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Relazione Scientifica conclusiva

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During the stage at the Department of Chemistry, the University of Western Ontario, the research activity has been focused on the synthesis of oxide-based nanosystems and the study of their size- and shape-dependent optical responses. The absorption and emission properties of nanostructures depend crucially on the intrinsic defect concentration, type and amount of dopants, degree of crystallinity as well as orientation.

In particular, object of the scientific activity has been the study of the luminescent behaviour of ZnO and GeO_2 nanostructures, pure and doped with optically active rare-earth impurities (Eu, Tb), grown by Vapor Solid synthesis.[1] Particular attention was devoted to the role of the synthesis parameters (nature of molecular precursors, nature and concentration of the doping elements) and processing conditions (deposition atmosphere, annealing temperature) in determining the composition, microstructure as well as the optical behaviour of the nanostructures.

The study of the luminescence, both in energy and time domain, was performed using synchrotron techniques called X-ray excited optical luminescence (XEOL) and time-resolved X-ray excited optical luminescence (TR-XEOL).[2-4] XEOL bares the essential features necessary for the study of advanced nanostructured materials like element specificity, 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 phenomenological correlation of structural, optical, and electronic properties. By tuning the photon energy to a particular absorption edge of an element, those sites responsible for the optical emission are thereby preferentially excited. The optical yield, in turn, is used to monitor the absorption; this technique is often called optical XAFS (X-ray Absorption Fine Structure). Although the mechanism of XEOL is complex for it involves the decay of super-excited states, it is generally realized that a radiative de-excitation channel results from the effective coupling of the super-excited state with the chromophore, producing electron-hole pairs that recombine radiatively. Besides structural aspects, the time behavior of nanostructures has been investigated using the time structure of synchrotron radiation. In third generation synchrotron the light pulses have subnanosecond duration and hundreds of nanoseconds repetition rate, thus being suitable to study the variable and sometimes relatively long life times of luminescence (nanoseconds to milliseconds). In particular, the time structure of the luminescence decay from oxide nanosystems excited by X-ray pulses and the time gated XEOL can be measured by counting photons coming through a selected time window.

ZnO nanostructures

ZnO is expected as the innovative material for the future optoelectronic devices. ZnO has a wide band-gap energy (3.37 eV at room temperature) and it is suitable as host material for the doping with optically active impurities such as transition-metal and rare-earth ions. The optical features of pure and doped ZnO nanostructures are matter of intense investigation, being of fundamental importance for the use of such light-emitting materials in advanced applications, but they are not known in detail. It is well known that the optical features of pure and doped ZnO nanostructures depend crucially on the intrinsic defect concentration, type and amount of dopants as well as degree of crystallinity. In particular, by lanthanide doping the luminescent properties can be tailored towards strong emission at selected wavelengths suitable for potential light emitting applications.

To this aim, pure ZnO, Eu-doped and Tb-doped nanosystems have been synthesized (see experimental).[1] Samples simultaneously doped with both REs have been also prepared to study the combined optical emission of (Eu+Tb) in the oxide matrix. The samples where synthesized in a tube furnace system kept at 550°C with argon as a carrier gas. Zn powder and $RECl_3$ (RE = Eu, Tb) salts were evaporated from a crucible onto a silicon wafer, placed downstream of the furnace tube.

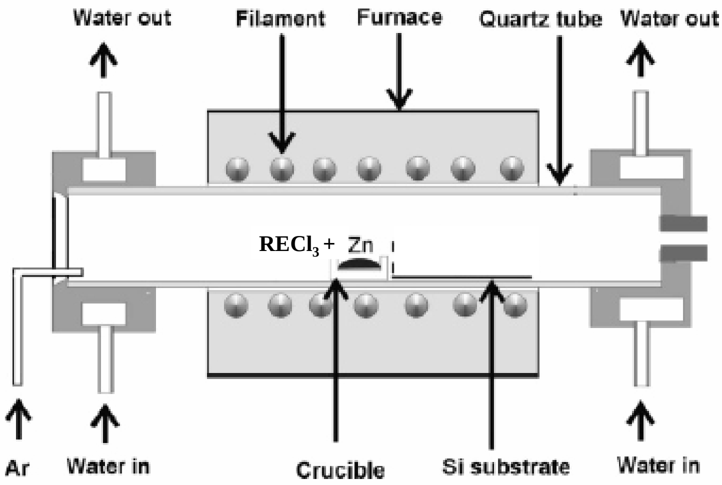


Figure 1. A schematic diagram of the experimental apparatus for growth of ZnO nanostructures by the solid−vapor phase process.

