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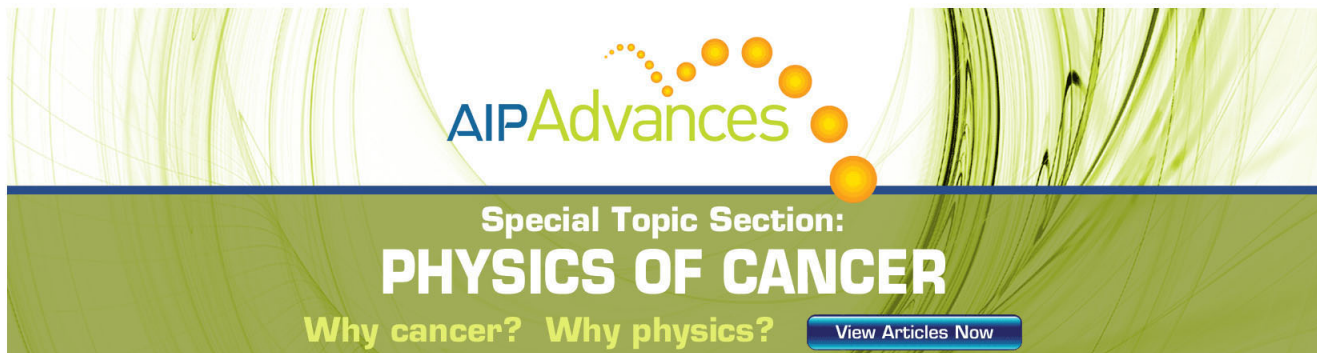
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Enhanced ultraviolet emission and optical properties in polyvinyl pyrrolidone surface modified ZnO quantum dots

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Optical properties of ZnO quantum dots (QDs) capped with polyvinyl pyrrolidone (PVP) molecules have been investigated. It is demonstrated that surface modification by PVP can dramatically change the emission spectra of the ZnO QDs. At the optimized condition with a PVP/Zn²⁺ ratio of 3:5, the photoluminescence (PL) spectrum of ZnO QDs shows a strong ultraviolet (UV) emission while the low energy green emission is fully quenched. This is a result of the surface passivation of the ZnO QDs by the PVP molecules. The origin of the green emission is attributed to the surface states associated with oxygen vacancies. Temperature and excitation power dependent PL studies suggest that the UV emission is associated with localized states. © 2001 American Institute of Physics. [DOI: 10.1063/1.1406973]

I. INTRODUCTION

Similar to GaN and ZnS, ZnO as a wide band gap semiconductor has attracted much attention due to the strong commercial desire for blue and ultraviolet (UV) light emitters and detectors.¹ Low threshold for optical pumping and large exciton binding energy (60 meV) allow lasing action to be reached at extremely low pumping power at room temperature.² Excitonic stimulated emission has even been observed at temperatures as high as 550 K.³ Furthermore, a ZnO device is unlikely to suffer from dislocation degradation during its operation as it is one of the “hardest” materials in the II–VI compound family.⁴

In recent years, intensive development of nanomaterials and nanotechnology has occurred worldwide since carriers on the nanoscale behave extraordinarily due to quantum confinement effects. Novel devices based on nanomaterials (especially quantum dots and wires) have attracted a great deal of interest by many researchers. In the past decade, various methods^{5–11} have been employed to produce ZnO quantum dots (QDs). In most of the previous work, visible emission dominates the photoluminescence (PL) spectra of ZnO QDs. PL spectra of ZnO QDs with purely strong UV emission have never been reported. In this article, we report on the optical properties of ZnO QDs capped with polyvinyl pyrrolidone (PVP) molecules. The PL spectrum with only strong UV emission was observed while the visible emission was fully quenched. This is a result of the surface passivation of the ZnO QDs by the PVP molecules. The visible emission of

ZnO QDs is attributed to surface oxygen vacancy states. Studies using excitation and temperature PL measurements suggest that the UV emission of QDs is associated with deep localized states.

