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Temperature-dependent growth mode of W-doped ZnO nanostructures

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ABSTRACT

We report on the effects of glass substrate temperature on the crystal structure and morphology of tungsten (W)-doped ZnO nanostructures synthesized by pulsed-laser deposition. X-ray diffraction analysis data shows that the W-doped ZnO thin films exhibit a strongly preferred orientation along a *c*-axis (000*L*) plane, while scanning electron and atomic force microscopes reveal that well-aligned W-doped ZnO nanorods with unique shape were directly and successfully synthesized at substrate temperature of 550 °C and 600 °C without any underlying catalyst or template. Possible growth mechanism of these nanorods is suggested and discussed.

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1. Introduction

The Assembly of nanostructures into the well ordered architectures has attracted wide interest lately because of their ability as building blocks for future optoelectronics and systems [1]. ZnO nanomaterials are promising candidates for nanoelectronic and nanophotonics, due to ZnO direct wide band gap (3.37 eV), excellent chemical and thermal stability, and its specific photonic and optoelectronic property with a large exciton binding energy (60 meV) [2].

The catalyst driven growth of ZnO nanorods using MBE or vapour transport have been demonstrated by many groups [3] and aligned growth of ZnO nanorods has been successfully achieved on a solid substrate via a vapour–liquid–solid (VLS) process, with the use of gold [4,5] and tin [6] as catalysts, in which the catalyst initiates and guides the growth. Other techniques that do not use any catalyst, such as metalorganic vapor-phase epitaxial growth [7] template-assisted growth [8] and electrical field alignment [9]

for vertically aligned ZnO nanorods motivated us to grow our films without any use of catalyst on glass substrate.

This work reports on the synthesis of well oriented W-doped ZnO nanorods at substrate temperature of 550 and 600 °C by pulsed laser deposition on soda lime glass substrate without any catalyst. Our experimental results suggested that, the nanorods growth is due to nucleation of the substrate around its transition temperature of 575 °C followed by a surface crystallization mechanism.

2. Experimental details

The films were deposited on the substrate held at temperatures ranging from 550 to 700 °C at deposition time of 30 min. An excimer laser, wavelength of 248 nm, fluence of 2.7 J/cm², repetition rate of 10 Hz, was incident on target of ZnO containing 1 wt% of WO₃. The substrates–target distance was kept at 30 mm. The deposition was carried out in an oxygen atmosphere at a pressure of 3 × 10^{−1} mbar. X-ray diffraction (XRD) patterns using an AXS Bruker diffractometer equipped with a position sensitive detector determined the crystalline structure. The surface morphology was characterized via scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surface chemical analysis was investigated by X-ray photoelectron spectroscopy (XPS) on a VG-ESCALAB

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MKII equipped with a dual X-ray source (Mg/Al) and an ion gun (Type EXO5). We have used the aluminum anode ($K\alpha$, 1486.6 eV). The energy resolution of the spectrometer was about 1 eV at pass energy 20 eV. All normal XPS spectra were calibrated by the C 1s peak from contamination. The photoluminescence (PL) measurements were conducted on a Hitachi F-4500 ultraviolet–visible spectrophotometer with a Xe lamp as the excitation light source at room temperature. The excitation wavelength was 325 nm.

3. Results and discussions

Fig. 1 shows the X-ray diffraction patterns of the W-doped ZnO thin films grown with different substrate temperatures. The observation of (000 L) peaks indicates that the films have grown preferentially along the c -axis orientation. “ c ” lattice parameter from a least square fit to the peak positions of the 0002 and 0004 Bragg reflections including the 2θ offset, was estimated to be 5.2074 ± 0.0036 , 5.2084 ± 0.0036 , 5.1957 ± 0.0040 and 5.1998 ± 0.0036 for substrate temperatures of 550 °C, 600 °C, 650 °C and 700 °C respectively compared to bulk ZnO value of 5.2066 Å (JCPDS card No. 36-1451). We observe that for temperatures of 550 and 600 °C the lattice constant is quite similar to the ZnO bulk value which suggest that at this temperature range W is forming interstitial impurity, while at high temperatures the lattice constant decreases which would mean that W is now a substitutional

Fig. 1. XRD of W-doped ZnO thin films with substrate temperatures shown in the figure.

Fig. 2. SEM and AFM images of the films deposited at 550 °C (a and b), 600 °C (c and d) and 700 °C (e and f) substrate temperatures respectively.

Fig. 2. (Continued)

impurity given the fact that the radius of W^{6+} (0.062 nm) is smaller than that of Zn^{2+} (0.074 nm).

Fig. 2 shows SEM and AFM images of the W-doped ZnO thin films grown at substrate temperature of 550 (a and b) 600 (c and d) 650 (e and f) and 650 °C (g and h) respectively. The films grown at glass substrate temperature of 550 and 600 °C show well oriented nanorods like structure while the films grown at higher temper-

atures the rodlike structure disappears into granular morphology with large uniform grains on the entire substrate with the surface roughness decreasing from 20.8 ± 1.2 nm at 550 to 17.6 ± 0.9 nm at 700 °C respectively.

