

Seed/Catalyst-Free Growth of 2D And 3D ZnO Nanostructures on Glass Substrate by Thermal Evaporation Method: Effects of Carrier Gas Flow Rate

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Abstract

Here, we report the seed/catalyst-free growth of 2D and 3D ZnO nanostructures on a glass substrate by thermal evaporation of Zn powder in the presence of O₂ gas. These nanostructures were grown on (75 ± 5 nm) ZnO seed layers, which were deposited on glass substrates by radio frequency magnetron sputtering. Prior to synthesized ZnO nanostructures, the sputtered ZnO seeds were annealed using the continuous wave CO₂ laser at 450 °C in air for 15 min. The effects of carrier gas flow rate on the morphological, structural, and optical properties were systematically studied using field emission scanning electron microscopy, X-ray diffraction and UV-Vis spectroscopy.

Keywords: ZnO nanostructure; Seed layer; CW CO₂ laser; Thermal evaporation

الخلاصة

هنا ، نقوم بالإبلاغ عن النمو الخالي من البذرة / المحفز للبنى النانوية ثنائية وثلاثية الأبعاد على ركيزة زجاجية بواسطة التبخر الحراري لمسحوق الزنك في وجود غاز الاوكسجين. نمت هذه البنى النانوية على طبقات من بذور الزنك (75 ± 5 نانومتر) والتي تم ترسيبها على ركائز زجاجية بواسطة طريقة الرش. قبل تركيب البنى النانوية لأكاسيد الزنك ، تم ترسيب بذور أكسيد الزنك باستخدام ليزر ثاني اوكسيد الكربون ذو الموجة المستمر عند 450 °C في الهواء لمدة 15 دقيقة. تم دراسة تأثير معدل تدفق الغاز الناقل على الخصائص المورفولوجيا والبنية والبصرية بشكل منهجي باستخدام انبعثات مجال مسح المجهر الإلكتروني ، حيود الأشعة السينية والتحليل الطيفي للأشعة فوق البنفسجي .

Introduction

Zinc oxide (ZnO) is semiconductor with a direct wide-bandgap of 3.37 eV and large exciton binding energy of 60 meV. ZnO nanostructures have significant interest because of its potential in different applications [1]. In addition, ZnO nanostructure is low cost, high thermal stability, non-toxic, easily fabricated, high transmittance in the visible region [2]. ZnO nanostructures have been extensively used in different fields, such as environmental science [3], optoelectronics [4], catalysts [5], actuators and piezoelectric transducers [6], and solar cells [7]. ZnO nanostructures including zero-dimensional (0D) such as nanoparticles and quantum dot, one-dimensional (1D) such as nanowires, nanorods, and nanoneedles, two-dimensional (2D) nanoribbons and nanoleaves,

and three-dimensional (3D) such as tetrapods and spherical grains [8-10].

Many physical and chemical methods are available and can be used to synthesis ZnO nanostructures, such as spray pyrolysis [11], pulsed laser deposition [12], magnetron sputtering (RF) [13], sol-gel method [14], atomic layer deposition [15], and thermal evaporation[16]. Among these methods, thermal evaporation is considered to be one of the important methods employed to prepare ZnO because of its cost-effectiveness, simple, unique features, catalyst-free growth namely and easily controlled growth parameters, such as distribution on the substrate, growth rate, and film thickness. In addition, thermal evaporation presents a wide range of nanostructures with different morphologies.

In the present study, the catalyst-free growth of 2D and 3D ZnO nanostructures on ZnO seeds-coated glass substrates by thermal evaporation method was investigated. In addition, the morphological, structure, and optical properties of ZnO nanostructures was conducted by using varying Ar flow rates at a low growth temperature. The objectives of this study are to use a low cost substrate in a fabricated a different morphology and dimension of ZnO nanostructures and obtains the optimized parameters for the control of different morphologies of these nanostructures

Materials and Methods

Experimental details

A horizontal tube furnace with a two-zone tube furnace was used to growth ZnO-Ts by thermal evaporation method. High-purity metallic Zn powder (Aldrich Chemical Company- Inc, USA, 99.99 %) loaded in a quartz boat. This Zn powder with boat was transferred into the first zone in center of the furnace using a quartz tube. The ZnO seed layer was deposited onto glass substrates by RF sputtering system. The base pressure of the RF chamber was at 10⁻⁷ mbar with power of 100 W with. The thickness of the ZnO seeds was approximately 75 ± 5 nm thicknesses. A CW CO₂ laser beam at wavelength of 10.6 μm was used for ZnO seed layer annealing at 450 °C in air for 15 min, in accordance with our previous study [17]. The ZnO seeds/glass substrate was placed vertically in second zone in the downstream direction of the Zn powder. The Zn powder in the first zone was gradually heated up from room temperature to 550 °C at a rate of 10 °C / min. High-purity Argon gas as a carrier gas was introduced into the quartz tube at a rate of 10, and 40 ml/min, respectively. High-purity Oxygen gas employed was introduced into the furnace at a rate of about 10 ml/min after reaching a maximum temperature in the first zone at 550 °C. The pumping of Oxygen gas into the reaction zone continued for 90 min. After the oxidation process, the furnace was turned off and cooled to room temperature. White material formed on the substrate after the evaporation was completed.

