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Aqueous synthesis towards vertically-aligned and selective pattern of ZnO nanostructures arrays

Ghim Wei Ho[1,a], Andrew See Weng Wong[2,b]

[1]Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive, Singapore 117576

[2]Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602

[a]elehgw@nus.edu.sg, [b]wonga@imre.a-star.edu.sg

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Abstract. For any future cost-effective applications of inorganic nanostructures in particular hybrid photovoltaic cell, solution processable and selective printable of inorganic nanomaterials is essential. The patterning and growth of highly ordered arrays of crystalline ZnO inorganic nanostructures use simple soft lithography technique and mild reaction conditions; both low in temperature and free from harmful organic additives. Variable yet controllable anisotropic growth of ZnO nanowires has been demonstrated on the transferred patterns of ZnO nanocystals.

Introduction

A revolutionary breakthrough in cutting cost and increasing throughput of manufacturing photovoltaic or electronic devices can be achieve through reel-to-reel coating of material from solution onto large flexible and light weight platform. Thus, it is important to develop a low temperature, cheap and large-scale solution-based synthesis method and patterning of inorganic nanostructures. Recently, patterning and self-assembly growth of nanostructures have received considerable attention. However, many of these methods require expensive equipments, multiple complex steps as well as the use of photoresist and other harmful chemicals to obtain selective growth of nanostructures whilst the soft-lithography techniques can easily be employed to pattern any nanomaterials and biomaterials on desired sites [1-3]. Here we've looked into growing vertically-aligned inorganic nanomaterials which in this case is ZnO on selective area using solution processable, simple, low temperature, substrate independent and environmental friendly method. In previous cases, the photoactive layer of photovoltaic cells are made of randomly interdispersed electron accepting and hole conducting polymer/inorganic material, where charge transport are limited by the hopping of electrons along the poorly connected network [4-5]. To improve electron transport in these photovoltaic cells, arrays of one-dimensional nanostructures infiltrated with inorganic material or conjugated polymers are designed to provide a direct path to the electrode [6-10].

Recently, there are many reports on solution-based synthesis of ZnO nanostructures using Zn metal nitrate and acetate along with organic amine additives namely oleylamine, hexadecylamine, dioctylamine, dodecylamine, methenamine etc. [11-18]. The commonly employed amine-mediated additives being a non-polar chelating agent would preferentially attach to the non-polar facets thereby exposing the polar planes (c-axis) for anisotropic growth [11]. However, in view of environmental importance to eliminate harmful and corrosive organic additives in the synthesis process as well as developer solvents in the patterning process, we have successfully developed a simple way to transfer patterns of ZnO nanocrystals onto various substrates and then using a facile solution based synthesis to grow highly ordered ZnO nanostructures on selective areas.

Experimental

Patterned poly(dimethylsiloxane) PDMS stamps were cleaned in isopropyl alcohol, ethanol and deionised water before O_2 plasma oxidized to create hydrophilic surfaces. The PDMS stamp was immersed in aqueous zinc acetate dihydrate solution of 5 mM for 10 min, blown dried with N_2 gas and stamped on clean substrates (glass, plastics and Si) for 10 min. The substrates were then rinsed in clean ethanol, blown dried with N_2 gas and annealed in furnace at 200-350 °C. Subsequently, the growth of the ZnO nanowires were then carried out using aqueous zinc acetate dihydrate without adding any organic additives at relatively low temperature of 85 °C. Finally, the products were washed with distilled water to remove any residual salts and organic material and then dried at 100 °C for at least 60 min. The crystal structure of the as-synthesized nanostructures were analysed using transmission electron microscope (TEM, Phillips FEG CM300) and X-ray diffractometer (XRD, Philip X-ray diffractometer equipped with a graphite monochromator Cu Kα radiation λ = 1.541 Å). The morphologies were characterised using scanning electron microscope (SEM, JEOL FEG JSM 6700 F, secondary electron imaging) and atomic force microscope (AFM, Digital Instruments). Photoluminescence (PL) properties were measured using Rapid Photoluminescence Mapping Accent rpm 2000 He-Cd laser at 325nm and 1.8 mW.

Results and Discussion

Fig. 1a-b show SEM images of ZnO nanowires grown on patterned substrates. Most of the PDMS stamps patterns were successfully printed and transferred onto substrates, regardless of the shapes and sizes of the patterns on the PDMS stamps. The concentration of the inking solution plays an important role in the success of pattern transfer. An optimized concentration of the inking solution is 5 mM since it is observed that the transferred and post-annealed film is uniformly covered with nanocrystals as shown in the AFM image (Fig. 1c). The average diameter of the nanocystals ca. 5 nm is determined from the height profile rather than the surface topography due to the poor lateral resolution of tip-shaped convolution. Fig. 1d shows the two-dimensional XRD Debye diffraction pattern obtained on the nanocrystals film. A high intensity and non-dispersive Debye ring shows only the existence of ZnO (002) plane which indicate that complete c-axis textured alignment had occurred on the film [15]. This result complements with the XRD pattern where a sharp and narrow full-width-half-maximum (FWHM) peak at $2\theta = 34.4°$ attributed to ZnO (002) crystal plane (lattice constant of 5.206 Å) was observed [17]. This is not surprising as it has been reported that decomposition of zinc acetate starts at ~ 235 °C and converts completely to ZnO at 300-350 °C based on the differential thermal analysis and thermogravimetric analyses [19].

