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Development of ZnO:Ga as an Ultrafast Scintillator

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Abstract– **We report on several methods for synthesizing the ultra-fast scintillator ZnO(Ga), and measurements of the resulting products. This material has characteristics that make it an excellent alpha detector for tagging the time and direction of individual neutrons produced by t-d and d-d neutron generators (associated particle imaging). The intensity and decay time are strongly dependent on the method used for dopant incorporation. We compare samples made by diffusion of Ga metal to samples made by solid state reaction between ZnO and Ga$_2$O$_3$ followed by reduction in hydrogen. The latter is much more successful and has a pure, strong near-band-edge fluorescence and an ultra-fast decay time of the x-ray-excited luminescence. The luminescence increases dramatically as the temperature is reduced to 10K. We also present results of an alternate low-temperature synthesis that produces luminescent particles with a more uniform size distribution. We examine possible mechanisms for the bright near-band-edge scintillation and favor the explanation that it is due to the recombination of Ga^{3+} donor electrons with ionization holes trapped on H$^+$ ion acceptors.**

I. INTRODUCTION

ZnO:Ga has been known as an ultrafast semiconductor scintillator since the 1960's [1] but has not been developed as a detector material because of its low stopping power for gamma rays and because of the difficulty of growing crystals. However, it has recently been recognized that even in polycrystalline form, it has unique capabilities for detecting alpha particles in t-d and d-d neutron generators [2-4]. A fast, high-efficiency, associated alpha-particle detector makes possible time and direction tagging of neutrons from the deuterium-tritium fusion reaction. The alpha particle detector is mounted inside the neutron generator and must meet specific requirements: 1) nanosecond timing accuracy, 2)

maximum event rates >50 MHz, 3) no degradation or fouling of the deuterium source at bake temperatures of 350˚C for over 72 hours, and 4) the total absence of organics.

ZnO is a direct band-gap semiconductor, and it is known that the impurities In and Ga act as donors to generate a metastable population of electrons near the bottom of the conduction band [1]. Fast, sub-nanosecond decay times of the luminescence are observed from these doped materials. A variety of scintillation schemes have been proposed, but at the present time no consensus has been reached as to the exact nature of the luminescence centers or the energy transfer mechanisms that are actually responsible for scintillation in this material. In previous work [5] we reported on the luminosities and decay times of ZnO doped with the donor Ga^{3+} and co-doped with H, with the acceptor N^{3-}, and with the isoelectronic hole trap S^{2-}, and showed that co-doped samples exhibit a large increase in luminosity and a fast mono-exponential decay. In this paper we study the impact of sample preparation on the photo and radioluminescence characteristics.

II. PROCEDURES

A. *ZnO:Ga made by reacting ZnO with Ga$_2$O$_3$ and H$_2$*

Our most luminous samples were made by first reacting Ga$_2$O$_3$ with ZnO at high temperature and then by reducing with hydrogen gas. The samples were prepared using high-purity ZnO crystalline powder (Strem) and Ga$_2$O$_3$ crystalline powder. In the first step, the ZnO and Ga$_2$O$_3$ were mixed, reacted at 1100˚C under vacuum (10^{-3} torr) for 10 to 15 hrs, cooled, and ground. In the second step the reaction was repeated at 900˚C for 10 to 15 hrs. This two-step process was used to insure homogeneous Ga diffusion in the sample. In the third and final step a 3% H$_2$ in Ar gas mixture was passed over the sample at 800˚C for 30 minutes.

B. *ZnO:Ga made by reacting ZnO with Ga metal*

These samples were prepared by reacting metal Ga with high-purity ZnO crystalline powder (Strem). The charge (0.04 mole% of Ga mixed in ZnO) was sealed in a quartz ampoule under vacuum (10^{-5} torr) and was allowed to react at 1200˚C for 12 hrs.

C. *Characterization:*

The resistance measurements were done using a high-pressure cell for compaction of the powder samples, similar to the design described in [6]. Photoluminescence spectra of

powdered samples in quartz cuvettes were measured using a Horiba Fluorolog FL3-11 dual monochromator spectrofluorimeter. Luminosity and luminescence decay times were measured using the pulsed x-ray system previously described in [7]. A Displex CSW-202 cryostat configured for use with both the Fluorolog FL3-11 and the pulsed x-ray system was used to acquire data between 10 K and 400 K.

