Time-resolved X-ray excited optical luminescence using an optical streak camera

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Abstract. We report the development of a time-resolved XEOL (TR-XEOL) system that employs an optical streak camera. We have conducted TR-XEOL experiments at the Canadian Light Source (CLS) operating in single bunch mode with a 570 ns dark gap and 35 ps electron bunch pulse, and at the Advanced Photon Source (APS) operating in top-up mode with a 153 ns dark gap and 33.5 ps electron bunch pulse. To illustrate the power of this technique we measured the TR-XEOL of solid-solution nanopowders of gallium nitride – zinc oxide, and for the first time have been able to resolve near-band-gap (NBG) optical luminescence emission from these materials. Herein we will discuss the development of the streak camera TR-XEOL technique and its application to the study of these novel materials.

1. Introduction

X-ray excited optical luminescence (XEOL) is now a routinely used X-ray photon-in optical photon-out technique for studying optical decay channels and their relation to core-level specific absorption processes. In order to further the applications of XEOL we have developed a time-resolved (TR-XEOL) system using an optical streak camera which makes use of the inherent time structure of synchrotron radiation. TR-XEOL is a powerful technique that monitors the temporal behaviour of the emission intensity (decay curve) following absorption of a synchrotron X-ray pulse [1]. TR-XEOL experiments were conducted on the Spherical Grating Monochromator (SGM) beam-line at the Canadian Light Source (CLS) operating in single bunch mode with a 570 ns dark gap, a 35 ps root-mean-square (RMS) electron bunch pulse, and at the Advanced Photon Source (APS) operating in regular top-up fill mode with a 153 ns dark gap and 33.5 ps RMS electron bunch pulse.

To illustrate the power of this technique we have measured the TR-XEOL of solid-solution nanopowders of gallium nitride – zinc oxide (GaN-ZnO). GaN and ZnO are both wide band-gap semiconductors, however, when alloyed together to form a solid solution, the band-gap is narrowed over the parent material [2]. When these solid solutions are investigated with conventional photoluminescence (PL) or XEOL techniques no near-band-gap (NBG) related emission is observed and we only see a broad defect luminescence peak of complex origin. For the first time, however, we have been able to use the temporal resolution of a streak camera, combined with the intense, tunable, and pulsing light from a synchrotron, to directly resolve fast NBG luminescence components in this material. Herein we will briefly discuss the development of our streak camera TR-XEOL technique and its application to the study of these novel materials.
2. Instrument Development and Testing

The TR-XEOL apparatus employs a Hamamatsu C5680 streak camera with a M5677 slow single sweep unit, a Bruker IS200 spectrograph, and a 30 mm WD lens system composed of 1 inch lenses and a sapphire UHV window. The streak tube is operated in single sweep mode and is triggered at CLS by a highly stable pulse generated by resynchronization of the orbit clock to the 500 MHz storage ring RF signal. At APS the streak tube is triggered by a bunch clock signal from the APS Ring RF system.

Spectacle cameras operate by converting a temporal event into a spatial profile, and thus are able to achieve sub-picosecond time resolution. The primary benefit of streak camera based TR-XEOL over other time resolved methods is the ability to simultaneously collect both lifetime decay and emission wavelength data, thus producing a temporally resolved 2D map of the XEOL emission pattern. This 2D temporal mapping capability is achieved by first passing XEOL collected from the sample through a spectrograph to disperse the light across the photocathode of the streak camera. Photoelectrons are subsequently generated at the front of the streak tube with a horizontal profile that is determined by the XEOL spectrum. The streak tube then applies a vertical deflection to the transiting photoelectrons, and thus, the original horizontal XEOL emission pattern is retained at the detector. The resulting 2D map contains XEOL spectral information on the horizontal axis and temporal information on the vertical axis. The ability to differentiate between multiple luminescence decay processes that are occurring with different lifetimes by applying appropriate integration windows (both temporal and spectral) to the resultant streak image is the greatest advantage that this technique provides over other TR-XEOL methods[3].

A M5677 slow sweep unit was chosen for the TR-XEOL apparatus due to the specified resolution of 50 ps, which makes it an ideal match for the pulse duration of 35 ps at CLS. Due to the large reduction in ring current at CLS while operating in single bunch mode vs. regular fill-up mode (16 mA vs. 250 mA at injection) the XEOL collected from a single excitation pulse is very weak. In order to overcome the weak XEOL signal data is usually collected in photon counting mode, which produces a final streak image that is a composite of single photon events captured over many (thousands to tens of thousands) individually triggered streak processes. Thus minimizing trigger jitter, which produces a blurring of the streak image in time, is of great importance to achieve a high level of temporal resolution. In order to minimize trigger jitter effects custom in-house triggering electronics were developed with the following features: 1) The streak camera is triggered by resynchronization of the orbit clock to the 500 MHz master oscillator, which produces a highly stable pulse with the same period as a single electron bunch orbiting the storage ring [4]. 2) The streak camera is inhibited during the periodic bunch cleaning. 3) The trigger pulse can be delayed in 2 ns steps to synchronize the timing of the camera with the single bunch in the storage ring.

