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Preparation and Characterization of Ga-doped ZnO (GZO) Thin Films via Chemical Vapor Deposition using Diethyl Zinc in N-Hexane as the Low Cost Precursor

Van Thi Thanh Ho[1*], Nam Giang Nguyen[2]

[1]Hochiminh City University of Natural Resources and Environment (HCMUNRE), Vietnam
[2]Department of Engineering, Alstom Phu My Power Service, Vietnam

ABSTRACT

Highly transparent conducting Ga-doped ZnO (GZO) films have been successfully grown by using low pressure chemical vapor deposition (LPMOCVD) technique using n-hexane diluted diethyl zinc (DEZn/n-C6H14) and trimethyl gallium (TMGa) as Zn and Ga precursors, respectively. As the first time, we used Diethyl Zinc (DEZn) 1M in n-hexane solution, the cheap source to supply Zn, instead of pure DEZn as commonly used in synthesis doped ZnO by CVD. Trimethylgallium (TMGa) was used as doping gas for Ga. The GZO films grown at 400 oC under a doping ratio of [TMGa/DEZn] = 10.3% exhibited a satisfactory of over 85% in the visible wavelength range, and a low resistivity of 4.98 × 10-4 Ω cm. The results indicated GZO films with qualified opto-electric properties can be prepared on glass using a cost friendly solution based Zn precursor.

Keywords: Low cost, MOCVD, ZnO, GZO, low resistivity.

INTRODUCTION

Transparent conducting oxides (TCOs) layers are the critical component which is used in thin films silicon solar cell as an electrode and several optoelectronic devices such as flat panels, light emitting diodes as well as flexible displays.[3-6] Flourine-doped tin oxide (FTO) glass is the most widely used TCO glass for the fabrication of thin film solar cell; however, the supply of large-area FTO glass is dominated by a few glass company. TCOs with optical transmittance more than 80% in the visible region and resistance less than 10^{-3} Ω cm are required to be used in solar cells.[7,8] Recently, doped ZnO is quickly attracting more attention as an alternative material to substitute tin doped indium oxide due to low cost material and non-toxicity. Doped ZnO, such as Al doped ZnO (AZO), B doped ZnO (BZO) and Ga doped ZnO (GZO), have been widely studied and remarked as a promising material for TCO layer with resistivity in the range order of 1×10^{-4} Ω cm.[9,10] However, the AZO requires a high degree control over the oxygen source in the sputter and chemical vapor deposition techniques because of the high reactivity of Al with oxygen to become Al_2O_3 clusters which lead to increase the resistivity of AZO films.[11] Furthermore, for the synthesis of BZO films are faced with very toxic and expensive of B_2H_6 source. Moreover, pure Zn precursor, which was commonly used for the synthesis doped ZnO by metal organic chemical vapor deposition (MOCVD) technique, is also expensive. Therefore, a new approach to synthesis doped ZnO by low cost source with the properties can be comparable is needed. The previous efforts suggest that GZO has better conduction stability than AZO due to Ga is less reactive and more resistant to oxidation than Al.[12] Moreover, the ion radius of Ga (0.54 Å) is closed to Zn (0.74 Å) and the covalent length of Ga-O (1.92 Å) is similar to that of Zn-O (1.97 Å). Therefore, the used of Ga as a dopant will offer the advantage of reducing the deformation of ZnO lattice at high level Ga doping concentrations.[13] Many methods have been employed to deposit GZO on glass such as RF/DC magnetron sputtering,[14,15] pulsed laser deposition (PLD),[16,17] metal organic chemical vapor deposition (MOCVD).[18,19] Among these

Address for correspondence:

httvan@hcmunre.edu.vn

methods, MOCVD shows the significant advantages since high growth rate over large area and high quality of GZO could be achieved and operated at low pressure. The great potential benefit of MOCVD method is the ability to control the growth condition such as doping level and growth rate.

In this work, GZO films were grown on glass substrate by using low pressure metal organic chemical vapor deposition (LPMOCVD) process which is a simple fabrication process and low cost. As the first time, we used Diethyl Zinc (DEZn) 1M in n-hexane solution, the cheap source to supply Zn, instead of pure DEZn as commonly used in synthesis doped ZnO by CVD. Trimethylgallium (TMGa) was used as doping gas for Ga. The results show the low resistivity and high optical transmittance in the visible range can be achieved in the optimized GZO films.

