

## Investigation of sol-gel yttrium doped ZnO thin films: structural and optical properties

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2016 J. Phys.: Conf. Ser. 682 012023

(<http://iopscience.iop.org/1742-6596/682/1/012023>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 139.165.209.80

This content was downloaded on 03/06/2016 at 16:48

Please note that [terms and conditions apply](#).

# Investigation of sol-gel yttrium doped ZnO thin films: structural and optical properties

T Ivanova<sup>1</sup>, A Harizanova<sup>1</sup>, T Koutzarova<sup>2</sup> and B Vertruyen<sup>3</sup>

<sup>1</sup>Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, blvd. Tzarigradsko chaussee 72, Sofia, Bulgaria

<sup>2</sup>Institute of Electronics, Bulgarian Academy of Sciences, blvd. Tzarigradsko chaussee 72, Sofia, Bulgaria

<sup>3</sup>LCIS/SUPRATECS, Institute of Chemistry B6, University of Liege, Sart-Tilman, B-4000 Liege, Belgium

E-mail: tativan@phys.bas.bg

**Abstract.** Nanostructured metal oxide films are extensively studied due to their numerous applications such as optoelectronic devices, sensors. In this work, we report the Y–Zn–O nanostructured films prepared by sol-gel technology from sols with different concentration of yttrium precursor, followed by post-annealing treatment. The Y doped ZnO thin films have been deposited on Si and quartz substrates by spin coating method, then treated at temperatures ranging from 300-800°C. XRD analysis reveals modification of the film structure and phases in the doped ZnO films.

## 1. Introduction

ZnO gains a great scientific research in respect to its interesting properties such as wide band gap (3.37 eV at room temperature) with large exciton binding energy (60 meV), high chemical stability, low dielectric constant, large electrochemical coupling coefficient, high thermal conductivity, binding, antibacterial and UV protection [1,2]. ZnO films possess high transmittance in the infrared and visible spectral regions and high refractive index, which extend their application range. They are used as chemical and biological gas sensors, UV light emitters, thin film transistors, solar cell windows [3].

The doping of ZnO with rare earth impurities such as Y has also been reported as its ionic radius is very close to that of Zn [4]. ZnO:Y nanostructures are studied in respect to improved photocatalytic properties, enhance intensity of UV emission in photoluminescence, conducting transparent coatings etc [5, 6].

In this work, we report the Y–Zn–O nanostructured films prepared by sol-gel technology from sols with different concentration of yttrium precursor, followed by post-annealing treatment. Sol-gel technology has been proved to be very successfully for obtaining doped ZnO films. The sol-gel approach offers possibility to control the film stoichiometry, composition modification (mixing on a molecular level), cost effective process, inexpensive equipments resulting in homogeneous and smooth thin films [7].

<sup>1</sup> To whom any correspondence should be addressed.



The sol-gel Y doped ZnO thin films have been deposited on Si and quartz substrates by spin coating method, then treated at the temperatures ranging from 300-800°C. XRD analysis reveals the modification of the film structure and phases in the doped ZnO films. Vibrational properties are investigated by FTIR spectroscopy and optical behavior has been studied by UV-VIS spectrophotometry (transmittance and reflectance spectra). Optical band gaps are estimated as a function of the annealing temperatures.