High bunch purity, the ratio of the amount of charge in the excitation pulse vs. the amount of charge in the dark gap before and after the excitation pulse, is very important for TR-XEOL experiments due to the necessity of having a well-defined excitation pulse. In order to improve bunch purity in the CLS storage ring a transverse feedback (TFB) kicker system was installed, the implementation and testing of which is described elsewhere: An improvement in the bunch purity from 10 to $10^5$ was observed resulting in stable excitation pulses with the time structure of a true single bunch [5].

Extensive testing of this system was carried out at CLS and APS [6]. Although the streak camera TR-XEOL apparatus was designed to be fully implemented for routine use on the SGM beam-line at CLS during single bunch operation, the ability to run TR experiments during regular top-up mode operations at APS provided highly necessary testing and commissioning time due to the limited number of single bunch shifts available at CLS.

3. Results and Discussion

Applying our streak camera based TR-XEOL technique to study the electronic structure of GaN-ZnO solid solutions we have been able to observe several distinct components in the optical emission
spectrum by choosing appropriate time windows and slices. For our study we used a well characterized sample of GaN-ZnO solid solution nanoparticles (GZNO) with an approximate composition of \((\text{GaN})_{0.75}(\text{ZnO})_{0.25}\) \[7\]. Initial streak camera measurements of GZNO (not shown) collected at the 20 BM beam-line (APS), taken below and above the Zn and Ga K-edges using a 20 ns sweep time, indicated that there was a fast luminescence emission component at ca. 480 nm, which was not observed previously via conventional un-gated XEOL \[8\]. A XEOL streak image of GZNO collected on the SGM beam-line (CLS) using a 5 ns sweep time with excitation energy of 550 eV is shown in figure 1(a). By taking a 0.1 ns horizontal slice (figure 1(c), 550 eV fast) of this image from immediately after excitation with a 550 eV X-ray pulse (0.5-0.6 ns) we observe a broad, asymmetric emission band centered at 471 nm (2.63 eV), with a shoulder on the low energy side. When we take a 0.1 ns slice (figure 1(c), 550 eV slow) ~1 ns after excitation (1.45-1.55 ns) we observe another broad band centered at 512 nm (2.42 eV). Lifetime decay spectra shown in figure 1(b), taken from the high energy (blue) and low energy (red) side of the XEOL map respectively, exhibit a shorter luminescence lifetime from the high energy side of the XEOL emission spectrum. Using a phenomenological argument we can interpret this as a shorter lifetime for the 471 nm band vs. the 512 nm band, however, further work must be done to provide quantitative lifetime information. XEOL spectra collected from GZNO using a conventional un-gated apparatus (Ocean Optics QE 65000 spectrometer) exhibit a broad, long lifetime, emission band at ca. 640 nm (figure 2) \[8\]. In contrast, by employing our streak camera TR-XEOL apparatus with CLS operating in single bunch mode and applying appropriate time windows, the long lifetime emission band is completely suppressed and we can resolve two bands, one centered at 471 nm (0.5-0.6 ns slice, figure 2: blue spectra) and one centered at 512 nm (1.45-1.55 ns slice, figure 2: red spectra) when the sample is excited with 550 eV X-rays (above O K-edge).
Integrating over the entire 5 ns window immediately after excitation (0.5-5 ns, figure 2: green spectra), we observe one broad band composed of the 471 nm and 512 nm components, centered at 500 nm (2.48 eV). The appearance of short wavelength emission in TR-XEOL that is not observed in un-gated XEOL has been previously reported for systems where a significant portion of the photon energy absorbed was transferred to the defect emission channel, which is a relatively slow process [9]. The band-gap for GZNO has previously been estimated to be ~2.53 eV from UV-vis diffuse reflectance measurements, which is in good agreement with the wavelength of maximum emission observed using the 5 ns time window (integrated over the entire window, 0.5-5 ns) to record the TR-XEOL spectra [6], hence the possibility of two separate NBG emission bands with different decay lifetimes. The implications of this observation will be fully addressed in a future publication.

4. Conclusion
A time-resolved X-ray excited optical luminescence apparatus employing an optical streak camera has been tested at CLS and APS and successfully integrated into the SGM beam-line (CLS) for regular operation during single bunch fill operation mode. Applying this new TR-XEOL technique to study the electronic structure of GaN-ZnO solid solution nanoparticles we have been able to temporally resolve several components in the X-ray excited optical emission spectrum. Our results suggest that we need to re-examine our current model for band-gap narrowing observed in these important photocatalytic materials.

References
[1] Sham T K and Rosenberg R A 2007 ChemPhysChem 8 2557
[2] Maeda K et al 2006 Nature 440 295
[3] Heigl F et al 2007 AIP Proceedings CP879 1202
[4] Tanaka Y, Hara T, Kitamura H, and Ishikawa T 2001 Nucl. Inst. Meth. A 467 1451
[5] Vogt J M et al 2009 Proceedings of PAC09, Vancouver, Canada
[6] T Z Regier, J M Vogt, R Sammynaiken and T K Sham 2010 AIP Conf. Proc. 1234 838
[7] Han W Q, Ward M J, and Sham T K 2011 J. Phys. Chem. C 115 3962
[8] Ward M J, Han W Q, and Sham T K 2011 J. Phys. Chem. C 115 20507
[9] Zhou X-T, Heigl F, Regier T, Coulthard I, and Sham T K App. Phys. Lett. 89 213109

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