Imprinting of Nanoporosity in Lithium-Doped Nickel Oxide through the use of Sacrificial Zinc Oxide Nanotemplates

Vinod E. Sandana[1], David J. Rogers[1], Ferechteh H. Teherani[1], Philippe Bove[1], Ryan McClintock[2] and Manijeh Razeghi[2]

[1]Nanovation, 8 Route de Chevreuse, 78117 Châteaufort, France
[2]Center for Quantum Devices, Department of Electrical and Computer Engineering, Northwestern University, Evanston, IL60208, USA

ABSTRACT

Methods for simultaneously increasing the conductivity and the porosity of NiO layers grown by pulsed laser deposition (PLD) were investigated in order to develop improved photocathodes for p-DSSC applications. NiO:Li (20at%) layers grown on c-Al_2O_3 by PLD showed a sharp drop in conductivity with increasing substrate temperature. Layers grown at room temperature were more than two orders of magnitude more conductive than undoped NiO layers but did not show evidence of any porosity in Scanning Electron Microscope (SEM) images. A new method for imposing a nanoporosity in NiO was developed based on a sacrificial template of nanostructured ZnO. SEM images and EDX spectroscopy showed that a nanoporous morphology had been imprinted in the NiO overlayer after preferential chemical etching away of the nanostructured ZnO underlayer. Beyond p-DSSC applications, this new process could represent a new paradigm for imprinting porosity in a whole range of materials.

Keywords: NiO:Li, sacrificial nanostructured ZnO, imprint, Pulsed Laser Deposition, p-DSSC.

1. INTRODUCTION

Nickel oxide (NiO) was one of the first reported p-type transparent conducting oxides (TCOs). This fcc material has a direct [1] wide bandgap (Eg ~ 4.3 eV) [2], excellent electrochemical stability, an elevated conduction band energy level and a relatively high ionization potential. While stoichiometric NiO is electrically insulating, as-grown NiO is invariably reported to be Ni deficient [3] and shows p-type conduction with a hole concentration that increases with oxygen content. This is attributed to positive charge compensation (formation of two Ni^{3+} ions in order to maintain charge neutrality) at thermodynamically-favored Ni^{2+} vacancies [4]. As a result of these properties, and their tunability, NiO has been investigated for a number of emerging uses including photocatalysis [5], water treatment [6], electrochromics [7], UV photodetectors [8], thermoelectrics [9], chemical/gas sensing [10], hole transport/electron blocking in organic electronic devices [11], super capacitor electrodes, lithium ion battery anodes [12], fuel cells [13], p-type field effect transistors [14] and as p-type photocathodes for use in novel tandem dye sensitized solar cells [15]. This latter application (termed "p-DSSC") employs a photosensitized (p-type semiconductor) cathode as a means to boost the solar conversion efficiency compared with conventional DSSCs, in which the sole photoelectrode is a nanoporous photosensitized anode (e.g. TiO_2) and the counter-electrode is in platinum. So far, NiO is the only photocathode found to give significant photocurrent and photovoltage when adopted instead of the Pt counter-electrode. Obtaining the required combination of a mesoporous morphology and a relatively low resistivity has proven challenging, however, since NiO (and all currently available p-type TCOs) show relatively poor conductivity compared to n-type TCOs. Moreover, the situation is compounded by the poor electrical connectivity between the grains in the sintered nanopowders of NiO which are generally used in order to obtain sufficient porosity for dye loading.

In previous work we described attempts to resolve this through the use of pulsed laser deposition (PLD) of NiO layers on fluorine-doped tin oxide (FTO)/glass substrates. These layers proved to be not just too insulating (~90 Ω.cm) but also insufficiently porous for p-DSSC applications, however. The new approach described in this paper

Oxide-based Materials and Devices VIII, edited by Ferechteh H. Teherani, David C. Look, David J. Rogers, Ivan Bozovic. Proc. of SPIE Vol. 10105, 101052C · © 2017 SPIE
CCC code: 0277-786X/17/$18 · doi: 10.1117/12.2263713

tries to combat these two challenges by (a) using Li doping to improve the conductivity of NiO (Li+ substitutional on the Ni site is a known shallow acceptor) [16] and (b) using nanostructured ZnO as a sacrificial template [17,18] in order to imprint a porosity in the NiO.

2. EXPERIMENT

In order to increase the NiO conductivity PLD was conducted using a sintered NiO target containing 20at% Li and c-sapphire (c-Al_2O_3) substrates. The ablation was done using a pulsed KrF excimer laser (248nm) and substrate temperature was varied from room temperature (RT) up to 400°C (Li is known to diffuse out of the structure at higher temperatures).
In order to render NiO nanoporous, self-forming (catalyst-free) ZnO nanostructure arrays were first grown on c-Al_2O_3 substrates [19-21] by PLD. NiO was then grown on the nano ZnO (again by PLD) and bonded to a glass substrate using Apiezon W wax. The whole structure was then immersed in a bath of a chemical etchant (0.1M HCl) in order to preferentially remove the nano ZnO and leave behind an imprinted porosity in the NiO. Figure 1 illustrates the process flow.

