



# The shift of optical band gap in W-doped ZnO with oxygen pressure and doping level



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## ABSTRACT

Tungsten-doped (W-doped) zinc oxide (ZnO) nanostructures were synthesized on quartz substrates by pulsed laser and hot filament chemical vapor co-deposition technique under different oxygen pressures and doping levels. We studied in detail the morphological, structural and optical properties of W-doped ZnO by SEM, XPS, Raman scattering, and optical transmission spectra. A close correlation among the oxygen pressure, morphology, W concentrations and the variation of band gaps were investigated. XPS and Raman measurements show that the sample grown under the oxygen pressure of 2.7 Pa has the maximum tungsten concentration and best crystalline structure, which induces the redshift of the optical band gap. The effect of W concentration on the change of morphology and shift of optical band gap was also studied for the samples grown under the fixed oxygen pressure of 2.7 Pa.

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## 1. Introduction

Zinc oxide (ZnO) nanomaterials are promising candidates for nanoelectronic and nanophotonics, due to its direct wide band gap (3.37 eV), excellent chemical and thermal stability, and its specific photonic and opto-electronic property with a large exciton binding energy (60 meV) [1]. During the past several years, various methods have been employed to prepare ZnO films such as chemical vapor deposition (CVD) [2], magnetron sputtering [3], sol-gel process [4], atomic layer deposition [5], spray pyrolysis [6], molecular beam epitaxy (MBE) [7], and pulsed laser deposition (PLD) [8]. Among those techniques, CVD gives rise to high quality films and is applicable to large-scale production and PLD technique is permitting high quality film grow at low substrate temperature [9].

The properties of ZnO highly rely on deposition parameters, dopants [10] and post-deposition treatments [11]. For example, properties of ZnO can be enhanced by doping with Li, Al, Cu, Mn, and Co. However, there are scanty reports on the optical properties of tungsten (W) doped ZnO. The optical properties of ZnO thin films are important because of their potential applications in electro-optic devices. The existing literatures reveal that the band-gap shifts have been attributed to factors such as the grain size effect, stress, defect and the amorphous nature of the films.

The aims of the present study are to improve the information on ZnO by preparing thin films of W-doped ZnO on quartz substrates using pulsed laser and hot filament chemical vapor co-deposition technique and study their morphological, structural and optical properties. The dependence of the morphological, structural and optical properties of the grown films on oxygen pressure and W doping levels was also investigated.

## 2. Experimental

The synthesis process involves two techniques including PLD and hot filament chemical vapor deposition (HFCVD) in the same chamber. Quartz substrates were placed into a bowl-like substrate holder, where tungsten coil was used as a heater placed at the backside of the substrates (Fig. 1). The chamber was pumped down to  $2.7 \times 10^{-3}$  Pa. Then, oxygen gas was introduced into the chamber and the pressure was kept at 1.1, 2.7, and 6.5 Pa during the deposition, respectively. An ArF Lambda Physik 1000 excimer laser (193 nm, ~20–30 ns, and 10 Hz repetition rate, and 30 mJ pulse energy) was used to irradiate the commercial ZnO target (99.99%). The distance between the target and the substrate was 3 cm and the duration of each deposition was 30 min. The substrate temperature remained at 400 °C. During the depositions, the tungsten reacted with oxygen yielding tungsten oxide that vaporized and partially spread to the whole surface of substrate, finally formed the W-doped ZnO nanostructures. The morphology of the W-doped ZnO nanostructures was characterized by scanning electron microscopy (SEM). The chemical bonds were examined

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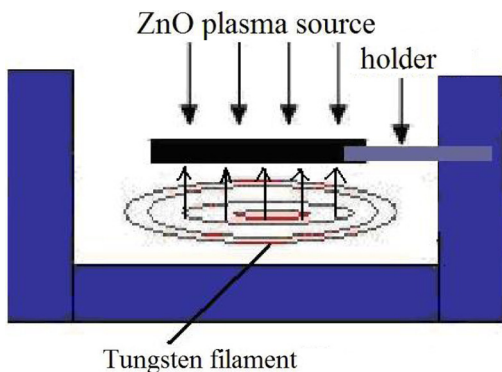


Fig. 1. Schematic of setup to synthesize W-doped ZnO nanostructures.

using X-ray photoelectron spectroscopy (XPS) with an MgK $\alpha$  X-ray source. Room temperature micro Raman scattering was performed using a Jobin-Yvon T64000 Triple-mate system with excitation at 514.5 nm by a coherent argon ion laser and a liquid nitrogen cooled CCD camera to collect and process the scattered data. The optical transmission spectra were recorded using an ultraviolet visible spectrometer (PerkinElmer model RS-2).

### 3. Discussion

W-doped ZnO nanostructures with different morphologies were synthesized by varying the oxygen pressures during depositions as shown in Fig. 2. At oxygen pressure of 1.1 Pa, nanopores structure (Fig. 2(a)) was formed. When increasing the oxygen pressure up to 2.7 Pa, the formation of nanorod arrays (Fig. 2(b)) on quartz substrates was observed. As we keep increasing the oxygen pressure up to 6.5 Pa, the nanoparticles (Fig. 2(c)) were formed. The great differences in morphologies when varying the oxygen pressures may result from the different kinetic and thermal energies of ions ( $\text{Zn}^{2+}$ ,  $\text{O}^{2-}$ ). High pressure of oxygen may enhance the collisions between the oxygen molecules and vaporized materials, and lead to the loss of kinetic and thermal energy of ions, which causes different formations of nanostructures on quartz substrates.