The variation of solely zinc acetate concentration provides a very effective and simple way to control the dimensions of the ZnO nanostructures. This additive-free synthesis method here has successfully synthesized bundles of high aspect ratio ZnO nanowires prepared using 1 mM zinc acetate (Fig. 2a). The individual long and thin ZnO nanowires have an average diameter of ~ 20 nm and length of ~ 2 μm. When the zinc acetate concentration is kept at 5 mM, vertically-aligned and discrete nanowires of diameter 30-60 nm and length ~ 200 nm are produced (Fig. 2b). It is noted that at a controlled intermediate concentration, the synthesized nanostructures are no longer randomly-aligned as evidently shown by the cross-sectional SEM image of Fig. 2c. As the zinc acetate concentration is drastically increased to 0.1 M, it is observed that the one-dimensional nanostructures have transformed into three-dimensional monodispersed hexagonal ZnO crystals of diameter ~ 250 nm (Fig. 2d). For ordered solar cell architecture, small diameters nanowires and closely spaced neighbouring nanowires is necessary to ensure a high efficient charge separation [20-22].

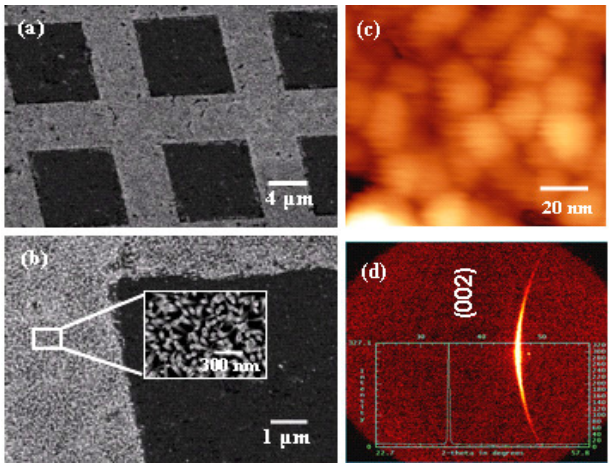

Fig. 1. (a-b) low and high magnification SEM images of the ZnO nanowires pattern growth. (c) AFM topographic image and (d) two-dimensional XRD Debye pattern of the microcontact printed ZnO nanocrystals.

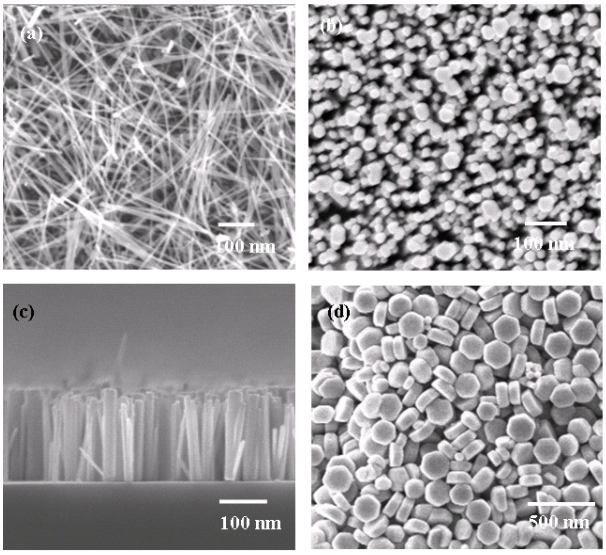

Fig. 2. SEM images of ZnO nanostructures grown at (a) 1 mM and (b-c) 5 mM and (d) 0.1 M.

We have reasoned that the presence of a pre-printed seeding nanocrystals film has facilitated the growth and orientation of ZnO nanowires. Deionized water acts as a nucleophilic reactant which leads to hydrolysis and polymerization of the zinc acetate complexes to form zinc hydroxide clusters [23]. Zinc hydroxide embryonic clusters grow into nuclei on the seeded substrates by heterogeneous nucleation which then transformed into zinc oxide. It is known that the zinc hydroxide undergoes decomposition reactions to form zinc oxide at 70-140 °C [24]. The growth of the ZnO nanostructures involves mass transport and nucleation of solute from bulk zinc acetate dihydrate solution onto the nanocrystals film driven by the solute concentration gradient. The designated growth morphology is determined by the initial degree of supersaturation. When the solute concentration is relatively low (1 mM), the growth of randomly-aligned bundles of ZnO nanowires are observed (figure 2a). These small but highly uniform diameters nanowires tend to bundle and align in the same growth direction can be described by the phenomena of multiplication growth through oriented attachment process [25]. However, at an intermediate concentration (≥ 5 mM), aligned growth of the ZnO nanowires on the seeded substrate becomes predominant (Figure