EXPERIMENTAL SECTION

Materials and Methods

The GZO thin films were deposited by a home-made shower head injector LPMOCVD system on corning EAGLE 2000 glass (20 mm × 20 mm × 0.7 mm) which was cleaned by sonication in acetone for 5 min followed by ethanol for another 5 min, then rinsed with DI water and blown dry by nitrogen. TMGa (US Epichem), DEZn 1M in n-hexane (Sigma Aldrich) and Millipore water were used the source of Ga, Zn and O respectively. Nitrogen was employed as the carrier gas. The GZO was grown at 400 ^{o}C on a buffer layer undoped ZnO with thickness 20-30 nm which was deposited on glass at 150 ^{o}C and flow rate ratio of [H_2O/DEZn] = 6.5. The thickness of GZO is about 740 nm. After growing, the GZO films were annealed at various temperatures under N_2 (99.999%) atmosphere at pressure 1 Torr, the flow rate of N_2 was 20 sccm.

The crystalline properties of the GZO films were characterized using X-ray (Bruker D2 PHASER**)** diffraction (XRD). Scanning electron microscopy (JEOL JSM-6500F) was used to characterize the thickness of GZO films. The optical properties of GZO were obtained using UV-visible spectrophotometer (JASCO V-670) in the wavelength from 300 to 1500 nm. The chemical composition and bonding state of the GZO films were investigated through X-ray photoelectron spectroscopy (XPS) using a monochromatic Al Kα radiation source. The resistivity, carrier concentration and mobility of films were measured at room temperature by van der Pauw method using Hall Effect measurement system. The sheet resistance was measured by a standard four point probe technique (KeithLink Technology, Taiwan).

RESULTS AND DISCUSSION

Figure 1 shows the plan and cross-sectional view of ZnO:Ga films were deposited on glass at 400 ^{o}C which the thickness is about ~ 740 nm. It was found that the surface of GZO films show a homogeneous surface and highly dense. The GZO exhibits typical columnar structure showing clear column structure boundaries, indicating while the columnar grains are growing and together gaining in width. Further study the effect of Ga doping to the electrical properties of GZO films, different flow ratio of [TMGa/DEZn] were carried out. The structural properties of films were examined by XRD. Figure 2 shows XRD pattern of GZO films with different [TMGa/DEZn] ratios.

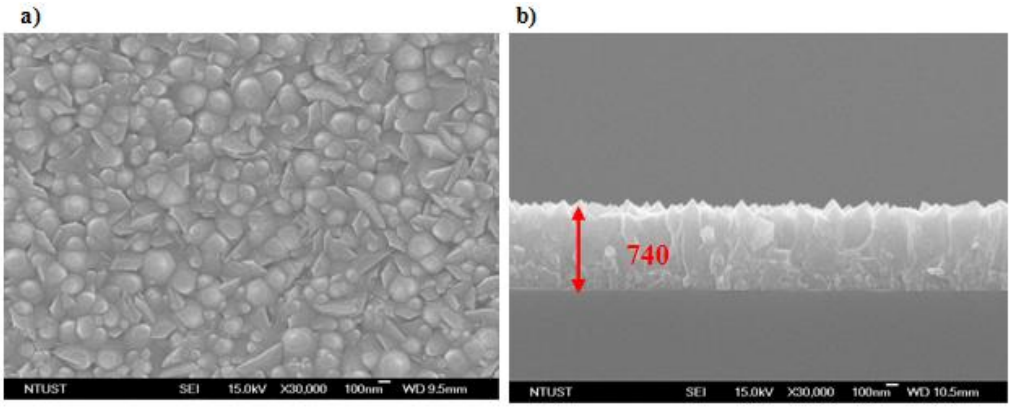

Figure1. *SEM images of ZnO:Ga thin films a) plan view and b) cross-sectional view. The [TMGa/DEZn] ratio = 0.103.*

From the figure 2, all the films with different gas flow ratio show the wurtzite structure with prefer c-axis growth orientation. The XRD spectrum of GZO films exhibit a strong peak at $2\theta = 34.4^{o}$ which belong to (002) plane. Other peaks (100, 110, and 103) with low intensity were also observed.[18] It is interesting to note that at the beginning stage of deposition has various of nucleation orientations were formed and each nucleus competed to grow. The strong and dominating nature of the peak corresponding to the (002) reflection indicates the preferential *c*-axis orientation of crystallites and the (002) orientation was the lowest surface energy. Noticeably, no signal corresponding to Ga_2O_3 phase was found from XRD patterns.[20] To evaluate the quality of GZO films, the full width half maximum (FWHM) of (002) peak of GZO films are used to evaluate the crystallinity. With increasing the [TMGa/DEZn] flow rate ratios, the FWHM first decreases and increases and has the minimum value (0.15^{o}) at the ratio 0.103 of [TMGa/DEZn]. However, further increasing in Ga content deteriorates the crystallinity of GZO films, which may be effect of the formation of the compressive stresses due to more ions Ga occupies in the interstitial sites of ZnO under high doping level of Ga.[10]

