XANES and photoluminescence studies of crystalline GeO$_2$ (Tb) nanowires

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Abstract. We report a synchrotron study of GeO$_2$ nanowires (NWs) prepared by a vapor-liquid-solid (VLS) method on a silica glass substrate. The electronic and local structure of GeO$_2$ NWs were studied by X-ray Absorption Near-Edge Structure (XANES) at the O K- and Ge L$_{3,2}$-edges. X-ray Excited Optical Luminescence (energy and time resolved) were used to monitor the optical emission upon X-ray absorption with the excitation energy tuned across absorption edges of interest. Using this method one obtains site specific insight into the chemical origin of luminescence.

1. Introduction
One-dimensional nanostructures provide a testing ground for the dependence of electrical, thermal, transport and mechanical properties on dimensionality and size (quantum confinement). Renewed interest in Ge as a material for future electronics is more recent and is due to its significantly higher electron and hole mobility than Si [1]; this is desirable as electronic devices are scaled down to the sub-micrometer range. In this range optical confinement effects become important as the exciton Bohr radius and the characteristic size of the nanostructure are in the same order of magnitude. As a result one observes the optical band gap or defect transitions shifted to higher energies. This is particularly

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true for Ge which has a large exciton radius (24.3nm) [2]. Although recent reports show that both Ge and GeO$_2$ nanostructures are light emitters, studies of germanium based nanowires (NW) have been scarce [2-4]. In general, Ge based NWs growth using Au nanoparticles as catalyst benefits from the low eutectic temperature of Ge-Au alloy (360°C), and follows the vapor–liquid–solid (VLS) [5] process. Here we report a synchrotron study of terbium doped GeO$_2$ NWs prepared with VLS without using any catalyst [6]. Nanocrystalline GeO$_2$ is a blue photoluminescence (PL) material, with peaks observed at energies around 3.1 eV (400 nm, violet) and 2.3 eV (539 nm, green) [7, 8]. In the present sample the characteristic size of the NWs covers a range of 50-500 nm. The role of the rare earth dopant, in the present case Tb, is generally quite complex. Depending on the oxidation state, the rare earth dopant can directly enhance or quench the optical emission, or may also act as a nucleation center for defects. In this study, the electronic and local structure of GeO$_2$ NWs have been investigated with X-ray absorption near-edge structure (XANES) and X-ray excited optical luminescence (XEOL) at the Ge L$_{3,2}$-edge. XEOL monitors the optical response from the specimen upon X-ray absorption (scintillation efficiency) and can be site specific if the excitation is tuned across the absorption edge of interest.

2. Experiment

GeO$_2$ (Tb) NWs on a SiO$_2$ (silica) substrate were prepared by vapor deposition in a horizontal tube furnace as described previously [9-11]. Ge powder (99.9%, Alfa Aesar) was used as source compounds for GeO$_2$. TbCl$_3$·6H$_2$O (Aldrich, 99.9%), was used as the starting material for the terbium doping of germanium dioxide. The precursors were used as received. Silica slides were used as the substrate. Before deposition, they were cleaned by sonication in ethyl alcohol and acetone. Tb-doped GeO$_2$ nanostructures were synthesized as follows. 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. Silica slides 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 of 55sccm (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 products were found covering homogeneously the silica substrates. The NWs were found to have a thickness of 50-500nm.

![Figure 1: SEM and TEM images of Tb doped GeO2 nanowires with a thickness ranging 50-500 nm. The XRD analysis is shown in the inset on the right.](image-url)

Most synchrotron measurements were conducted at the SGM beamline of the Canadian Light Source, a third generation 2.9 GeV ring operating at an injection current of 250 mA at the present time. Total electron yield (TEY) was measured from the sample drain current. Fluorescence yield was
measured with a pair of micro-channel-plates (MCP). The X-ray excited optical luminescence (XEOL) was collected by a scientific-grade spectrometer, QE650000, Ocean Optics via optical fibre. Time resolved XEOL was measured at the 4 ID beamline line (SGM) of the Advance Photon Source. The optical signal was referenced to the bunch clock of the electron storage ring with a time gap of 153 ns between consecutive bunches in normal top-up mode at 100 mA ring current. A detailed description of this technique is given in Ref [12]. Images of the GeO₂(Tb) NWs by SEM and TEM are shown in Fig.1. The NWs are generally uniform. The thickness of the NWs covers a wide range of sizes: 50-500 nm (cf. scale in Fig.1).