II. EXPERIMENT

The key step in the sample preparation is the introduction of PVP in the precursor as the capping molecules for the ZnO quantum dots. It serves to stabilize the ZnO quantum dots and to passivate the surface. The size of the ZnO QDs is closely related to the PVP/Zn²⁺ ratio. High resolution transmission electron microscope images of the ZnO QD samples showed that the mean dot sizes were 2.8 ± 0.4 , 2.6 ± 0.3 , 3.6 ± 0.5 , and 4 ± 0.5 nm for the ZnO samples corresponding to the PVP/Zn²⁺ ratio of 5:5, 3:5, 1:5, and 0:5 (no PVP), respectively. For the ZnO QDs without PVP modification, the dots take the shape of ellipsoids, while the dots with PVP modification are spherical in shape. A detailed synthetic procedures and structure analysis of the ZnO dots can be found elsewhere.^{12,13}

Optical absorption spectra were recorded on a Philips 3000 spectrophotometer. In the measurements, appropriate blank solutions of pure 2-propanol and PVP/2-propanol mixtures were used as references. In the PL measurements, either the 325 nm line from a He–Cd laser or the 266 nm fourth harmonic from a Nd:YAG laser were used as the excitation light. Light emission from the samples was collected into the Spex500 spectrometer and detected by a photomultiplier tube with GaAs as the cathode.

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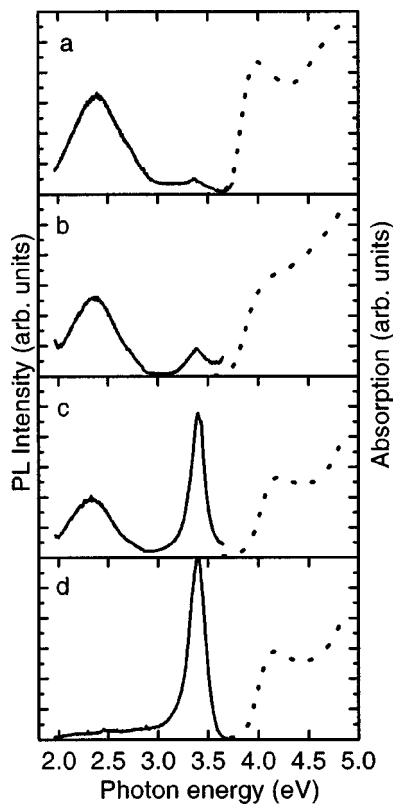


FIG. 1. Absorption (dotted lines) and PL (solid lines) spectra of four ZnO QDs samples with PVP/Zn²⁺ ratios: (a) 0:5, (b) 1:5, (c) 5:5, and (d) 3:5, respectively. The excitation power density in taking the PL spectra was 42 W/cm².

III. RESULTS AND DISCUSSION

In Fig. 1 the room temperature optical absorption (dotted lines) and PL (solid line) spectra of different ZnO quantum dots with and without PVP captions are shown. The absorption spectra largely depend on the concentration of PVP used to prepare the precursor. These ZnO nanoparticles exhibit strong free exciton absorption at room temperature with strong quantum size effects. With the increase in PVP concentration, the excitonic absorption peak shifts to higher energy. The onset energy position of the absorption can be obtained by extrapolating $(\alpha h\nu)^2$ against $h\nu$ to zero, where α is the absorption coefficient and $h\nu$ is the photon energy. The absorption edges for the four samples are then obtained as 3.778 eV [Fig. 1(a) without PVP capping], 3.816 eV [Fig. 1(b) PVP/Zn²⁺=1:5], 3.974 eV [Fig. 1(d) PVP/Zn²⁺=3:5], and 3.934 eV [Fig. 1(c) PVP/Zn²⁺=5:5], respectively. These values are all much larger than the absorption edge of the bulk ZnO (3.3 eV),¹⁴ showing the quantum confinement effect. The corresponding blueshifts are consistent with the observed variation of the dot sizes previously mentioned.