## 2. Experimental details

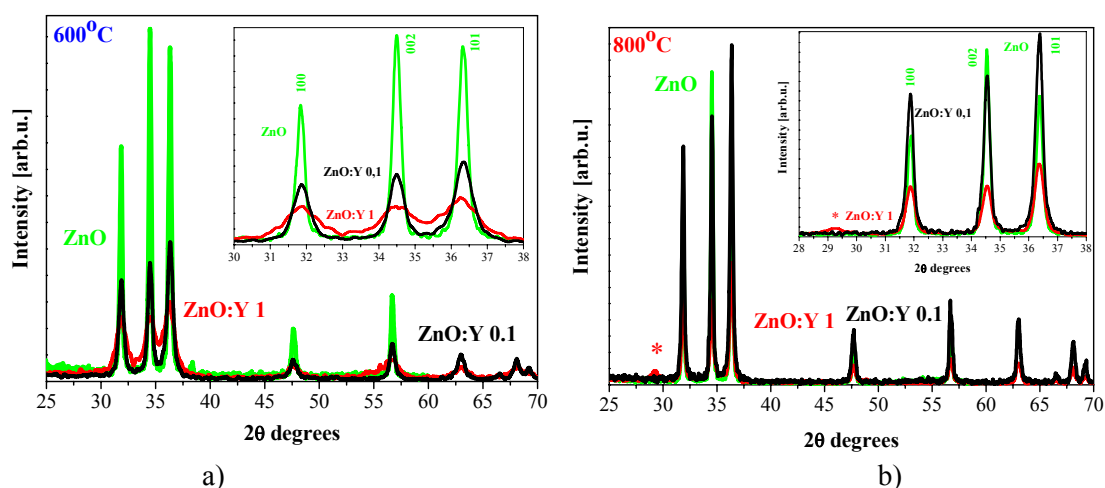
The sol solution for ZnO deposition has been previously reported [8]. The precursor used is zinc acetate, dissolved in an absolute ethanol (0.4 M concentration). The complexing agent and stabilizer used is monoethanolamine (MEA). The molar ratio MEA/Zn is fixed to 1. The yttrium has been involved by adding  $Y(NO_3)_3$  monohydrate in the following weight percents: 0,1 and 1. The corresponding sols and thin films obtained from them are labeled ZnO:Y 0.1 and ZnO:Y 1 and they are referred with these labels throughout the text. For depositing ZnO:Y thin films, the Zn solutions with Y additive were homogenized by ultrasonic treatment for few hours. The sol solutions are found to be very stable retaining their film forming properties for more than three months.

The films were deposited by spin coating method at 4000 rpm on Si wafers and quartz substrates, the samples undergo five layer depositions. The preheating temperature used (heating between layers) is 300°C for 10 minutes. After repeating the coating procedures five times, the films have been subjected to annealing at temperatures of 300 to 800°C in air ambient for 1 hour. The heating rate for the preheating and annealing temperatures has been kept constant 10°C/minute.

XRD spectra of the sol-gel films have been recorded by means of XRD diffractometer Bruker D8, at the grazing angle  $2^\circ$  and step time of 8 s and step a of  $0.1^\circ$  FTIR measurements are performed in the spectral region  $350-4000\text{ cm}^{-1}$  by Shimadzu FTIR Spectrophotometer IRPrestige-21. Optical measurements have been done by using UV-VIS-NIR Shimadzu 3600 spectrophotometer.

## 3. Results and discussions

The ZnO and ZnO:Y films, annealed at 600 and 800°C have been subjected to XRD measurements and the recorded diffraction patterns are presented in figure 1.



**Figure 1.** XRD spectra of ZnO:Y films compared to ZnO and annealed at 600 (a) and 800°C (b). The inset figures represent enlarged diffraction patterns in the  $2\theta$  range 25 - 39°.

The yttrium doping leads to suppress film crystallization as it is clearly observed for the films, annealed at 600°C. At the highest annealing temperature (800°C) only the film with the lower Y addition reveals a degree of crystallization close to that of ZnO films. The XRD patterns of ZnO,

ZnO:Y 0.1 and ZnO:Y 1 show predominantly diffraction peaks due to wurtzite ZnO phase (JSPDS 01-070-8070) with weak lines related to ZnO<sub>2</sub> phase (JSPDS 04-005-4315). Interesting features appear in the XRD spectra of ZnO:Y1 (very weak line) (figure 1b). The extra peak at  $2\theta=29,1^\circ$  (marked with asterisk) can be assigned to (222) reflection of cubic Y<sub>2</sub>O<sub>3</sub> phase [JCPDS 01-073-1334, 9]. Additional experiments with higher yttrium concentrations reveal that cubic yttrium oxide appeared as separate phase after high temperature annealing.

The average crystallite sizes can be estimated from the XRD data according to Scherrer's formula (using XRD peaks: 100, 002 and 101) and the results obtained are given in table 1. Table 1 presents also the calculated lattice parameters of the wurtzite ZnO phase and the dislocation density of the films. Dislocations are an imperfection in a crystal associated with misregistry of the lattice in one part of the crystal with respect to another part. The dislocation density of the films is given by the Williamson and Smallman's relation [10]:  $\delta = n/d^2$  (1), where  $n$  is a factor, which equals unity giving minimum dislocation density and  $d$  is the grain size. Dislocation densities manifest a decrease with increasing annealing temperatures, which indicates a lower concentration of lattice imperfections.

