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Low temperature and large-scale growth of ZnO nanoneedle arrays with enhanced optical and surface-enhanced Raman scattering properties

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ABSTRACT

Large-scale ZnO nanoneedle arrays have been grown on four-inch silicon wafers with ZnO seed film by an aqueous chemical growth method at a low growth temperature and short reaction time. The volumes of 1,3 diaminopropane play an important role in controlling the dimension and optical emission properties of ZnO nanoneedle arrays, which exhibit a very prominent green emission and weak UV emission from defect and band gaps in the cathodoluminescence spectrum, respectively. The ZnO nanoneedle arrays with large alignment variations display broadband and omnidirectional antireflection properties from the gradual index profile, and can provide a higher surface-to-volume ratio and stronger defect emission, which results in a peak photocatalytic performance at a light irradiation of 10 W UV. The appropriate Ag sputtering durations on the ZnO nanoneedle arrays have been optimized to yield the greatest surface-enhanced Raman scattering effect in the rhodamine 6G molecule. The ZnO/Ag composite arrays provide a facile, high enhancement, low detection limit and low cost fabrication, which shall be of significant value for practical applications of other SERS sensing systems.

1. Introduction

Zinc Oxide (ZnO) is one of most promising oxide materials, which has attracted considerable interest due to its unique physical properties, such as its direct and wide band gap (3.37 eV), n-type semiconductor, large exciton binding energy (60 meV), high electron mobility (100 $cm^2 V^{-1} s^{-1}$), and piezoelectricity [1–3]. It is an important functional oxide, exhibiting high photoreactivity, near-UV emission, visible light transparency, biosafety, and biocompatibility [4,5]. ZnO nanostructures have great potential for application in ultraviolet (UV) lasers [6,7], light-emitting diodes [8–10], thin-film transistors [11,12], field emission (FE) devices [13,14], solar cells [15], photocatalysis [4,16], and piezo-nanogenerators [17,18].

ZnO nanostructures have be synthesized by various methods, such as metal organic chemical vapor deposition [19], molecular beam epitaxy (MBE) [20], physical vapor deposition (PVD) [21,22], pulsed laser deposition [23], and thermal evaporation [24,25]. However, these methods generally require high temperature, involve complicated equipment, and have a low yield [5]. The aqueous chemical growth (ACG) method is more attractive attributed to its low cost, low temperature and feasibility for industrial-scale fabrication [4,16,26]. Previous works on ACG processes have been controlled to grow different morphologies by adjusting reaction conditions, including pH [27,28], precursor concentrations [29], temperature [30], and surfactants [31–33], etc. Recently, ACG methods have been developed for fabrication of ZnO nanostructures in various geometrical morphologies, including nanowires [34,35], nanorods [29,36], nanotubes [37], nanopagodas [4,26], nanoneedles [30], nanoplates [4,38], nanoparticles [39], and nanoflowers [27], etc. Among them, ZnO nanoneedles can provide for sharp curvatures of tips, which are expected to be of particular importance in field emissions [40], photocatalysis [41], and optical properties [30,42]. However, there are fewer reports about low temperature and large-scale growth of ZnO nanoneedle arrays with high performance antireflective, photocatalytic, and surface-enhanced Raman scattering properties.

The present work has synthesized well-aligned ZnO nanoneedle arrays by the ACG method on four-inch silicon wafers with ZnO seed film. The appropriate volumes of 1,3-diaminopropane (DAP) can be used to grow the highest aspect ratio of ZnO nanoneedle arrays at a relatively low growth temperature of 80 °C for 1.5 h. Hexamethylenetetramine plays an important role in inhibiting the influence of high pH values with large dimensions. The ZnO

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nanoneedle arrays exhibit a very weak UV emission and very strong green emission from a defect in the cathodoluminescence spectrum. The ZnO nanoneedle arrays have good geometric structures for antireflection coatings, which display broadband reflection suppression from 400–1950 nm. ZnO nanoneedle arrays can provide a higher surface-to-volume ratio and better stability against aggregation, resulting in greater photocatalytic activity. In addition, ZnO nanoneedle arrays have good geometric structures for deposition three-dimensional Ag nanoparticles, which lead to high performance surface-enhanced Raman scattering (SERS) detection. The present work can provide insight into further structural design for nanostructured optical and SERS applications.

2. Experimental

2.1. Synthesis

A Si (0 0 1) wafer was cleaned ultrasonically for 10 min in ethanol. A thin film of zinc acetate was then coated on the substrate by spinning a layer of solution of 5 mM zinc acetate dihydrate (98% Aldrich) in ethanol and repeating for ten times. 5–10 nm thick ZnO seed film was produced after annealing at 300 °C in air for 20 min [4,43]. The ZnO nanoneedle arrays were grown by an ACG method in 100 mL of aqueous solution containing 10 mM equimolar zinc nitrate hexahydrate (98% Aldrich) and hexamethylenetetramine (99% Aldrich) (HMTA), with the addition of different volumes of 1,3-diaminopropane (98%, Alfa Aesar) (DAP). The substrate with ZnO seed film was pasted at the side of a sealed bottle containing the above solution and heated to about $T = 80$ °C for 1.5 h.