Grown in a gas flow furnace ZnO can assume a large variety of morphologies. In Fig. 2 SEM images from ZnO structures (a, b), and structures of ZnO co-evaporated with Eu (c, d) are shown; both were deposited under the same conditions. In the present case ZnO exhibits thin needles, whereas ZnO(Eu) shows some bulky pyramid-like shapes.[5,6]

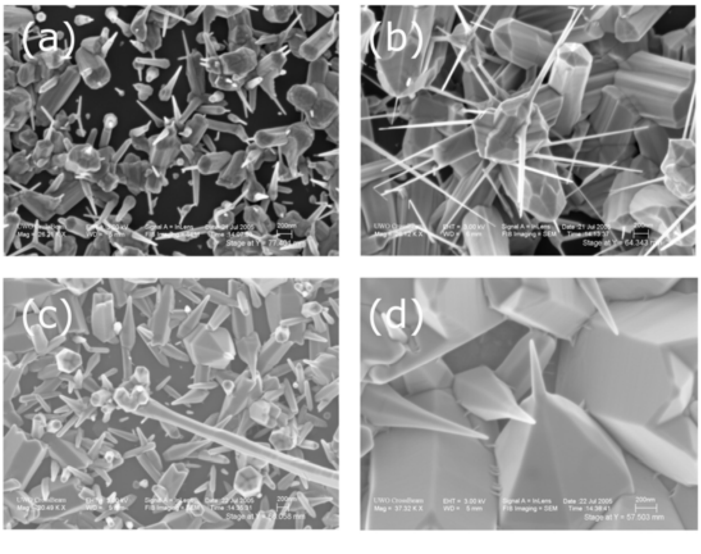


FIGURE 2. SEM images of ZnO (a, b), and ZnO(Eu) (c, d), grown on Si substrate under the same conditions.

As revealed by XRD analysis, a sole crystalline phase was adopted by all samples, despite the diverse morphologies. Both undoped and ZnO(Eu) systems show the ZnO hexagonal wurtzite structure. The sharp diffraction peaks suggest that the ZnO nanostructures are highly crystalline. Moreover, diffraction peaks from other phases such as europium oxides are not detected, thus suggesting a high dispersion of the guest species in the host oxide matrix.[5]

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.

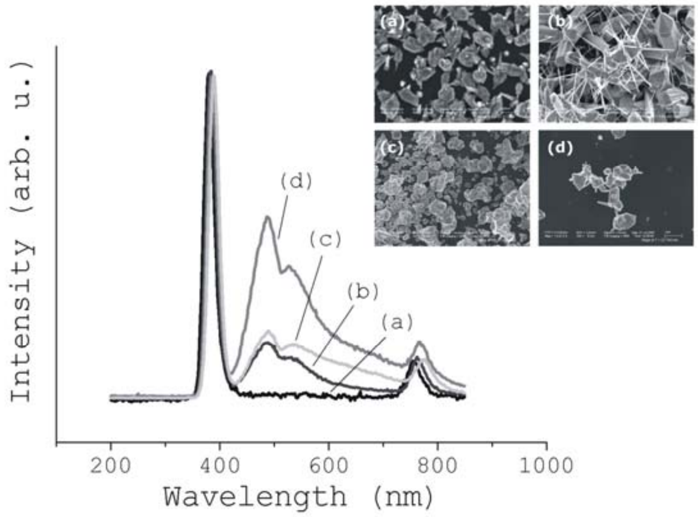


FIGURE 3. XEOL spectra (excited at 2300eV) and SEM images from Zn grown on a silicon substrate (a-d, respectively). The spectra are normalized to the band-gap emission.

Typical features in the ZnO luminescence spectrum exhibit a sharp band-gap emission at ~386nm and broadband emission features at ~488, and ~535nm 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.[6]

Time gated optical luminescence of ZnO(Eu) excited at 9661eV is shown in Fig. 4. Using the time structure of the synchrotron (153ns time gap between ~300ps wide electron bunches at

APS), the XEOL intensity was integrated within a selected time window. Integrating 0-10ns after excitation only the bandgap is visible, whereas at 10-150ns after excitation, i.e. just cutting the first 10ns, 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. 3).