III. RESULTS

A. *ZnO:Ga made by reacting ZnO with Ga_2O_3 and H_2*

Fig. 1 shows the luminescence and the decay time of the X-ray excited luminescence measured at room temperature for a sample synthesized with ZnO, Ga_2O_3 and H_2 as described in II.A. The luminescence spectrum shows a narrow emission at 389 nm (Fig. 1a). There is no 'green' or 'yellow' luminescence usually observed in undoped ZnO samples and attributed to native defects; an ionized oxygen vacancy and an oxygen interstitial, respectively [8]. The decay of the X-ray excited luminescence is fast (0.8 ns), monoexponential in time over four decades which indicates that the luminescence arises from a homogeneous excited state. The x-ray-excited luminescence intensity is 54% that of YAP (Phosphor Technology, Inc. YAlO$_3$:Ce, Product QM58/N-S1). In contrast, the luminosity of the ZnO starting reagent is 77 times lower, only 0.7% that of YAP.
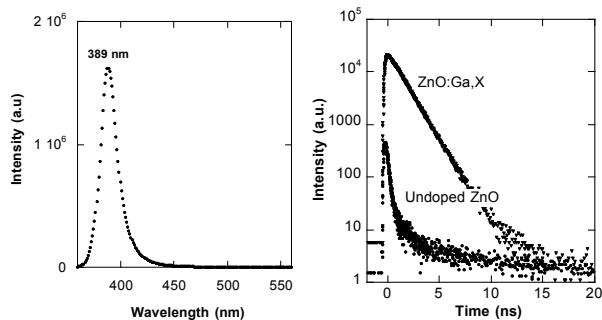

Fig. 1: Room temperature photoluminescence spectrum of a ZnO:Ga sample made by reaction of ZnO with Ga_2O_3 (left), and decay time of the room temperature X-ray excited luminescence of the same sample compared to an undoped sample (right).

To optimize the temperature of the hydrogen processing in Section IIA, step 3 we produced a series of samples where the processing temperature was varied from 400°C to 1100°C. Figure 2 shows measurements of the photoluminescence spectrum, the electrical resistance, and the X-ray excited scintillation light yield for these samples. As expected, the Ga_2O_3 in the initial sample produces an excess of oxygen, and the luminescence spectrum shows a broad band around 560 nm. This situation persists for hydrogen processing temperatures up to 600°C. Above this temperature the excess oxygen is eliminated by reaction with hydrogen and some of the Ga^{3+} ions become charge compensated with electrons near the top of the energy gap by the following reaction:

$$Ga_2O_3 + H_2 => 2[GaO]^{+1} + 2e^- + H_2O$$
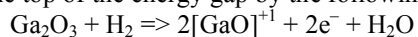
It is important to note that this reaction creates zinc vacancies as an excess O remains.

At 800 °C pure, intense emission at 389 nm is observed and the electrical resistance decreases by a factor of 5000 compared with the unreacted material. (Fig. 2, right). At higher temperatures, the broad green band related to oxygen vacancies appears (Fig. 2 left), the electrical resistance increases and the overall luminosity decreases significantly. Above 1000°C, ZnO starts to decompose under hydrogen, and a multitude of native defects are created.

From these data it is evident that the highest luminosity is achieved when the stoichiometry is nearly balanced, with neither yellow emission from excess oxygen or green emission from oxygen vacancies.

It is not obvious why the electrical resistance increases and the overall luminosity decreases at higher temperature in the presence of hydrogen, but one possible explanation is that upon decomposition above 1000°C, the Zn^{2+} capture electrons from the donor band becoming neutral Zn^0 following the reaction:

$$Zn^{2+} + 2e^- => Zn$$
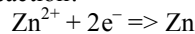
The result is the loss of the donor band, an increase in resistance and the creation of a zinc-rich material that emits in the green (fig.2). Note that ZnO doped with only 30 ppm Zn is an intense green phosphor (P24, available from Phosphor Technologies, Inc.).
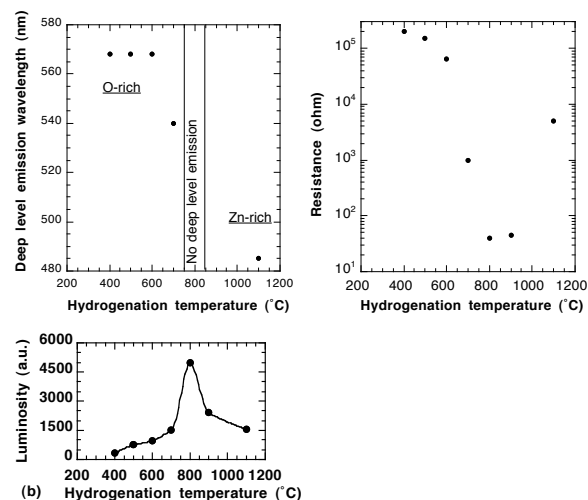

Fig. 2: Evolution of the deep level emission as a function of the hydrogenation temperature (left) and related variation in resistance of the samples (right).

