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UV Sensing Properties of Single 2D ZnO Nanostructure

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Abstract: The performance of nanostructured devices depend significantly on the morphology and structure of the used nanostructures. We report the hydrothermal synthesis of high quality 2D ZnO nanostructures and the fabrication of ultraviolet (UV) sensors based on single 2D ZnO nanostructures. The grown nanostructures are characterized using SEM, STEM, SAED, and XRD. The single 2D ZnO nanostructure UV sensor demonstrates high photosensitivity of 980 and speed of response and recovery of 19 and 25 s, respectively. The high performance is attributed to the high quality of the ZnO 2D crystals and its high surface to volume ratio.

Key words: Nanostructures, ZnO, sensors, single crystal, nanodisks, hydrothermal, synthesis, UV.

1. Introduction

Rationally controlled hydrothermal synthesis of nanostructures has advanced significantly in recent years, because of its role in the development large scale fabrication of many devices [1-5]. Zinc oxide (ZnO) is a main nanomaterial which is predicted to have great impact on a large range of devices in many areas such as flexible electronics, optoelectronics, piezo electronics, photovoltaic technologies, and ultraviolet (UV) sensing [6-9].

UV sensing has been applied in many applications like pollution monitoring, secure space communications, water purification, flame and missile plume detection, etc. Excellent sensing properties including photosensitivity and fast response and recovery are expected for these uses.

In the literature, one can find large number of studies on the preparation of different ZnO nanostructures via wide range of methods and their UV sensing properties. Hydrothermal synthesis methods are preferred because of many advantages including simplicity, cost effectiveness, suitability to large area scalability, low processing temperature, non-hazardous nature, reproducibility, and compatibility with flexible organic substrates [1-4]. ZnO nanostructures prepared via hydrothermal growth process have a tendency to take the one-dimensional (1D) shapes because they grow faster in the [0001] direction [10, 11]. Yet, the morphology of these nanostructures can be modified stopping the growth along the [0001] direction. Several shapes have been prepared by introducing some additives like citrate ions [12], CTAB [13], and polymers [14-16] into the growth system.

Nanostructures with high surface-to-volume ratio and excellent crystallinity are regarded as great candidates in the fabrication of UV sensors. They are expected to show superior performance (photosensitivity and speed of response) in comparison with bulk and thin film UV sensors. However, the majority of reported studies investigating UV sensing properties of nanostructures are focusing on 1D nanostructure [6]. As for the two-dimensional (2D) nanostructures, most of the reports found on the literature are dealing with their synthesis. Few reports

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can be found on the use of a network of 2D nanostructures as the active material in sensing applications.

Here, we present a hydrothermal technique to prepare single crystal 2D ZnO nanostructures. The morphology and structure of the grown nanostructures are characterized. Finally, the UV sensing properties of a single 2D ZnO nanostructure are investigated.

2. Materials and Methods

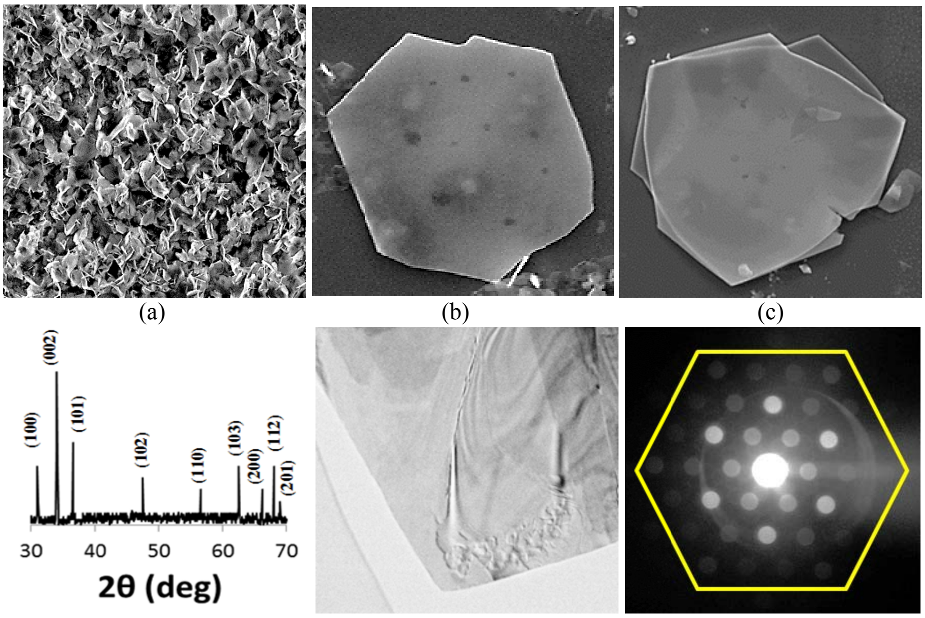
Used reagents in the growth process to produce 2D ZnO nanostructures are analytical grade. The growth solution consists of 100 mM $ZnSO_4$ and 100 mM hexamethylenetetramine (HMTA), which was heated to 75 °C in an oven for 3h. Next, the solution containing the 2D ZnO nanostructure was spin cast onto a substrate with pre-patterned Au electrodes. The substrate was then dried on a hotplate at 0 °C for 2 h for further characterization.

