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Improvement of UV emission from highly crystalline ZnO nanoparticles by pulsed laser ablation under O₂/He glow discharge

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Pulsed laser ablation under an O₂/He glow discharge was studied to improve the surface crystallinity and UV luminescence of ZnO nanoparticles ~ 10 nm in size. X-ray photoemission spectroscopy, scanning transmission electron microscopy, and cathodoluminescence spectroscopy were used to analyze the crystalline structures and chemical components. The results indicated that highly crystalline ZnO nanoparticles were fabricated under the O₂/He plasma discharge. The near band gap UV emission intensities from these particles were roughly five times those of samples fabricated under O₂ gas. The present results suggest the possibility of synthesizing high quality ZnO quantum dots or nanoparticles without requiring any post-treatment. © 2011 American Institute of Physics. [doi:10.1063/1.3551534]

Zinc oxide (ZnO) has numerous potential applications in ultraviolet (UV) light emitting diodes, gas sensors, solar cells, and transparent thin film transistors due to its direct wide band gap of 3.37 eV and its 60 meV binding energy at room temperature.^{1–5} ZnO nanomaterials, such as quantum dots and nanoparticles with a relatively high surface area to volume ratio, exhibit physical and chemical properties remarkably differently from the bulk materials.^{3,6,7} Compared to bulk ZnO, however, ZnO nanoparticles usually exhibit lower UV luminescent efficiency, related to surface defects.⁸ Therefore, it is a significant challenge to enhance the UV emission efficiency of ZnO nanomaterials. The UV luminescence of ZnO nanoparticles is important in optoelectronic applications. Hitherto, various methods have been used to enhance the UV luminescence efficiency of ZnO.^{6,9–12} It is well known that the UV emission arises from the near band edge emission, corresponding to the degree of crystallinity of the ZnO nanoparticles.^{9,13} Hence, the preparation of defect-free ZnO nanostructures with a controlled size and morphology is a major focus of current nanoscience research.

In this letter, our motivation is to provide a feasible method to realize predominantly UV luminescence in as-grown ZnO nanoparticles or quantum dots without requiring any post-treatment. The ZnO nanoparticles were fabricated by pulsed laser ablation under an O₂/He glow discharge. A fine crystalline structure was achieved, and oxygen-related defects were suppressed, resulting in a roughly fivefold enhancement of the UV emission intensity.

ZnO nanoparticles were prepared using a pulsed Nd:YAG laser with a wavelength of 1064 nm, to ablate a pure Zn metal target (with a purity of 99.99%) with a pulse energy of ~ 9.0 J/pulse in an O₂/He mixed gas atmosphere. The working pressure varied from 0.5 to 1.8 kPa. The power of the DC plasma was roughly 110 W. The experimental laser ablation setup was described in detail in a previous paper.¹⁴ ZnO nanoparticles fabricated by pulsed laser ablation under normal oxygen ambience were used as a reference. Except for the plasma, the reference ZnO samples were fabricated under the same conditions as the other samples.

The morphology and structure of the samples were characterized using scanning transmission electron microscopy (STEM). The luminescence properties of the ZnO nanophosphors were measured by cathodoluminescent (CL) spectral measurement using an energy-controllable electron beam.¹⁴ X-ray photoelectron spectroscopy (XPS) was used to investigate the electronic structure of the nanoparticles.

Figure 1(a) shows high resolution TEM images of ZnO nanophosphors fabricated under a normal oxygen ambience at an oxygen pressure of 1000 Pa. These nanoparticles were surrounded by an amorphous-like layer. As shown in the enlargement, amorphous-like layers, possibly attributed to dislocations and stacking, were obvious along the ZnO particle edge. This result indicates that unsaturated bonds (i.e., surface defects) existed on the surface of the ZnO nanoparticles. Therefore, most of the excitation electron beam energy

FIG. 1. High resolution TEM images of ZnO nanoparticles prepared (a) under a normal O₂ gas ambience and (b) in O₂/He mixed plasma.

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FIG. 2. CL spectra of ZnO nanoparticles, fabricated (a) under a normal O_2 gas ambience and (b) in an O_2/He mixed plasma.

would have been dissipated in heating these surface defects. As a result, amorphous-like layers would affect the luminescence of the ZnO nanoparticles. Figure 1(b) shows high resolution TEM images of ZnO nanoparticles fabricated in plasma with an oxygen partial pressure of 900 Pa and a helium partial pressure of 600 Pa. The size of the ZnO nanoparticles varied from several nanometers to ~ 20 nm. In the images, the lattice structure is prominent, and is observable in the particle interior as well as at the surface. Therefore, the as-grown ZnO nanoparticles had a fine crystalline structure,¹⁵ and contained few dislocations or stacking defects. As shown in the enlarged image, the lattice image of the (0002) plane could be seen clearly.¹⁵ After comparing Figs. 1(a) and 1(b), it was hypothesized that the plasma played a role in removing the amorphous layer from the surface of the ZnO nanoparticles.

