

Radioluminescence in ZnO: effect of chemical modification

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The radioluminescence (RL) response of zinc oxide (ZnO) was investigated for alpha particle detection. The present study reports the chemical modification of bulk ZnO for enhancing the RL property of oxide. The treated oxide samples were characterized with different techniques such as XRD, XPS, SEM and in terms of average pore radius. The photoluminescence (PL) and RL properties of all samples were also investigated. Results showed an important relation between the PL integrated emission intensity of the green-yellow bands and the type of solvent. This was mainly explained by the increase of the oxygen defects in ZnO, which was confirmed by the XPS results. The RL results of the treated ZnO were improved by the chemical treatment of the bulk oxide. The obtained results confirmed the chemical treatment as an alternative method for ZnO preparation with improved properties. The preliminary results showed an increase in the PL and RL response with the decrease of the average pore radius. However, further experiments are still needed in order to better study the correlation between chemically produced defects and RL response.

(Received July 26, 2015; accepted June 7, 2017)

Keywords: ZnO, Chemical modification, Photoluminescence, Radioluminescence

1. Introduction

Zinc oxide (ZnO) is an interesting n-type semiconductor material with a wide band gap of 3.2 eV (~ 387 nm) and large excitation binding energy of 60 meV at 300 K [4,10,15]. Recently, ZnO has attracted great attention due to its promising optoelectronic applications such as ultraviolet light-emitting diodes and laser diodes [5].

The structure of ZnO can be described in terms of planes composed of tetrahedrally coordinated Zn^{2+} and O^{2-} ions stacked alternately along the c axis without central symmetry. This coordination gives rise to piezoelectric and pyroelectric properties [14]. Generally, ZnO has wurtzite structures (hexagonal) with space group P6₃mc at ambient conditions. Liu et al. [7] reported that the application of pressure above 9 GPa leads to a transition from the wurtzite structure to the cubic structure with space group Fm3m and an increase in the coordination number from 4 to 6.

The study of nano zinc oxide doped with various impurities was widely reported in literature leading to several publications [2,12,8,6,9,11,17]. The role of impurities and vacancies has not been clearly understood. However, it is well known that vacancies and defects play an important role in photoluminescence (PL) and radioluminescence (RL) of inorganic oxides, and that the decrease in crystallite size leads to changes in optical, electrical and sensing properties of nano-powders [10,12]. The treatment of ZnO can modify the structure with new vacancies and defects. This could play an important role in sensing properties [10,7,12,1,3].

Yanagida et al. developed Cd-doped ZnO scintillator by the liquid phase epitaxy (LPE) method to enhance the defect related emission in ZnO for α -ray detectors. The enhancement of the light yield was attributed to the dynamization of the defect emission around 500 nm [16].

As an innovative method, the modification of bulk ZnO structure was studied using a cheap and easy chemical method. Thus, the present investigation aims at finding out the structural, photoluminescence and radioluminescence properties of ZnO powders modified with new vacancies and defects in structure. The use of treated oxide samples in the preparation of scintillation films for alpha particle detection was studied and effect of different solvent was investigated.

2. Materials and Methods

2.1. The chemical modification of ZnO

The ZnO (99.5 % from Honeywell Riedel-de Haën®) was used as a bulk sample. The oxide structure was chemically modified using four organic solvents i.e. water (H_2O), Tetrahydrofuran (THF), Ethanol (Et) and Dimethylformamide (DMF). For each experiment, bulk oxide (2.0 g) was mixed with 100 mL of solvent. Samples were aged for 2 h, and then sonicated for 10 min. The mixture was filtered and the modified oxide was dried in air for 24 h at room temperature, and then in oven for 4 h at 323 ± 3 K.

2.2. XRD, XPS and PL characterization

The elemental and chemical compositions of the treated oxide have been measured by an X-ray photoelectron technique. The XPS analyses were performed using a SPECS UHV/XPS/AES system with a hemispherical energy analyzer. The monochromated Al K α X-ray (1486.6 eV) is used as the excitation source and is operated at 250 W. High resolution spectra of the Zn-2p and O-1s peaks are treated and deconvoluted, with CasaXPS version 2.3.16Dev52, using a non-linear least-squares method with a Gaussian/Lorentzian peak shape GL(30) and the background was subtracted using the Shirley method (Shirley, 1972).

Sample morphology and thickness were obtained with a Tescan Vega II XMU Scanning Electron Microscope (SEM).

The crystalline phase of all samples was determined by X-ray diffraction (Stoe StadiP Transmission X-ray diffractometer).

