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Photoluminescence study of interstitial oxygen defects in ZnO nanostructures

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ABSTRACT

ZnO defect luminescence is a fascinating but still highly controversial issue. Herein, the role of interstitial oxygen played on the photoluminescence (PL) property of ZnO nanostructures is investigated through oxygen plasma exposure and low temperature O_2 annealing. In contrast to previous reports, no interstitial oxygen related deep level emission was observed in PL spectra from room temperature (RT) to 7 K after oxygen-rich treatments, except apparent suppression of the exciton emission due to the upward band bending effect. This work illustrates that the isolated interstitial oxygen seems not to cause the widely reported yellow/orange emission regardless of the ZnO growth method.

1. Introduction

ZnO is a promising wide band-gap semiconductor that exhibits multiple applications ranging from optoelectronic to biomedical area [1]. Although intensive efforts have been focused on this special material, there are many fundamental issues unclear yet, such as the p-type conductivity challenge. A clear understanding of defect luminescence is of significance towards its potential application. Theoretical calculation predicts that interstitial oxygen (O_i) has a relative high formation energy and independent of O-poor or O-rich conditions, [2] while a group of experimental works reported that O_i produces the yellow/orange luminescence in ZnO, especial in solution-grown ZnO nanostructures [3–5]. Compared to bulk ZnO, the light emission properties of solution-based ZnO are strongly influenced by the lattice termination, surface defects, reconstruction or amorphization of the crystalline arrangement, dangling bonds, and chemisorbed or physisorbed atoms et, al. Therefore, it is meaningful to clarify whether O_i contributes to the as-reported visible emission in ZnO nanostructures.

In our previous work, we found that low temperature O_2 ambient annealing can greatly increase interstitial oxygen defect in ZnO. On the other hand, O plasma is also well addressed to tune chemical balance of oxides, which contains various oxygen ions and radicals, such as O^+, O^{2+}, O^- and O^*. In this work, we systematic studied the influence of oxygen-rich treatments on the photoluminescence property of ZnO nanostructures. Both commercial and solution-grown ZnO nanostructures are tested to explore the role O_i played on the luminescence property of ZnO. Our work offers direct experimental evidence that the yellow/orange photoluminescence in solution grown ZnO nanostructures is likely correlated to either lithium related impurities or surface ligands rather than interstitial oxygen defects.

2. Experimental

ZnO nanocrystals (Sigma-Aldrich, 99.99% purity) with an averaged diameter of 90 nm were used as starting materials. ZnO nanorod arrays were synthesized on glass substrates by chemical bath deposition method using $Zn(Ac)_2$ and monoethanolamine at a low temperature of 90 °C. The experimental details can be found elsewhere [6]. Oxygen exposure treatments were performed by annealing ZnO in a flowing O_2 ambient at 150 °C for 4 h and exposing with oxygen plasma (100 W, 30 Pa) for 1 h, respectively.

The samples' morphology and composition were observed using S-5400 type scanning electron microscope (SEM) equipped with Energy Dispersive Spectrometer (EDS). Micro-Raman spectra of samples were recorded on a JY-HR800 micro-Raman spectrometer using a 488 nm wavelength Ar^+-ion laser. The XPS (X-ray photoelectron spectroscopy) was measured on a PHI 5300 ESCA instrument using an Al-Kα X-ray source at a power of 250 W. The PL spectra were recorded using an excitation wavelength of 325 nm. Low temperature measurements were performed in an attached closed-cycle liquid-helium cryostat capable of reaching 7 K.

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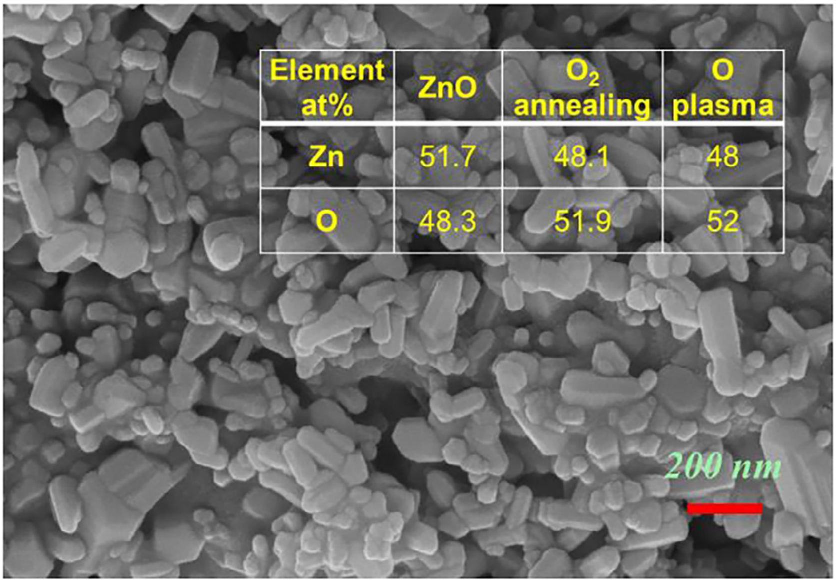

Element at%	ZnO	O_2 annealing	O plasma
Zn	51.7	48.1	48
O	48.3	51.9	52

Fig. 1. SEM image of ZnO nanocrystals, the inset table lists the EDS of ZnO before and after oxygen exposures. The error bar for oxygen determination from EDS is about ±0.2%.