2b and c). Further increase in concentration to 0.1 M, gives a highly supersaturated solution, whereby homogeneous nucleation and growth of ZnO structures within the bulk solution becomes predominant (figure 2d). At this point, the homogeneous nucleation becomes evident as white precipitates were visibly observed in the reaction solution itself. Highly supersaturated solution leads to the formation of well-formed three-dimensional hexagonal nanostructures. Thus, a clear correlation can be derived between the aspect ratio (length/diameter) and the zinc acetate concentration as such it is inversely related.

Fig. 3a shows a low resolution image of nanowires which were dispersed on holey carbon copper grid. High resolution TEM observations (Fig. 3b) reveal single-crystal structures with lattice spacing of ~ 0.52 nm perpendicular to the longitudinal axis direction of the nanowire. The diameters of the nanowires are ~ 30-50 nm. This corresponds to the growth direction of [002] c-axis hexagonal ZnO [26]. According to the TEM energy dispersive X-ray (EDX) analysis as shown in Fig. 3c, the atomic concentration of the Zn and O elements in the nanowire is 0.51:0.49 which confirms the chemical composition and stoichiometry of ZnO nanowires.

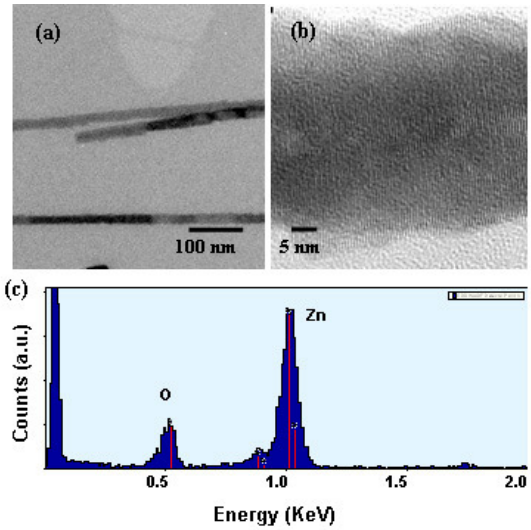

Fig. 3. (a) Low and (b) high resolution TEM images and (c) TEM-EDX spectrum of the as-produced nanowire

Fig. 4 shows the XRD patterns of the hydrothermally prepared ZnO nanostructures. All the diffraction peaks can be indexed to wurtzite structured ZnO (JCPDS card no. 3-1451) with no traces of impurities [27]. The relative intensities peaks were different from the standard powder diffraction of bulk ZnO which can be explained by the preferential growth or alignment of the synthesized ZnO nanostructures. XRD patterns obtained from the 5 mM and 50 mM samples show strong peaks at $2\theta = 34.4^{\circ}$ attributed to ZnO (002) crystal plane with lattice constant of 5.206 Å. The enhanced (002) diffraction peaks of 50 mM and 5 mM samples are consistent with the SEM images which show oriented growth of ZnO nanowires arrays along c-axes [17]. The FWHM of the diffraction peaks is small which indicates the high crystal quality of the synthesized nanostructures. On the other hand, XRD patterns obtained from 1 mM and 0.1 M samples do not show any preferential alignment.

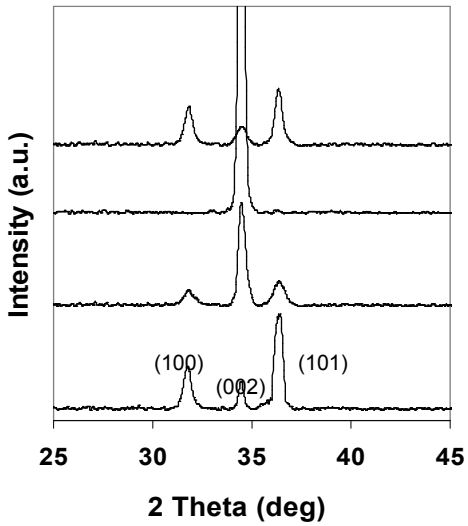

Fig. 4. XRD patterns of ZnO nanostructures prepared at various concentrations.

Conclusion

We have demonstrated the selective growth of ordered single-crystal ZnO nanostructures based on microcontact printing of nanocrystals seeding film. The pattern transfer quality is dependent on the concentration of the inking solution. The optimized concentration of the inking solution was found to be 5 mM since the transferred and post-annealed film is uniformly covered with nanocrystals. The success of patterning and growth of these inorganic nanostructures uses simple soft lithography technique and mild reaction conditions; both low in temperature and free from harmful organic additives. Finally, we expect that with a good control of the ZnO nanocrystals seeding layers and reaction parameters, the dimension, gap separation and the density of the ZnO nanowires can be tailored for various applications.

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