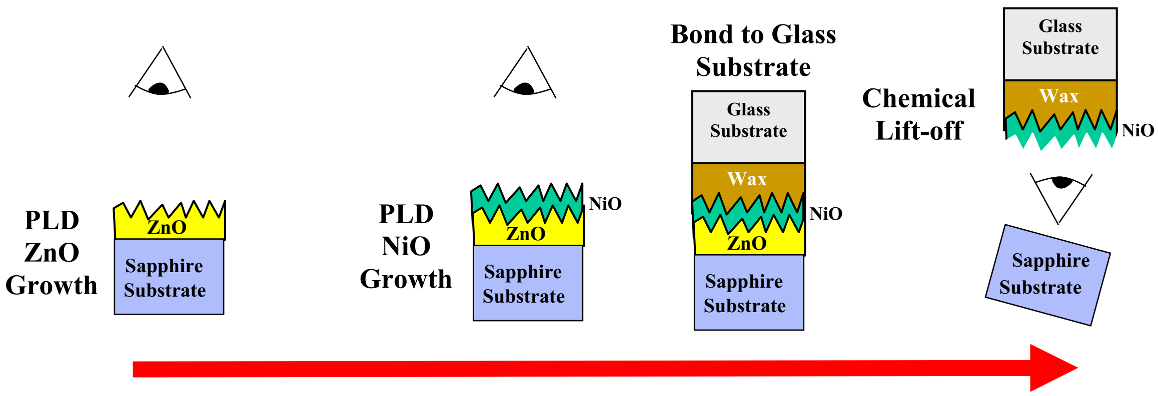


Figure 1. Schematic of the proposed process flow for the sacrificial nanotemplate imprinting and lift-off approach.

A Philips XL-30 Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) combined with Energy-dispersive X-ray spectroscopy (EDX) was used to examine the surface morphology and to analyse the chemical composition. Electrical resistivity was measured with a Keithley 2400 source-meter and a Signatone four-collinear-probe system. Hall effect measurements were conducted with an Ecopia HMS-3000 system.

3. RESULTS & DISCUSSION

3.1 NiO:Li Film deposition on cAl_2O_3

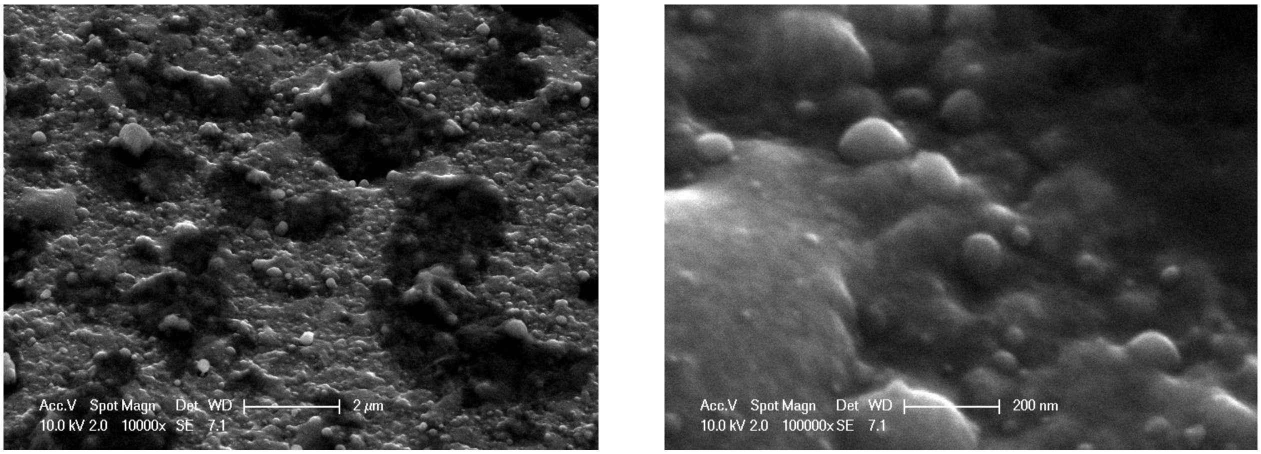
NiO:Li conductivity was seen to drop dramatically with increasing substrate temperature and growths performed above RT were too insulating for p-DSSC applications. Table 1 shows the result of Hall effect measurements on a NiO:Li layer grown at RT.