Interesting features are found in the PL spectra of the ZnO quantum dots synthesized using different PVP/Zn²⁺ ratios shown in Fig. 1 as solid lines. The spectra were taken under an excitation power of 42 W/cm². For the ZnO QDs without PVP capping [Fig. 1(a)], the PL spectrum consists of a very weak UV peak at about 3.41 eV and a strong and broad green peak at about 2.4 eV. The full width at half maximum of the broad green peak is about 0.25 eV. With the

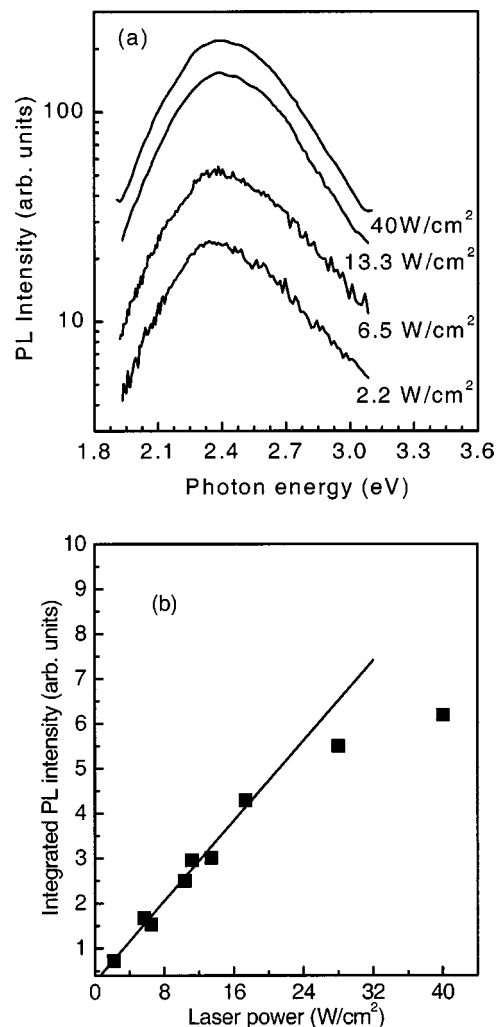


FIG. 2. (a) PL spectra of the green emission peak for ZnO QDs sample without PVP capping at different excitation intensities indicated. (b) Excitation power dependence (solid squares) of the integrated PL intensity for the green emission. The solid line is a guide for the eyes.

introduction of PVP [Figs. 1(b)–1(d)], the intensity of the UV peak increases dramatically at the expense of the green peak, but the position of the UV peak does not vary. At the optimized ratio of PVP/Zn²⁺ of 3:5 [Fig. 1(d)], the green emission is fully quenched and we obtain purely strong UV emission from the ZnO QDs.

A. Green emission from the QDs

It is commonly believed that the green emission from ZnO originates from oxygen vacancies (V_O).^{5–13,15} Vanheusden *et al.*¹⁶ further suggest that the green emission in ZnO is due to the recombination of electrons in singly occupied oxygen vacancies with photoexcited holes in the valence band. A recent first-principles calculation by Zhang *et al.*¹⁷ supports this identification and shows that V_O defects have low formation enthalpy and hence are readily formed. The photo-generated electrons can be trapped into oxygen vacancies through a nonradiative decay and then recombine with the holes in the valence band. Shown in Fig. 2(a) are the green emission peaks for the sample without PVP with different excitation intensities. We found that the peak energy shifted

from about 2.34 to 2.4 eV when we changed the excitation power from 2.2 to about 40 W/cm². Xu *et al.*¹⁸ recently have also observed the peak shift when changing the excitation power for sulfur vacancy related emissions from CdS nanoparticles. They suggest that the shift implies that the emissions are likely from donor–acceptor (*D–A*) pairs. It is well known¹⁹ that one of the characteristics of *D–A* recombination is a shift to higher energy as the excitation intensity increases. This energy shift has been attributed to a dependence of the pair transition energy on the separation between the donor and acceptor. In our case it seems more likely that the shift is due to the carrier occupation variations in the V_O states with different energy levels when the excitation power is changed. The broadness of the emission band originates from inhomogeneous broadening induced by the different surroundings of the V_O in dots. The higher excitation power will induce more carrier occupation into those V_O states with higher energies, hence causing the blueshift of the spectrum. The integrated PL intensity of the green peak against the excitation power for the same sample is given in Fig. 2(b). At the lower excitation power range (<16 W/cm²), the PL intensity is linearly dependent on the power. But as the excitation power is further increased, the PL intensity tends to saturate. This behavior is attributed to a nonlinear change in the carrier occupation of the radiative and nonradiative centers with excitation intensity.²⁰