The depth-resolved luminescence of ZnO nanoparticles was studied using a CL technique with an energy-controlled electron beam, as shown in Fig. 2. When the accelerating voltage of the CL equipment was increased from 1.0 to 2.0 keV, the primary electron penetration depth varied from ~ 7 to ~ 30 nm.¹⁶ However, the electron beam can be expected to lose energy with increasing depth because of energy dissipation by surface defects. Therefore, the above penetration depth values were likely overestimated. Figure 2(a) shows CL spectra of ZnO nanocrystals fabricated under normal oxygen ambience of 1000 Pa at different accelerating voltages. The CL spectrum was dominated by a broad defect-related emission peak and a UV emission peak. Kingsley *et al.* found that the CL intensity in a bulk crystal increases linearly with accelerating voltage.¹⁷ Similarly, the CL inten-

FIG. 3. CL spectra of ZnO nanoparticles fabricated under different partial pressure of He gas at a fixed oxygen gas pressure of 900 Pa.

sities of both the UV and green emissions increased with acceleration voltage. Figure 2(b) shows the CL spectra of ZnO nanoparticles fabricated in plasma with an oxygen partial pressure of 900 Pa and a helium partial pressure of 600 Pa. These CL results revealed a predominant UV luminescence, even at room temperature, and a broad green peak that was significantly suppressed to the background noise level. The intensity of the UV emission peak increased significantly after increasing the acceleration voltage to 2.0 kV, with no obvious effect on the intensity of the green light peak. The UV emission from ZnO nanoparticles can be attributed to the near band edge emission, attesting to the highly crystalline structure of ZnO nanoparticles.¹⁸ The broad green peak can be attributed to defect-related deep-level emissions, indicating the existence of intrinsic defects. Moreover, intrinsic defects can act as trapping centers to compete with the near band edge emission and quench the excitonic luminescence of ZnO nanocrystals.¹³ Thus, the CL spectra provided clear evidence for the high crystallinity of the as-grown ZnO nanocrystals, and indicated that the growth of intrinsic defects in the ZnO was inhibited. Figure 2 shows that the intensity of the UV emission peaks of ZnO nanocrystals fabricated in plasma were enhanced approximately fivefold, compared to samples fabricated under normal oxygen conditions. It is possible that the existence of many nonradiative defects in the ZnO nanoparticles fabricated without plasma quenched the UV emission.

Figure 3 shows the CL spectrum of ZnO nanoparticles, fabricated in plasma. The detail information of oxygen partial pressure and helium partial pressure is signed in the figure. The relative intensities of green peak decrease with the enhancement of helium gas pressure.

In the plasma, some of oxygen molecules would be transformed into two types of atomic oxygen states (O^*) with high chemical activity. The energy of helium in neutral excited metastable states is larger than the first ionization potential of oxygen molecules. Therefore, helium gas (He) was added to improve the stability of the plasma discharge, and to produce oxygen radicals.^{19,20}

where He_m^* is He in an excited metastable state, and O_2^+ is the molecular oxygen ion. Optical emission spectroscopy mea-

FIG. 4. (Color online) The O 1s XPS spectra of samples fabricated (a) under a normal O_2 gas ambience and (b) in an O_2/He mixed plasma.

measurements indicated that the presence of He in the discharge promoted an increase in the emission intensity of the 777.2 nm line, which corresponds to a transition of atomic oxygen radicals $OI(3p^5P \rightarrow 3s^5S)$. The presence of He in the discharge promoted to produce atomic oxygen radicals efficiently. Combining the glow discharge analysis with the crystalline structure analysis of the ZnO nanoparticles, it is likely that the existence of radical atoms/ions with high chemical activity in plasma can give rise to the higher oxidation rate of the decomposed Zn atoms from the target and restrict the growth of oxygen vacancy during pulsed laser ablation process. For sufficient concentrations of oxygen radical atoms (O^*), the enhanced collision frequency involving oxygen atoms/ions and zinc atoms/ions can give rise to the synthesis of a better crystalline structure of ZnO.¹⁸ Therefore, the presence of radical atoms/ions can improve the UV luminescence intensity of ZnO nanoparticles fabricated by pulsed laser ablation in plasma.

Figures 4(a) and 4(b) show XPS O 1s spectra of ZnO nanocrystals, synthesized (a) under a normal oxygen gas ambience and (b) in an O_2/He mixed plasma. A high-energy Ar ion beam was used to etch the surfaces of the samples, which was used to reduce the effect of adsorbed oxygen ($-CO_3$, $-OH$, etc.) on the XPS results. The O 1s peaks were deconvoluted into two Gaussian peaks, centered at 531.5 ± 0.2 eV and 532.8 ± 0.2 eV. The peak (P_1) at binding energy 531.5 ± 0.2 eV can be attributed to oxygen ions surrounded by Zn ions in the wurtzite structure, and the intensity of this peak is a measure of fully oxidized oxygen atoms.¹³ The peak (P_2) at binding energy 532.8 ± 0.2 eV is associated with the protoxide ZnO, and the variation in its intensity may be related to changes in oxygen vacancies.¹⁴ Since XPS is a surface sensitive diagnostic, which can probe about 5 nm deep into a material, the XPS results mainly reveal the chemical composition near the surface of ZnO nanoparticles. In the samples fabricated under a normal oxygen ambience shown in Fig. 4(a), the integrated intensity of peak P_1 can be compared with that of peak P_2 using the P_1 to P_2 integrated intensity ratio “R,” which was approximately 1.1. As shown in Fig. 4(b), the plasma affected the high binding energy shoulder of the O 1s peak and caused the integrated intensity of P_1 to dominate that of peak P_2 , with R larger than 2.5. Therefore, the lattice positions of the wurtzite structure near the surface of the samples, fabricated in plasma, were mainly occupied by oxygen and Zn ions.

In summary, ZnO nanoparticles, with a minimum diameter of about 7 nm, were fabricated using a pulsed laser in an

O_2/He mixed plasma. Structural and chemical composition analysis of the ZnO nanoparticles by STEM and XPS indicated that samples fabricated under an oxygen pressure of 900 Pa and a helium pressure of 600 Pa were highly crystalline and contained few defects. CL results demonstrated that ZnO nanoparticles can produce a strong UV luminescence. This work suggests the possibility of fabricating fine crystalline as-grown ZnO quantum dots or nanoparticles for commercial application.

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