

Time Resolved Studies of ZnO (Eu) Nanostructure Luminescence Using Short Synchrotron Radiation Pulses

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Abstract. X-ray excited optical luminescence (XEOL) is a well established technique to study nanostructured light emitting materials. XEOL bares the essential features necessary for the study of advanced nanostructured materials like element specifity, good quantum efficiency, and easy approach for time resolution. Being sensitive to the geometry of the material on a nano-scale, luminescence gives insight into the phenomenologic correlation of structural, optical, and electronic properties. Besides structural aspects we study the time behavior of nanostructured ZnO (Eu) in a pump-probe like experiment, using the time structure of synchrotron radiation.

Keywords: XEOL, Timing, Synchrotron Radiation, Nanotechnology.

PACS: 07.85.Qe, 78.47.+p, 78.55.-m, 61.46.-w

INTRODUCTION

Wide band gap ZnO semiconductors ($E_g \sim 3.3\text{eV}$ at RT) exhibit remarkable luminescent properties, which are related to many possible shapes of nanosized structures, e.g., nanowires, nanoneedles, or nanoflowers etc., that have been realized so far. By rare earth doping the luminescent properties can be tailored towards strong emission at selected wavelengths suitable for potential light emitting applications. However, the structural and luminescence properties of impurity-doped ZnO nanocrystals are not clearly understood [1]. X-ray excited optical luminescence (XEOL) is a suitable technique for element-resolved studies of correlations between crystallinity and optical properties. Time-resolved XEOL permits the study of different optical decay channel contributions to the total luminescence yield over time, e.g. fast band gap emission (ns) and considerably slower emission from structure related defects ($>100\text{ns}$). We have studied the time dependence of the optical properties of nanostructured ZnO (Eu), using short pulses ($<\text{ns}$) from synchrotron radiation for excitation.

In this paper we present a study of luminescence from ZnO(Eu) using synchrotron techniques called X-ray excited optical luminescence (XEOL) [2,3] and time resolved X-ray excited optical luminescence (TRXEOL) [4,5], as well as a brief description of the applied techniques.

EXPERIMENTAL

X-ray excited optical luminescence (XEOL) describes the emission of optical photons due to absorption of X-rays (photon energy).

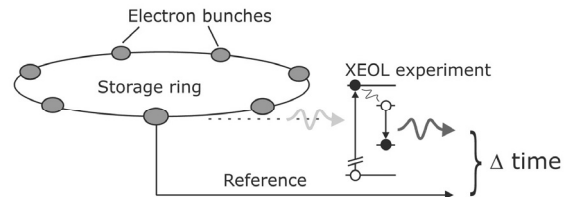


FIGURE 1. Schematic of X-ray excited optical luminescence (XEOL), and time resolved X-ray excited optical luminescence (TRXEOL) using the time structure of the RF cavity of the synchrotron storage ring.

The power of this technique lies in the tunability of the exciting X-rays, which permits to ramp the photon energy across absorption edges of selected elements. Emitted optical photons are collected by a lens system which focuses on the optical monochromator. The detector is a fast photomultiplier (PMT). For time resolved XEOL the time structure of the RF cavity of the synchrotron storage ring is used (cf. Fig. 1). The short X-ray pulses separated by a relatively wide time gap are suitable for a pump-probe like experiment. The time elapsed between the X-ray excitation and the emission of an optical photon is a measure for the lifetimes involved in the decay process. Details of this technique have been reported elsewhere [5]. XEOL and TRXEOL experiments were conducted at the PNC-CAT of the Advanced Photon Source at Argonne National Laboratory, the VLS-SGM beamline of the Canadian Light Source in Saskatoon, and the DCM beamline of the Canadian Synchrotron Radiation Facility at the Synchrotron Radiation Center in Madison, Wisconsin.

Nanostructured ZnO and ZnO(Eu) samples were synthesized in a tube furnace system with argon as a carrier gas. Zn powder was evaporated from a crucible onto a silicon wafer, placed downstream of the furnace tube. Details of this technique were reported elsewhere [6].