For PL characterization of the prepared samples, the experimental set-up consisted of UV excitation using a 325 nm He/Cd laser, and spectral measurements via a grating monochromator with 1200 groves/mm equipped with a cooled PMT (HAMAMATSU). A long-pass filter was used to reject plasma and laser light from the helium-cadmium laser below 360 nm. Synchronous detection technique was implemented by chopping the laser beam and employing a lock-in amplifier to process the electrical output of the PMT. Via a set of optical devices, the excitation beam was guided and focused on to the tested sample.

2.3. Radioluminescence study

For radioluminescence experiments, the treated oxide was prepared as films by spraying on transparent plastic sheet using N₂ as a holder gas to optimize the homogeneity of the oxide deposition. All samples were prepared under the same conditions and for the same thickness. The prepared ZnO scintillation films were dried at room temperature for 2 h, and then at 343 ± 3 K for 3h.

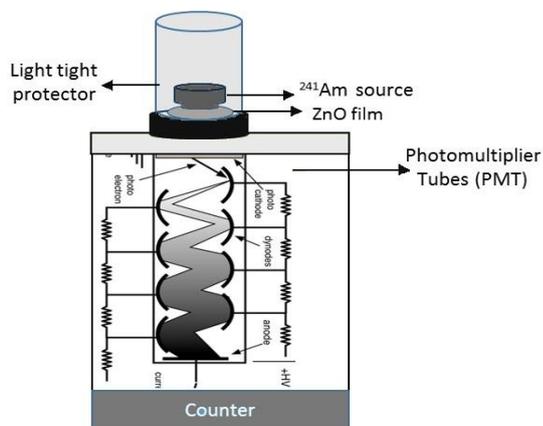


Fig. 1. The experimental set-up for testing the response of ZnO

The scintillation properties of the prepared films were tested using alpha sources (Am-241) with an activity of 7.5 kBq. The scintillation response of ZnO due to 1 min alpha particles exposure was measured using a nuclear counting system (AB-5) manufactured by Pylon Electronics Inc. The experimental set-up is shown in Fig. 1.

2.3.1. Effect of oxide layer thickness

The main purpose of the chemical treatment was the preparation of scintillation films of ZnO. To optimize the preparation method, the effect of layer thickness of ZnO films was studied using a ZnO modified sample with DMF. The thickness of the ZnO layer was measured using a micrometer with an accuracy of $\pm 0.5 \mu\text{m}$, and confirmed using the scanning electron microscope (SEM). The ZnO films were then exposed for 1 min to an Am-241 alpha source and the response was measured using the AB-5.

3. Results and discussions

3.1. ZnO samples characterization

The X-ray diffraction (XRD) results are shown in figure 2. It was observed that the oxide of different samples was crystalline and had the hexagonal wurtzite structure of bulk ZnO lattice parameters matching those in the literature (Santos, 2010).

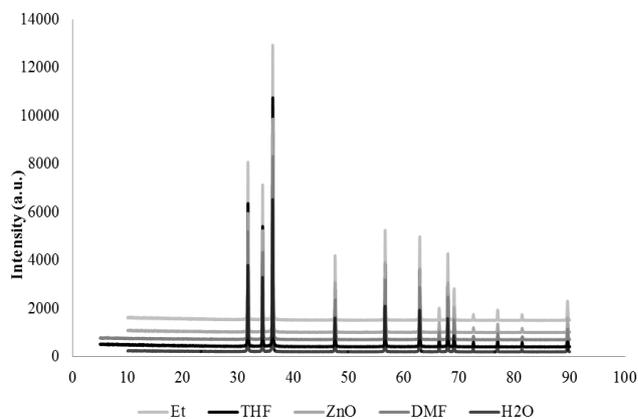


Fig. 2. XRD patterns of bulk ZnO

Surface structure plays an important role in determining the electrical, optical and radioluminescence properties of nanomaterials. Accordingly, SEM studies of modified oxide powders were carried out and presented in Fig. 3 (a-d). The oxide structures in all cases look like hexagonal plate like crystallites with irregular shape. The average pore radius of ZnO samples varied depending on the used solvent. The lowest average pore radius was noted in the case of sample treated with THF. Further study on the effect of the different used solvents (THF, Et, DMF and H₂O) on the size of pores is needed, as the primary study showed that the average pore radius of the treated samples had the following arrangement ZnO(THF) < ZnO(Et) < ZnO(DMF) < ZnO(H₂O).