2.2. Characterization

The morphology of nanostructures was examined with a field emission scanning electron microscope (FESEM) using a JEOL JSM-6500F SEM operating at 10 kV accelerating voltage. A JEOL-2010 transmission electron microscope (TEM) operating at 200 kV was used to examine the microstructures. The crystalline phase of the ZnO nanostructures was determined using the X-ray powder diffraction method (Shimadzu XRD-6000, $CuK_{\alpha 1}$ radiation ($\lambda = 0.1505$ nm)). The cathodoluminescence (CL) spectra were acquired with an electron probe microanalyzer (Shimadzu EPMA-1500) attached to a SEM. CL spectra were accumulated in a single shot mode within an exposure rate of 1 nm/s. All the CL spectra were taken at room temperature. The reflection spectra were obtained with a Hitachi Model U-4100 spectrophotometer. The degradation of methylene blue solution was used to evaluate the photocatalytic activity of ZnO nanoneedle arrays. The methylene blue solutions were exposed to a 10 W UV lamp. For the photocatalytic activity evaluation, the concentration of photodegraded methylene blue was recorded by a Hitachi U-2900 UV–vis spectroscopy. Ion sputtering (EMITECH KSC7620) was used to deposit Ag nanoparticles on the surface of ZnO nanoneedle arrays. The Raman spectra were performed by Confocal Raman Microscope (HORIBA, LabRAM HR) at room temperature in the backscattering configuration. The light source was a He-Ne laser emitting a wavelength of 632.8 nm.

3. Results and discussion

3.1. Evaluation of ZnO nanoneedle arrays

Fig. 1a–d show the cross-sectional SEM images depicting the vertical ZnO nanoneedle arrays grown from equimolar (10 mM) zinc nitrate and HMTA, and the different volumes of DAP solution by an ACG method at the growth temperature of 80 °C for 1.5 h. The volumes of DAP were 0.25, 0.5, 0.75, and 1 mL,

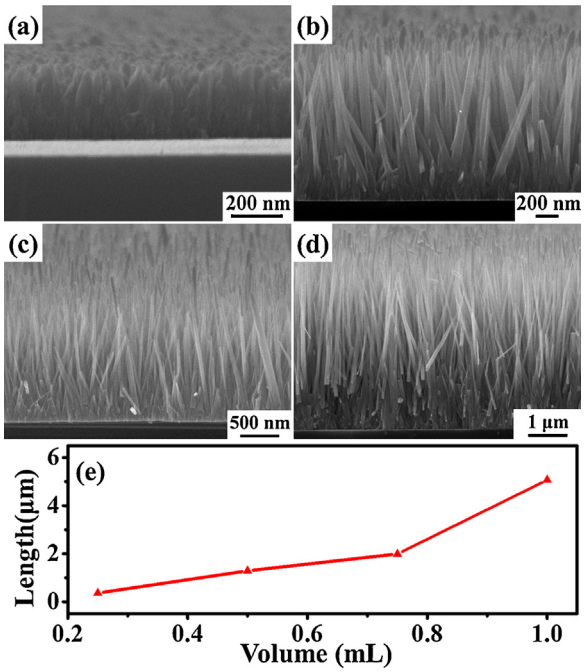

Fig. 1. The cross-sectional SEM images of the ZnO nanoneedle arrays were grown on the silicon substrates with ZnO seed film at different volumes of DAP. The volumes of DAP are (a) 0.25, (b) 0.5, (c) 0.75, and (d) 1 mL, respectively. (e) The average length of ZnO nanoneedle arrays as a function of the volumes of DAP.

respectively. The lengths of ZnO nanoneedles gradually increased with an increase in DAP volumes, as shown in Fig. 1e. The average lengths of ZnO nanoneedles were 0.36, 1.29, 1.99, and 5.07 μm, respectively. And the medium diameters of ZnO nanoneedles were 82.3 ± 9.4, 55.5 ± 10.4, 53.9 ± 16.7, and 66.5 ± 14.1 nm, respectively. In addition, the aspect ratios (length /diameter) of ZnO nanoneedles were 4.4, 23.2, 36.9, and 76.2, respectively. The ZnO nanoneedle arrays had the longest length and highest aspect ratios at a DAP volume of 1 mL. In general, the solubility of ZnO in an alkali solution was found to increase with an increase in the alkali concentration and temperature [44]. The pH value turned from 6.94 to 11.45 by the addition of DAP (1 mL) in the growth solution. If the volumes of DAP are higher than 1 mL, the solution becomes too alkaline to restrain the growth of ZnO nanoneedle arrays. The excessive amount of DAP not only influenced the growth of ZnO nanoneedle arrays, but also etched the ZnO seed film. On the other hand, appropriate volumes of DAP lead to the growth of ZnO nanoneedle arrays with long length and high aspect ratio.

The seed film has been found to be beneficial for fabricating ZnO nanowire or nanorod arrays with a wafer-scale production by the ACG method with a neutral pH value [45]. And in order to ensure that the alkaline condition would not influence the growth the uniformity of ZnO nanoneedle arrays for a four-inch wafer scale, high concentrations (20 mM) of zinc acetate dihydrate were used to prepare a thicker ZnO seed film for the growth of ZnO nanoneedle arrays. In addition, a bigger reaction chamber and a copious reaction solution were needed to grow aligned and regular ZnO nanoneedle arrays over a large area. Fig. 2a shows that ZnO nanoneedle arrays successfully covered a four-inch Si wafer. SEM images taken from several four-inch samples revealed that entire wafer can be grown with highly uniform and aligned ZnO nanoneedle arrays, as shown in Figs. 2b and c. The medium diameters and average lengths of ZnO nanoneedles were 71.2 ± 16.8 nm and 4.76 μm, respectively. In addition, the average density of ZnO nanoneedle arrays was 4.3×10^9 cm^{-2}. And the dimensions of ZnO nanoneedle arrays were not changed by an increase in size of the reaction chamber or adding