

Synthesis of ZnO Nanosheets by Using PECVD at Low Temperatures

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ABSTRACT

A simple method for fabricating ZnO nanosheets at low temperatures via PECVD is presented. The fabrication was carried out by exposing Zn nanosheets to oxygen chemical vapors at temperatures below 380°C. ZnO nanosheets with well-defined crystallinity were found to be formed above at 280°C. The morphological and optical properties of the ZnO nanosheets grown at 380°C were characterized by using SEM, TEM, Raman, XRD and PL measurements. The resulting ZnO nanosheets were shown to have a wurtzite hexagonal structure. The Raman shift and PL peaks located near 275 cm⁻¹ and 370 nm, respectively, were also found, showing that nitrogen is incorporated into the nanosheets. It is suggested that the growth of ZnO nanosheets is achieved via a self-catalyzed vapor-solid mechanism.

Keywords: zinc oxide nanosheets, oxygen vapors, self-catalyzed vapor-solid mechanism

1 INTRODUCTION

Zinc oxide (ZnO) has various favorable properties, including good transparency, high electron mobility, wide bandgap, and strong blue luminescence at room temperature. As a consequence, these properties allow ZnO to be produced in a wide variety of nanostructures, such as nanoparticles [1, 2], nanowires [3, 4], nanobelts [5, 6], nanosheets [7, 8, 9], and nanorods [10, 11]. A variety of techniques have been employed for the growth of ZnO nanostructures: solution-[12, 13] and gas-based synthesis [14, 15]. The former is generally carried out below 300 °C, but requires several processing steps. Whereas, the latter uses gaseous environments in closed chambers and is carried out at high temperatures ranging from 500 °C to 1500 °C, requiring special substrates.

In this work we demonstrate a simple method for fabricating ZnO nanosheets on arbitrary substrates at low temperatures below 380 °C. The method was based on simply exposing Zn nanosheets to oxygen chemical vapors produced by PECVD using N₂O as a gas source. The

resulting ZnO nanosheets were found to have a wurtzite hexagonal structure with lattice constants of $a = 0.3250$ nm and $c = 0.5211$ nm. The vapor-solid mechanism self-catalyzed by Zn is proposed for the growth of ZnO nanosheets.

2 EXPERIMENTAL

ZnO nanosheets were fabricated by exposing Zn film composed of Zn nanosheets to oxygen chemical vapors produced by using a conventional plasma-enhanced chemical vapor deposition (PECVD) reactor with capacitively coupled two electrodes. Zn film of ~250 nm in thickness composed of Zn nanosheets (~16 nm thickness) was formed onto (100)-oriented *p*-type silicon wafer (0.4 Ω-cm ~ 0.9 Ω-cm) and glass (Corning 7059) substrates by a conventional thermal evaporation method. The substrates coated with Zn nanosheets were then placed on the bottom electrode, which is grounded and placed at a 20 mm distance from the top electrode, and were subsequently exposed to oxygen chemical vapors generated between two electrodes with N₂O gas for 30 min. The substrate temperature was varied from 240 °C to 380 °C. The morphologies of ZnO nanosheets were analyzed by using a field-emission scanning electron microscope (SEM) and a field-emission transmission electron microscope (TEM). X-ray diffraction (XRD) spectroscopy was performed for phase analysis. The optical properties were characterized by using Raman and photoluminescence (PL) spectroscopy. The PL spectra were measured using the 325 nm line of a He-Cd laser as the excitation source at room temperature under vacuum. Emitted light was measured by using a photomultiplier tube (PMT: R928, Hamamatsu).

3 RESULTS AND DISCUSSION

Fig. 1(a) shows SEM image of Zn film as-evaporated onto Si substrate. The image clearly shows that the film is composed of numerous thin nanosheets in hexagonal shape. XRD analysis (Fig. 2(a)) shows that the phase of the nanosheets is pure Zn crystal. Figs. 1(b), 1(c) and 1(d) represent SEM images of Zn nanosheet-coated Si substrates