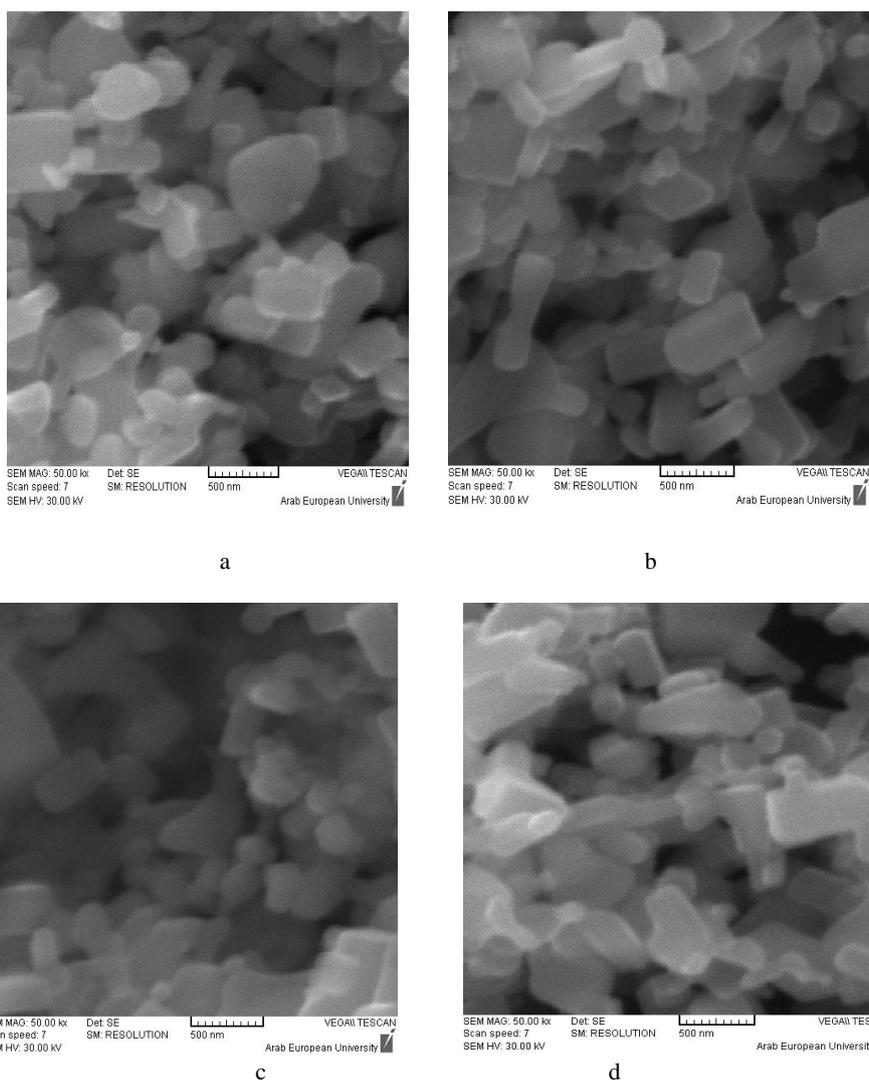


Fig. 3. SEM images of modified ZnO with different solvents (a) H₂O, (b) THF, (c) Et, (d) DMF

The SEM image of the scintillation film, consisting of ZnO layer on transparent plastic sheet, is presented in Fig. 4. The SEM image revealed a good homogeneity of the oxide layer, and was used to confirm its thickness measurement.

The surface and sub-surface components and oxidation states of ZnO samples treated with different solutions were investigated by XPS analysis. XPS analysis of the oxide shows asymmetric O-1s spectra that can be deconvoluted into three peaks, as shown in Fig. 5. The binding energy values at 530.2 eV, 531.2 eV, and 532.8 eV are observed in all samples. These peaks are associated with O²⁻ species in the lattice (O-Zn), oxygen vacancies or defects (O-H) and chemisorbed or dissociated (O ab.) oxygen species.

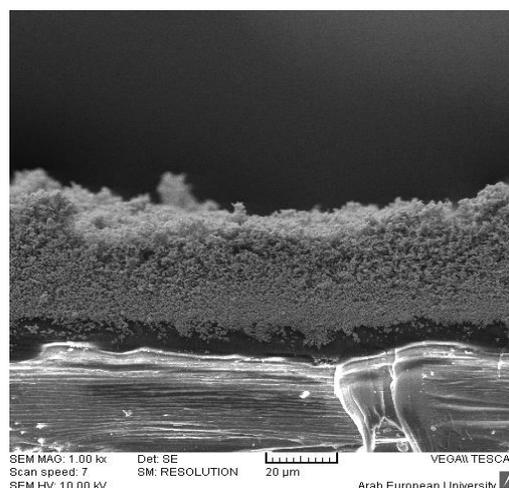


Fig. 4. SEM images of modified ZnO coated on transparent plastic sheet (ZnO modified with DMF)

