

Scintillation of Un-doped ZnO Single Crystals

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ABSTRACT

Scintillation properties are often studied by photo-luminescence (PL) and scintillation measurements. In this work, we combine X-ray-induced luminescence (XRIL) spectroscopy [Review of Scientific Instruments 83, 103112 (2012)] with PL and standard scintillation measurements to give insight into the scintillation properties of un-doped ZnO single crystals. XRIL revealed that ZnO luminescence proportionally increases with X-ray power and exhibits excellent linearity - indicating the possibility of developing radiation detectors with good energy resolution. By coupling ZnO crystals to fast photomultiplier tubes and monitoring the anode signal, rise times as fast as 0.9 ns were measured.

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INTRODUCTION

Radiation detectors are crucial in a number of fields, such as mining [1], national security [2], astrophysics [3], high-energy physics, medical diagnostics and nuclear medicine - as well as many others [4]. Scintillation detectors, in particular, have been widely used in the aforementioned applications. The process referred to as scintillation can be defined as luminescence arising from exciton recombination, induced by ionizing radiation, and these scintillation photons can be converted into an electrical signal using photo-amplifying instruments [4]. Some metal oxides are considered suitable materials for radiation sensing and scintillation, due to their optical and electrical sensitivity to ionizing radiation [5]. An ideal combination of physical properties for an inorganic scintillator would consist of sufficient stopping power, intense light output, high radiation resistance, and ultrafast decay time [6]. In this work, we study some of the scintillation properties of ZnO single crystals grown by chemical vapor transport (CVT). The interest in ZnO as a scintillator stems from its very fast sub-nanosecond excitonic emission, low materials cost, and high radiation resistance [7, 8]. The wide band gap of ZnO (3.4 eV) with its exciton binding energy of 60 meV [9-12] yields intense luminescence, ideal for scintillation applications. In fact, limited use of ZnO in powdered and

ceramic forms has been known for decades [13-15] and many studies were carried out on Ga- and In-doped ZnO ceramic scintillators for efficient alpha – particle detection (see, e.g. Refs. [13,14]). However, only a few studies have investigated the scintillation properties of un-doped bulk ZnO single crystals that are the focus of this work.

Here we use X–ray-induced luminescence (XRIL) spectroscopy [17] in conjunction with photoluminescence (PL) and standard scintillation measurements to provide insight into the scintillation of un-doped ZnO single crystals. PL measurements reveal the emission efficiency of luminescence centers and the spectral emission range; however, they do not provide information about the charge-carrier generation efficiency, the presence of trapping defects, or the efficiency of energy transfer from the carriers to the luminescence centers. Typical scintillation measurements, on the other hand, often do not provide information about the spectral range or emission efficiency, instead, they show the overall device efficiency. The advantages of using XRIL spectroscopy is that it can be utilized as a quick and efficient method of studying the scintillation efficiency of materials while simultaneously gaining information about the spectral range, the charge carrier production efficiency and the carrier energy transfer to the luminescence centers [17]. We will also show that XRIL can examine the dependence and linearity of the luminescence intensity of scintillation materials on ionizing radiation intensity and can predict, to some extent, the energy resolution of the detector to be developed.

EXPERIMENT

Un-doped ZnO single crystals were grown at the Oak Ridge National Laboratory by the chemical vapor transport (CVT) method. Polycrystalline spheres of ZnO are heated to 1250 °C inside an alumina tube in a mixture of flowing hydrogen and either argon or nitrogen gases [18]. Zinc vapor is formed during the reduction reaction: $\text{ZnO(s)} + \text{H}_2(\text{g}) \rightarrow \text{Zn(g)} + \text{H}_2\text{O(g)}$ and a nitrogen or argon gas transports the Zn vapor to the cooler region of the growth chamber, where ZnO single crystals are formed by the reaction: $\text{Zn(g)} + (1/2)\text{O}_2(\text{g}) \rightarrow \text{ZnO(s)}$. This reaction is accompanied by $\text{H}_2(\text{g}) + (1/2)\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(g)}$ [18]. Here g and s represent the gas and solid phases. Then, test samples were prepared in sizes of $(10 \times 7 \times 1) \text{ mm}^3$ for scintillation studies