The temperature dependence of the photoluminescence for samples processed in hydrogen at 800°C is shown in Fig. 3. The intensity of the near-band-edge emission increases dramatically at low temperature. The wavelength of emission also decreases from 389 nm to 373 nm at 10 K. The peak luminescent intensity at 10 K is about 14 times more intense than at room temperature. The decrease of the luminescence intensity with raising temperature is due to thermal quenching. In the 10 K spectrum a shoulder at 367 nm appears that is attributed to the free exciton. The decay time of the x-ray excited luminescence is unchanged from room temperature down to 10K.

We must note that our samples are produced from a process that is quite different from that used by Lehmann [1]. His

process uses $ZnCl_2$ or HCl in the ZnO-Ga_2O_3 mixture, and produces samples that have about 3 times lower luminosity but exhibit a faster decay time of 0.8 ns.
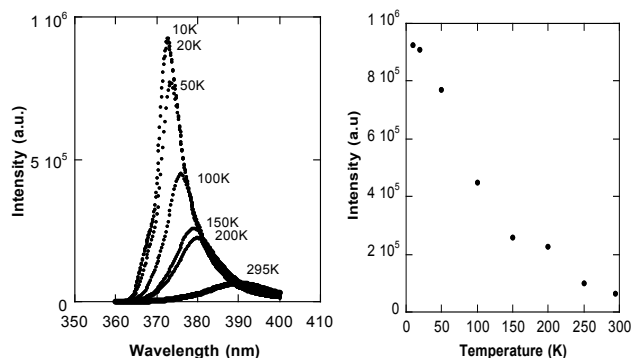

Fig.3: Temperature dependence of the photoluminescence of ZnO:Ga made by reaction of ZnO with Ga_2O_3 (left) and plot of the luminescence intensity vs temperature.

B. *ZnO:Ga made by reacting ZnO with Ga metal*

Fig. 4 shows the emission wavelength spectrum and the decay time of the x-ray excited luminescence measured at room temperature for a sample synthesized by diffusion of Ga into ZnO as described in II.B. The luminescence spectrum exhibits two main emission bands: a narrow band peaking at 392 nm and a broad band peaking around 480 - 500 nm characteristic of the 'green' luminescence of ZnO:Zn. The diffusion of excess Ga atoms into Zn sites results in an increase in ionized oxygen vacancies responsible for the green luminescence. The decay of the x-ray excited luminescence is non-exponential. Both fast decay of the near- band-edge luminescence and slow decay of the green luminescence are present. About 50% of the light has decays in less than 2.5 ns, 16% between 7 and 40 ns and the rest decaying more slowly. While the samples have low resistance indicating that the Ga atoms have been incorporated to create a donor band their x-ray-excited luminosity is only 0.2% that of YAP and 27 times less than the material prepared by reacting ZnO with Ga_2O_3 and H_2.

From these data we conclude that the intense near-edge emission of the brighter preparation is not due to the recombination of donor-band electrons with ionization holes at the top of the valence band, but with ionization holes that have been trapped on shallow acceptor states that also serve as radiative centers. Since the emission energy is 150 meV from the band edge of ZnO and Ga3+ has a donor depth of 30 meV in ZnO, we conclude that this acceptor has a depth of 120 meV. Moreover, figure 3 indicates that these centers compete with thermally activated traps that are dominant at room temperature and are non-radiative centers.
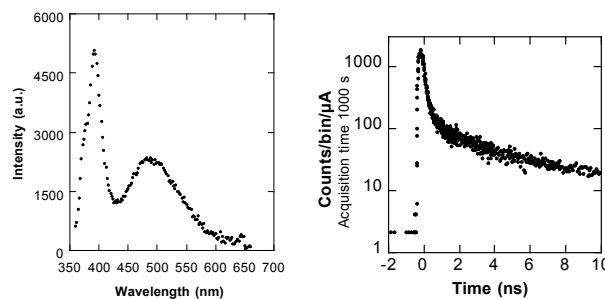

Fig. 4: Room temperature photoluminescence spectrum of a ZnO:Ga sample made by diffusion of Ga metal in ZnO (left), and decay time of the room temperature x-ray excited luminescence of the same sample (right).