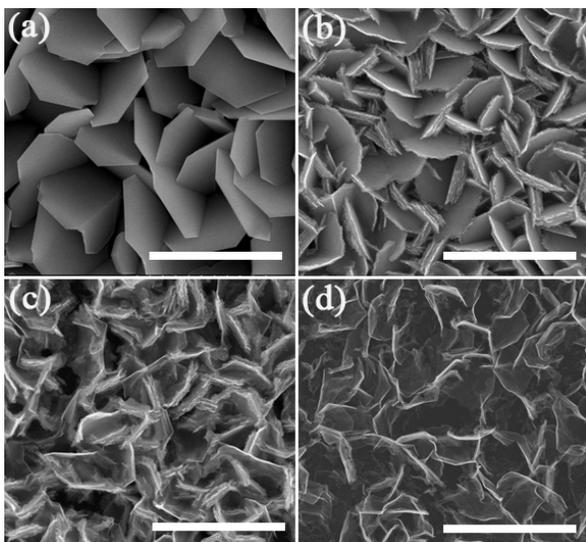


Figure 1. SEM images of Zn-coated Si samples. (a) As-deposited and after exposing to oxygen vapors at (b) 240, (c) 280, and (d) 380 °C for 30 min. The scale bars denote 2 μm.

after exposing to oxygen chemical vapors at 240 °C, 280 °C, and 380 °C for 30 min, respectively. The images show that the edge of Zn nanosheets gets whiter, and that their thickness is getting thinner as the vapor-exposing temperature is increased. However, it is shown that the hexagonal shape remains nearly unchanged. The mean thickness of the sheets was estimated to be about 6 nm after exposing at 380 °C. These features were also observed for the Zn-coated glass substrates.

To make exact phase identification of the nanosheets achieved by the present method, XRD analysis was performed on the products shown in Fig. 1. Fig. 2(a) shows XRD patterns obtained from the as-deposited Zn film together the diffraction patterns of hexagonal Zn (ICDD card no. 01-071-4620). Fig. 2(b) represents XRD patterns of Zn-coated samples after exposing to the oxygen vapors at 240 °C, 280 °C, and 380 °C for 30 min together the diffraction patterns of ZnO crystal (ICDD card no. 01-075-0576). The XRD peaks of as-deposited Zn film are well in agreement with those of Zn crystal, indicating that the Zn nanosheets shown in Fig. 1(a) are crystalline hexagonal structure. On the other hand, it is shown that the XRD pattern of the oxygen vapor-exposed Zn films is dependent on the vapor-exposure temperature. In the case of exposure at 240 °C, the small peaks associated with ZnO crystal appears besides Zn-related peaks, suggesting the partial formation of ZnO crystal. For the Zn film exposed at 280 °C, however, the Zn-related peaks disappear, accompanied with an increase in the ZnO-related peak intensities, which

further increase when the Zn film is exposed at 380 °C. These results suggest that the formation of ZnO nanosheets can be completed at temperatures higher than 280 °C with the present experimental conditions. Using the XRD peaks of the ZnO nanosheets formed at 380 °C, the hexagonal lattice parameters of the ZnO nanosheets were calculated. These parameters are $a = 3.250 \text{ \AA}$ and $c = 5.211 \text{ \AA}$, which is in good agreement with those of ICDD No. 01-075-0576 ($a = 3.243 \text{ \AA}$, $c = 5.195 \text{ \AA}$), further confirming that the nanosheets have hexagonal crystal structure.

The crystal structure of the nanosheets was further analyzed by TEM studies using the nanosheets grown at 380 °C. Fig 3 shows the HRTEM image and its fast Fourier Transform (FFT) pattern (inset). Electron beam was