Results and Discussion

Morphological studies

The morphologies of the catalyst-free growth of ZnO nanostructures on the ZnO seed layer coated glass substrates were measured by FESEM as shown in Fig. 1. The effect of the carrier gas flow rate on the shape and diameter of the ZnO nanostructures is significantly observed. The 3D ZnO nanostructures grown on seed layer at a low flow rate of 10 ml/min were agglomeration of small spherical grain with high-density growth, as shown in Fig. 1(a). The average diameters of these spherical grains were estimated to be 30-40 nm. Significant conversion in the morphology of ZnO nanostructures that were grown at a flow rate of 40 ml/min is appears as a 3D, large area and high-density growth of ZnO resembles the tree leaves, as shown in Fig. 1(b). Therefore this structure can be called a nanoleaf structure. The diameter of most of these leaves ranges approximately 50 nm width and 1-2 μm length.

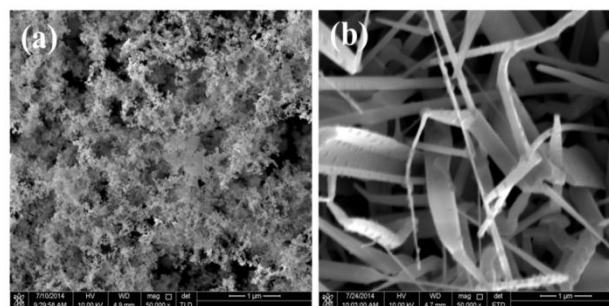


Figure 1: FESEM image of the catalyst-free growth of 2D and 3D ZnO nanostructures on ZnO seed layer under different Ar flow rates (a) 10 ml/min, and (b) 40 ml/min.

Crystalline Structure

The X-ray diffraction patterns of the catalyst-free growth of ZnO nanostructures on ZnO under different Ar flow rates of 10 and 40 ml/min, respectively via thermal evaporation method are shown in Fig 2. All the peaks indicate that the ZnO nanostructures were successfully grown on glass substrates at varying Ar flow rates, with match the hexagonal wurtzite phase of bulk ZnO (ICSD Card No.01-080-0075). The strong intensity of the (0 0 2) peak indicates that the ZnO nanostructures have a preferential growth direction along the c-axis orientation.

The highest intensity of the (002) direction was obtained under Ar flow rates of 40 ml/min. This finding indicated that the highest crystallinity was at this sample [18].

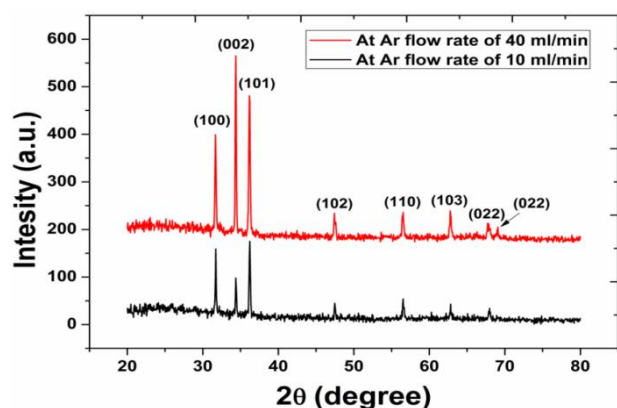


Figure 2: EDX spectra of the catalyst-free growth of 2D and 3D ZnO nanostructures on ZnO seed layer under different Ar flow rates.

Optical properties

Fig. 3 shows the UV–Vis optical transmission spectra of the catalyst-free growth of ZnO nanostructures on ZnO under different Ar flow rates of 10 and 40 ml/min, respectively via thermal evaporation method in a wavelength range of 300– 800 nm, and the absorption spectra of the samples, inset of Fig. 3. It can be seen that the transmittance of the ZnO nanostructure at a flow rate of 40 ml/min is higher than the other sample in the whole wavelength range. The reason is that when this nanostructure grows at a flow rate of 40 ml/min it will have a better uniform interspace amongst all the samples, which is in agreement with FESEM (Fig. 1). This can cause less light scattering and better transmittance of the spectrum [19]. The absorption spectrum of the prepared nanostructures (inset of Fig. 3) demonstrates a high absorbance and sharp absorption shoulder in wavelengths between 300 and 400 nm (UV region).

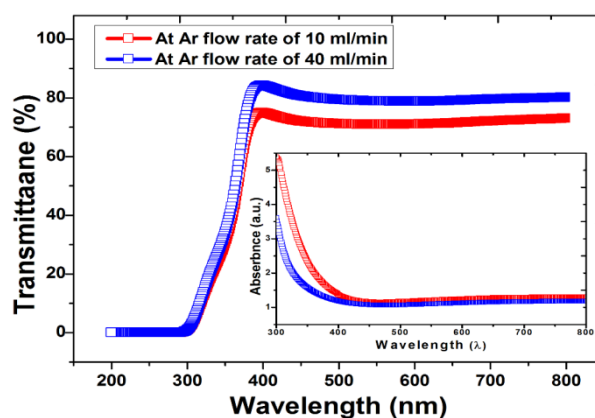


Figure 3: UV–Vis transmissions of the 2D and 3D ZnO nanostructures under different Ar flow rates. The absorption spectrum is shown in the inset.

Conclusion

In conclusion, catalyst-free growth of 2D and 3D ZnO nanostructures was successfully fabricated on a glass substrate via thermal evaporation method. This was demonstrated using a sputtered ZnO seed layer after laser-treatment by CW CO₂ laser as a heat source. Controlling the growth mechanism for these nanostructures at different Ar flow rate at growth temperature of 550 °C was proposed. It has been shown that the carrier gas flow rates leads to a different in the nucleation site, which in turn leads to significant influence on the dimensions, sizes and geometric shapes of ZnO nanostructures. In addition, observed that the morphology of the ZnO nanostructures play a critical role in determining their crystal quality and optical properties.

Acknowledgements

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