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Up conversion from visible to ultraviolet in bulk ZnO implanted with Tm ions

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We report on the up-converted ultraviolet near-band edge emission of bulk ZnO generated by visible and ultraviolet photons with energies below the band gap. This up-converted photoluminescence was observed in samples intentionally doped with Tm ions, suggesting that the energy levels introduced by the rare earth ion in the ZnO band gap are responsible for this process. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2128491]

ZnO with a high energy band gap, 3.37 eV at room temperature, has been in the last few years one of the most studied materials. The main driving force for research in this oxide semiconductor is the potentialities of ZnO for optoelectronic and spintronic applications.

Nominally undoped ZnO samples grown by seeded chemical vapor transport show a highly structured near-band edge emission with above band gap excitation.[1–8] At low temperatures the ultraviolet luminescence is dominated by the recombination processes of donor bound excitons, two electron satellites and LO phonon replicas as well as donor acceptor pairs.[1–8] Even having a rather wide distribution of electronic states within the band gap, as pointed out by photoluminescence (PL) excitation measurements,[8,9] when excited with photons with lower energy than the band gap, these as-grown samples do not show ultraviolet up-converted luminescence. Similar conclusions can be drawn when ZnO is intentionally doped with Er despite the observed intraionic Er^{3+} emission.

On the contrary, in all the studied ZnO samples intentionally doped with Tm ions, for which the intra-4f emission is present, we observed ultraviolet recombination when the samples were excited with visible radiation.

The samples used in these studies were implanted at room temperature with 150 keV Tm^+ ions with a nominal fluence of 5×10^{15} Tm^+/cm^2 and subsequently air annealed for 30 min at 800, 900, and 950 °C. The implantation damage and annealing effects were investigated with Rutherford backscattering/channeling spectroscopy. We observed that following implantation the majority of Tm ions are incorporated into Zn sites.[10] The optical properties of as-implanted and annealed samples have been studied by photoluminescence (PL) measurements[10–12] carried out with a 325 nm continuous wave He–Cd laser and an excitation power density typically less than 0.6 W cm^{-2}. In-gap excitation was accomplished with the 457.9, 476.5, and 514.5 nm argon laser lines. The PL was measured at 7 K using a closed cycle helium cryostat and collected in 90° geometry. The luminescence was dispersed by a Spex 1704 monocromator and detected by a cooled Hamamatsu R928 photomultiplier. With above band gap photoexcitation the ZnO samples intentionally doped with Tm^+ ions exhibit multi Tm-related optical centers, for which the dominant intraionic emission occurs near 1.56 eV and can be assigned to the $^3H_4\rightarrow{}^3H_6$ transition.[10–12]

Figure 1 shows typical high energy spectra of as-grown and Tm doped ZnO samples obtained with above [(a) and (b)] and below (c) band gap excitation. It can be observed that the as-grown and the Tm doped samples show nearly the same optical active centres under above the band gap excitation. The main observed changes in the Tm doped samples are the decrease in relative intensities in the bound exciton spectral region (namely I_4 line) as well as two new emission lines at 3.27 and 3.26 eV.

Comparing the photoluminescence spectra obtained with above and below band gap excitation, a spectral narrowing in the high energy side (3.38–3.37 eV) is clearly observed together with a new line at 3.35 eV (370 nm) that can be correlated with the $^1D_2\rightarrow{}^3H_6$ transition of the Tm^{3+} already observed in other wide gap materiais.[13,14]

Using the same pump power and different excitation energies, it is evident that the intensity of the up-converted luminescence decreases one order of magnitude when the photon excitation energy decreases from violet to green (Fig. 2).