**Table 1.** Crystallite sizes ( $d$ ), dislocation density and lattice parameters of ZnO and ZnO:Y films.

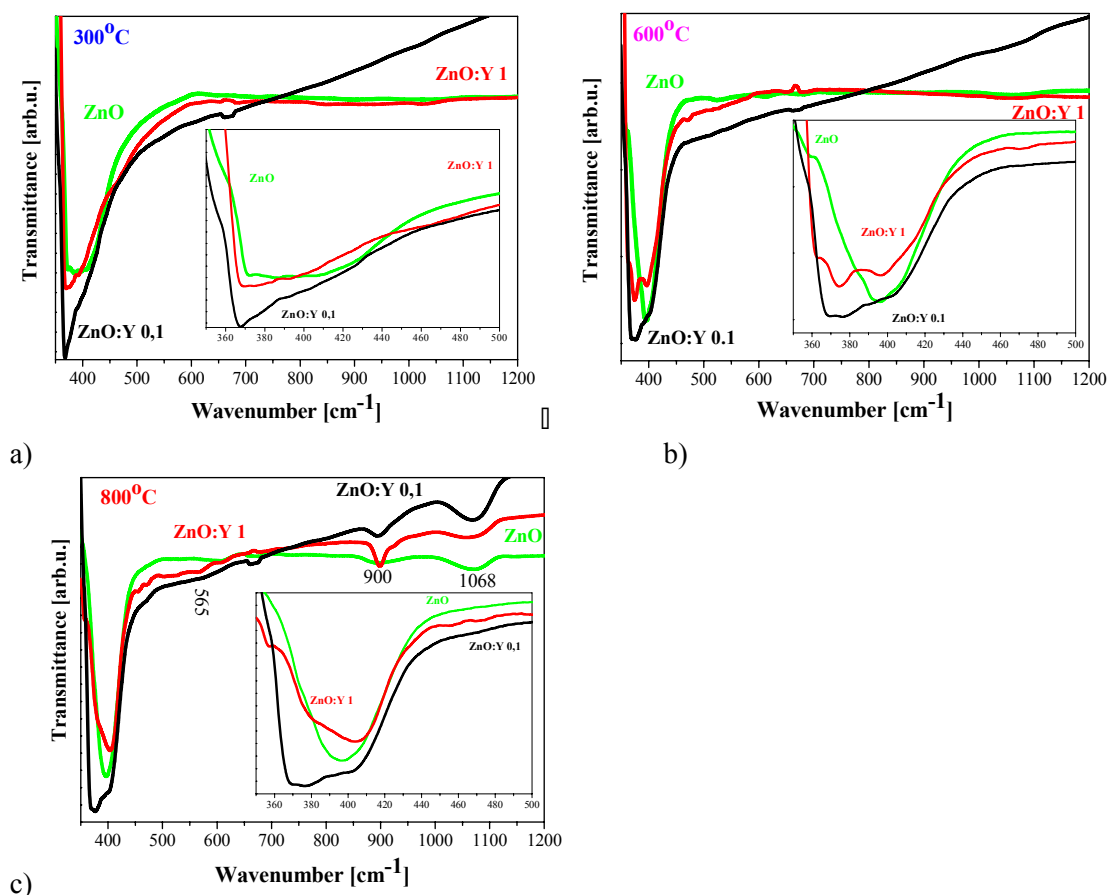
	ZnO	ZnO:Y 0.1	ZnO:Y 1
<b>600°C</b>			
<b>d, (nm)</b>	30.9	15.8	8.9
<b><math>\delta \times 10^{-4}</math>, (1/nm<sup>2</sup>)</b>	10.5	40.1	126.2
<b>a (Å)</b>	3.243	3.246	3.243
<b>c (Å)</b>	5.193	5.197	5.191
<b>800°C</b>			
<b>d, (nm)</b>	36.2	31.6	24.0
<b><math>\delta \times 10^{-4}</math>, (1/nm<sup>2</sup>)</b>	7.6	10.0	17.4
<b>a (Å)</b>	3.241	3.245	3.243
<b>c (Å)</b>	5.185	5.190	5.195

The yttrium component influences the crystallization of the films and respectively the crystallite sizes are found to be smaller than those of ZnO films for the two annealing temperatures. XRD study reveals that yttrium doping content affects considerably the crystalline structure of sol-gel ZnO:Y thin films and formation of Y<sub>2</sub>O<sub>3</sub> phase begins at higher Y concentrations.