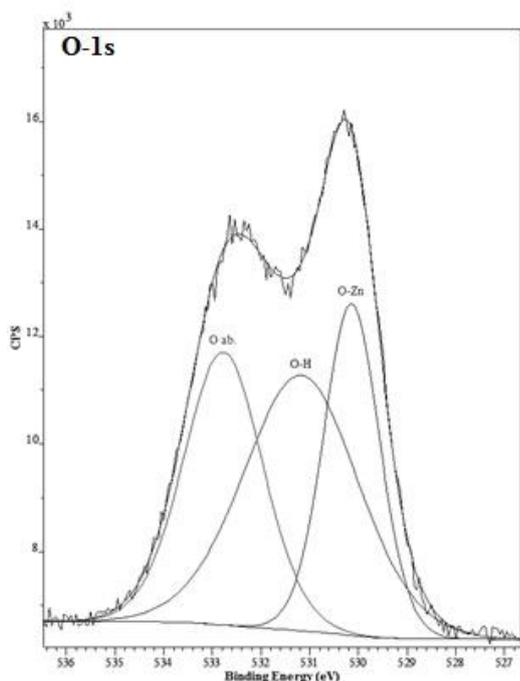


Fig. 5. XPS O-1s spectra for ZnO powder

As shown in Fig. 5 and Table 1, a high percentage of the physically absorbed hydroxyl groups on ZnO was observed, which could be mainly due to the low vacuum condition of the used XPS system. The distinct signals of hydroxyl groups observed should be due to hydroxyl groups, i.e. Zn-OH and H₂O, strongly bound to surface defects on ZnO. In other words, the hydroxyl groups in XPS are associated with surface defects and the visible hydroxyl groups should indicate the existence of surface defects on ZnO samples. According to the XPS results, the O-H (531.2 eV) values of O-1s were widely varied depending on the type of the used solvent, which implies that ZnO have different amount of surface defects. This could play an important role in facilitating the trapping of radio-induced electrons and holes, thus enhancing the PL and RL properties.

Table 1. XPS analysis for different ZnO modified samples

Solvent	O-1s			Zn 2p 3/2
	O ab. %	O-H %	O-Zn %	Zn-O %
ZnO	25.0	34.0	21.4	19.6
ZnO+ DMF	24.9	35.3	19.1	20.7
ZnO+ H ₂ O	30.2	32.1	19.4	18.3
ZnO+ Et	29.3	16.9	25.2	28.6
ZnO +THF	36.3	38.0	13.1	12.5

3.2. PL Characterization

PL is a very useful technique to disclose the efficiency of charge carrier trapping, migration and transfer in a semiconductor. Generally, the PL emissions on semiconductor materials are originated from the radiative recombination of photo-generated electrons and holes, and two major photo-physical processes can give rise to photoluminescence signals.

PL spectra obtained from the samples prepared with different solvents H₂O, THF, Et and DMF are shown in Fig. 5. PL results show the typical two emissions of narrow violet (~380 nm) and broad green-yellow bands (~510 nm). A comparable results were found by Yanagida et al., using high crystalline quality Cd²⁺ doped ZnO (Cd:ZnO) scintillator (Yanagida, 2014). To scrutinize the green defect emission (broad band in the visible region), the peaks of the near band edge (NBE) emission in the spectra were normalized to the same value. The broad emission band revealed in the visible region in our samples is due to the superposition of green and yellow emissions. ZnO commonly exhibits luminescence in the visible spectral range due to different intrinsic or extrinsic defects, and the absence of visible luminescence suggests the high crystal quality of ZnO. According to the chemical process, the defects formed in our system are likely to be due to an oxygen vacancy and interstitial oxygen, corresponding to the green and yellow bands in PL, respectively. The two different oxygen defects are competing with each other, presenting in the competition of green and yellow bands in PL. As the redox reactions might occur on the surface of oxygen vacancies and interstitial oxygen defects, the oxygen defects can be considered to be the active sites of the ZnO radioluminescence. As seen in Fig. 6, the PL integrated emission intensity (for the green-yellow bands) widely varied depending on the used solvent, suggesting the increase of the oxygen defects in ZnO structure.