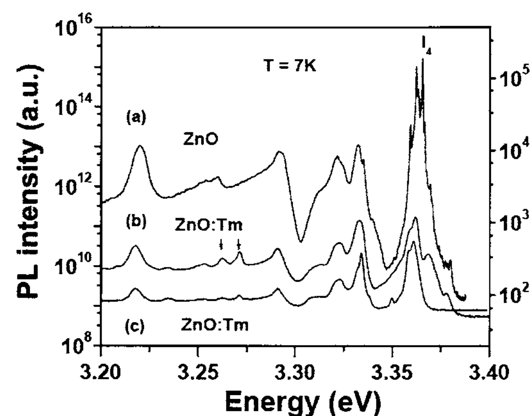

FIG. 1. PL spectra of ZnO samples: (a) as-grown ZnO, excited with above band gap He–Cd laser line (325 nm), (b) ZnO:Tm, excited with above band gap He–Cd laser line (325 nm), (c) the same ZnO:Tm sample excited with below band gap excitation (457.9 nm).

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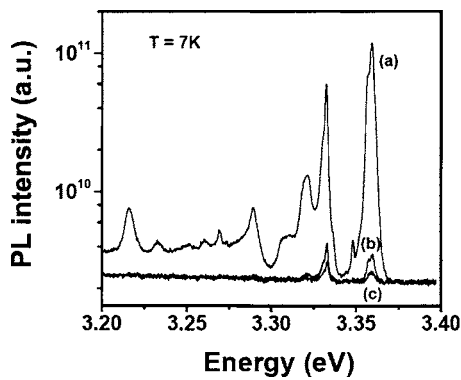

FIG. 2. Normalized 7 K PL spectra obtained with different below band gap excitation wavelengths: (a) 457.9 nm, (b) 476.5 nm, and (c) 514.5 nm.

Following the Auzel[15] treatment for the up-conversion processes, we have analyzed the up-converted emission intensity as a function of excitation density at 2.71 eV (457.9 nm). The results are shown in Fig. 3.

The observed up-converted photoluminescence lines follow a nonlinear dependence with the excitation density giving slopes ~1.7 which can be explained assuming a two-step process.[15]

As suggested by the energy dependence of the up-converted luminescence, the two-step process requires a deep level close to 1.1 eV below the conduction band in order to absorb the lowest photon excitation energy. In one step, an electron is excited from the valence band to the deep level

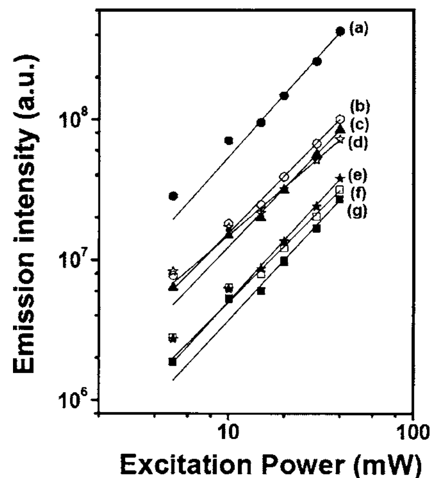

FIG. 3. Log-log plot for the up-converted luminescence intensity as a function of excitation power of the 457.9 nm laser of an Ar^+ laser. Results are shown for the different emission lines observed in ZnO:Tm samples: (a) 3.36 eV, (b) 3.35 eV, (c) 3.323 eV, (d) 3.333 eV, (e) 3.29 eV, (f) 3.27 eV, and (g) 3.22 eV.

while the other step involves the transfer of the electron from the deep level to the conduction band. Electrons and holes are thus created, respectively, in the conduction and valence band, whose recombination after impurity capture is responsible for the ultraviolet near-band edge emission of bulk ZnO.

This deep level involved must be related to Tm-defect complexes because ultraviolet recombination is always observed in ZnO intentionally doped with Tm ions when the samples are excited with visible radiation and cannot be observed when ZnO is intentionally doped with other rare earth ions.

In summary, we have reported the observation of up-converted ultraviolet photoluminescence in ZnO bulk samples intentionally doped with Tm by ion implantation. As this up-converted luminescence is only observed in intentionally doped samples we must conclude that the energy levels of the thulium ions are to be involved at least in one of the two-step processes.

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