Sample	Film Thickness (nm)	Field (T)	Current (μA)	Type	Rs (Ω/cm^2)	Resistivity (Ω.cm)	n (cm^{-3})	m (cm^2/Vs)
NiO:Li/ c-Al_2O_3	**90**	**1**	**1**	**p**	**9.9×10^4**	**0.8**	**1×10^{20}**	**6.1**

Table 1. Hall measurement of RT NiO:Li/c-Al_2O_3 .

At 0.8 Ω.cm the resistivity is more than 2 orders of magnitude lower than for undoped NiO layers grown on c-sapphire [22].

Figure 2 shows typical SEM images for the NiO:Li grown on c-Al_2O_3 at RT.



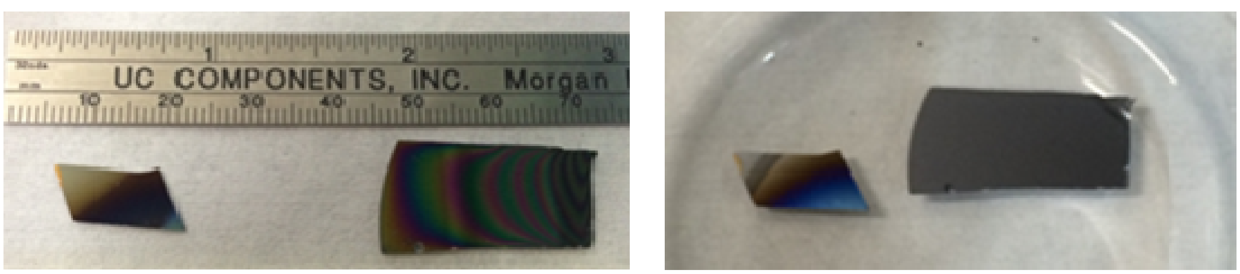
a) b)

Figure 2. SEM images (at two different magnifications) of NiO:Li grown on c-Al_2O_3 at RT.

The film showed a continuous NiO:Li coating with a relatively rough topology but no sign of cracking. There are particulate features on the surface ranging from about 20 to 500 nm in diameter. The morphology does not show any sign of the porosity necessary for p-DSSC applications, however.

3.2 Nanoimprinting Porosity into NiO with Sacrificial Nano ZnO Templates

Figure 3 shows pictures of a chemical etching test on ZnO/Si and NiO/Si with 0.1M HCl.



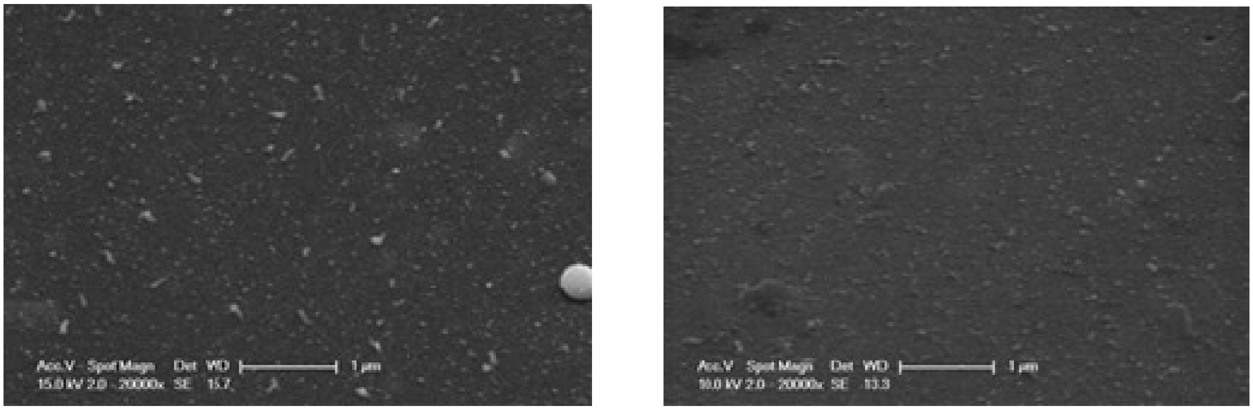
NiO/Si(111) ZnO/Si(111) NiO/Si(111) Si(111)

a) **b)**

Figure 3. Photos of the NiO/Si and ZnO/Si sample a) before etching b) after 100 minutes of immersion in HCl.

The chemical etching tests showed that the ZnO disappeared almost instantaneously while the NiO was still clearly present after 100 minutes of immersion. Hence NiO was much more resistant to chemical etching in dilute HCl than ZnO.

Figure 4 shows SEM images of NiO before and after the chemical etching test in HCl.