3. Results
The total fluorescence yield (FY) and total electron yield (TEY) from GeO₂(Tb) NWs at the O K-edge and at the Ge L₃,₂-edge are shown in Fig. 2. The peaks in the O K-edge spectrum appear as a result of O 1s transitions to the O 2p σ* states hybridized with metallic s, p, and d orbitals, mapping the unoccupied density of states (band structure). A pronounced peak in FY at 540 eV appears much less intense in TEY, which is more surface-sensitive compared to the FY. In TEY we see a small pre-edge shoulder and noisy signal overall, which most likely is due to charging (the substrate is an insulator in this case), and has undesirable effects on the thermalization of the electrons and holes and hence the total electron and luminescence yield. PLY shows a more or less even curve with some signal inversion features. As the nanowires are grown on silica most of the TEY and FY signal comes from the substrate (not from the nanowires), and PLY changes little when crossing the O K-edge, thus the conversion of X-ray energy to optical photons appears equally efficient below and above the edges.

![Figure 2: Total fluorescence yield (FY) and total electron yield (TEY) at the O K-edge (left) and at the Ge L₃,₂-edge (right). PLY is in zero order, i.e. total luminescence yield.](image)

![Figure 3: Optical emission of GeO₂(Tb) NWs at different excitation energies: in the vicinity of the O K-edge (left), at the Ge L₃-edge and the Tb M₅-edge (right).](image)
The Ge L\textsubscript{2,3}-edge XANES probes primarily the s character of the unoccupied densities of states above the Fermi level via a 2p to 4s transition. Both, FY and TEY, follow the same footprint, whereas PLY (zero order) does not change across the Ge L\textsubscript{3,2} edge. As the wires are not more that 500 nm in diameter, thickness effects (self-absorption) are not expected to be a problem. This confirms the assumption that the NWs are highly homogeneous.

The optical emission excited at the O K-edge and the Ge L\textsubscript{3}-edge is shown in Fig. 3. In the spectra we can clearly distinguish three important emission bands (fitted Gaussians) and some weak components at higher energies (~4 eV and ~5 eV). Excited in the vicinity of the O K-edge the peaks are centered at 3.02 eV (violet), 2.36 eV (green), and 1.57 eV (red), with the green peak being the most intense. With the excitation energy tuned to the Ge L\textsubscript{3}-edge the violet peak becomes the most intense by far dominating the other peaks. While the peaks of the violet and red emission bands are centered at similar energies, namely at 3.11 eV and 1.56 eV, the green emission peak appears to be considerably shifted to 2.74 eV. It is interesting to note that although change in the branching ratio of the emission peaks resulting from different excitation energy has been observed previously, this observation is perhaps most dramatic.

![Figure 4: Partial luminescence yield of selected emission bands (left) and X-ray attenuation length (right) versus excitation energy (CXRO calculator).](image)

The luminescence yield (proportional to the branching ratio) of the violet, green and red peaks at excitation energies ranging from below the oxygen K-edge to above the Ge L\textsubscript{3,2}-edge are shown in Fig. 4 (left panel). The yield of the violet emission band starts to increase at around 900 eV and drops back

![Figure 5: Time gated X-ray excited (h\textsubscript{ex}=530eV) optical luminescence of GeO\textsubscript{2} (Tb) NWs (left). Angular dependence of the violet, green, and red emission yield (right).](image)
to the initial yield when crossing the Ge L$_3$-edge (Fig. 4 / left). Except for a small increase at the Ge L$_3$-edge, the yield of the green and red emission peak remains roughly the same. For comparison: the attenuation length at 900 eV is 500 nm (typical NW thickness), increasing to 1µm at the Ge L$_3$-edge (Fig. 4 / right). This notion is confirmed by the angular dependence of the partial optical yield at the Ge L$_{3,2}$-edge (Fig. 5 / right), which shows how the accessibility of the deeper laying transitions increases with increasing angle of incidence, i.e. increasing penetration depth of the exciting X-rays, with reference to the substrate surface to which the randomly oriented NWs align.

