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Graphical abstract

Thermal treatment of ZnO seed layer into Atomic layer deposition to improve crystal quality of ZnO nanorod arrays

Abstract

Vertically arrayed ZnO nanorods were synthesized by a hydrothermal method on homo-seed layers deposited using atomic layer deposition (ALD) and heat-treated at various temperatures ranging from 200 to 600 °C in air. The effect of the annealing temperatures on nanorod formation was investigated. With increasing temperature, the microstructure of the ZnO seed layers changed from nanocrystals to coarse polycrystals with a preferred orientation, which led to an increase in the length and diameter of the solvothermally

Keywords

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Thermal treatments

grown nanorods. The effects of the post-heated ZnO seed layers on the structural and optical properties of the ZnO nanostructures were investigated by scanning electron microscopy (SEM), x-ray diffraction (XRD) spectroscopy and UV-Vis spectroscopy. The average grain sizes in the ZnO seed layers increased with increasing post-heating temperature. The ZnO seed layers post-heated in the range 200 – 600 °C affected the residual stress, lattice distortion in the ZnO nanostructures and the intensity, positions, and full widths at half maximum of 2θ in the XRD for the ZnO nanostructures. In this work, it is demonstrated that the heat-treatment temperature of ZnO seed layer plays an important role in the crystallinity and alignment of the ZnO nanorods.

Tratamiento térmico de la capa de semillas ZnO en deposición de capa atómica para mejorar la calidad de los cristales de las matrices de nanocables

Resumen

Los nanorods de ZnO agrupados verticalmente se sintetizaron mediante un método hidrotermal sobre capas de homo-semillas depositadas usando Deposición de Capa Atómica (ALD) y tratadas térmicamente a diversas temperaturas que varían de 200 a 600 °C en aire. Se investigó el efecto de las temperaturas de recocido en la formación de nanorod. Con el aumento de la temperatura, la microestructura de las capas de semillas de ZnO cambió de nanocristales a policristales gruesos con una orientación preferida, lo que condujo a un aumento en la longitud y el diámetro de los nanoalimentos cultivados por vía solar. Los efectos de las capas de semillas de ZnO precalentadas sobre las propiedades estructurales y ópticas de las nanoestructuras de ZnO se investigaron mediante microscopía electrónica de barrido (SEM), espectroscopía de difracción de rayos X (XRD) y espectroscopía UV-Vis. Los tamaños promedio de grano en las capas de semillas de ZnO aumentaron con el aumento de la temperatura de postcalentamiento. Las capas de semillas de ZnO postcalentadas en el rango de 200 - 600 °C afectaron el estrés residual, la distorsión de la red en las nanoestructuras de ZnO y la intensidad, las posiciones y los anchos completos a la mitad como máximo de 2θ en la XRD para las nanoestructuras de ZnO. En este trabajo, se demuestra que la temperatura de tratamiento térmico de la capa de semilla de ZnO juega un papel importante en la cristalinidad y la alineación de los nanorods de ZnO.

Palabras clave

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Abstract

Vertically arrayed ZnO nanorods were synthesized by a hydrothermal method on homo-seed layers deposited using atomic layer deposition (ALD) and heat-treated at various temperatures ranging from 200 to 600 °C in air. The effect of the annealing temperatures on nanorod formation was investigated. With increasing temperature, the microstructure of the ZnO seed layers changed from nanocrystals to coarse polycrystals with a preferred orientation, which led to an increase in the length and diameter of the solvothermally grown nanorods. The effects of the post-heated ZnO seed layers on the structural and optical properties of the ZnO nanostructures were investigated by scanning electron microscopy (SEM), x-ray diffraction (XRD) spectroscopy and UV-Vis spectroscopy. The average grain sizes in the ZnO seed layers increased with increasing post-heating temperature. The ZnO seed layers post-heated in the range 200 – 600 °C affected the residual stress, lattice distortion in the ZnO nanostructures and the intensity, positions, and full widths at half maximum of 2θ in the XRD for the ZnO nanostructures. In this work, it is demonstrated that the heat-treatment temperature of ZnO seed layer plays an important role in the crystallinity and alignment of the ZnO nanorods.

Keywords

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1. Introducción

The study of materials in one dimension (1D) has become a competitive advantage in the field of nanoscience and nanotechnology. 1D ZnO nanostructures such as nanotubes [1,2], nanorods [3], nanobelts [4] and nanowires [5] and nanonails [5] stimulate interest in scientific research because of their importance in fundamental physics studies

and its applications in nanoelectronics, nanomechanics and flat panel display devices.