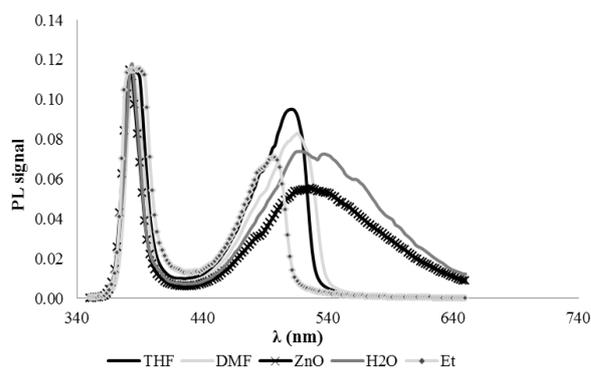


Fig. 6. Photoluminescence spectra of ZnO treated with different solvents

3.3. Radioluminescence study

3.3.1. Effect of solvent

To study the effect of solvent used in the chemical modification of bulk ZnO, scintillator films were prepared

with modified oxide powders and tested for their response to alpha particle irradiation. The range of 5 MeV alpha particles in ZnO was calculated by SRIM software, and found to be about 14 μm . Thus, studied samples had a thickness of about 20 μm . This means that the incident alpha-particle can be fully absorbed by the

sample and the thickness of the sample was enough to detect alpha-particles in the following experiment.

The prepared films were tested using alpha sources (Am-241), and the recorded scintillation counts are shown in table 2. Each experiment was repeated fifteen times to study the measurement repeatability, and the film surface homogeneity.

Table 2. The count rate variation with different ZnO modified films.

Solvent	Number of measurements	Count rate (cpm)			
		Average (cpm)	RSD (%)	max	min
H ₂ O	50	115220	0.7	116921	113239
THF	50	91514	0.8	92886	89855
Et	50	92242	1.0	94903	90123
DMF	50	103098	0.8	104481	101728

Looking to Table 2, the average counts of different films were increased from 91514, 92242, 103098 and 115220 for THF, Et, DMF and water, respectively. The relative standard deviation (RSD) values were very low and do not exceed 1.0 %. The obtained results could be explained that the hydroxyl group can be useful in the formation of hydrogen bonds within the structure of the oxide. This can play an important role in changing the outer shape of ZnO. Therefore, the radioluminescence of the ZnO can be changed using a chemical modification as results of the abundant surface oxygen vacancies or defects exist in ZnO.

It is worth noting that PL, XPS and pore size results could be correlated with radioluminescence results, however, further studies still be needed in order to better understand the correlation between defects and radioluminescence results.

3.3.2. Effect of oxide layer thickness

As an important factor affecting the radioluminescence of ZnO, the thickness of oxide layer has been studied. As shown in Fig. 7, the ZnO response to alpha particles was found to vary as a function of the thickness of the oxide layer.

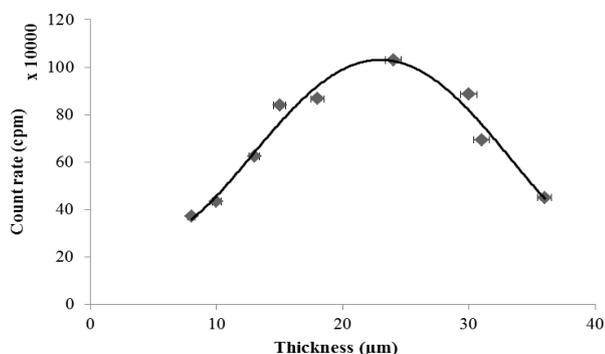


Fig. 7. The count rate (cpm) relation with ZnO layer thickness

It is noted that the response of ZnO increases with the thickness increase and reach to a maximum value for the thickness of about 24 μm . The count rate then decreased when thickness of oxide increased, which could be explained by the ZnO self-absorption of the optical photons.

4. Conclusions

The present work mainly focuses on the chemical modification of bulk ZnO and the resulting defects in the oxide structure. The structural, photoluminescence and radioluminescence properties of modified ZnO powders were studied. Two emission peaks were observed in photoluminescence spectrum. The first at approximately 380 nm due to free excitations peaking and the second one is a defect-based emission peaking at approximately 510 nm. An important variation in the PL integrated emission intensity (for the green-yellow bands) increased with changing the used solvent, suggesting the increase of the oxygen defects in ZnO. The XPS results showed that the O-H values of O-1s were widely varied depending on the type of the used solvent, which imply that ZnO have different amount of surface defects.

The radioluminescence of the ZnO can be changed using a chemical modification as results of the abundant surface oxygen vacancies or defects exist in ZnO. It is worth noting that PL results could be correlated to the radioluminescence results, however, further experiments are needed in order to better study the correlation between defects and radioluminescence results.

Acknowledgements

The authors gratefully acknowledge Prof. I. Othman (Director General of AECS) and Prof. M.S. Al-Masri (Head of Protection and Safety Department), for their continuous encouragement and support.

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