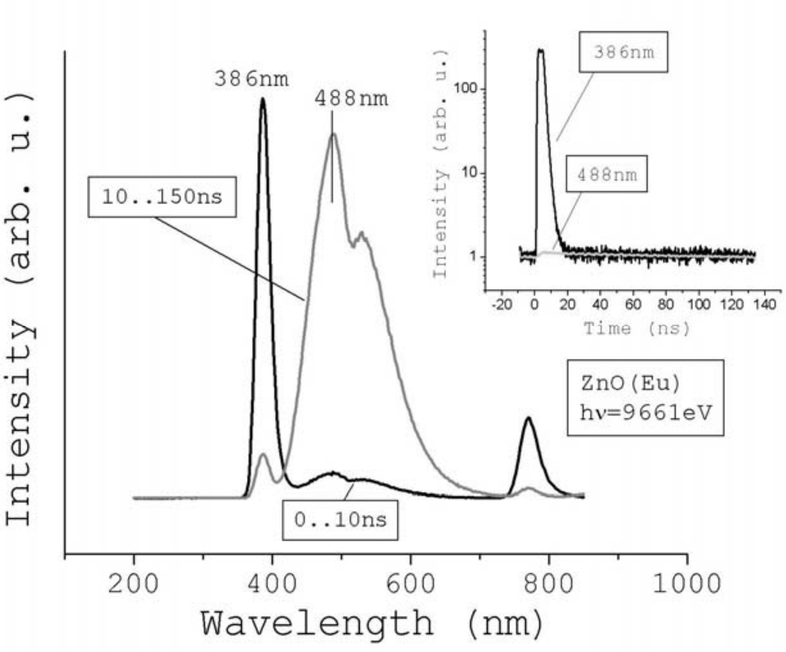


FIGURE 4. Time gated optical emission from co-evaporated europium and zinc on silicon (hν= 9661eV).

The time behavior of the optical luminescence depends on the various decay channels involved. Tuning to the selected wavelengths 384, 488, and 535nm we find the lifetime involved with the optical bandgap transition (383nm) is very short (~10ns), 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, or strong luminescence from the host (Fig.4).

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.

A similar analysis will be performed also on ZnO(Tb) and ZnO(Eu+Tb) nanostructures.

Experimental

Chemicals. Zn powder (99.9%, Alfa Aesar) was used as source compounds for ZnO. $RECl_3$ $6H_2O$ (Aldrich, 99.9%) was used as staring material for the europium or terbium doping of zinc oxide. The precursors were used as received. Silicon wafers were used as the substrate. Before deposition, they were cleaned by sonication in acetone.

Synthesis. ZnO and RE-doped ZnO nanostructures were synthesized according to a previously reported procedure.[1] In a quartz tube, mounted inside a horizontal tube furnace, an alumina boat containing the source precursors was placed at the middle of the high-temperature zone of the furnace. For the preparation of pure ZnO samples, only the Zn powder was used, whereas a mixture of both Zn and $RECl_3$ $6H_2O$ (RE/Zn = 0.1 at.) was adopted for the deposition of RE-doped nanosystems. The silicon wafer was placed at a position downstream of the carrier gas (Ar), which was introduced at one end of the quartz tube at a flow rate of 100 sccm (standard cubic centimeters per minute), whereas the other tube end was open to air. The temperature of the furnace was increased to 550° C and kept for 60 min. After the reaction, the system was cooled to room temperature and gray- or white-colored products were found covering the silicon substrate. The deposited layers consisted of ZnO-based nanostructures characterized by various morphologies depending on their position on the substrate as well as on the presence of the doping element.

Structural characterization. The morphology and microstructure of the as-synthesized samples were characterized by Scanning Electron Microscopy (SEM, LEO 1540XB) and X-ray Diffraction (XRD, Rigaku, Co Kα radiation, $\lambda = 0.1792$ nm).