Sakohara *et al.*²¹ have proposed a correlation between the visible emission and the surface states in ZnO QDs. The fact that we can effectively reduce and even quench the oxygen vacancy related green emission by the PVP surface capping implies that the oxygen vacancies are mainly located on the dot surfaces. If we consider the sizes of our quantum dots (2–5 nm), this is not a surprising result as the surface-to-volume ratio is very large in such small dots.

B. UV emission from the QDs

The UV emission from ZnO is commonly attributed to band-to-band or near band edge emissions.^{11,22} In the ZnO QDs studies,^{8–11} it is commonly observed that the excitonic peak in the absorption spectra exhibits increasing blueshift with decreasing dot size. Large Stokes shift toward red from the absorption edge is also observed in the UV emission from ZnO quantum dots. In general, electron–phonon coupling, lattice distortions, and localization of charge carriers due to interface defects or point defects may cause the redshift of emission line from the absorption edge. In the case of a bundle of quantum dots, the redshift may also be caused by the preferential emission from larger dots in the sample.¹⁰ In our case, as shown in Fig. 1, we find that there is a large energy difference between the absorption edge and the emission peak. For the sample with PVP/Zn²⁺=3:5, the redshift of the UV peak from the absorption edge is as large as 0.39 eV [see Fig. 1(d)]. Such a large shift cannot be simply explained by the electron–phonon interaction or lattice distortions. In addition, the UV peak energy is independent of the dot sizes and is located at about 3.41 eV for all samples in spite of the fact that the absorption edges show a blueshift consistent with the reduction of the quantum dot sizes.

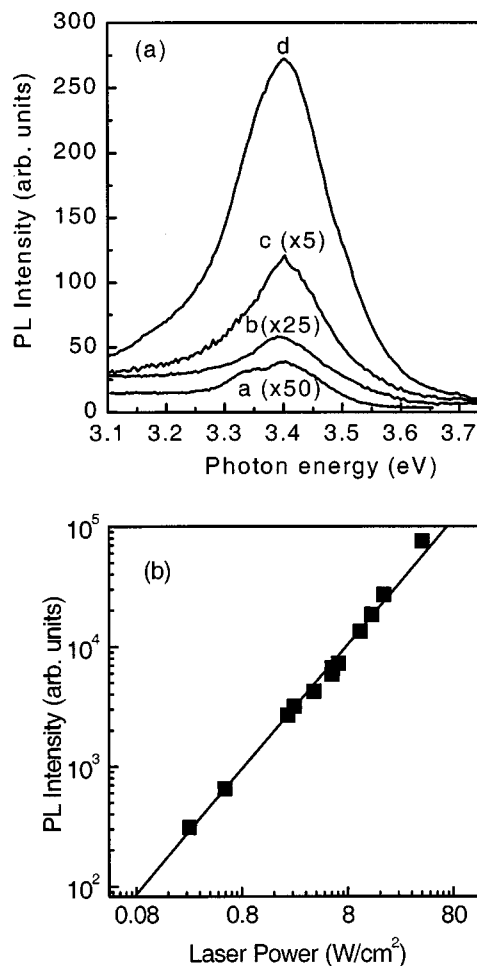


FIG. 3. (a) PL spectra of the UV emission for ZnO QDs with PVP capping (PVP/Zn²⁺=3:5) at different excitation intensities. Spectra a, b, c, and d are with excitation intensity at 0.2, 0.5, 4.2, and 42 W/cm², respectively. (b) Excitation power dependence (solid squares) of the integrated PL intensity for the UV emission. The solid line is a guide for the eyes.