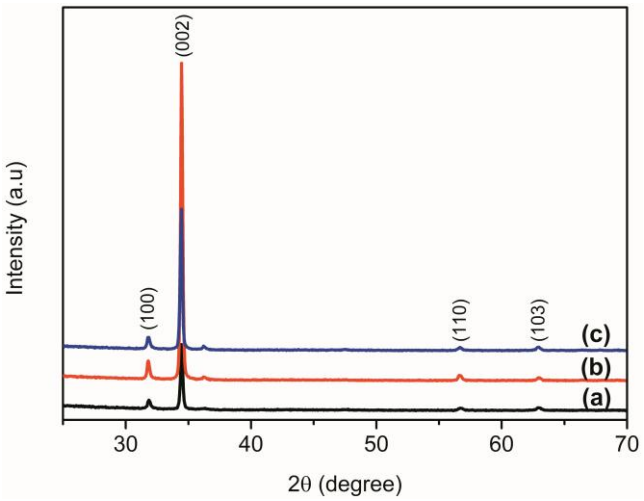

Figure2. *XRD patterns of GZO films with various gas flow ratio [TMGa/DEZn] a) 0.09, b) 0.103, c) 0.117.*

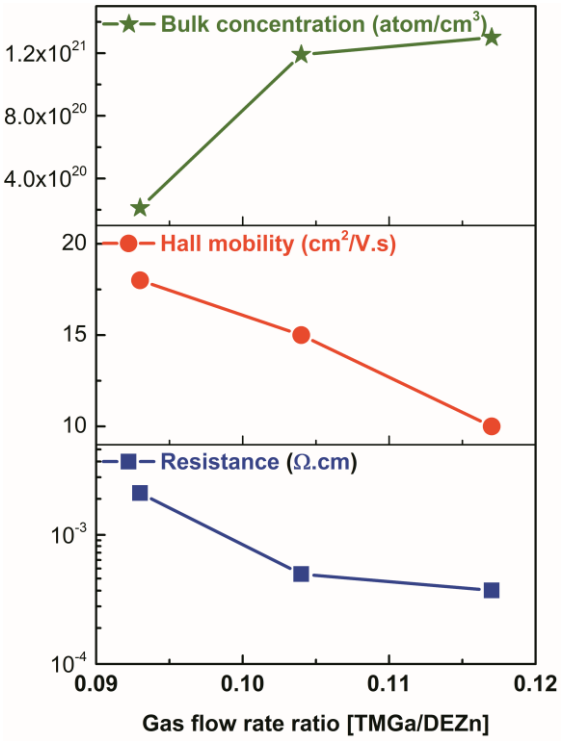

Figure3. *Resistivity, Hall mobility, and carrier concentration as a function of gas flow rate ratio [TMGa/DEZn].*

Figure 3 shows the measured films resistivity, Hall mobility and carrier density of GZO films as a function of gas flow ratio. The films resistivity decrease dramatically from 2.11 × 10^{-3} Ω cm and reaches the value of 3.72 × 10^{-4} Ω cm as the gas flow ratio is increased from 0.09 to 0.117. On the other hand, the carrier concentration is increased from 2.12 × 10^{20} cm^{-3} to 1.3 × 10^{21} cm^{-3}. This behaviour could be explained due to Ga is a *n*-type dopant that replaces zinc atoms which causes the increasing of free electron concentration in the films. It is known that the improvement of electrical properties of GZO as the result of increasing the Ga content in the precursor's mixture that leads to more substituting Zn in lattice site. However, the Hall mobility of GZO films decrease with further more Ga is supplied.