XANES and optical XANES. Experiments were performed at the Grasshopper beamline (Eu N-edge), and the Double Crystal Monochromator (DCM) beamline (above Zn L-edge) of the Canadian Synchrotron Radiation Facility (CSRF) located at the Synchrotron Radiation Center (SRC, University of Wisconsin-Madison), at the PNC-CAT beamline (Zn K-edge) of the Advanced Photon Source (APS, Argonne National Laboratory), and at the spherical grating monochromator (SGM) beamline (O K-edge) of the Canadian Light Source (CLS, University of Saskatchewan).

XEOL and TR-XEOL. The optical properties of ZnO and Eu-doped ZnO nanosystems were studied by x-ray excited optical luminescence (XEOL) and time resolved x-ray excited optical luminescence (TR-XEOL). XEOL spectra were scanned with a JY optical monochromator. The optical detector was a Hamamatsu R943-02 photomultiplier (PMT) with 2 ns rise time. Time Resolved XEOL (TR-XEOL) experiments were performed at the SGM beamline (CLS) using single bunch mode (60 ps pulse width, 570 ns repetition, 10-15 mA ring current) and at PNC-CAT beamline (APS) using the normal fill pattern (100 ps pulse width, 153 ns repetition, ~100mA ring current in top-up mode).

GeO_2 nanostructures

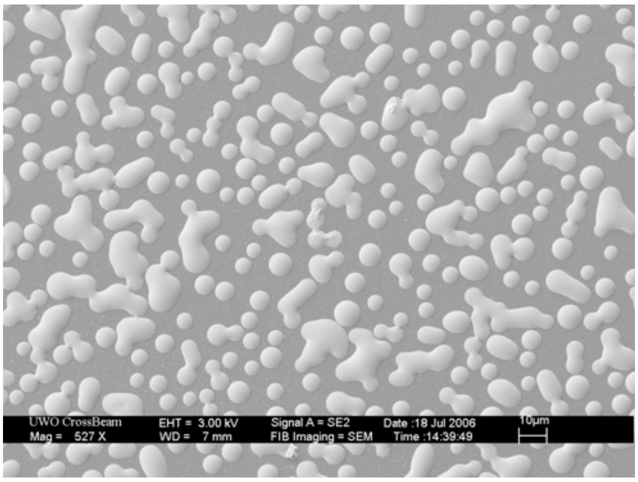
GeO_2 is an important material for optical fibers and it has a blue luminescence around 3.1 eV (*ca.* 400 nm) and 2.2 eV (*ca.* 563 nm). Pure and RE doped GeO_2 nanostructures would be useful for future optical communication devices. Few works are reported in literature on the synthesis of GeO_2 nanostructures, and most concern the preparation of nanowires.[7,8]

The synthesis of GeO_2-based nanostructures is thus interesting to investigate he dependence of the optical emission on the system dimensionality as well as on the presence of RE dopants.

To this aim, a great experimental work has been done to optimize the deposition conditions, as described in the following. Pure GeO_2, Eu-doped and Tb-doped nanosystems (RE/Ge atomic ratio 0.1) have been prepared by Vapour-Solid synthesis. The samples where synthesized in the tube furnace system used for ZnO at various temperatures (900-1200°C) with argon as a carrier gas (flux: 50-100 sccm). Ge powder and $RECl_3$ (RE = Eu, Tb) salts were evaporated from a crucible onto silicon or alumina wafers, placed downstream of the furnace tube. Samples simultaneously doped with both REs have been also prepared to study the combined optical emission of (Eu+Tb) in the oxide matrix.

In particular, the following aspects have been considered: i) the experimental conditions for actual synthesis of GeO_2 nanostructures, ii) the variety of nanosystems shape as a function of synthesis conditions, iii) the emission properties of GeO_2 as a function of their nanostructure, iv) the role (electronic and/or structural) of REs on the emission properties of GeO_2, v) the local structure of REs in the doped GeO_2 nanostructures.

At the moment, the morphology of a few samples has been investigated by SEM analysis. In particular, GeO_2 presents a very different structure as a function of the substrate nature. In Fig. 5 GeO_2 nanostructures deposited in the same conditions on Si wafer (a) or porous alumina (b), are reported.



