Passivation of defects in ZnO nanowires by SiO₂ sputtering deposition

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ABSTRACT

Passivation of native point defects in ZnO nanowires was successfully achieved by SiO₂ deposition. The ZnO nanowires were grown on sapphire by vapor-liquid-solid method and coated with SiO₂ through reactive sputtering deposition. The samples were post-annealed at different temperatures in Argon atmosphere. Photoluminescence measurements at room temperature and electron transmission microscopy were performed. The coated nanowires present a core-shell structure. A strong oxygen vacancies passivation were observed resulting in a drastic suppression on visible light emissions in favor of UV ones. On the other hand, annealing at increasingly higher temperatures favored the oxygen desorption and the increase of deep-level states.

KEYWORDS: Zinc oxide nanowires, SiO₂ matrix, photoluminescence, native point defects passivation.

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1. Introduction

Zinc Oxide (ZnO) is a transparent semiconductor with a direct band gap of about 3.37 eV [1]. Its large exciton binding energy (60 meV) makes it suitable for short-wavelength optoelectronics devices operating at room temperature. Many ZnO-based optical devices have been reported over the past years [1–3], among them UV light emitting diodes [2] and lasers [3]. Room temperature photoluminescence (PL) of ZnO usually presents two main emissions. The first, known as near-band-edge (NBE) emission, is observed in the near UV range and is related to the recombination of the electron-hole pair close to band-gap edge [4]. The second, known as deep level emission (DLE), is a broad band centered on 525 nm and mainly related to a variety of native point defects [4,5]. Past works report these defects as being predominately oxygen vacancies (V_O), zinc vacancies (V_{Zn}), interstitial oxygen (O_i) and interstitial zinc (Zn_i) [4,5]. In the case of nanostructured ZnO, such as nanowires (NWs), the higher surface to volume ratio increases the number of surface-related trap states, directly affecting the NBE emission. Previous studies report a boost of PL emission in the near UV for ZnO nanostructures synthesized by sol-gel technique embedded in dielectric matrices [6–8]. This effect is mainly correlated to the surface defect passivation. In this work we investigate the behavior of the PL emission peaks of ZnO NWs before and after covering them with silicon dioxide (SiO_2) using sputtering technique. In order to study the SiO_2 passivation mechanism, we perform thermal annealing under Argon atmosphere using different temperatures. Transmission Electron Microscopy (TEM) measurements and electron energy loss spectroscopy (EELS) confirm the presence of ZnO/ SiO_2 core-shell structure.

2. Experimental

ZnO nanowires were grown by vapor-liquid-solid (VLS) method using sapphire coated with Au film of about 2 nm as substrate and ZnO:graphite powder as source [9]. A gas mixture of purified Ar and O₂ (123 sccm and 14 sccm, respectively) flowed into the furnace under a pressure kept in 2 mbar during the growth. At the end of the process - set for 30 minutes – vertically aligned ZnO nanowires with about 50 nm diameter and 4 μm length are obtained [10] (Fig. 1(a)). The high-resolution TEM in Figure 1 (b) shows a typical defective nanowire surface.

Without removing the ZnO NWs from the sapphire substrate, a SiO₂ film was deposited by RF sputtering. It was used Ar plasma at 6.7 mTorr and 1 kW RF power supply to sputter from an 8 inch diameter SiO₂ target. Afterwards, the samples were annealed during 5 minutes under Ar atmosphere in a temperature range of 500 – 900°C. Photoluminescence (PL) spectra at room temperature were acquired using a Crylas CW 266 nm laser as an excitation source. The laser power was kept in 1 mW and the sample emission was collected by a CCD camera attached to a grating monochromator. A Zeiss Libra microscope operated at 120 kV, a FEI Tecnai F20 UT and Titan 80-300 machines operated at 200 and 300 kV characterized the structure of ZnO/SiO₂ system. In order to distinguish the chemical composition, we used high-angle annular dark field images (under STEM mode) combined with electron energy loss spectroscopy (EELS).

3. Results and discussion

Fig. 2 shows the TEM studies of the as-deposited ZnO NWs. Figure 2 (a) is a low magnification Bright Field-TEM micrograph showing an overview of the dispersed NWs walls covered by a thin SiO₂ layer (white arrow). High-Resolution image (Figure 2 (b)) confirms the presence of an approximately 10 nm thick SiO₂ layer. STEM images

(Figure 2 (c)) were obtained by scanning the electron beam across the sample and collecting the electrons scattered elastically at high angles using an annular dark field detector (ADF). Its contrast is mainly due to interactions with phonons (thermal diffuse scattering), resulting in incoherent imaging with chemical Z-contrast. Therefore, Figure 2 (c) clearly proves the compositional difference between the ZnO and the SiO₂ cap layer through the image contrast.

Figure 2 (d) and (e) show additional EELS analysis from the squared regions d and e, respectively. Both present an exponential background removed EELS spectrum after intensity normalization using the zero loss peak. EELS spectrum from the region (d) shows the characteristic Silicon L₂ and L₃ energy loss edges located respectively, at 104 and 149 eV together with the Oxygen K edge at 532 eV. EELS spectrum taken from the ZnO confirms the Zinc L₁ edge at 1200 eV and Zinc L₂ edge at 1050 eV together with the Oxygen K edge (blue). It is important to notice that in the spectrum taken from SiO₂ area it does not show any Zn related edge.