RESULTS AND DISCUSSION

Grown in a gas flow furnace (see Experimental) ZnO can assume a large variety of morphologies. In Fig. 2 we show SEM images from ZnO structures (a, b), and structures of ZnO co-evaporated with Eu (c, d); both were deposited under the same conditions. In the present case ZnO exhibits thin needles, whereas ZnO(Eu) shows some bulky pyramid-like shapes.

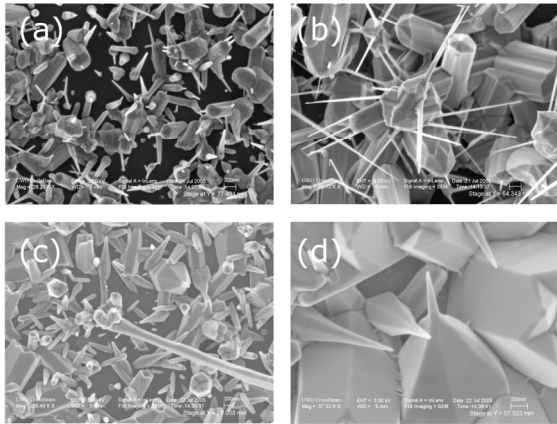


FIGURE 2. SEM images of ZnO (a, b), and ZnO(Eu) (c, d), grown on Si substrate under the same conditions.

Structural changes in the sample morphology on a nanoscale can strongly influence the emission of optical photons. Fig. 3 shows the XEOL spectra from different ZnO morphologies. Typical features in the ZnO luminescence spectrum exhibit a sharp band-gap emission at ~ 386 nm and broadband emission features at ~ 488 , and ~ 535 nm from defect states. The most stunning observation is the change in branching ratio between band-gap and defect state emission as we look at the XEOL related to different ZnO structures. A closer look reveals that there are slight shifts of the band-gap emission as well.

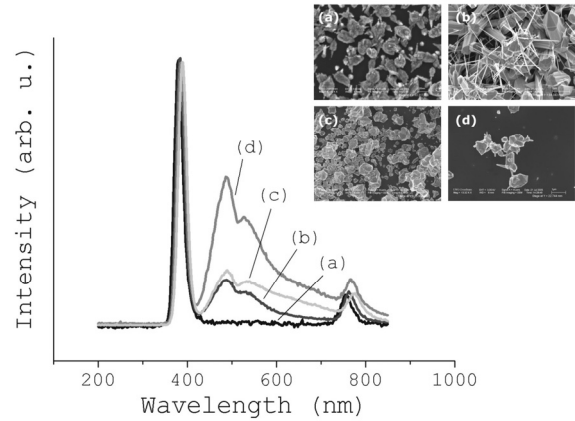


FIGURE 3. XEOL spectra (excited at 2300eV) and SEM images from ZnO grown on a silicon substrate (a-d, respectively). The spectra are normalized to the band-gap emission.

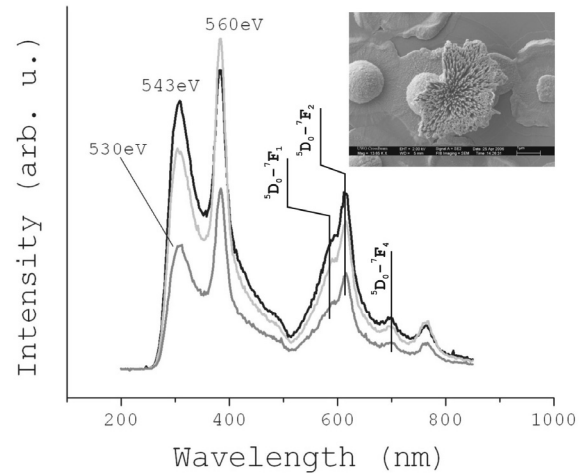


FIGURE 4. Optical emission of Eu^{3+} deposited on Si substrate, excited around the O K-edge. (The SEM image shows the morphology of the sample.)