Particularly, the application of devices ZnO nanostructures based optoelectronic dimensional (1D) have become a priority area of scientific and technological interest [6-8]. Novel applications of vertically arrayed ZnO nanorods include piezo-nanogenerators, UV lasers, gas sensors cells and photocatalysis [9].

For applications of nanostructured materials, usually it required that the crystalline morphology, orientation and surface architecture nanostructure can be controlled during the preparation process. There different methods for synthesis of ZnO nanostructures, such as Vapor Phase Transport (VPT) [10-12], Pulsed Laser Deposition (PLD) [13], Chemical Vapor Deposition (CVD,) [14, 15], Electrochemical Deposition [16] and arc discharge [16], which have been widely used for prepare ZnO nanostructures. These aforementioned techniques are very complex processes, sophisticated equipment and high temperatures which make it very difficult for large scale manufacturing of these nanostructures to commercial applications. Contrary to these techniques, chemical aqueous methods show great advantages because of its easy operation and low temperature (95 °C) [17, 18], which makes it very low cost. However, the ZnO nanostructures grown by these chemical methods show low reproducibility, difficulty in controlling the size, however, it still remains a major challenge control the growth of ZnO nanostructures.

In applications for ZnO nanostructures, it is required that not only its crystal morphology, and surface orientation are controlled during preparation process, but the quality will also improve their optical and electronic properties. Unfortunately, ZnO nanostructures grow relatively at low temperature (< 100 °C) show a poor crystallization and not good optical properties.

To grow ZnO nanorods, various synthesis methods have been utilized, such as vapor-liquid-solid (VLS) growth [19,20] chemical vapor deposition [21] and electrochemical deposition [22, 23]. However, those methods require severe conditions or a catalyst for nanorod growth.

The hydrothermal solution method has many merits that can make ZnO nanorods grow at low temperatures at low cost. To fabricate ZnO nanorods in liquid solution, the effects of zinc salt, concentration of zinc salt, pH, growth temperature, and growth time affect growth rate, morphology and aspect ratio. By decreasing the growth temperature from 90 to 60 °C, the average diameter of the ZnO nanorods decreases [24]. By increasing the concentration of the zinc source, the length and diameter of the ZnO nanorods increase [25]. By controlling the pH of the aqueous solution, the ZnO nanostructure morphologies and growth rate can be changed [26]. The length and

diameter of the ZnO nanorods are affected by the growing time [27].

In addition, the seed material is also important for the growth of high-quality ZnO nanorods [28]. Nevertheless, until now, it is not well understood the seed layer role on the growth mechanism for ZnO nanorods. Some reports state that by forming layers of textured ZnO films by ALD on a substrate, a seeded surface can be used to fabricate high density vertical nanorod arrays [29, 30]. From the results, it is observed that thickness influences the texture of ALD ZnO layer and thus, the crystallographic nature of the seed layer that determines the ulterior nanorod growth type.

In this study, homo-ZnO thin films prepared by an ALD process were used as a seed layer to grow vertically aligned nanorods. The degree of crystallization in the seed layers was changed using different annealing temperatures after formation of the seed layers. Complementary to all available papers, this work is focused exclusively on the thermal treatment effect of ALD ZnO seed layer to improve crystal quality of vertical ZnO nanorod arrays. We study the dimensional, morphological, orientation and optical properties of the ZnO nanorods using a hybrid growth method that consists in three steps: i) a textured seed layer obtained by ALD, ii) a thermal treatment for ALD ZnO seed layer and iii) vertical ZnO nanorods growth by hydrothermal method. The reported contributions have considered only two steps [29,30].

2. Experimental section

The fabrication procedure for the growth of the nanorods consisted of three steps: preparation of a seed-textured ZnO thin layer by ALD, thermal treatment in oxygen atmosphere of seed layer and the nanorod array growth by hydrothermal.