One possibility is that some N^{3-} is present in our brightest samples and that these are the shallow donors that trap ionization holes and act as radiative centers for the near-band-edge emission. The work of Wang et al [9] shows that N^{3-} in ZnO has an acceptor depth of 160 meV which is consistent with the observed emission wavelength. It would also be expected that N^{3-} ion incorporation would be facilitated by the oxygen vacancies in this material.

To explore this possibility, samples of ZnO:Ga produced by diffusion of Ga metal were subsequently annealed at 800˚C for 30 minutes with flowing nitrogen (Fig. 5). The luminosity increased from 0.2% to 0.4% that of YAP, and most of the emission was not band-edge. From this we conclude that N^{3-} is not the shallow acceptor responsible for the emission of our brightest samples.

In addition, we annealed samples of ZnO:Ga produced by diffusion of Ga metal at 800˚C for 30 minutes with flowing oxygen and hydrogen (Fig. 5). The annealing under oxygen does reduce the intensity of the 'green' luminescence and confirms the assignment of that luminescence to the presence of ionized vacancies.

Hydrogen further reduces ZnO, and the intensity of the green luminescence is increased. The band-edge emission is also increased, which provides some evidence that hydrogen plays a direct role in that emission process.
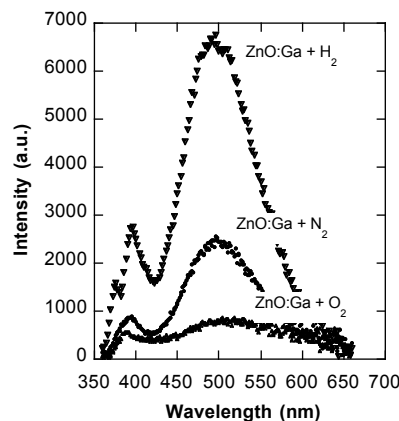

Fig. 5: Room temperature photoluminescence spectra of a ZnO:Ga sample made by diffusion of Ga metal in ZnO and reacted at 850˚C with hydrogen, nitrogen and oxygen gases.

IV. ALTERNATE LOW TEMPERATURE SYNTHESIS

The luminescent screens used for alpha detection in the neutron generators are made by sedimentation using the ZnO:Ga powder mixed with a binder (potassium silicate 1% in water) and an electrolyte ($SrNO_3$). The powders fabricated by reaction at high temperature consist of irregularly shaped particles with a wide size distribution. A scanning electron microscope image is shown in Fig. 6 (left). By sifting the powder and measuring its x-ray excited luminescence we found that the particle size affects the luminescent output. The coarser the particles are, the higher is the luminosity of the sample (Fig. 6, right). The decay time remains constant, pointing to a uniform distribution of dopant in the particles of various sizes. Matsumoto et al. [10] reported the influence of particle size on the photoluminescence of undoped ZnO. In addition, they not only observed an increase in luminescence intensity but also an increase in the decay times. The radioluminescence that we observe in this work is directly related to the presence of Ga.
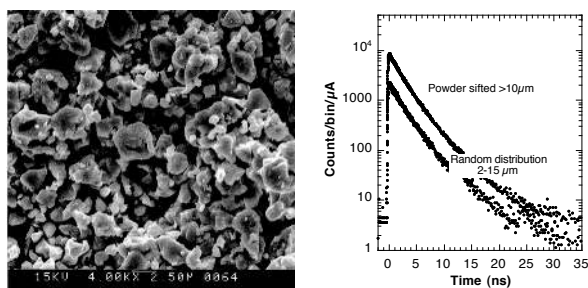

Fig. 6: Right: SEM image of the ZnO:Ga powder (not sifted) used for fabrication of alpha detector screen. Left: X-ray excited luminescence of powder sifted for particle size larger than 10 μm.