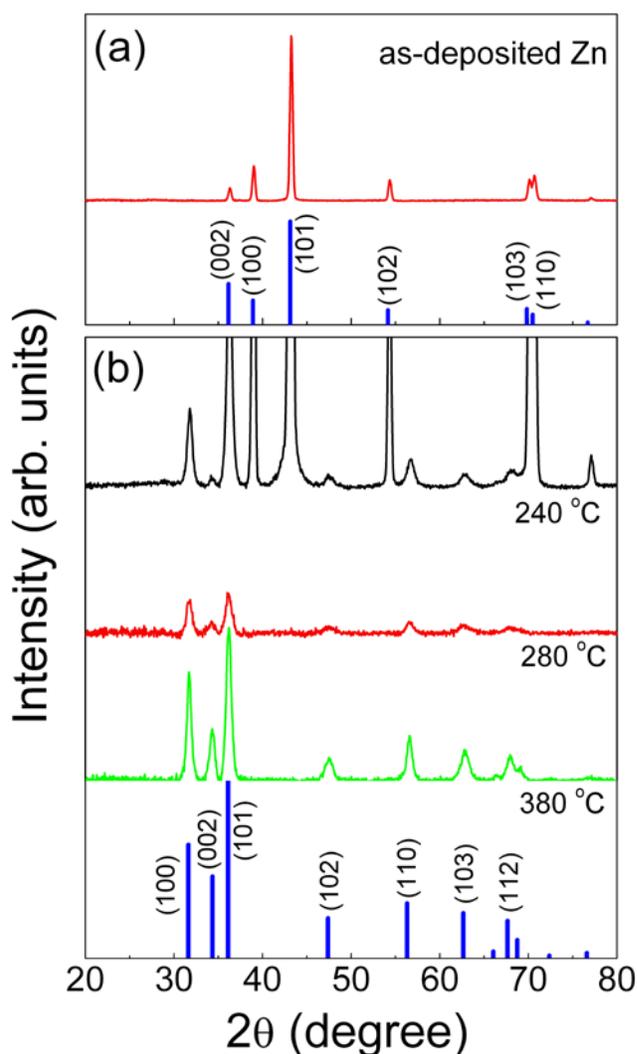


Figure 2. XRD spectra of Zn films (a) as-deposited and after exposing to oxygen vapors at (b) 240, 280, and 380 °C for 30 min.

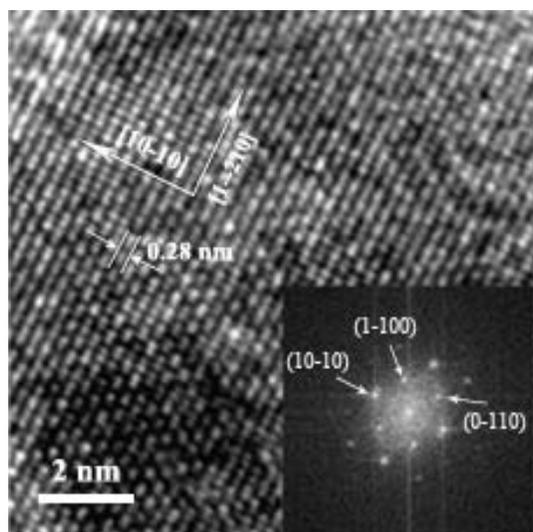


Figure 3. HRTEM and FFT (inset) images of the nanosheet grown at 380 °C. The electron beam is incident along [0001] direction.

irradiated along the [0001] zone axis, perpendicular to the wide surface of the sheet. The image clearly reveals a hexagonal lattice structure characteristic of (0001) lattice plane of hexagonal ZnO crystal. The measured lattice spacing of 0.28 nm corresponds to the (10-10) planes of wurtzite ZnO. The FFT pattern recorded over the same position of the ZnO sheet also reveals the (10-10) orientation of the sheet. Furthermore, it is clearly shown that the lattices geometrically form a hexagonal structure, demonstrating that the ZnO nanosheet has a hexagonal shape bounded by $\pm(10-10)$, $\pm(01-10)$ and $\pm(-1100)$ planes.

Finally, the optical properties of the nanosheets were analyzed by using Raman and PL measurements. Fig. 4(a) represents the Raman spectrum of the nanosheets grown onto glass at 380 °C. The spectrum shows five peaks: two intense peaks near 275 cm^{-1} and 583 cm^{-1} , and three small peaks near 436, 510 cm^{-1} , and 645 cm^{-1} . Two Raman lines at 436 and 583 cm^{-1} are due to the E_2 high frequency (E_{2H}) and longitudinal optical (LO) modes, which are typical peaks observed in the wurtzite crystal structure of ZnO [16]. Other peaks (275 cm^{-1} , 510 cm^{-1} , and 645 cm^{-1}) are closely associated with N-related vibration modes [17]. The present ZnO nanosheets were formed by using N_2O as a source gas. As a result, it is possible that N atoms may be incorporated into the ZnO structure, resulting in N-related Raman peaks. Fig. 4(b) presents the PL spectrum of the nanosheets grown at 380 °C as measured at room temperature. The spectrum clearly exhibit two distinct peaks; one is centered at near 380 nm (UV) and the other is centered at near 500 nm (Green).