2.1 Synthesis of ZnO films by ALD

ZnO films with a thickness of 80 nm were deposited on glass substrates by ALD using a Savannah 100 ALD system from Cambridge Nanotech. Diethylzinc (DEZn) was used as the precursor for zinc and deionized water was used as the oxidation source. The growth cycle consists of precursor exposures and N₂ (99.9999 %) purge following the sequence of DEZn/N₂/H₂O/N₂ with

corresponding duration of 0.1 s/5 s/0.1 s/5 s. After each N₂ purging, the reactor was pumped down to 0.1 Torr. DEZn and H₂O were fed into the chamber through separate inlet lines and nozzles. In the ALD method reagents (precursors) are introduced sequentially into the growth chamber and when precursors reach the substrate are interspersed by cycles of purging with inert gas (N₂). The opening and closing sequences of the valves were controlled by a computer. Precursor introduction was done by opening the inlet valve between the reservoir and reactor chamber while the outlet valve was closed. The pressures of the DEZn and H₂O in the reactor chamber were approximately 1 and 2 torr, respectively, monitored by a vacuum gauge. The substrate temperature was maintained at 177 °C during the deposition. The reaction was repeated 800 cycles to obtain the ZnO films with a thickness of 80 nm.

2.2 Thermal treatment of seed layer under oxygen atmosphere

The ALD ZnO seed layer films were annealed at various temperatures ranging from 200 to 600 °C for 1h under oxygen to induce crystallization. The thickness of the ZnO seed layers was approximately 80 nm.

2.3 Growth of ZnO nanorods through hydrothermal process

In this process, Zn(NO₃)₂ (ZNT) and hexamethylenetetramine (HMT) purchased from Sigma-Aldrich (St Louis, MO) were used as reagents. The ZnO nanorods were grown in aqueous solutions of zinc nitrate (Zn(NO₃)₂·6H₂O) 0.05 M and hexamine (CH₂)₆N₄ 0.05 M in deionized water; the ZNT:HMT molar ratio was always {1:1}. The thermal treated ALD-ZnO seed layer were placed in face up position into glass reactor with screw cap and then equal amounts of both ZNT and HMT solutions were added. The reactor was immersed in a water bath at 90 °C with mild agitation during 4 hours. Finally, the samples were rinsed with deionized water for several times and dried at 90 °C for several hours before characterization. The samples were structurally and morphologically characterized by X-ray diffraction (XRD) using a Philips X'Pert PW3040 diffractometer with Cu-Kα radiation and field-

emission scanning electron microscopy in a Hitachi S-5500 Field Emission Gun (FEG) ultra high-resolution scanning electron microscope (SEM) (0.4 nm at 30 kV) with a BF/DF Duo-STEM detector. Additionally, the composition was determined by energy dispersive X-ray spectroscopy (EDS, Inca Oxford, attached to the FE-SEM) and the seed-textured ZnO layer surface was analyzed by atomic force microscopy (AFM).

3. Results and discussion

3.1 ZnO seed layer

SEM was used to examine the morphology of the thermal treated ZnO seed layers. Figure 1 shows the morphology of the ZnO seed layer (80 nm) obtained by ALD with the experimental conditions mentioned above with and without thermal treatment at 200 °C, 300 °C, 400 °C, 500 °C and 600 °C. Figure 1a shows SEM image of the ZnO seed layers as deposited by ALD.

Figure 1. SEM images of the 80 nm ZnO seed layer deposited by ALD with and without thermal treatment. a) 80 nm ZnO seed layer without heat treatment, b) – f) ZnO seed layer with heat treatment at 200 °C, 300 °C, 400 °C, 500 °C and 600 °C respectively.

The ALD-fabricated ZnO seed layer without post-thermal treatment showed a less dense and inhomogeneous film with grains of different sizes. However, the ZnO seed crystals were densely grown and the grain size increased gradually with increasing annealing temperature. The average grain size of the seed crystals evaluated from SEM images was increased from 28 nm at 200 °C to 65 nm at 600 °C. The increase in grain size can be understood by an Ostwald ripening mechanism [31]. In particular, Ostwald ripening occurs frequently over a wide range of temperatures when the density of nucleation sites is dispersed randomly. The degree of crystallization is expected to affect the morphology and distribution of the ZnO nanorods. As shown in Figure. 1a to 1f, the change in annealing temperature of the seed layers impacts the morphology and density of the ZnO crystals on seed layer. It is observed that the morphology changes from small grains to larger grains forming mosaics. It also increases the crystal volume until obtain a quasi-planar surface on the ZnO seed layer.

