Research Article

Luminescence and Structure of ZnO Grown by Physical Vapor Deposition

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Received 15 August 2012; Revised 18 November 2012; Accepted 7 December 2012

Academic Editor: Markku Leskela

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Nanostructured ZnO was deposited on different substrates (Si, SiO2, and Au/SiO2) by an enhanced physical vapor deposition technique that presents excellent luminescent properties. This technique consists in a horizontal quartz tube reactor that uses ultra-high purity Zn and UHP oxygen as precursors. The morphology and structure of ZnO grown in this work were studied by electron microscopy and X-ray diffraction. The XRD patterns revealed the highly crystalline phase of wurtzite polycrystalline structure, with a preferred (1011) growth direction. Room temperature cathodoluminescence studies revealed two features in the luminescence properties of the ZnO obtained by this technique, first a high-intensity narrow peak centered at 390 nm (∼3.2 eV) corresponding to a near band-to-band emission, and secondly, a broad peak centered around 517 nm (2.4 eV), the typical green-yellow luminescence, related to an unintentionally doped ZnO.

1. Introduction

Zinc oxide (ZnO) has been an object of growing attention in the last decade due to its potential applications in electronics and optoelectronics. ZnO is a wideband gap semiconductor with a hexagonal crystalline structure (wurtzite type) showing a direct band gap of ∼3.3 eV. As a direct wide band gap semiconductor material, ZnO has attracted much attention towards applications, such as UV photodetectors, solar cells, light emitting diodes and laser diodes [1, 2]. Several techniques have been adopted to synthesize ZnO nanostructures such as metalorganic chemical vapor deposition (MOCVD) [3], microwave plasma deposition [4], hydrothermal synthesis [5–7], electrochemical deposition [8–11], and ultrasonic spray pyrolysis [12]. Nevertheless, physical vapor deposition (PVD) technique is an easy, reproducible, low-cost method that can be scaled up and used for the production of wide range of nanostructures such as nanowires, nanobelts, nanohelixes, nanorings, and nanoneedles [13–16].

In this work, nanostructured ZnO has been grown on different substrates (Si, SiO2, and Au/SiO2) by physical vapor deposition technique; the nanostructures obtained were sheets and plaques.

2. Experimental Procedure

The schematic setup for the physical vapor deposition of ZnO is shown in Figure 1. The reactor consists of a quartz tube heated in a three-zone horizontal furnace. A boat with UHP Zn is placed at the first zone of the quartz tube, and a boat that holds the substrates (silicon wafer, fused silica disk and a gold-covered fused silica disk) is placed in zone 2. The quartz tube used in this work was a 2.5″ tube, but this system allows to change the size of the tube thus being able to scale up the deposits. This PVD method instead of
A flow of UHP oxygen is started through the 2.5″ diameter quartz tube by argon (allows doping the samples with different materials such as Al, Ag, and In).

The following reactions take place in the quartz tube:

\[
\text{Zone 1 at 600}^\circ \text{C: } \text{Zn}_{(l)} \rightarrow \text{Zn}_{(g)}
\]

\[
\text{Zone 2 at 900}^\circ \text{C: } \text{Zn}_{(g)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{ZnO}_{(s)} \quad (1)
\]

A gold layer (~50 nm) was deposited on a 1″-diameter fused silica substrate by sputtering, with a following thermal treatment at 900°C. This process made the gold film form disperser ~100 nm size islands that act as catalysts and nucleation sites for ZnO nanorods.

Once the boats containing the substrates (Si, SiO₂, and Au/SiO₂) and the Zn (~1.5 g) are placed inside the quartz tube, the tube is flushed with argon while being evacuated with a mechanical pump down to 1 Pa. The temperature is increased, and when the central zone of the tube reaches 900°C, the argon flushing and evacuation are stopped, and a flow of UHP oxygen is started through the 2.5″ diameter tube (200 sccm, ~7000 Pa). At that point the temperature at the entrance of the reactor is 600°C, and the Zn starts to evaporate. The vapor is carried through an inner 3/4″ diameter quartz tube by argon (~200 sccm). When the Zn vapor reaches zone 2, at 900°C, it is ready to react with the oxygen that is flowing by annular space. The Zn and the oxygen react on the surface of the substrate yielding ZnO. The growth is maintained for around 15 min. The boat with the substrate and the deposit (ZnO) is moved rapidly to the coldest part of the reactor using a magnetic manipulator. After the system is cooled down to room temperature, the boat is taken out of the reactor. Then, ZnO samples are stored for later analysis.