FTIR spectroscopy has been used for studying the vibrational properties of ZnO:Y films as it is well known that FTIR spectroscopy is a very sensitive characterization method and can contribute to XRD conclusions. Figure 2 shows FTIR spectra of ZnO and ZnO:Y films, treated at temperatures of 300°C and 800°C.

The lowest annealing temperature of 300°C results in FTIR spectra revealing a weak band at 668 cm<sup>-1</sup> (Zn-O stretching mode). This band can be observed for all studied films independently of thermal treatments. The effect of yttrium additive is clearly seen: the shape and the intensity of the main absorption bands are considerably different than those of undoped ZnO. The main band of ZnO film is broad and strong centred at 372 cm<sup>-1</sup> (300°C) and shifting to 395 cm<sup>-1</sup> for higher annealing temperatures. The doped films manifest broader bands with doublets or triplets peaks depending on annealing above 300°C. In this spectral range, there is obviously an overlapping of IR lines, contributions both from ZnO and Y<sub>2</sub>O<sub>3</sub> phases. Other authors [11, 12] reported that cubic yttrium oxide shows peaks at 375, 383, 395, 420, 435 and 468 cm<sup>-1</sup> (for Y<sub>2</sub>O<sub>3</sub> films). Some of these lines are seen in figure 2. This result confirms that there is yttrium oxide presence even at the lowest annealing temperature although the XRD analysis do not show any traces of this phase. It must be noted that the spectra of ZnO:Y 0.1 (for all thermal treatments (FTIR spectra of annealed films at 400, 500 and 700°C were measured and analyzed but not given here) matches ZnO spectrum without a sign for

yttrium oxide with exception of the highest annealing at 800°C, where its main absorption band clearly indicates some contribution of Y-O phase.



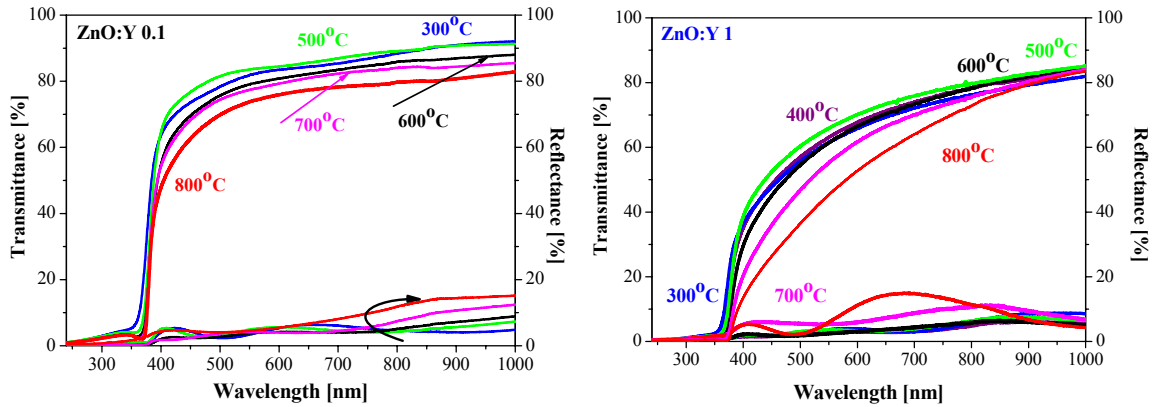
**Figure 2.** FTIR spectra of ZnO and ZnO:Y films annealed at 300 (a), 600 (b) and 800°C (c). The inset figures show enlarged main absorption band in the spectral range 350-500  $\text{cm}^{-1}$ .

The FTIR spectra of ZnO based films, annealed at 800°C shows some additional features. The clear band at 1068  $\text{cm}^{-1}$  can be assigned to Si-O bonds and it is due to the Si substrate. New weak bands appeared at 471, 465  $\text{cm}^{-1}$  and a clear line at 565  $\text{cm}^{-1}$  for ZnO:Y 1 sample. The absorption band at 565  $\text{cm}^{-1}$  is assigned to Y-O lattice vibration or Y-O stretching bond [13]. FTIR study shows that a fraction of yttrium oxide can exist in ZnO:Y 1 independently of the annealing temperatures.