(a)

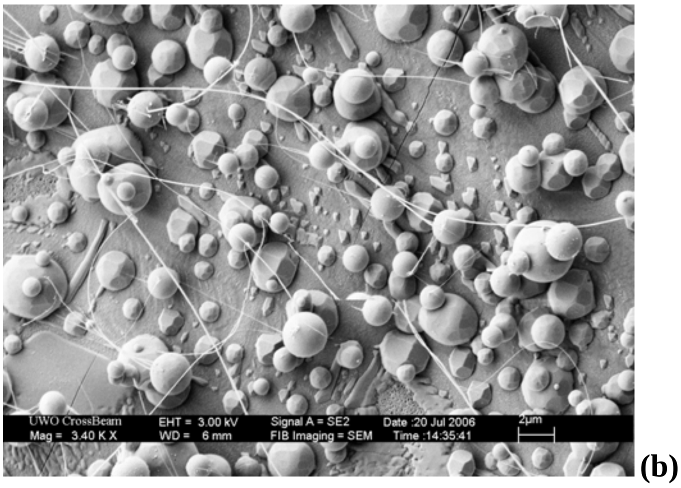


FIGURE 5. SEM images of GeO_2 grown on Si substrate (a) and porous Al_2O_3 (b) under the same conditions.

When deposited on Si wafers (Fig. 5 (a)), GeO_2 is in the form of droplets, likely due to the low wettability of Si surfaces by germanium dioxide. On porous alumina (Fig. 5 (b)) , the formation of spheres is observed, with few faceting and long thin wires connecting them. The reference porous alumina clearly shows the honeycomb structure (Fig. 6).

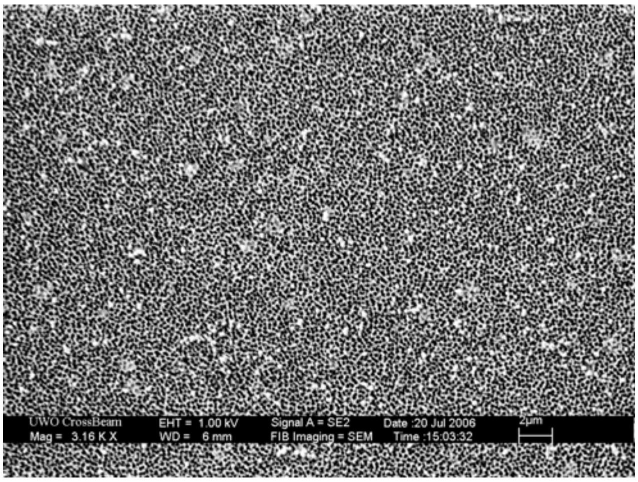


FIGURE 6. SEM image of the porous alumina substrate.

The points to be investigated and clarified are: i) the morphology of doped-GeO_2 nanostructures, ii) the actual chemical composition (atomic ratio RE/Ge), iii) the sample microstructure, iv) the role of RE on the morphological features and optical emission behaviour.

Experimental

Chemicals. Ge powder (99.9%, Alfa Aesar) was used as source compounds for GeO_2. $RECl_3$ $6H_2O$ (Aldrich, 99.9%) was used as staring material for the europium or terbium doping of germanium dioxide. The precursors were used as received. Silicon wafers or porous alumina were used as the substrate. Before deposition, they were cleaned by sonication in acetone.

Synthesis. GeO_2 and RE-doped GeO_2 nanostructures were synthesized according to a previously reported procedure.[1] In a quartz tube, mounted inside a horizontal tube furnace, an alumina boat containing the source precursors was placed at the middle of the high-temperature zone of the furnace. For the preparation of pure GeO_2 samples, only the Ge powder was used, whereas a mixture of both Ge and $RECl_3$ $6H_2O$ (RE/Ge = 0.1 at.) was adopted for the deposition of RE-doped nanosystems. A set of samples was prepared using $Fe(NO_3)_3$ as oxidizing agent for Ge.[8]

The silicon wafer or the porous alumina were placed at a position downstream of the carrier gas (Ar), which was introduced at one end of the quartz tube at a flow rate ranging between 50 and 100 sccm (standard cubic centimeters per minute), whereas the other tube end was open to air. The temperature of the furnace was increased to a maximum value of 1200°C by a step by step procedure and kept for at least 6 hours. After the reaction, the system was cooled to room temperature and white-coloured products were found covering the substrates. The deposited layers consisted of GeO_2-based nanostructures characterized by various morphologies depending on the substrate nature.

Structural characterization. The morphology and microstructure of the as-synthesized samples were characterized by Scanning Electron Microscopy (SEM, LEO 1540XB).

References

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