A new synthesis technique was developed to obtain microcrystals of well-defined shape and size. The synthesis is done at a low temperature that is expected to prevent formation of a number of native defects. The micro crystals are formed in solution by the reaction of zinc nitrate tetrahydrate and hexamethyltetramine, and the dopant, Ga, is introduced by addition of gallium nitrate. The reaction produces well-defined microcrystals of hexagonal cross-section and elongated in the c direction. The diameter and length of the microcrystals are strongly dependent on the temperature used for the precipitation. SEM images of microcrystals produced at different temperatures are shown in Fig. 7. At 67˚C, the crystals are about 250 nm in diameter by 500 nm long. The size increases to 500 nm in diameter by about 1μm long for a precipitation done at 78˚C, to about 1 μm in diameter by about 5 μm long at 95˚C, and to 1 to 2 μm in diameter by 5 to 8 μm long at 100˚C. Because of the absorption of the alpha particle in ZnO, a 7 microns thick detector screen is optimum; we see from the previous data that

microcrystals of that length can be achieved if the synthesis is done at 100˚C. In future work, the microcrystals could be aligned in a very compact array.

Fig. 8 shows the room-temperature photoluminescence spectra of micro crystals synthesized at 100˚C. The spectrum has three main emission bands: a relatively narrow near-band-edge emission at 380 nm and two broad bands centered around 420 nm and 600 nm. The 600-nm band is the yellow luminescence that is attributed to excess oxygen (interstitials). The origin of the 420-nm band is unknown. We observe it in both undoped and Ga-doped micro crystals, and it is removed upon hydrogenation of the samples. Because it is not observed in samples prepared at high temperature, it is tentatively assigned to hydroxyls from the aqueous solution. We used an Osprey hydrogen atom source to react the doped samples with hydrogen at room temperature. The samples were maintained under the hydrogen beam for 15 minutes. The surface of the sample directly exposed to the beam changed color from white to a pale yellow, indicating that the hydrogenation was not uniform throughout the sample. This hydrogenation process needs further optimization. Nevertheless, the hydrogenation resulted in a significant decrease of the two broad bands and an increase in the intensity of the near-band-edge emission with a small shift of the emission wavelength to 382 nm. The data indicate that the hydrogenation of the sample was not complete but that activation of the Ga-related luminescence can be achieved for the micro crystals using hydrogen in a manner very similar to that used for samples synthesized using Ga_2O_3.
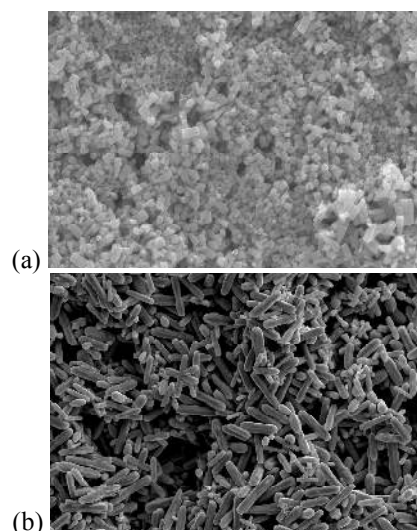

Fig. 7: SEM images of ZnO:Ga produced by precipitation at (a) 67˚C, (b) 100˚C. The micro crystals size range are (a) 250 nm by 500nm long, (b) 1 to 2 μm by 5 to 8 μm long.
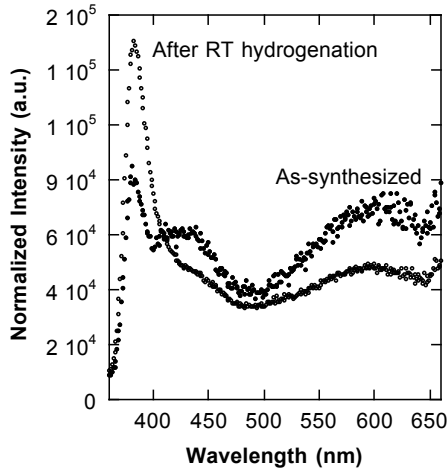
Fig. 8: Room temperature photoluminescence spectra of ZnO:Ga micro crystals as synthesized at 100˚C and further reacted with hydrogen atoms at room temperature.