The optical transmittance and reflectance spectra of sol-gel ZnO:Y films are shown in figure 3 (the films are deposited on quartz substrates). It can be observed that the thermal annealing influences the optical behavior of the films considerably. The transparency in the visible spectral range is decreasing with raising the annealing temperatures. It can be seen that the transmittance diminishes from 94 % (for 500°C annealed ZnO:Y 0.1 films) to 74 % (800°C) at the wavelength of 550 nm. The ZnO:Y 1 films show lower transmittance in comparison to ZnO:Y 0,1 films, but the optical transparency also shows strong reduction after high temperature treatment. This had been observed for sol-gel ZnO films, as their transmittance drops from 78% at 400°C annealing down to 65 % at 800°C.

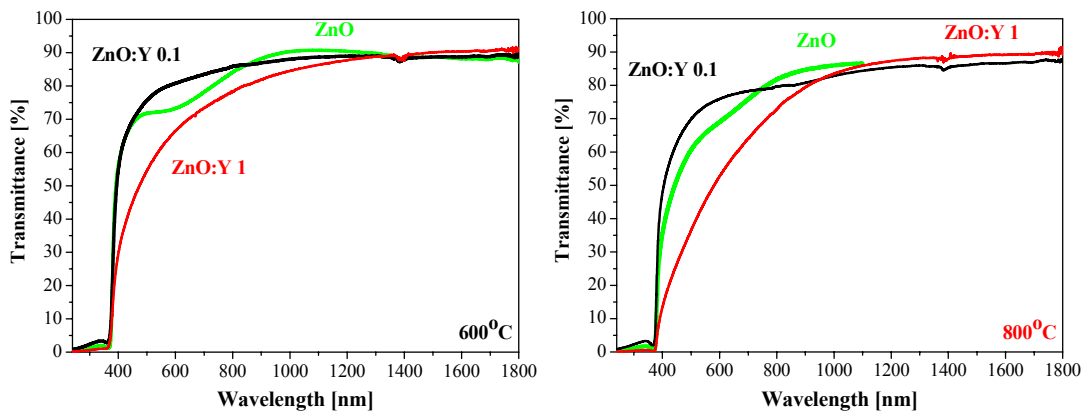
The specific bands which have been observed in the optical spectra of ZnO:Y 0.1 (annealing temperatures 500°C and above) below the absorption edge are due to the excitonic absorption of ZnO. The excitonic feature of the bulk ZnO is located near to 373 nm. ZnO films reveal excitonic absorption features even after 300°C treatment. The appearance of excitonic peak is reported to be a sign of high optical quality and good crystallinity of ZnO [14]. The excitonic absorption peaks prove that these sol-

gel ZnO and ZnO:Y 0,1 thin films have good optical properties. On the other hand, no excitonic band can be observed for ZnO:Y 1 even at the highest annealing temperatures.

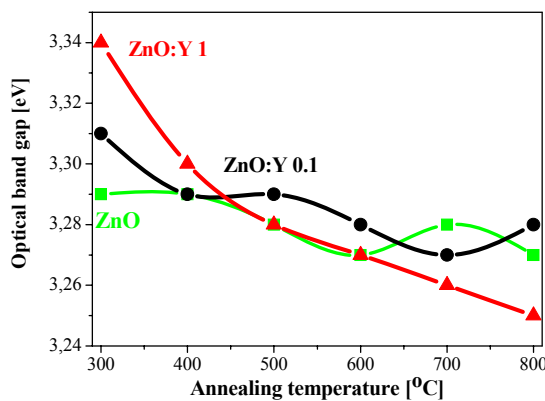


**Figure 3.** UV-VIS spectra of ZnO:Y 0,1 and ZnO:Y 1 films, annealed at different temperatures.

Figure 3 shows comparison of ZnO and ZnO:Y film transmittance for two annealing temperatures. The lower yttrium concentration leads to slight improvement of the optical transparency in respect of undoped ZnO. The higher yttrium doping results in lower transmittance of ZnO:Y 1 film which might be due to higher scattering.



