2D XAFS-XEOL Spectroscopy – Some recent developments

M J Ward¹, J G Smith¹, T Z Regier², T K Sham¹,³

¹The University of Western Ontario, London, Ontario, CANADA, N6A 5B7
² Canadian Light Source Inc., Saskatoon SK, CANADA, S7N 0X4
³ To whom correspondence may be addressed, email: tsham@uwo.ca

Abstract. The use of optical photons to measure the modulation of the absorption coefficient upon X-ray excitation, or optical XAFS, is of particular interest for application to the study of light emitting semiconducting nanomaterials due to the additional information that may be gained. The potential for site-selectivity, elemental and excitation energy specific luminescence decay channels, and surface vs. bulk effects all make the use of X-ray excited optical luminescence (XEOL) desirable as a detection method. Previous experiments have made use of a monochromator to select the optical emission wavelength used to monitor optical XAFS. This method of detection suffers from the primary limitation of only being able to monitor the optical response at one emission wavelength. By combining the high resolution soft X-ray Spherical Grating Monochromator beam-line at the Canadian Light Source with an Ocean Optics QE 65000 fast CCD spectrophotometer and custom integration software we have developed a technique for collecting 2D XAFS-XEOL spectra, in which the excitation energy is scanned and a XEOL spectra is collected for every energy value. Herein we report the development of this technique and its capabilities using the study of the luminescence emitted from single crystal zinc oxide as an example.

1. Introduction

The phenomenon of X-ray excited optical luminescence (XEOL) has been around since the discovery of X-rays by Röntgen in 1895, and has been commonly used to “see” X-rays [1]. Despite its popularity the XEOL process has not been fully understood because of both the complexity of the energy transfer process involving the decay of a core-hole and subsequent decay cascade dynamics, and its strong dependence on the composition, structure, morphology, size, crystallinity and defects of the scintillation material [2-4]. The advent of third generation light sources combined with the advancement of the nanoscience field has changed this and XEOL is now routinely employed in the study of luminescence and defect processes in nanomaterials [5]. XEOL has become particularly useful for understanding energy transfer in semiconducting nanostructures where the dynamics leading to band-gap and defect luminescence processes are of great importance [6]. X-ray absorption fine structures (XAFS) measures the modulation of the absorption coefficient across a given absorption edge and thus provides elementally specific information about the nature of an absorbing atom in a chemical environment. Typically XAFS spectra are recorded using either transmission or yield methods. For low Z elements or shallow core levels where the corresponding energy is in the VUV region, total electron yield (TEY) or total fluorescence yield (TFY) detectors are often used. However, it is also possible to use XEOL as a mode of XAFS detection provided the sample has an optical luminescence response to X-ray excitation. This so called photoluminescence yield (PLY) mode of XAFS detection, sometimes known as optical XAFS, benefits from the site-specificity that XEOL is often capable of achieving, especially in the soft X-ray region and...
in nanostructures, and thus is a valuable tool for studying a specific absorbing atom in a multi-site sample [6,7]. By combining these techniques we can produce 2D XEOL intensity maps as a function of luminescence wavelength and X-ray excitation energy by simultaneously collecting a XEOL spectrum at every value of the excitation energy during an XAFS scan. Herein we will discuss the experimental set-up for this technique and give an example of its application to the study of luminescence decay processes in single crystal (SC) ZnO (0001).

2. Experiment Design and Apparatus
In order to rapidly collect high quality XAFS-XEOL spectra it is critical to have a fast, high resolution, spectrophotometer and a high resolution beam-line. Additionally, beam-lines that operate in the soft X-ray regime (~200 – 2000 eV) are particularly suited to this type of experiment for the following reasons: (1) at low excitation energy the quantum efficiency of XEOL is much higher than at high X-ray energy where X-ray fluorescence processes dominate (X-ray can escape the solid without contributing to the secondary process which in turn leads to energy transfer to the luminescence channel); (2) at these energies the X-ray attenuation length (1/e) is sufficiently short to allow for probing of surface, interfacial, and bulk regions of the sample, for example, the attenuation length at the Si L$_{1,2}$-edge (~100 eV) of elemental Si is 56 nm, allowing the probing of various layers of a nanodevice; (3) the mean free path for electrons in condensed matter excited using soft X-rays is relatively short, i.e. according to the universal inelastic mean free path of the electron, which has a minimum at ~0.5 nm with kinetic energy at ~50 eV, and thus their energy is more readily transferred through inelastic scattering creating shallow holes and low kinetic energy (secondary) electrons which results in short thermalization paths, whereas hard X-ray yields higher kinetic energy electrons hence longer thermalization paths, thus the effect would be much less localized; (4) electrons in the K and L shells of many important light emitting semiconducting nanomaterials (ZnO, GaN, Si, etc.) are accessible at these energies.