The morphological and structural characterizations of the grown nanostructures are carried out by applying Philips XL-20 scanning electron microscope (SEM) at 10 kV. The grown structures are also analyzed through powder X-ray diffraction (XRD) using a Panalytical X-pert diffractometer with Cu Kα radiation. Scanning transmission electron microscopy (STEM) and electron diffraction characterizations are applied using a Hitachi HD2300A microscope operating at 200 kV. The electrical characteristics of the fabricated sensor are analyzed using a probe-station attached to Keithley 4200 semiconductor analyzer. The excitation source for the UV sensing properties was a UV lamp (UVGL-55 Hand Lamp from UVP LLC) with 50 $\mu W/cm^2$ intensity at a wavelength of 365 nm.

3. Results and Discussion

3.1 Morphology and Structure

An SEM image of a film of spin cast ZnO nanostructures and a single 2D ZnO nanostructure grown at 75 °C for 3h are presented in Figs. 1a and 1b. These nanostructures are very thin as one can see in the SEM images of Fig. 1 and in many cases the 2D ZnO nanostructures become stacked on the top of each other as depicted in Fig. 1c. Even though their thicknesses differ from one nanostructure to another, the thickness of each nanostructure is uniform.



(d) (e) (f)

Fig. 1 SEM images of (a) a film of 2D ZnO nanostructures, (b) single 2D ZnO nanostructure, (c) 2D nanostructures stacked on top of each other; (d) XRD pattern, (e) STEM image, and (f) the corresponding SAED pattern of a single2D ZnO nanostructure.

The high crystallinity of the 2D ZnO nanostructures is evident from the XRD pattern shown in Fig. 1(d). Each diffraction peak represents the ZnO hexagonal wurtzite-type. Moreover, we further validate the crystallinity of the produced 2D ZnO nanostructures by STEM imaging and electron diffraction. Fig. 1e represents an STEM image of a single 2D ZnO nanostructure. Despite the fact that the image does not cover all the top facet of the 2D nanostructure, we can see it is very transparent confirming its low thickness. The selected area electron diffraction pattern of a single 2D ZnO nanostructure recorded as the electron beam was normal to the top facet, accepted as the [0001] axis of the hexagonal ZnO lattice. This analysis confirms that the ZnO 2D nanostructure is single crystal and their exposed facets are the polar {0001} planes.

3.2 UV Sensing Properties of Single 2D Nanostructure

Figs. 2a and 2b show low and high magnification SEM image of a UV sensor that was fabricated based on a single 2D ZnO nanostructure. A schematic of the sensor is presented in Fig. 2c for more clarification.

The active area in this device is about 50 μm^2 while the thickness of the nanostructure is around 80 nm. The photosensitivity of the single 2D ZnO nanostructure UV sensor is about 980 as shown in Fig. 2d. The response time and recovery time are 19 and 25 s, respectively. The photocurrent of the sensor was measured to be 19.6 μA, while the dark one was 20 nA.

Fig. 3 presents the *I-V* curve of the single 2D ZnO nanostructure sensor, where its electrical behaviour seems to be asymmetrical and nonlinear [17]. The origin of this could be the difference between the two contacts of the ZnO nanostructure with the two electrodes. The UV sensing mechanism of the single 2D ZnO nanostructure sensor is depicted in Fig. 4. When the ZnO nanostructure are in dark and room temperature conditions, oxygen molecules (O_2) are adsorbed on the surface of the ZnO nanostructure and become negative ions (O_2^-) seizing electrons from the conduction band of ZnO [4,6]. Subsequently, this builds a depletion layer close to the surface (Fig. 4).