Fig. 3 (a) shows the PL spectrum of the as-grown ZnO NWs (black line) compared to the NWs after SiO₂ deposition (red circles). Both spectra were collected with identical experimental parameters. We observe the ZnO band-edge transition in the near UV – around 375nm - for both structures. However, this characteristic emission is about two times higher for the sample after the SiO₂ coating. In the case of as-grown sample, the high PL emission centered at the green region (525 nm) characterizes the transitions related to the presence of deep level defects. After SiO₂ deposition, this band dramatically decreases while the UV band increases, compared to the as grown nanowires, clearly indicating a surface defect passivation phenomena. This effect can easily be observed by the analysis of the I_{UV}/I_{Vis} ratio: the higher this ratio is, fewer

defects on the surface of the nanostructure are present [11]. For as-grown nanowires, I_{UV}/I_{Vis} ratio is around 0.46 while for the nanowires after the SiO_2 deposition it reaches 4.4, indicating an effective passivation of the native point defects on the ZnO surface. Oxygen vacancies are known to be responsible for green emission in ZnO nanostructures [4]. Our results suggest that oxygen reacts with the V_O on the NWs surface, passivating these defects during the SiO_2 film deposition. This leads to a decrease in PL emission for this band. On the other hand, the band centered at 1.9 eV did not decrease after the film deposition. Since this band is associated with interstitial oxygen sites [12], the SiO_2 deposition did not directly affect this transition levels.

Fu et al. suggested the passivation of the dangling bonds and O^{2-} ions in the surface reduces the trap density within the band gap and favors the radiative recombination in the near band edge, consequently, increasing the UV peak emission [7,13].

In order to investigate the effects of defect passivation, Fig. 3 (b) presents the PL spectra of the samples coated with SiO_2 for different annealing temperatures during 5 minutes. We observe that the amplitude of the near UV transition increases until it reaches its maximum at 700°C (blue triangles).

A possible explanation for this behavior is an improvement of the ZnO/ SiO_2 interface formation under high temperature. Since the Si-O bond strength is higher than Zn-O (4.80eV and 1.89eV, respectively), only after certain temperature the formation of the Zn-O-Si bond at the interface reaches a stable form. Zn-O-Si structures have less probability of visible and non-radiative transitions and facilitates the UV emission [7]. Also, excited carriers in SiO_2 can tunnel to the SiO_2 /ZnO interface or even to the ZnO nanostructure and recombine, emitting UV light [7].

Annealing at 900°C results in a decrease of the UV intensity and an increase of the intensity of visible band compared to the 700°C annealed sample. The visible emission increases with each annealing step and has a dramatic increase at 900°C. Reduction of UV peak may be related to the oxygen desorption after annealing at high temperatures [14]. Zhang et al annealed ZnO nanospheres in Ar atmosphere and observed an increase in V_O emission, indicating similar oxygen desorption mechanism [14].

To further investigate the annealing effect on ZnO nanowires, we prepared new samples without the SiO_2 film and performed identical annealing steps in Ar ambient. Fig. 3 (c) shows the PL spectra of the nanowires, before and after annealing. We observe that the UV band decreases while the visible band emission slightly increases with annealing temperature. Presumably, oxygen desorption from ZnO nanowires occurs during annealing in Ar, creating V_O [14]. However, this mechanism is less observable in nanowires annealed without SiO_2 since it already presents high levels of V_O .

4. Conclusions

Passivation of native point defects on ZnO nanowires surface were successfully achieved by SiO_2 sputtering coating. The PL measurements showed a strong decrease in the visible band emission consistent with a V_O passivation mechanism during SiO_2 deposition. The defect passivation also decreases the probability of non-radiative transitions, contributing to an increase in the UV NBE emission. After annealing in Ar atmosphere, the visible band becomes pronounced due probably to oxygen desorption. ZnO nanowires without SiO_2 coating were submitted to thermal treatment and also presented an increase in visible emission band, strongly indicating similar oxygen

desorption mechanism. (S)TEM images confirm the formation of ZnO/SiO₂ core-shell like structures.

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Figure Captions:

Fig. 1: (a) Scanning electron microscopy and (b) transmission electron microscopy of ZnO nanowires as grown in sapphire substrate.

Fig. 2: (S)TEM/EELS studies of as deposited SiO₂/ZnO nanowires. (a) Low magnification BF TEM micrograph. (b) Close view of the SiO₂/ZnO interface. (c) STEM image showing the contrast difference due to the composition. (d) and (e) are EELS spectra from the squared areas marked on (c).

Fig. 3: PL spectra at room temperature of ZnO nanowires: (a) as grown (line) and after SiO₂ deposition (circles); (b) with SiO₂ film covered (line) and submitted to rapid thermal annealing at 500°C (circles), 700°C (triangles) and 900°C (stars); (d) as grown (line) and submitted to rapid thermal annealing at 500°C (circles), 700°C (triangles) and 900°C (stars).

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Figure 1

Figure 2

Figure 3