V. Discussion

Ultra-fast, intense UV emission was observed in ZnO that was first reacted with Ga_2O_3 and then annealed in hydrogen. The luminosity was greatest and the conductivity was lowest when the stoichiometry was balanced and luminous emissions from either excess oxygen or oxygen vacancies were minimized. The UV emission photon energy is shifted 0.15 eV from the band edge, indicating that the radiative emission is due to the transition of Ga^{3+} donor band electrons to ionization holes trapped on shallow acceptors and not on ionization holes at the top of the ZnO valence band. The decay is monoexponential over four decades, indicating that a single shallow acceptor dominates. These measurements are consistent with the hydrogen playing two roles: 1) removing the excess oxygen to produce a donor electron band and 2) filling zinc vacancies as a H^+ ion acceptor . In our brightest samples, reacting ZnO with Ga_2O_3 provide a significant number of zinc vacancies for the following reaction with hydrogen to occur:

$[V_{Zn}]^{2-} + H_2 => 2[H_{Zn}]^-$ (charge relative to the lattice), thus creating ionized acceptors. When an ionization event occur (upon excitation) the holes migrate through the valence band and are trapped by the $[H_{Zn}]^-$. They then annihilate with the abundant donors and the electron-hole pair recombination results in the observed bright and ultra fast scintillation.

Much lower emission was seen from ZnO that had been reacted with gallium metal, even though it had a high electrical conductivity indicating the presence of a Ga^{3+} donor electron band. This shows that radiative emission between Ga^{3+} donor electrons and ionization holes at the top of the ZnO valence band or ionization holes trapped on unintentional N^{3-} impurities is very weak.

Even lower UV emission was seen in ZnO that had been reacted with gallium metal and then annealed in nitrogen. Since this preparation promotes N^{3-} ions on oxygen vacancy sites, this is additional evidence that the ultra-fast, intense UV emission seen in this work is not due to N^{3-} acceptors.

It is not surprising that there is little UV emission from ZnO that had been reacted with gallium metal and then annealed in hydrogen because this preparation does not provide zinc vacancies. Instead, this preparation produces oxygen vacancies and the characteristic emission from that defect. Therefore a H^+ ion on a zinc vacancy that could serve as an acceptor, is not favored in this material because it is cation rich.

VI. Conclusion

The preparation of ZnO:Ga with ultra-fast, intense UV emission requires both oxygen-rich starting conditions and processing in hydrogen to eliminate the excess oxygen and provide a shallow acceptor. Processing ZnO in Ga metal followed by annealing in nitrogen produces very weak UV emission, indicating that nitrogen does not play a significant role in the UV emission.

We have developed a low-temperature aqueous process that produces micro crystals of well-defined shape and narrow distribution size.

References

[1] W. Lehmann, "Edge emission of n-type conducting ZnO and CdS," *Solid-State Electronics,* vol. 9, pp. 1107-1110, 1966.

[2] J. C. Cooper, D. S. Koltick, J. T. Mihalczo, et al., "Evaluation of ZnO(Ga) coatings as alpha particle transducers within a neutron generator," *Nucl Instr Meth,* vol. A505, pp. 498-501, 2003.

[3] P. A. Hausladen, J. S. Neal and J. T. Mihalczo, *Nucl Inst Meth,* vol. A241, pp. 835-838, 2005.

[4] J. S. Neal, L. A. Boatner, N. C. Giles, et al., "Comparative investigation of the performance of ZnO-based scintillators for use as a-particle detectors," *Nucl Instr Meth,* vol. A568, pp. 803-809, 2006.

[5] Bourret-Courchesne ED, Derenzo SE, Weber MJ, "Semiconductor scintillators ZnO and PbI2: co-doping studies" *Nuclear Inst. and Methods in Physics Research, A,* vol.579, no.1, 21 Aug. 2007, pp. 1-5.

[6] R. Wang, A. Sleight and D. Cleary, "High conductivity in gallium-doped zinc oxide powders," *Chem Mater,* vol. 8, pp. 433-439, 1996.

[7] S. C. Blankespoor, S. E. Derenzo, W. W. Moses, et al., "Characterization of a pulsed x-ray source for fluorescent lifetime measurements," *IEEE Trans Nucl Sci,* vol. NS-41, pp. 698-702, 1994.

[8] X. L. Wu, G. G. Siu, C. L. Fu, et al., "Photoluminescent and cathodoluminesce studies of stoichiometric and oxygen-deficient ZnO films," *Appl Phys lett,* vol. 78, pp. 2285-2287, 2001.

[9] H. Wang, H.P. Ho, K.C. Lo, K.W. Cheah "Preparation of p-type ZnO films with (N,Ga) co-doping by MOVPE" Materials Chemistry and Physics 107 (2008) 244–247.

[10] T. Matsumoto, H. Kato, K. Miyamoto, et al., "Correlation between grain size and optical properties in zinc oxide thin films," *Appl Phys Lett,* vol. 81, pp. 1231, 2002.