Fig. 3 shows the full XPS spectrum of the three samples. The concentrations of W in at.% are found approximately to be 0.5%, 1.5%, and 0.5% under oxygen pressure of 1.1, 2.7 and 6.5 Pa, respectively. The reaction rate of  $\text{O}_2$  and W increases with the oxygen pressure, but the produced vapor is partially blocked by the dense oxygen molecules. Therefore, the W concentration of the W-doped ZnO reaches the highest value (1.5%) at a certain oxygen pressure (2.7 Pa). The detected peaks of C 1s and N 1s are due to contaminants. All the O 1s state peaks at 531.7 eV can be due to the O–Zn bond formation, which is attributed to  $\text{O}^{2-}$  ions on the wurtzite structure of a hexagonal  $\text{Zn}^{2+}$  ion array [12], surrounded by the substitution of W atoms [13]. Fig. 3 shows that the Zn 2p $_{3/2}$

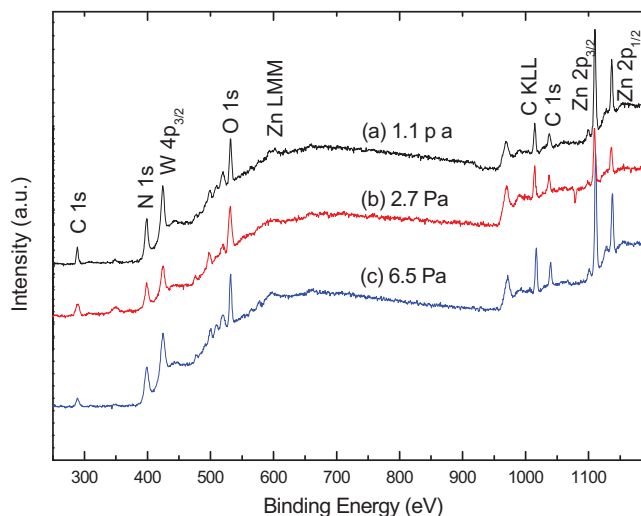


Fig. 3. XPS of W-doped ZnO nanostructures grown under different oxygen pressures.

peak for ZnO nanostructures is located at 1016.8 eV, which are lower than that of the host material ZnO (1021.4 eV) [14]. The decrease in the binding energy may be due to the decrease in the surface energy of the W-doped ZnO nanostructures. No metallic Zn with a binding energy of 1021.50 eV [15] was observed, which confirms that Zn exists only in the oxidized state.

Micro-Raman measurements have been carried out for W-doped ZnO samples and results are shown in Fig. 4. The peak at  $491\text{ cm}^{-1}$  is from quartz substrate. Three optical modes of ZnO at  $99.58$ ,  $438.09$ , and  $579.64\text{ cm}^{-1}$  corresponds to  $E_2^{\text{low}}$ ,  $E_2^{\text{high}}$ , and  $E_1$  (LO), respectively for ZnO nanoholes grown at oxygen pressure of 1.1 Pa, which is indicative of the ZnO wurtzite crystal structure. The bands marked with  $K_1$  and  $K_2$  at  $275.08\text{ cm}^{-1}$  and  $808.44\text{ cm}^{-1}$  are related to tungsten oxide [16].

Those peaks are still visible when the oxygen pressure increases up to 2.7 Pa but  $E_2^{\text{low}}$  and  $E_2^{\text{high}}$  peaks become sharp. To further increase oxygen pressure up to 6.5 Pa,  $E_2^{\text{low}}$  and  $E_2^{\text{high}}$  peaks become weak and broad. Experimental data above indicate the better crystalline structure of ZnO can be obtained at the oxygen pressure of 2.7 Pa. Structural degradation is observed when the oxygen pressure increases to 6.5 Pa. For the samples grown under 1.1 and 6.5 Pa which have the same W concentration (0.5 at.%), the latter has worse crystallinity than that of the former. The result that overhigh oxygen pressure induces poor crystallinity is also observed by Bylsma et al. [17].

To compare the transmitting property of W-doped and pure ZnO, additional sample was synthesized under vacuum where a metal hat was used to cover tungsten filament in order to isolate tungsten oxide on to the surface of substrate but otherwise identical growth conditions. The optical transmission spectra of

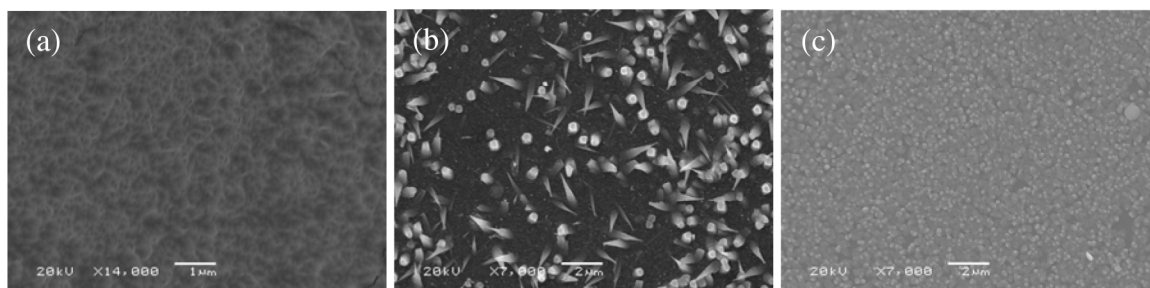


Fig. 2. SEM images of W-doped ZnO nanostructures grown under oxygen pressure of (a) 1.1, (b) 2.7, and (c) 6.5 Pa.

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