For optical application, the high transmittance in the visible range is very important. Figure 4 shows the optical properties of GZO films with various ratios [TMGa/DEZn] in the wavelength 300-1500 nm. The GZO films show the high transparent in the visible light. This result is associated with a good structural homogeneity and crystallinity. However, the films transmittance decreases with the increasing of ratios [TMGa/DEZn]. A drastic change in transmittance can be seen with different doping ratios, especially in the near infrared range. This is caused by the free carrier absorption, which increases with the increasing of Ga doping level.[21]

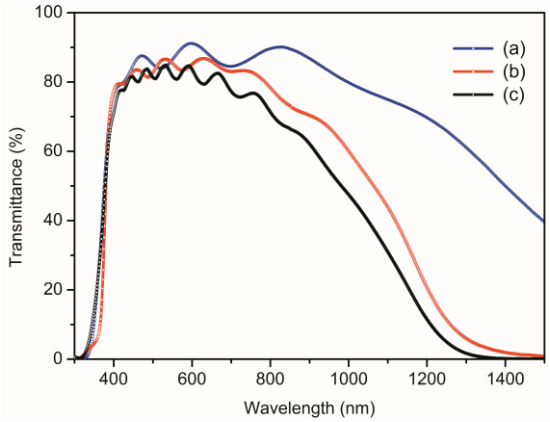

Figure4. *The total transmittance of GZO films with various ratios [TMGa/DEZn] a) 0.09, b) 0.103, c) 0.117.*

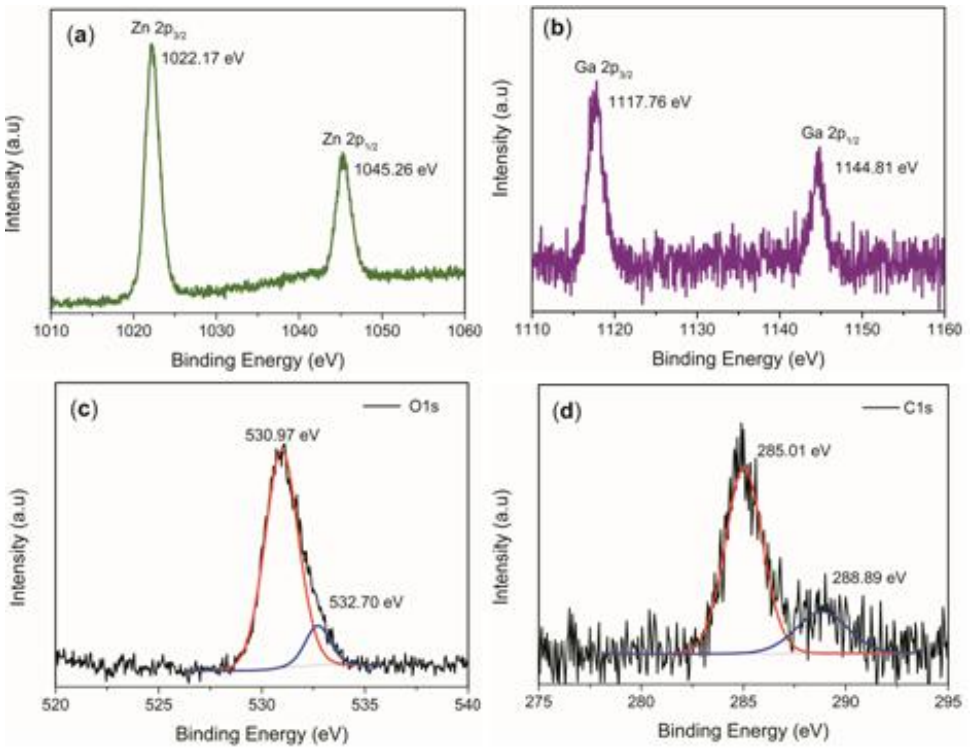

Figure5. *XPS spectra of (a) Zn $2p_{3/2}$, (b) Ga $2p_{3/2}$, (c) O 1s and C 1s (d) for GZO films with thickness ~ 740 nm.*