The X-ray diffraction patterns of the ZnO seed layer with the different heat treatments are shown in Figure 2. The diffraction X-ray pattern of the ZnO seed layer of is observed without and their respective heat treatments can be observed the single-phase and textured character of the ZnO ultrathin (80 nm) layer obtained by the ALD technique. The diffraction Peaks correspond to a single phase, with hexagonal Wurtzite structure type (ICSD 31052, PDF 36-1451), described by the reflections of the crystallographic planes (100), (110) and (002), the latter being the most intense. The diffraction pattern reveals a preferential growth along the direction [002]. With the heat treatment promoted the crystallization and the growth of the grain size in the ultrathin ZnO layer. The peak intensity in the (002) increases with increasing the heat treatment temperature which favors the atomic diffusion, crystallization processes, crystallographic order and increasing the grain size which was observed by SEM. The formation and faceting of the hexagonal phase observed are indicative of the preferential orientation in the plane (002).

Figure 3 shows the transmittance spectrum curves of ZnO layer with and without heat treatments. It is observed that the transmittance increases in the visible region while decreases in the UV region

with increasing the treatment temperature. The increase of the transmittance in the visible region may be due to a surface effect by increasing the temperature, which forms a flat surface preventing the dispersion of light, unlike the ultrathin ZnO film obtained by ALD which is entirely rough. Similarly, the heat treatment improves the ZnO transmittance due to the reaction with the oxygen.

Figure 2. The X-ray diffraction patterns of the ZnO seed layer with the different heat treatments.

Figure 3. Transmittance spectrum curves of ZnO seed layer with and without heat treatments.

Figure 4. SEM images of the ZnO nanorods grown on thermal treated seed layer, a) and b) Top and lateral view of the ZnO nanorods growth on ZnO seed layer annealed at 300 °C, c) and d) Top and lateral view of the ZnO nanorods growth on ZnO seed layer annealed at 600 °C.

The change in the absorption edge can be attributed to the quality of the ZnO ultrathin film with the increase of heat treatment temperature. When temperature increases, the number of defects decreases improving the quality of the ZnO film. This means that the electronic structure of ZnO changes with temperature rise, making it a more perfect structure. These results can be validated by the previously obtained SEM images and the diffraction patterns, showing the changes of the ZnO seed layer with the increase of the heat treatment temperature to get a planar and textured surface.

3.2 ZnO nanorods grown on thermal treated seed layer

In the second stage, the ZnO nanorods were synthesized under the same conditions by a hydrothermal method on these seed crystals. As shown in Figure 4 the change in annealing temperature of the seed layers impacts in the morphology and density of the ZnO nanorods. The most striking difference in the SEM images is that the average length of the nanorods increases with increasing annealing temperature of the seed layers where the average length of the nanorods increased from 450 nm at 300 °C to 1200 nm at 600 °C. The diameter of the nanorods also increased slightly.

For example, the samples thermally annealed at 300 and 600 °C had diameters of 80 and 120 nm, respectively. All the ZnO nanorods were generally grown along the c-direction with polar axis. It is also expected that thermal treatment promotes the enhancement in the degree of the c-axis-preferred orientation of the seed layers. Therefore, the increase in the annealing temperature may induce the rapid growth along the c-axis. From the plan-view SEM images in Figure 4a and 4c, the number of nanorods per-unit area was approximately 55 and 34 per $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ for the samples annealed at 300 and 600 °C, which are proportional to the density of the seed crystals.

As observed by SEM, the diameter of the nanorods increased with increasing annealing temperature, i.e. an enlarged grain size in the seed crystals results in an increase in the diameter and length of the nanorods produced subsequently, as shown in Figure. 4. Consequently, the increase in the grain size by thermal annealing is expected to promote the reaction rate along the vertical and lateral directions simultaneously, and the resulting volume of nanorods increases significantly. Even though there is a slight inclination of the nanorods, all vertically arrayed nanorods fabricated by the hydrothermal method have a hexagonal surface shape and a preferential orientation along the c-axis, regardless of the annealing temperature. On the basis of the SEM, the crystallization of seed layers by post-thermal annealing promotes the formation of vertically arrayed nanorods, and also augments the width of the nanorods by coarsening the grains in the seed layers.