Whether a 325 nm (3.82 eV) laser or a 266 nm (4.66 eV) laser with higher power was used as the excitation source, no difference was observed in the emission spectra. This means that the preferential emission from larger dots cannot explain the large redshift in our case. Therefore, we suggest that the observed UV emission is from bound excitons due to deep levels. The excitonic nature will be discussed below. The deep levels might be induced by impurities or defects, or surface states as in silicon nanocrystals.²³ Consequently, band gap resonant emission cannot be observed and the deep level related states dominate the luminescence spectra in our ZnO quantum dots.

Figure 3(a) shows the UV emission spectra of the sample with PVP/Zn²⁺=3:5 at different excitation levels. At very low excitation intensity (0.2 W/cm²), curve a in Fig. 3(a), the main peak at 3.41 eV is accompanied by a small peak in the low energy tail. With the increase of the excitation power, the small peak in the tail saturates very quickly and the main peak dominates the UV emission spectra. The peak energy of this main UV emission located at 3.41 eV does not shift with variation of the excitation power. The relationship between the integrated intensity of the UV emission and the excitation

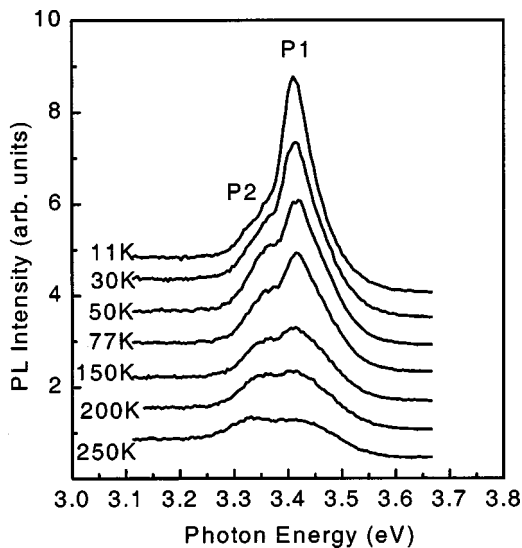


FIG. 4. PL spectra of a ZnO quantum dot film (with PVP/Zn²⁺=3:5) at different temperatures.

power is shown in Fig. 3(b). An almost linear dependence is evident. No evidence of saturation for the PL intensity is detected when the excitation power is increased by more than 2 orders of magnitude. Because of the large excitonic binding energy in ZnO the recombination is probably excitonic. Although not sufficient, the close-to-linear excitation dependence of the main UV peak supports the idea of an excitonic process.²⁴ As suggested above, the excitons are bound to deep centers (localized states). Bound excitons related to Li⁺ or Na⁺ centers^{25–27} in ZnO have been reported by several groups before. Na⁺ is an inevitable dopant in our ZnO QDs since we used NaOH in the synthesis precursor. Surface defects are other candidates. These states are radiative and compete with the oxygen vacancy related states. Whatever the deep centers are, they must have a larger density of states since the PL intensity associated with the centers does not saturate at the excitation levels we used. The binding of an exciton to the defect centers can be explained qualitatively using the well-known Hopfield-Thomas-Lynch²⁸ model. Normally, according to whether an electron or hole is captured by the deep center, the bound exciton is classified as an acceptor-like or donor-like bound exciton. The study of the thermal quenching of the luminescence through the disassociation of the electron, hole, or exciton was useful for determining the binding mechanism.

To provide more information for understanding the origin of the UV emission, we have studied the optical properties of ZnO quantum dot thin films with PVP/Zn²⁺=3:5 at various temperatures. The quantum dot film was formed by spin coating the stable colloidal solution onto a silicon substrate. Figure 4 presents the PL spectra of the ZnO quantum dot film at various temperatures, which show a main peak *P1* and a lower energy shoulder *P2* in the tail. For clarity, the temperature dependences of the peak energy and integrated PL intensity of these two peaks are shown in Figs. 5(a) and 5(b), respectively. As can be seen in Fig. 5(a) the energy of *P1* (3.41 eV) hardly changes with temperature. It does not follow the band gap or the free exciton temperature