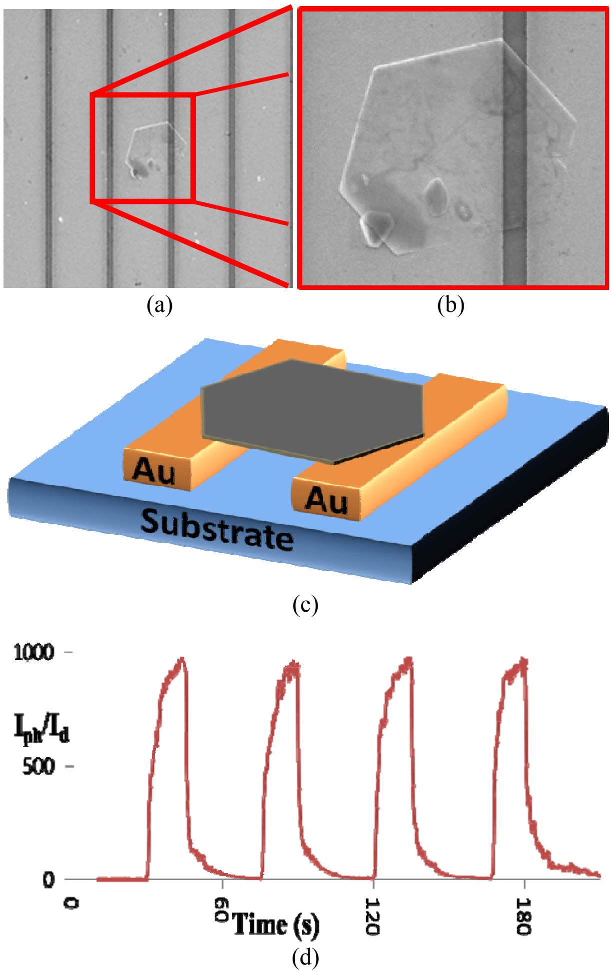


Fig. 2 (a) Low, (b) high magnification SEM image, (c) schematic, and (d) photoresponse characteristics of a single 2D ZnO nanostructure sensor.

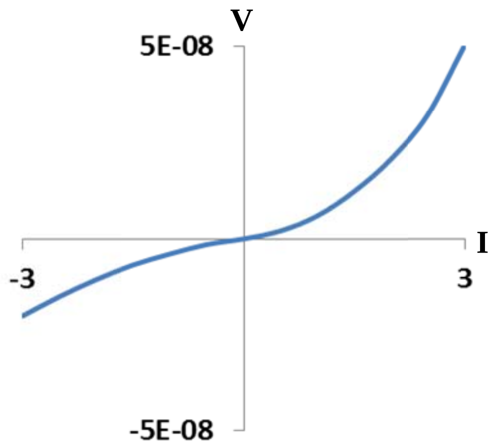


Fig. 3 *I-V* curve characteristics of a single 2D ZnO nanostructure sensor in dark conditions.

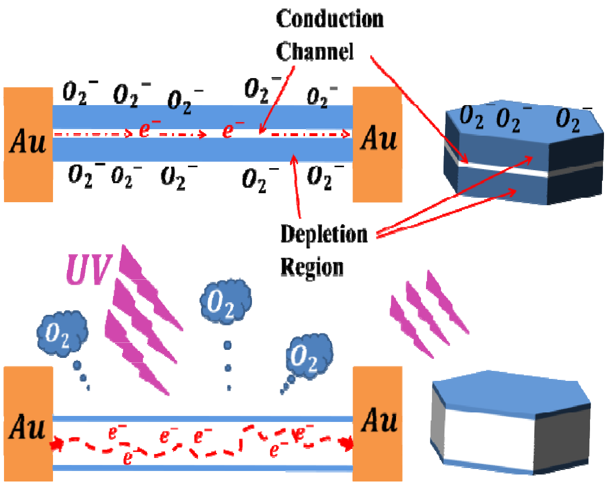


Fig. 4 Schematic illustration of the UV sensing mechanism in the single 2D ZnO nanostructure under UV irradiation and dark conditions.

Upon UV illumination, electron-hole pairs are photo generated lowering the thickness of the depletion layer and increasing the number of free electrons in the ZnO SNWs as shown in Fig. 4. After turning the UV light off, oxygen molecules are readsorbed again on the surface of the ZnO nanostructure decreasing its conductivity. The charge transport in this single 2D ZnO nanostructure sensor is controlled by the surface oxygen exchange process [4, 6].

4. Conclusions

In conclusion, a low temperature hydrothermal method to prepare 2D ZnO nanostructures was presented. Single 2D ZnO nanostructures based UV sensors were fabricated and tested under ambient conditions. The single 2D ZnO nanostructure showed a high photosensitivity of 980 and speed of response and speed of recovery of 15 and 25 s, respectively. The high performance of this sensor is attributed to the high quality of the grown nanostructures, high surface to volume ratio and reduced dimensionality. This work represents a cost effective technique to produce ZnO UV sensors.

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