Rare earth ions are known as strong light emitters and therefore are used in light emitting semiconductor design. In Fig. 4 we show optical emission from Eu^{3+} , excited at the O K-edge. The observed features at

~590, ~620, and ~708 nm are characteristic for this material, and are identified as $^5D_0\text{--}^7F_1$, $^5D_0\text{--}^7F_2$, and $^5D_0\text{--}^7F_4$ optical transitions [7,8]. Additionally, there are two pronounced peaks on the UV side of the luminescence spectrum. Their branching ratio changes when tuning the photon energy across the O K-edge (Fig. 4).

Time gated optical luminescence of ZnO(Eu) excited at 9661 eV is shown in Fig. 5. Using the time structure of the synchrotron (153 ns time gap between ~300 ps wide electron bunches at APS), the XEOL intensity was integrated within a selected time window. Integrating 0-10 ns after excitation only the bandgap is visible, whereas at 10-150 ns after excitation, i.e. just cutting the first 10 ns, the bandgap luminescence is much reduced and the dominant contribution to the XEOL intensity comes from the defect states. The ungated emission spectrum is shown as well (Fig. 5).

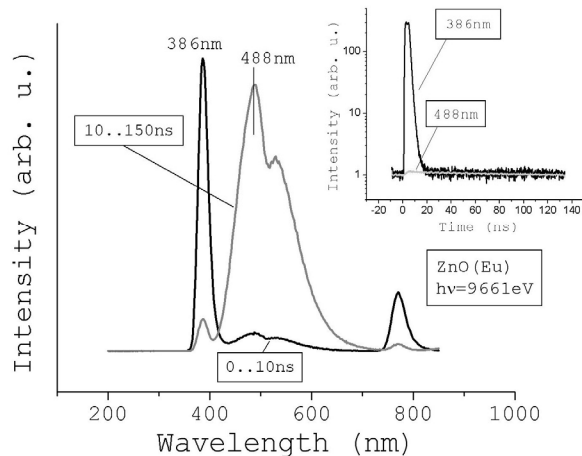


FIGURE 5. Time gated optical emission from co-evaporated europium and zinc on silicon ($h\nu=9661$ eV).

The time behavior of the optical luminescence depends on the various decay channels involved. Tuning to the selected wavelengths 384, 488, and 535 nm we find the lifetime involved with the optical bandgap transition (383 nm) is very short (~10 ns), whereas the defect states decay over much longer time. However, there is no direct evidence of the role of the Eu^{3+} dopant. This is most likely related to strong non-radiative decay mechanism which couples to Eu^{3+} ions in case of multiphonon excitation [9], or strong luminescence from the host (Fig. 3).

The presented data give clear evidence for the capabilities of XEOL and TRXEOL as techniques to the study phenomenological optical-structural correlation in nano-sized light emitting materials. On the other hand nanostructured ZnO compounds are promising light emitting materials which already are

being used in, e.g., scintillator design, because they are strong and fast light emitters even at room temperature. More efforts will be required to better understand the role of rare earth dopants in light emitting materials. The opening of new Eu^{3+} related decay channels, as well as structure-induced morphology changes, where Eu^{3+} nucleates new morphologies, are equally likely scenarios.

ACKNOWLEDGMENTS

CSRF, CLS and the Canadian component at PNC-CAT/APS are supported by NSERC MFA grants. Some of the research was performed at the Canadian Light Source which is partially supported by NSERC, NRC CIHR and the University of Saskatchewan. The Synchrotron Radiation Center, UW-Madison, is supported by the NSF under Award No. DMR-0084402. The work performed at the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. W-31-109-ENG-38. The Italian Ministry of Education, University and Research (MIUR) is also acknowledged for the FIRB Research Program - RBNE033KMA(LA).

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