$\theta - 2\theta$ scan XRD was performed to compare the crystallinity of the ZnO seed layers and ZnO nanorods. As shown in Figure. 5 faint (002) diffraction peaks were observed for the samples annealed at high temperatures due to crystallization of the seed layers. The diffraction peaks from the ZnO nanorods in Figure 5 were also intensified when the annealing temperature was increased. Annealing at high temperatures induces a shift in the (002) ZnO peak for the nanorods to a lower angle. This suggests an increase in the c lattice constant from 0.5188 nm (200 °C) to 0.5198 nm (600 °C). In particular, the value estimated from the sample annealed at 600 °C was closer to the c-lattice parameter (0.5207 nm) of bulk ZnO, indicating reduced stress. The above means that longer and thicker nanorods with large dimensions

Figure 5. The X-ray diffraction patterns of the ZnO nanorods growth on the annealed ZnO seed layer.

Figure 6. Transmittance spectrum curves of the ZnO nanorods at different temperatures of seed layer heat treatment.

assisted by the crystallized seed layers induce lattice constant corresponding to the near bulk. The patterns for all nanostructures exhibit intense (002) diffraction peaks, indicating that the preferred growth orientation of nanorods is along (002) direction because their vertical growth rate is rapid and because their lateral growth is relatively limited. Figure 5b shows the full width at half maximum (FWHM) and the position of the peaks in the XRD patterns for the ZnO nanorods grown

on ZnO-ALD seed layers post-heated at various temperatures. The FWHM of the (002) diffraction peak for ZnO is reported to be closely related to both grain size and crystal quality. The FWHM is inversely proportional to grain size. Hence narrower FWHM and larger grain sizes imply better crystal quality. The position of the (002) peak in the XD spectra shifted with changing ZnO seed layers post-heating temperature, indicating that ZnO seed layers post-heating temperature affected the structural properties of the ZnO nanorods. The shift in the position of the (002) peak as a function of the ZnO seed layer post-heating temperatures implies a change in the amount of residual stress (σ) compared to that in strain-free ZnO. The residual stress σ is generated in the ZnO nanorods because of the differences in the lattice constant and the thermal expansion coefficient between the rods and the seed layer.

3.3 Effect of thermal treatment of ALD ZnO seed layer on the growth of ZnO nanorods

The results from SEM images suggest that the growth rate of the ZnO nanorods during hydrothermal synthesis is strongly dependent on the annealing temperature of the seed layer. In our study, the density of ZnO nanorods on the seed layer annealed at 600 °C was found to be $2 \times 10^{10} \text{ cm}^{-2}$. In contrast the nanorods grown at lower temperatures exhibited comparable densities but lower if compared to those grown on ALD seed layer without thermal treatment.

The nanorods grown on seed layers annealed at 600 °C exhibited larger average diameters when compared with diameters of seed layer before nanorods growth. Thus, the lower density of nanorods might be caused by the nanorods larger diameter. The lateral growth is not as effectively suppressed, resulting in larger-diameters rods. The influence of the seed layer is mainly showed in perfect and well faceted basal planes for all thermal treated substrates. The differences in the ZnO nanorod growth on different seed layers are explained by the competition between neighboring nanorods in addition to the preferential growth axis of the crystal.

Figure 6 shows the transmittance curves of ZnO nanorods at different temperatures of treatment on the seed, it is noted a decreasing of the transmittance visible region of the ZnO nanorods whit

increasing heat treatment temperature. This may be because that at higher temperatures are much larger diameters that if are not grown at the same height can be a loss by light scattering resulting in a decrease in the transmittance.

4. Conclusions

Vertically arrayed ZnO nanorods were successfully synthesized by a hydrothermal method on homo-seed layers deposited using ALD and heat-treated at various temperatures ranging from 200 to 600 °C in air. The average grain size of the seed crystals increased gradually with increasing annealing temperature.

The heat treatment promoted the crystallization and the growth of the grain size in the ultrathin ZnO layer. The peak intensity in the (002) increases with increasing the heat treatment temperature which favors the atomic diffusion, the crystallization processes into the preferential orientation in the plane (002). The change in annealing temperature of the seed layers impacts in the morphology and density of the ZnO nanorods. The average length of the nanorods increased from 450 nm at 300 °C to 1200 nm at 600 °C and diameters from 80 and 120 nm, respectively.

The number of nanorods per-unit area was approximately 55 and 34 per $1\ \mu\text{m} \times 1\ \mu\text{m}$ for the samples annealed at 300 and 600 °C, which are proportional to the density of the seed crystals. The heat treatment affected the residual stress, lattice distortion in the ZnO nanostructures and the intensity, positions, and full widths at half maximum of 2θ in the XRD for the ZnO nanorods.

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Conflict of interests

Authors declare that there are no conflicts of interest associated with the information contained in this work.

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