This variation of the surface morphology of the W-doped zinc oxide nanostructures with substrate temperature may be due to the nucleation of the glass substrate which happens around 575 °C [10]

Fig. 3. XPS of W-doped ZnO thin films. (a) Zn 2p, (b) O 1s and (c) W 4f (d) W and their Gaussian-resolved components.

Fig. 3. (Continued)

and followed by the process of crystallization of the W-ZnO. This observed well oriented nano-structures at these two temperatures could be due to the ad-atom mobility with the energy supplied via substrate heating and the nucleus formed at the substrate surface at the deposition substrates temperatures of 550 and 600 °C $\pm$ 25 °C of the transition glass substrate temperature, the nanoparticles which resulted in the condensation in the gas phase [11,12], fuse together to form the small seeds. These seeds then form the centres for the rod growth. These nanosized particles then coagulate with each other due to the presence of sufficient thermal energy to form rods and microcrystalline structures. The morphology and the direction of these nanorods indicate that the surface crystallization starts off in a preferential direction. These results agree with the results

obtained by the thermo-analytical study, in which, by the Ozawa method it was obtained that the crystallization mechanism is of surface type [13,14]. This reported behavior is the same phenomena that lead to our reported films morphology and this is also supported by the XRD results.

The tungsten incorporation into ZnO at growth substrate temperatures of 550 and 600 °C, seem to be also playing a major role in the orientation growth of these rods. The tungsten within this temperature range seems to be acting as a catalyst instead of a substitution of Zinc as suggest by the results in the lattice parameter *c* and seem to guide the growth in well oriented nano-rods.

In order to support our argument above, the surface chemical analysis was investigated by XPS.

Fig. 3. (Continued)

The XPS is used to obtain chemical nature and composition from the material surface (3–5 nm in depth) with a detection limit of 1 at.%. Approximate surface composition ratio of Zn:W in at.% is found to be 10:2 for the samples grown at substrate temperature of 550 and 600 °C and 15:3 for the substrate temperature of 650 °C and equal to 34:3 from the films grown at 700 °C.

Fig. 3a, b, c and d gives the typical XPS data of Zn 2p, O 1s and W 4f respectively. In all cases, the binding energy of Zn 2p_{3/2} remains at 1022.7 eV, which confirms that the majority of Zn atoms remain, for all the films, in the same formal valence state of Zn²⁺ [15].

The asymmetric O 1s peak (Fig. 3b) in the surface was coherently fitted by four nearly Gaussian components, centered at 530.4 eV and 530.5 eV, 531.8 eV and 532.9 eV, for the sample grown at 550

and 600 °C, with an additional nearly Gaussian component, centered at 531 eV, for the samples grown above 600 °C substrate temperature, as shown in Fig. 3b. The 530.4 eV peak is attributed to the O²⁻ ions on the wurtzite structure of the hexagonal Zn²⁺ ion array [16].

Fig. 3b apparently includes two functions centered at 530.4 eV and 530.5 eV, with their small energy, it is difficult to separate this two with fitting. These functions cannot be distinguished in the figures.

Free oxide surfaces contacting with the atmosphere are always hydrated, i.e. contain water molecules and hydroxyl groups. There are two types of OH-groups on the surface: single M–OH and double OH–M–OH [17], OH-groups (EpO1s = 531.1 eV) [16–18] and groups

Fig. 4. Room temperature photoluminescence spectra of W-ZnO thin films different substrate temperature.

C=O ($E_{\text{pO1s}} = 531.2$ eV), C–O–C, C–O–H ($E_{\text{pO1s}} = 532.5$ – 532.8 eV) [19] are present on the surface of the films, thus the structures of grown samples (Fig. 3b) are very complex. The presence of C=O, C–O–C, C–O–H groups may be caused by oxidation–reduction and acid–base transitions of CO_2 on catalytically active oxide surface.

Therefore the higher binding energy at 532.9 eV is attributed to chemisorbed or dissociated oxygen or OH species on the surface of the ZnO thin film, such as $-\text{CO}_3$, adsorbed H_2O or adsorbed O_2 . The component at the binding energy 531.8 eV is associated with O^{2-} ions that are in oxygen-deficient regions [16–18]. This additional peak centered at 531.8 eV found on the sample grown at substrate temperature above 600°C , can be attributed to O^{2-} ions on wurtzite structure of hexagonal Zn^{2+} ion array, surrounded by the substitution of W atoms as suggested by the XRD results.

At a substrate temperature of 700°C the most intense peak of the O 1s level correspond to the O^{2-} ions on the wurtzite structure of the hexagonal Zn^{2+} ion array, while for the sample grown at 600°C the maxima belong to weakly adsorbed species and O – oxygen states [16–18,20]. This could mean that the surface of the films for the sample grown at 600°C are mostly terminated by WO_x and/or ZnO_x intermediate oxides that lead to the catalytic growth of the nanorods.