Our experiments were performed on the spherical grating monochromator (SGM) beam-line at the Canadian Light Source (CLS), a high resolution - high flux undulator based beam-line with an energy range of 250-2000 eV and a resolving power greater than $10^4$ below 800 eV [8]. An Ocean Optics QE 65000 Scientific Grade spectrophotometer with a spectral range of 200-900 nm (UV-vis-NIR) and a resolution of ~0.88 nm was used for XEOL acquisition. The QE 65000 is a symmetrical crossed Czerny-Turner design spectrophotometer with a high quantum efficiency (QE 90% peak) Hamamatsu TE cooled S7031-1006 2D CCD detector. A lens system composed of a set of 1 inch lenses with a 30 mm WD and a sapphire UHV window is used to collect XEOL emission from the sample and transfer it out of the vacuum chamber to the spectrophotometer. Custom software was written using Java SDK purchased from Ocean Optics and allows the spectrometer to be controlled from any CLS beam-line via an EPICS application. The custom control software triggers the spectrometer to record a XEOL spectrum every time the beam-line monochromator increments the excitation energy. In this way it is possible to collect a 2D XAFS-XEOL intensity map during regular XAS data collection, allowing for the simultaneous collection of normal TEY and TFY spectral data.

3. Results and Discussion
Zinc oxide is a wide band-gap ($E_g = 3.37$ eV) semiconductor that has been observed to exhibit near-band-gap (NBG) emission at 380 nm as well as broad defect bands in the green, orange, and red regions of the visible spectrum [6]. In order to test our XAFS-XEOL technique we measured the optical emission from a ZnO (0001) single crystal (MTI ZnO 0001 ± 0.5°, hexagonal, surface roughness < 5 Å, O face polished) at 45° normal to the incident X-ray beam.

A 2D XAFS-XEOL map of the XEOL emission intensity taken across the O K-edge of single crystal (SC) ZnO with the oxygen face polished (i.e. the oxygen layer in the hexagonal structure is exposed) is
shown in figure 1(a). By taking vertical slices from figure 1(a), we obtain XEOL emission spectra at selected excitation energies. XEOL spectra taken below, at, and above the O 1s excitation threshold are shown in figure 1(b). Two main features can be observed in the XEOL spectra, a broad intense defect emission band at ca. 580 nm and a very weak band-gap (BG) peak at ca. 363 nm (figure 1(b), see inset for zoom in on BG peak). By taking horizontal slices from figure 1(a) we get wavelength selected PLY spectra. The PLY recorded at the BG is shown in figure 1(c), note the positive optical response across the O K-edge.

Figure 1 – (a) 2D XAFS-XEOL mapping across O K-edge of ZnO single crystal shown with O K TEY spectrum. (b) XEOL slices taken across the O K-edge from Fig. 1a (inset zoomed in on band-gap emission). (c) PLY slice taken at ZnO band-gap emission maximum across the O K-edge. (d) PLY slices taken at selected wavelengths from defect emission band across the O K-edge (d).

PLY spectra recorded at selected wavelengths from the broad defect peak are shown in figure 1(d), there is a negative optical response across the O K-edge. The increase in XEOL intensity at the O 1s resonance for BG emission is concomitant with a decrease in intensity for the defect emission band (figure 1(b)). Qualitatively, the PLY$_{580\text{nm}}$ inversion across the O K-edge suggests that the broad band at 580 nm is related to O defects in a thin surface layer. At the edge there is a rapid change in absorption cross section as competition for photons by the newly accessible O 1s core-level occurs, producing Auger electrons and
fluorescent X-rays. Auger electrons created in the surface and near-surface regions can escape the surface without contributing to the thermalization (secondary) process, and thus a surface layer with a thickness comparable to the attenuation length of electrons can truncate the thermalization path and lead to a reduction in e-h pair formation, and subsequently, a reduction in luminescence. The positive edge jump in the PLY$_{363\text{nm}}$ for BG emission across the O K-edge suggests a more complete thermalization process for this optical decay channel, which would be expected for an emission band originating within the bulk of the ZnO crystal. The effects of surface atom termination (Zn vs. O face polished) and angular resolution on the optical luminescence of SC ZnO will be addressed in a future publication.

4. Conclusions

2D XAFS-XEOL mapping has been demonstrated as a powerful technique for simultaneously collecting energy resolved XEOL and wavelength resolved PLY data. The application of this technique to the study of SC ZnO has shown that it is possible to track the optical luminescence decay behaviour of multi emission bands in a single experiment which helps increase the efficiency of detailed XEOL data collection using limited amounts of beam-time. A recent 2D XAFS-XEOL study of GaN-ZnO solid solution nanostructures by Ward et al [9] demonstrated that this technique can be used to trace the efficiency of X-ray excited optical emission channels across absorption edges of nanostructures of different size and morphology.

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