The XPS measurement were carried out to determine the chemical composition and bonding state of the GZO films which were synthesis at 400 ^{o}C under the ratios of [TMGa/DEZn] = 0.103, as shown in Figure 5.The energy peak of Zn $2p_{3/2}$ at 1022.17 eV in Figure 5a is attributed to interstitial Zn^{2+} ions bounded with O^{2-} ions in the wurtzite structure.[22] Furthermore, no metallic Zn with a binding energy of 1021.5 eV is observed, indicating that Zn exists only in the oxide states.[23] Concerning the role of doped Ga, the peak spectrum for Ga $2p_{3/2}$ is around 1117.76 eV in Figure 5b is originated from Ga^{3+} ions that substituted Zn^{2+} ions in wurtzite structure.[24] This result further confirms no Ga metallic was found, indicating that the Ga^{3+} ions were perfectly substituted Zn^{2+} sites in the GZO crystal structure. As shown in Figure 5c, the O 1s spectrum is composed of two peaks. The main peak located at 530.97 eV is contributed by lattice oxygen bonded as O^{2-} ions which are surrounded by Zn or Ga in the ZnO matrix. The shoulder peak with the binding energy at 532.70 eV is assigned to the loosely oxygen on the surface of GZO films belonging to specific –OH, –CO tails.[22] Figure 5d shows the fitted spectrum of C 1s. It could be suitable resolved into two state of C. The peak located at 285.10 eV is assigned to the hydrocarbon group state due to surface contamination resulted due to exposure to air before the XPS measurements.[25] The peak located at the highest energy of 288.89 eV illustrates the C=O bonding group which may come from the reaction of water vapor and hydrocarbon group at 400 ^{o}C. The calculated atomic composition percentages are determined to be Zn = 51.86 at.%, O = 42.6 at.%, Ga = 5.54 at.%, respectively.

For a reference, Table 1 shows the recent development of GZO by using various techniques. The results show the GZO done by this work have good electrical and optical properties, the films exhibited the lowest sheet resistance 6.75 Ω/square with thickness 740 nm. It is interesting to note that the GZO films which have been fabricated by simple method and low cost Zn precursor could be comparable with the other methods and techniques. The results further confirm GZO films can be used as TCO layer for thin films Si solar cells applications.

Table1. *Summary the properties of GZO thin films were prepared by various techniques.*

Synthesis method	Substrate	Films thickness (nm)	Sheet Resistance (Ω/square)	Resistivity × 10^{-4} (Ω cm)	Carrier concentration (cm^{-3})	Mobility (cm^2/V.s)	Transmittance Invisible (%)	Ref.
MOCVD	Glass	740	6.75	4.98	1.2×10^{21}	15.0	> 85	This work
MOCVD	Glass	600	10.70	3.60	1.7×10^{21}	10.1	~ 90	(18)
PECVD	Glass	410	18.00	7.50	5.5×10^{20}	15.0	~ 93	(19)
Sputter	Glass	620		4.48	1.7×10^{21}	7.5	> 90	(20)
MOCVD	Glass	800	13.00	2.60	4.0×10^{21}		> 85	(26)
Sputter	Glass	400	11.67	5.88	6.8×10^{20}	22.0	~ 90	(27)
Sputter	Glass	700		3.00	1.2×10^{21}	17.0	~ 85	(28)
Sputter	Glass	535		20.00	3.5×10^{20}	7.0	> 90	(29)

CONCLUSIONS

Highly conducting and transparent GZO films have been successfully grown by using low cost Zn precursor, simple fabrication LPMOCVD technique. In addition, the ratio of [TMGa/DEZn] at 0.103 can be used to obtain GZO films with the resistivity of 4.98 × 10^{-4} Ω cm and transmittance in visible range higher than 85%. The result of this work suggests that the ability to fabricate the larger area TCO with cost competitive for solar cells, LEDs (light emitting diodes) as a potential candidate for replacement ITO.

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REFERENCES

[1] J. Waldau, (2004). Solar Energy, 77 , 667-678.

[2] A.V. Shah, H. Schade, M. Vanecek, J. Meier, E. Vallat-Sauvain and N. Wyrsch, U. Kroll, C. Droz and J. Bailat, (2004). Prog Photovolt: Res Appl, 12**,** 113-142.

[3] M. Fukawa, K. Sato, T. Tsukamoto, K. Adachi, H. Nishimura, (1997). Sol. Energy Mater. Sol. Cells, 49, 107-112.

[4] S. I. Kim, S. H. Cho, S. R. Choi, M. C. Oh, J. H. Jang, P. K. Song, (2009). Thin Solid Films, 517, 4061-4064.

[5] H. Liu, V. Avrutin, N. Izyumskaya, Ü. Özgür, H. Morkoç, (2010). Superlattices and Microstructures, 48 , 458-484.

[6] T. P. Muneshwar, V. Varma, N. Meshram, S. Soni, R. O. Dusane, (2010). Sol. Energy Mater. Sol. Cells, 94, 1448-1450.

[7] Lennon, R. B. Tapia, R. Kodama, Y. Chang, S. Sivananthan, and M. Deshpande, (2009).J. Electron. Mater. 38,1568.