The asymmetric W 4f 7/2 peak in the surface was coherently fitted by four nearly Gaussian components, centered at 35.3–35.7 eV, 36.4–36.9 eV for the samples grown at substrate temperature of 700°C (Fig. 3c), while for the sample grown at 600°C there is only one component centered at 36.65 eV as shown in Fig. 3c. The peak centered at 35.3 eV and 35.7 eV correspond to W 4f 7/2-levels of tungsten atoms for W^{6+} – oxidation states [21] and hydroxide for W 4f 7/2 = 36.4–36.9 eV [21,22]. This component on the higher binding energy side of the W 4f 7/2 spectrum could be related to the formation of intermediate “ WO_x ” oxides that lead to the orientation of the nanorods which resulted in $\text{WO}_3 \cdot (\text{OH}_2)_n$ -phase formed after contact with air.

Fig. 4 shows the room temperature PL spectrum for W-doped ZnO nanostructures deposited on the soda lime glass substrate with different substrate temperature. The synthesized W-doped ZnO nanostructures exhibit at room temperature, four near-band-edge (NEB) UV and violet emissions located at 3.290, 3.243, 3.116 and 3.010–3.025 eV, with strong deep-level blue emissions at:

2.622, 2.71–2.78, 2.84–2.86, 2.881 and 2.918 eV and green emissions located at 2.29, 2.34–2.38 eV. The 3.243 eV peak is the phonon replicas which is linked to the emission observed at 3.29 eV in ZnO bulk and the nearband-edge emission at 3.110 eV should be assigned to the bound excitonic emission at neutral acceptors.

Sun et al. [23] had calculated the energy levels of the intrinsic defects in ZnO by applying full-potential linear muffin-tin orbital method. From the calculated defect levels, it can be seen that the violet peak centered at 415 nm (3.025 eV) was due to the Zn vacancies (V_{Zn}). The mechanism of deep-level emission is not clear yet, but it is suspected that structural defects, oxygen deficiencies, impurities [24,25], or oxygen interstitials created by excess oxygen are the main cause [26]. We believe that this can also originate from a higher surface-to-volume ratio for the thinner nanostructures, resulting in more surface and sub-surface oxygen vacancies [27]. Xu et al. [28] calculated the energy levels of the intrinsic defects in ZnO films using full-potential linear muffin-tin orbital method. The energy interval from the Zn interstitial level to the top of the valence bands is about 2.87 eV, consistent with the blue peak energy accompanied by the zero-phonon line at 2.8590 eV which is located at 2.84–2.86 eV in our data. So, the blue peak (2.84–2.86 eV) may come from the electron transition from the Zn interstitial level to the top of the valence bands [29] and the peaks at 2.622, 2.71–2.78 and 2.918 eV which we cannot find in the literature may be coming from the WO_x . The green emission at 2.29 eV is assigned to the electronic transition from the bottom of the conduction band to the interstitial oxygen (O level –2.28 eV), and donor–acceptor complexes [30]. It is generally accepted that the surface conditions play a crucial role in PL spectra of nano-material [31]. The green-yellow band emissions 2.34–2.38 eV are attributed to the radial recombination of a photon generated hole with an electron that belongs to a singly ionized oxygen vacancy in the surface and sub-surface lattices of ZnO materials [23] (dominant in bulk ZnO) and recombination at surface states (low-dimensional structures with reduced volume to surface ratio) [25,32]. The effect of the W-doping on the luminescence properties of the ZnO nanostructures have been reported and discussed in our previous work [27]. However the PL results show that the temperature plays an important role on the intensity of the deep level emission. The increase in intensity of the green band peaks at 2.34–2.38 eV for the samples deposited at 550°C and 650°C compared to intensity of those deposited at 600°C and 700°C , can be related to the structural point defects and small crystallites as suggested by the XRD. Increasing temperature from 650°C to 700°C , the intensity of the peak of the PL spectrum quickly decreases, which may be due to the small crystallites which coalesce together to form larger crystallites which improve the crystallinity of the films at 700°C [33]. The decrease in green emission when the temperature is beyond 650°C can also be related to the concentration of oxygen loosely bonded in the films which decrease due to the formation of WO_3 at very high temperature which lead to a quick decrease in the amount of intermediate “ WO_x ”. These results correlate very well with the XPS, XRD and AFM results.

4. Conclusion

We have demonstrated that the temperatures at which well oriented nanorods are observed are within $\pm 25^\circ\text{C}$ of the nucleation temperature of the soda lime glass substrate which is 575°C and that W at this temperature range is sitting at interstitial sites in the lattice. We therefore conclude that the arguments given above supported by our data suggest that nanorods like structure, happens with the nucleation of temperature of soda lime glass while their orientation is due to the surface crystallization and/or the incorporation of W. We have demonstrated the potential of PLD

technique to grow well-aligned nanorods, over a range of temperature on cheap soda lime glass, of a ZnO target containing 1 wt% of WO₃, in an oxygen atmosphere without underlying catalyst on the substrate or post-depositions treatments.

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