Time gated optical luminescence of GeO$_2$ (Tb) NWs excited at the O K-edge is shown in Fig. 5 (left). The ungated spectrum is shown together with the short-gate (0-50 ns) and long gated (50-150 ns) spectrum. The excitation repetition rate in this experiment was 153ns (APS, normal top-up mode). The long-gated spectrum looks very similar to the ungated case, which indicates that the dynamics are actually quite fast. Interestingly, even the ungated spectrum shows a violet emission component, whereas the red emission component is completely missing in any of the cases.

4. Discussion
The different types of oxygen state related defects which appear at the surface, the bulk and at the interface between Ge based nanostructures are depicted in Fig. 6 [3,14]. At the surface defects nucleate from GeOH species and from GeO$_2$ dangling bonds [14]. These surface defects induce very shallow levels giving rise to optical transitions at ~1.8 eV (~689 nm). Inside the NW bulk nonstoichiometric GeO$_{2-X}$ defects give rise to optical transitions in the range 2.2-2.7 eV (564-459 nm) [14]. The defects usually depend on the thickness of the NW as the stoichiometry varies along the diameter. At the interface between GeO$_2$ NWs and the silica substrate O-Ge.=O defects and divalent Ge defects (or dicoordinated Ge defects) are expected, since they are more stable in the presence of silica (SiO$_2$) [14,15]. Eventually these defects are also stable between adjacent NWs, which would explain the observed intense optical emission. These interface defects generate several PL bands, giving raise to optical transitions at about 3.1 eV (~400 nm) [14] of which the initial state is reached by an intersystem crossing process (singlet to triplet), and becomes important as the size of the sample is reduced, i.e. in films (interface contribution) [16].

Figure 6: Schematic model of the GeO$_2$ NWs on a SiO$_2$ substrate with surface, bulk, and interface defects.

In our model we assume three peaks corresponding to surface bulk and interface defects in order to analyse the optical emission spectrum. Using this simplified model we take into account that there is a broad variety of each type of defect (surface, bulk, and interface), each of them appearing as a band with the peak centered at the mean value of the distributed energies.

As the penetration depth of X-rays increases with increasing energy the deeper laying defects become gradually accessible and contribute to the optical spectrum. The opposite effect occurs as an absorption edge is crossed, steeply reducing the penetration depth as it is observed, e.g. at the Ge L$_3$-edge (cf. Fig. 4). This picture is supported by the angular dependence of XEOL, i.e. the dependence of the optical emission and the incident angle of the exciting X-rays. As shown in Fig. 5 (left) the violet component increases with the angle of incidence, whereas the intensity of the green and red peaks decreases. (Note that the penetration depth increases with steeper angle of incidence.)
Some minor effect is observed when crossing the Tb M edge, but the role of Tb is not yet clear. As confirmed by XPS, some segregation of Tb to the surface of the NWs, creating an additional interface, might be the reason for this minor effect.

5. Conclusion

Preliminary results of synchrotron light excited luminescence near the Ge L$_3$-edge and O K-edge and corresponding XANES have been reported. We show optical emission results from GeO$_2$ (Tb) NWs prepared by VSL technique and identify the different oxidation states and their contribution to the XEOL. Thus XEOL using a synchrotron source adds a new dimension in the analysis of nano-sized light emitting materials. The most evident effect is the vanishing of the violet peak which is attributed to optical transitions related to defects at the interface between NWs and substrate (O-Ge...-O), and probably also occur between adjacent NWs. Apparently the decreasing information depth when crossing the Ge L$_3$ edge plays a major role. Less pronounced, but still present, is the shift of the green emission peak which is attributed to optical transitions related to GeO$_2$:X defects. Keeping in mind the steep variation of the information depth this might be the footprint of an oxidation state gradient along the diameter of the NWs. The role of the Tb dopant could not be clarified so far and awaits future investigation.

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