The cathodoluminescence (CL) measurements were taken in a JEOL JSM 6300 scanning electron microscope equipped with a CL system. The following conditions were used: acceleration voltage 5 kV, beam current 300 pA, slit width 0.12 mm, and spot size 2 × 1.5 μm. The XRD measurements were done using the D500 SIEMENS diffractometer in a range of 10 to 70 degrees in position 2θ at room temperature. The following conditions were used: acceleration voltage 5 kV, beam current 300 pA, slit with 0.12 mm, and spot size 2 × 1.5 μm.

3. Results and Discussion

The crystalline structure of ZnO/Au/SiO₂ was characterized using XRD as shown in Figure 2. The sharp diffraction pattern indicates that the sample exhibits hexagonal ZnO polycrystalline structure with a preferred growth direction (1011), with lattice constant of a = 3.248 Å and c = 5.199 Å, which is reported in JCPDS (36-1451). The Scherrer formula was used for the calculation of the crystallite sizes, which is given by the following formula:

\[
D_{bdh} = \frac{K\lambda}{\beta \cos \theta},
\]

where K is constant, β is FWHM in radians, λ is the wavelength of X-ray used, which was 1.5406 Å, and θ is the bragg angle, which was 18.1°. K value is taken as 0.9 for the calculations. The crystallite size (D) calculated for ZnO nanostructures was approximately 50 nm. Secondary electron images of ZnO grown in this work are shown in Figure 3. The morphology of the ZnO grown on (a) Si (100) and (b) SiO₂ is very similar, mostly rectangular plaques (flat surfaces with average dimensions of 40 μm length × 10 μm width × 1 μm thick) and nanowires, around 100 nm diameter and more than 100 μm long. In contrast, the ZnO grown on Au nanoislands shows mainly rods and columns, with dimensions between 100 and 200 nm diameter and length between 1 and 4 μm. Figure 4 shows gold droplets formation after annealing of a 10 nm Au layer with narrow size particles.
Figure 3: Secondary electron images of as-grown ZnO. (a) on silicon (100), (b) on fused silica (SiO$_2$), and (c) and (d) on gold-covered fused silica (Au/SiO$_2$).

Figure 4: Gold islands after annealing of 10 nm Au layer over fused silica.

Figure 5: Room temperature CL spectra of ZnO samples grown on three different substrates by PVD.

distributed between 50 and 100 nm. It was found that the Au droplets promote the crystal growth and nucleation of ZnO over them. This means that the typical crystalline structure of ZnO is presented when deposited in SiO$_2$, but when in presence of Au droplets, it functions as nucleation center and catalyst, improving the column growth of ZnO.

In addition, XRD spectra confirmed that the ZnO grown by this PVD technique shows a hexagonal wurtzite structure. Cathodoluminescence has been used to further improve our understanding of the optical properties of the ZnO structures. Figure 5 shows the room temperature
luminescence characteristic of ZnO. The CL spectra of the three samples exhibit two broad peaks, one peak at around 390 nm (~3.2 eV) near the band edge of the material and a broad peak centered at 525 nm (~2.4 eV, the typical green emission). This green emission is the typical green emission for the undoped or unintentional doped ZnO which is attributed to oxygen vacancies (V0⁺) [16–18]. Also, Janotti and Van de Walle [19] have presented a model for the formation energy of oxygen vacancies in ZnO, which establishes a relationship between green emission and oxygen vacancies. Figure 6 shows monochromatic CL images of ZnO taken at the same location. In (a), it is possible to see that the 390 nm emission is from the flat surface, and in (b), we can see that the “green emission” is emitted principally from rods and wires. It gives the impression that the flat structures such as sheets and plaques have less oxygen vacancies (V0⁺) than the cylindrical structures such as nanorods.

4. Conclusions

An improved PVD method to grow high-quality nanostructures of ZnO on different substrates had been investigated. This method is very straightforward; it can produce large quantities of ZnO in a short time without later treatments as thermal annealing and can produce less contaminated samples. X-ray diffraction confirms that the ZnO grown by this method presents a hexagonal wurtzite polycrystalline structure with a preferred growth direction (1011). These structures are attributed to the Au droplets which promote this orientation over the typical crystalline orientation (002) of ZnO. These structures also show high-intensity luminescence in the UV (390 nm) and visible regions between 470 and 570 nm. It was found that the ZnO flat structures such as sheets and plaques show higher intensity luminescence than those in ZnO rods and wires. Also, in this research was found that a selective growth can be achieved when the substrate presents well defined structures, such as the gold nanoislands to the precursors (zinc vapors and oxygen).

Acknowledgments

The authors gratefully acknowledge the use of facilities within the University of Sonora (UNISON), Arizona State University (ASU), and Center of Nanoscience and Nanotechnology (CNYN-UNAM). This paper has been partially supported by CONACYT México, Project no. 102671.

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