XRIL measurements were carried out using the newly developed spectrometer, which uses an AEG FK 60-04 Cu X–ray tube to generate X–rays that pass through a monochromator and collimator to provide focused mono-energetic X–ray beams [17]. The light emitted from the sample is collected by a lens and transmitted through an optical fiber to an Ocean Optics USB2000+ spectrofluorometer that covers a spectral range of 200–800 nm, with a 1 nm resolution. The PL measurements were carried out using a JY-Horiba FluoroLog-3 spectrofluorometer with double-grating excitation and emission monochromators with a 1200 groove/mm grating. The excitation of the samples was done by a 450 W CW Xenon lamp source. The measurements include excitations by 325, 350 and 390 nm light, and they were carried out on both as-grown and annealed samples. Samples were annealed in H_2 atmosphere at 300 °C or O_2 atmosphere at 900 °C. Some samples were also annealed in both atmospheres

For the scintillation measurements, a detector was assembled by mounting an as-grown ZnO crystal on a Hamamatsu H3378-51 PMT. Black tape was used to shield the phototube from external light. A bias of negative 2900 V was applied to the detector, and the anode signal was monitored using a 500 MHz oscilloscope, Tektronix TDS – 640. A Co-60 source was used as a radiation source.

DISCUSSION

Figure 1 (a) shows the XRIL spectra for as-grown ZnO single crystals taken at different X-ray power with a gradual 5 mA increase in X-ray tube current from 5 to 35 mA. Both the near-band emission (NBE) at 390 nm and defect luminescence (DL) at 525 nm are present in the spectra. The graph shows that the emissions proportionally increase with X-ray current without saturation. The integrated NBE and DL emission intensities for the as-grown single crystal ZnO are plotted versus X-ray current and displayed in Fig. 1 (b) demonstrating excellent linearity. The high efficiency of XRIL and the almost perfect linearity indicate that ZnO-based scintillation detector can exhibit good energy resolution. In Fig. 4 (c), we have plotted the ratio between the defect luminescence and NBE as a function of X-ray tube current. It is interesting to observe that the ratio increases with increasing current at the beginning and then stays constant. This is probably because higher X-ray intensity induces more charge carriers. Thus oxygen vacancies can trap one or two electrons forming F centers that act as luminescence centers and lead to an increase in defect emission at 525 nm [19].

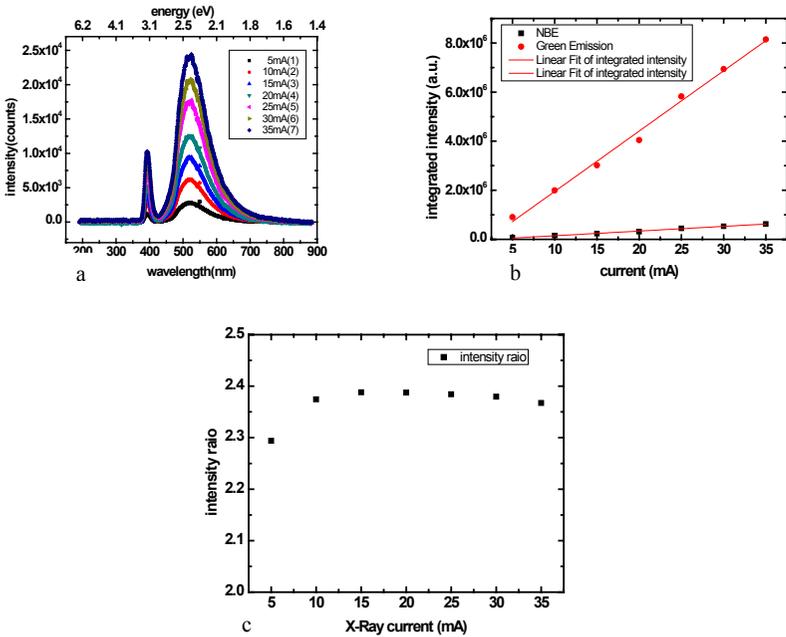


Figure 1. (a) XRIL spectra for as-grown ZnO single crystal at various X-ray tube currents ranging from 5 to 35 mA in 5 mA intervals. (b) The integrated DL and NBE emission intensities vs. X-ray tube current (mA) are fit with a straight line, demonstrating almost perfect linearity. (c) Plot of the integrated DL/NBE emission ratio plotted at various X-ray tube currents.