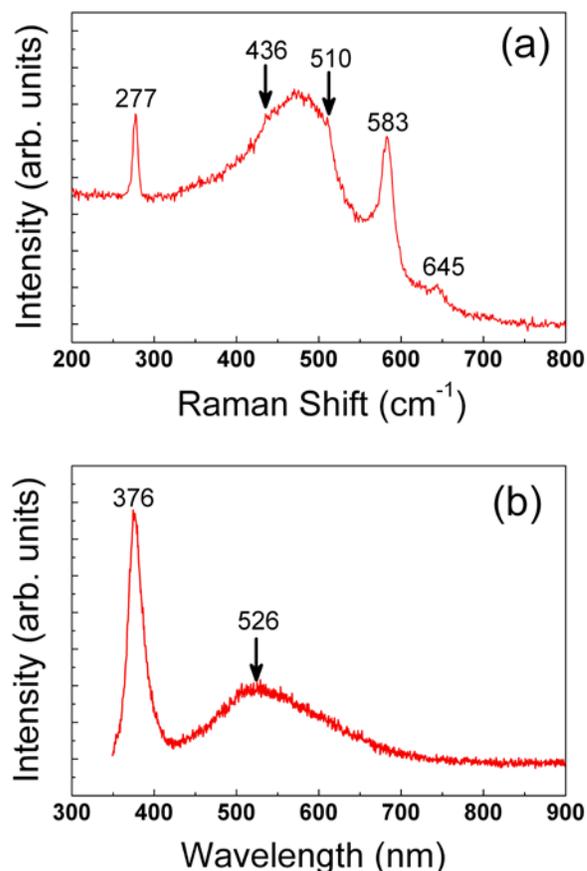


Figure 4. (a) Raman and (b) PL spectrum taken on the ZnO nanosheets grown at 380°C. The spectra were measured at room temperature.

It is well known that the UV emission is attributed to the band gap or excitonic emission [18], whilst the green emission is due to the singly ionized oxygen vacancy or other defects in ZnO [19]. Thus the UV intensity near 380 nm is much stronger than that near 500 nm, indicating well-crystallized ZnO nanosheets with a low concentration of oxygen vacancies.

The gas-based growth of ZnO nanostructures is generally believed to proceed via a vapor-liquid-solid (VLS) [14] or vapor-solid (VS) [15] growth mechanism depending on the catalyst employed. A typical evidence for VLS mechanism is the existence of liquid droplets which serve as the catalytic active site. In the present case, however, no such evidence was found, as shown in Fig. 1, demonstrating that the nanosheet growth is unlikely to be governed by the VLS process. In the general VS growth, on the other hand, ZnO nanostructures, even depending on temperature, pressure, atmosphere, and substrate, etc., were popularly achieved by a vaporization of ZnO at high temperatures over 1000 °C and subsequent vapor transport and condensation at low temperatures. However, the

present results have two particular features contrary to the VS mechanism. One is that there are no nanosheets outside Zn film, ruling out vapor transport and condensation process, and the other is that the hexagonal shape of the ZnO nanosheets is almost the same as the Zn nanosheets composed of Zn film as shown in Fig. 1(a). Of particular relevance to the present ZnO nanosheets may be the alternatives based on the VS process reported by Hu *et al.*[7] and Wang *et al.*[20]. Hu *et al.* obtained thin ZnO nanosheets from Zn nanosheets by annealing them at a temperature of 350 °C in air. They demonstrated that the formation of ZnO nanosheets might be achieved by the oxidation of Zn nanosheets. Wang *et al.* showed that ZnO nanocantilever arrays were grown from the (0001)-Zn surface, suggesting that Zn can act as the self-catalyst in the formation of ZnO. The growth of ZnO nanosheets by the present method is likely to be proceeded via a Zn-catalyzed VS mechanism. Initially, the ZnO formation via a reaction, $2\text{Zn} + \text{O} \rightarrow \text{ZnO}$, occurs at the six-sides of hexagonal Zn nanosheets where available Zn atoms for the reaction are most abundant, apparently shown in Figs. 1(b) and (c). During further process, the reaction occurs at the surface of Zn nanosheets, enlarging the ZnO area, and finally followed by a complete formation of ZnO nanosheets.

4 SUMMARY

In conclusion, ZnO nanosheets were synthesized by simply exposing Zn nanosheets formed onto arbitrary substrates to oxygen chemical vapors produced by PECVD using N_2O gas at low temperatures. The well-defined crystalline nanosheets were found to be formed at temperatures above 280 °C. The formation of the nanosheets is suggested to be likely due to the reaction between Zn sheets and oxygen vapors via self-catalyzed process.

Acknowledgement This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant Number: 2010-0021320).

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