[8] Y. Hsu, T. F. Ko, and Y. M. Huang, (2008), J. Eur. Ceram. Soc. 28, 3065.

[9] X. Q. Gu, L.P. Zhu, L. Cao, Z. Z. Ye, H. P. He, P. K. Chu,(2011), Materials Science in Semiconductor Processing, 14, 48-51.

[10] Q. B. Ma, Z. Z. Ye, H. P. He, S. H. Hu, J. R. Wang, L. P. Zhu, Y. Z. Zhang, B. H. Zhao, (2007). J Cryst Growth, 304, 64-68.

[11] H. J. Ko, Y. F. Chen, S. K. Hong, H. Wenisch, T. Yao, and D. C. Look, (2000). Appl. Phys. Lett. **77**, 3761

[12] J.I. Nomoto, M. Konagai, K. Okada, T. Ito, T. Miyata, T. Minami, (2010), Thin Solid Films, 518, 2937-2940.

[13] V. Assunção, E. Fortunato, A. Marques, A. Gonçalves, I. Ferreira, H. Águas, R. Martins, (2003). Thin Solid Films, 442, 102–106.

[14] S. W. Shin, K. U. Sim, J. H. Moon, J. H. Kim, (2010). Current Applied Physics, 10, S274-S277.

[15] Nam, Y. H. Kang, D. Jung, Y. S. Kim, (2010). Thin Solid Films, 518, 6245-6248.

[16] Z. F. Liu, F. K. Shan, Y. X. Li, B. C. Shin, Y. S. Yu, (2003). J Cryst Growth, 259, 130-136.

[17] S. M. Park, T. Ikegami, K. Ebihara, (2006). Thin Solid Films, 513, 90-94.

[18] J. L. Zhao, X.W. Sun, H. Ryu, Y. B. Moon, (2011). Optical Materials, 33 768-772.

[19] J. J. Robbins, J. Harvey, J. Leaf, C. Fry, C. A. Wolden, (2005). Thin Solid Films, 473, 35-40.

[20] Q. B. Ma, Z. Z. Ye, H. P. He, J. R. Wang, L. P. Zhu, B. H. Zhao, (2007). Vacuum, 82, 9-14.

[21] K. Ellmer, A. Klein, B. Rech, Transparent conductive zinc oxide: basics and applications in thin film solar cells, Springer, 2008, p378.

[22] M.N. Islam, T.B. Ghosh, K.L. Chopra, H.N. Acharya, (1996). Thin Solid Films, 280, 20-25.

[23] M. Chen, Z. L. Pei, C. Sun, L. S. Wen, X. Wang, (2001). Mater. Lett. 48, 194-198.

[24] Mitsugi, Y. Umeda, N. Sakai, T. Ikegami, (2010). Thin Solid Films, 518, 6334-6338.

[25] B. Saha, R. Thapa, K.K. Chattopadhyay, (2008). Solid State Commun, 145, 33-37.

[26] Y. Li, G. S. Tompa, S. Liang, C. Gorla, Y. Lu, and J. Doyle, (1997**)**. J. Vac. Sci. Technol. A15, 1063-1068.

[27] J. H. Park, K. J. Ahn, S.I. Na, H. K Kim, (2011). Sol. Energy Mater. Sol. Cells, 95, 657-663.

[28] Fortunato, L. Raniero, L. Silva, A. Gonçalves, A. Pimentel, P. Barquinha, H. Águas, L. Pereira, G. Gonçalves, I. Ferreira, E. Elangovan, R. Martins, (2008). Sol. Energy Mater. Sol. Cells, 92, 1605-1610.

[29] S. Liang and X. Bi, (2008). J. Appl. Phys. 104, 113533.

[30] L. B. Duan, X. R. Zhao, J. M. Liu, W. C. Geng, H. Y. Xie and H. N. Sun, (2012), Phys. Scr. 85, 035709.

[31] Jia, T. Matsui and M. Kondo, (2012). Prog. Photovolt: Res. Appl, 20, 111–116.

[32] K. Ellmer, (2001). Journal of Physics D: Applied Physics 34, 3097.

AUTHOR'S BIOGRAPHY

Dr Ho Thi Thanh Van, has worked in advanced nanomaterials for environment treatment, environmental sustainability, semiconductor materials (SiC, GaN, TCO…), renewable energy (fuel cells, solar cells) and electrochemistry, nanotechnology.