To examine the time response of the scintillation signal from ZnO, scintillation measurements were performed as described in the experimental section, by mounting an as-grown ZnO crystal on a H3378-51 Hamamatsu PMT that has a rise time of 0.7 ns and maximum sensitivity at 420 nm - an excellent match with the NBE emission from ZnO. Figure 2 presents the anode signal from a ZnO scintillator using Co-60 as a radiation source, and it shows a 0.9 ns rise time illustrating the very fast time response.

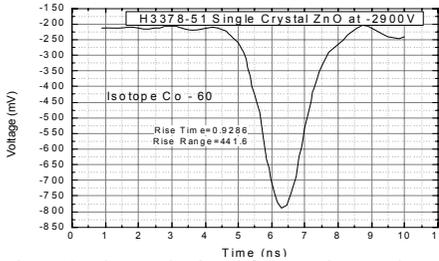


Figure 2. The anode signal from ZnO crystal mounted on H3378-51 PMT. The radiation source was Co-60.

Understanding the dependence of ZnO luminescence on the growth and annealing atmospheres is vital for developing ZnO for scintillation devices. PL measurements were carried on as-grown and annealed ZnO samples to study the effect of anneals. The results are summarized in Fig. 3 and Table (I). The figure shows the PL emission for different excitation wavelengths and illustrates the shift in emission peaks after various anneals. Anneal in O_2 atmospheres led to the suppression of NBE (3.28 eV). In fact, this emission peak was observed only for as-grown or H_2 -anneal samples (See Table I, not shown in Fig. 3.) Anneal in O_2 followed by H_2 led to a shift of the NBE to lower energy (from 3.28 to 3.01 eV).

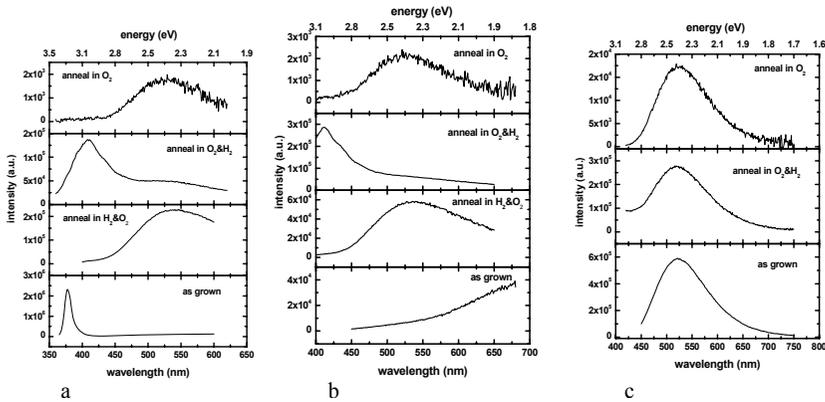


Figure 3. PL emission of as-grown and annealed ZnO samples for: (a) 325 nm excitation, (b) 350 nm excitation, (c) 390 nm excitation.

Table I: PL emission peak positions for as-grown and annealed ZnO crystals at different excitations.

sample	PL Excitation (nm)	PL Emission (eV)
As-grown	325	3.28
	350	
	390	2.38
Annealed in H ₂ &O ₂	325	2.27
	350	2.32
Annealed in O ₂ &H ₂	325	3.04
	350	3.01
	390	2.39
Annealed in O ₂	325	2.34
	350	2.38
	390	2.39
Annealed in H ₂	325	3.22
		3.12
	350	3.23
		3.13
390		

The 3.28 eV emission is known to arise from the recombination of free excitons while the 3.01 eV emission was expected to be associated with electron transitions from donor levels to the valence band [20, 21]. Thus, the presented results imply that most of the annealing procedures here except H₂ anneal suppress the formation of free excitons. Annealing in O₂ followed by H₂ generates new donors that lead to the NBE emission at 3.01 eV (410 nm). As seen from Fig. 3 (c) and table I, anneals in various atmospheres did not lead to a shift in the DL peak indicating that annealing did not create new defect luminescence centers. It might however modify their concentrations.

CONCLUSIONS

XRIL, PL, and scintillation measurements were applied to study the scintillation properties of annealed ZnO single crystals. They revealed that both the NBE and DL exhibit almost perfect linearity with increasing X-ray intensity - indicating the possibility of achieving good detector energy resolution. The rise time of the fast scintillation signal from ZnO coupled to a H3378-51 PMT detector was found to be 0.9 ns. PL measurements illustrated the effect of annealing atmospheres on the emission of ZnO that is expected to significantly affect the scintillation properties and efficiency of ZnO.

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