**Figure 4.** Transmittance spectra of ZnO and ZnO:Y films, annealed at 600 and 800°C.



**Figure 5.** The dependence of the optical band gap with the annealing temperatures.

The optical band gaps ( $E_g$ ) versus the annealing temperatures are presented in figure 5. For ZnO films, the obtained  $E_g$  values are in the range of 3.27 to 3.29 eV, which is below to the reported value

(3.37 eV) of bulk ZnO [15] but close to those given in the literature for ZnO thin films [16]. The bandgap difference between the thin film and crystal can be related to grain boundaries and imperfections of the polycrystalline film structure. The optical band gap values of ZnO:Y 0.1 and ZnO:Y 1 films decrease with increasing the annealing temperatures. This can be attributed to increase of the crystallites size (as it is proved by the XRD analysis); it is known that optical band gap increased with decreasing particle size [17]. Other authors claim that yttrium contribution in sol-gel ZnO films can lead either to higher or smaller optical band gap [18]. In this study, it can be seen a strong correlation with the annealing temperatures and yttrium concentration. The optical band gap of  $Y_2O_3$  is reported 5.5 eV [11] so it seems logically to expect that that ZnO:Y films will show higher Eg values than undoped ZnO. A more detail optical study will be further performed for sol-gel ZnO:Y films with higher yttrium doping.

#### 4. Conclusions

Sol-gel technology is found to be very suitable approach for obtaining nanocrystalline thin films and for deposition of undoped and doped ZnO films. The prepared sols remain stable and were usable for spin-coating within 3 months. ZnO and ZnO:Y films are polycrystalline and have wurtzite structure with a small trace of yttrium oxide phase for ZnO:Y 1 annealed at 800°C. This conclusion is confirmed by FTIR investigation. The optical transparency is improved by a low Y doping and then strongly decreases for higher yttrium concentration. The optical band gaps in ZnO and ZnO:Y films vary in the range of 3.25 eV to 3.34 eV. The obtained properties of ZnO and ZnO:Y films on Si and quartz substrates are promising for applications in optoelectronic devices or solar cells.

#### 5. Acknowledgements

This paper was presented at INERA Conference "Light in Nanoscience and Nanotechnology 2015", 20-22 October 2015, Hissar, Bulgaria. The Conference is part of the Program of INERA REGPOT Project of Institute of Solid State Physics, Bulgarian Academy of Sciences.

#### 6. References

- [1] You Q, Cai H, Hu Z, Liang P, Prucnal S, Zhou S, Sun J, Xu N and Wu J 2015 *J. Alloys Compounds* **644** 528–533
- [2] Choi H W, Lee K, Theodore N and Alford T 2013 *Sol. Energy Mater. Sol. Cells* **117**. 273 -278
- [3] Wang Y, Yang J, Kong J, Jia H and Yu M 2015 *Superlatt. Microstr.* **86** 228–235
- [4] Kaur R, Singh A V and Mehra R M 2006 *J. Non-Cryst. Solids* **352** 2335–2338
- [5] Zheng J H, Song J L, Jiang Q and Lian J S 2012 *App. Surf. Sci.* **258** 6735–6738
- [6] Heo S, Sharma S, Lee S, Kim Ch, Lee B, Lee H and Kim D Y 2014 *Thin Solid Films* **558** 27
- [7] Anandan S and Muthukumaran S 2013 *Optical Mater.* **35** 2241–2249
- [8] Ivanova T, Harizanova A, Koutzarova T and Vertruyen B 2010 *Mater. Lett.* **64** 1147-1149.
- [9] Khachatourian A M, Golestani-Fard F, Sarpoolaky H, Vogt C and Toprak M S 2015 *Ceramics Inter.* **41** 2006-2014
- [10] Ergin B, Ketenci E and Atay F 2009 *Int. J. Hydrogen Energy* **34** 5249
- [11] Chopade S, Barve S, Raman K H T, Chand N, Deo M N, Biswas A, Rai S, Lodha G, Rao G and Patil D S 2013 *Appl. Surf. Sci.* **285** 524
- [12] Barve S, Jagannath N, Mithal M, Chand N, Bhanage B M, Gantayet L and Patil D S 2010 *Surf. Coatings Techn.* **204** 3167
- [13] Gupta A, Brahme N and Bisen D 2014 *J. Electroluminescence* **155** 112
- [14] Xu L, Zheng G, Miao J and Xian F 2012 *Appl. Surf. Sci.* **258** 7760
- [15] Tsay Ch-Y and Wang M C 2013 *Ceramics Inter.* **39** 469
- [16] Zhang Y, Ji H, Li P, Yang F and Zheng Z 2011 *Optics Commun.* **284** 236
- [17] Thongsuriwong K, Amornpitoksuk P and Suwanboon S 2013 *Adv. Powder Techn.* **24** 275
- [18] Turgut G, Duman S and Keskenler E F 2015 *Superlatt. Microstr.* **86** 363