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

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(Received 19 May 2005; accepted 14 September 2005; published online 3 November 2005)

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 potentials 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. 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. Even having a rather wide distribution of electronic states within the band gap, as pointed out by photoluminescence (PL) excitation measurements, 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 Er3+ emission.

On the contrary, in all the studied ZnO samples intentionally doped with Tm ions, for which the intra-4f/4f emission is present, we observe 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 $5 \times 10^{15}$ 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. The optical properties of as-implanted and annealed samples have been studied by photoluminescence (PL) measurements 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 Tm ions.

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).

![Plotted image of 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).](http://apl.aip.org/apl/copyright.jsp)

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Following the Auzel\textsuperscript{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.\textsuperscript{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 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.

M.P. and E.R. thank FCT for their grants. This work was funded by Fundação para a Ciência e Tecnologia (POCTI/CTM/45236/02) and (POCTI/FAT/48822) supported by FEDER.