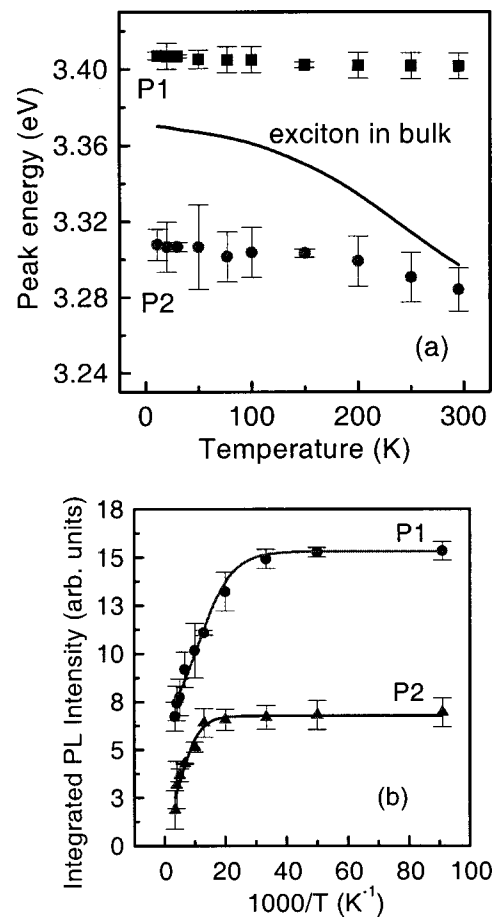


FIG. 5. (a) Temperature dependence of the peak energy for *P1* (solid squares) and *P2* (solid circles) in the UV emission (see Fig. 4). Solid line shows the temperature dependence for a free exciton in bulk ZnO (Ref. 28) for comparison. (b) Arrhenius plot of the integrated PL intensity against temperature for *P1* and *P2*, respectively. Solid symbols are experimental data and solid lines are fit using Eq. (1).

dependence in bulk ZnO up to room temperature. The *P2* peak energy is lower than that of the free exciton in bulk ZnO and is not strongly dependent on temperature either. This implies that both *P1* and *P2* originate from localized states.

Shown in Fig. 5(b) is the temperature dependence of the integrated PL intensity of *P1* and *P2*. Generally, the thermal quenching of luminescence intensity of a bound exciton can be expressed as²⁹

$$I(T) = \frac{I_0}{1 + C_1 \cdot \exp(-E_1/kT) + C_2 \cdot \exp(E_2/kT)}, \quad (1)$$

where C_i contains the ratios of optical-collection efficiencies and effective degeneracy between the unbound and bound states, and E_i is the thermal activation energy. This formula describes two dissociation processes associated with the bound excitons. But in our case we found that one process is predominant; i.e., $C_1=0$ in the formula. We conclude from the experimental data that the value of E_2 for *P1* and *P2* is 16 and 26.5 meV, respectively. It is known that the exciton binding energy of bulk ZnO is about 60 meV and this value is expected to increase further in a three-dimensional confined system. So E_2 here cannot be the binding energy of a

free exciton. It must correspond to the activation energy of several dissociation processes of a bound exciton, as analyzed in Ref. 29. In any case, the small thermal activation energies additionally indicate that *P1* and *P2* are not due to emissions of free excitons in the ZnO dots.

It is beyond the scope of this article to further identify the origin of the deep centers that bind excitons in the ZnO QDs. What we can conclude now is that they are localized with high density of states, and do not follow the properties of the band-to-band transition.

IV. CONCLUSION

Optical properties of PVP capped ZnO QDs have been investigated. It has been shown that the PVP/Zn²⁺ ratio in the precursor can dramatically enhance the UV emission intensity from the QDs. The green emission from the QDs is attributed to the oxygen vacancies at the surface and can be quenched by surface passivation of PVP. A large redshift from the absorption edge is observed for the UV emission. Temperature and excitation power dependent PL studies suggest that the UV emission is associated with localized states.

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