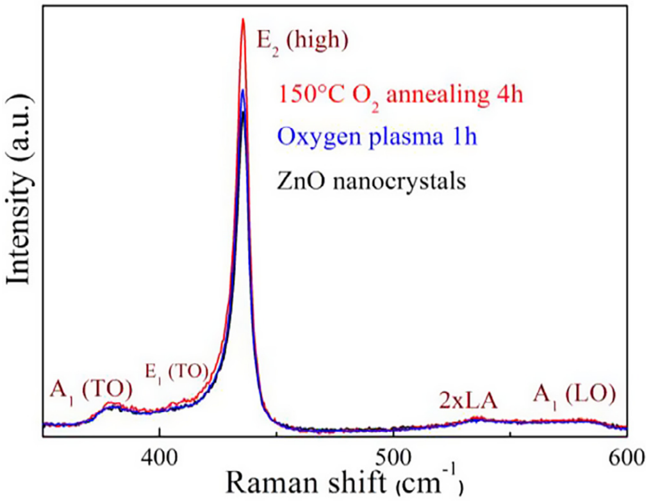

Fig. 2. Raman spectra of pristine ZnO, and O-rich treated samples.

3. Results and discussion

Fig. 1 shows the SEM image of as-received commercial ZnO nanocrystals. The ZnO particles exhibit uniform prism-like shape, and the averaged diameter is below 100 nm. While no visible morphology change was observed before and after O-rich treatments, it is apparent that the oxygen atom concentration significantly increased, suggesting the exposed surface is in rich of oxygen element.

Fig. 2 illustrates the Raman scattering spectra of pristine ZnO nanocrystals and oxygen-exposure treated samples. The E_2 high mode around 438 cm^{-1}, which indicates the crystalline quality of ZnO [6]. As it can be seen, both O_2 ambient annealing and O plasma treatment lead to intensification of the E_2 high mode, implying the improvement of the crystal structure.

Fig. 3 presents the PL spectra of ZnO nanostructures before and after O-rich treatments. As shown in Fig. 3(a), the pristine ZnO nanocrystals show a typical near band edge (NBE) emission around 379 nm and a broad visible emission. The 379 nm peak is attributed to the free exciton recombination process, while the deep level emission is related to defect and impurities in ZnO. Noticeably, both O plasma and O_2 annealing treatments affected little of the visible luminescence, while the NBE intensity reduced sharply. It is known that oxygen molecules can adsorb on the nanocrystal surface, primarily on the oxygen deficiency sites, and then become negatively charged ions through capturing free electrons [7]. This creates a depletion layer near the nanocrystal surface and causes upward band bending, which leads to suppress of the exciton recombination.

7 k PL spectra are also employed to trace the luminescence feature of ZnO before and after O-rich treatments. As shown in Fig. 3b, the 368 nm (3.37 eV), 373 nm (3.32 eV) and 382 nm (3.24 eV) emission can be assigned to donor-bound exciton (D^0X), structural defects related acceptor-bound exciton (A^0X) and donor-acceptor pair (DAP) transition, [8] respectively. The emission line at 385 nm (3.22 eV), 393 nm (3.15 eV) and 403 nm (3.07 eV) can be attributed to longitudinal optical (LO) phonon replicas of DAP. Like the case of RT PL spectra, no new visible peak can be observed.

We noticed that majorities of the reported O_i related yellow/orange emissions were observed in solution-grown ZnO [9]. To verify this case, we also performed a same O plasma treatment upon the solution-grown ZnO nano arrays. As shown in Fig. 3c, after O plasma treatment, the NBE emission declined remarkably while the visible luminescence changed little. Thus, in this work, we conclude that the isolated interstitial oxygen defect does not cause the DEL emission.

The effect of O_2 adsorption on the PL emission properties of nanoscaled ZnO has been well studied in literatures. Amir R. Gheisi et al. [4] reported that a broad yellow emission of 6–10 nm ZnO was substantially intensified when measuring the PL spectrum in an O_2 ambient, compared to the spectrum recorded in vacuum. They suggested that oxygen adsorption causes surface band bending and drives photogenerated holes into the surface near region. Subsequent hole trapping at oxygen interstitials as deep trap states enforced their recombination with photogenerated electrons yielding yellow photoluminescence emission. On the other hand, Gregory Spataro et al. [10] found that the nature of the yellow emitting site is not altered by the environment (medium or ligand type), while the quantum yield of colloidal ZnO is strongly dependent on the composition of the ligand shell. In a recent study, by