV–visible absorption spectra indicated that the ZnO nanoneedles show strong light-trapping effects. These findings firmly indicate that ZnO nanoneedle arrays have great potential for applications in solar energy harvesting and as a pyramidal structure template.

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References