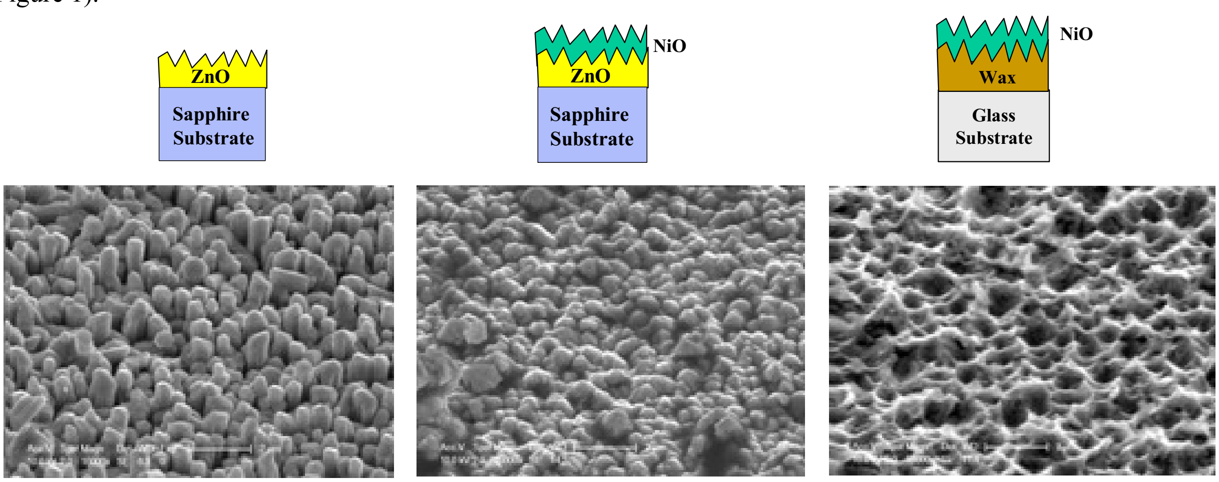


a) **b)**

Figure 4. SEM image of the NiO surface a) before and b) after chemical etching.

The SEM images of the NiO surface before and after the immersion show similar morphology apart from the removal of some surface debris/particulates.

Figure 5 shows SEM images of the surface of (a) nano ZnO deposited on c-Al_2O_3, (b) NiO deposited on top of the nano ZnO/cAl_2O_3 and (c) NiO after chemical removal of the underlying nano ZnO (see the flow chart illustrated in Figure 1).

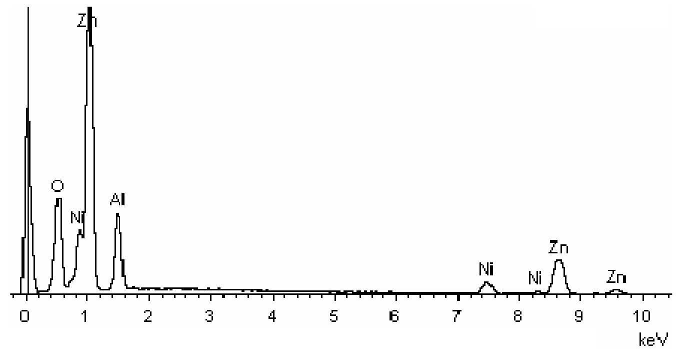


a) b) c)

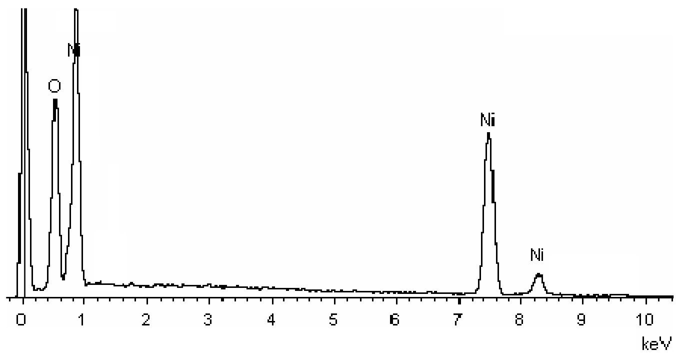
Figure 5. SEM Images of a) nanoZnO/cAl_2O_3 b) NiO on nano ZnO/ cAl_2O_3 c) NiO after chemical lift-off of nano ZnO

The last SEM image shows that we have succeeded in imprinting a tailor-made nanoporosity in the NiO layer.

Figure 6 shows the EDX spectra for the NiO surface before and after preferential chemical etching away of the nanostructured ZnO underlayer (i.e. corresponding to figures 5 (b) and 5 (c)).



a)



b)

Figure 6. EDX spectra a) before and b) after the chemical lift-off

EDX before and after the chemical lift-off showed that the Ni and O peaks were still present after chemical lift-off while the zinc peak (from ZnO) and the aluminium peak (from the c-Al_2O_3) were no longer present. This indicates that the nanostructured ZnO template had been completely dissolved.

4. CONCLUSIONS

The electrical conductivity of p-type NiO:Li (20at%) layers grown on c-sapphire by PLD decreased sharply with increasing substrate temperature. At 0.8 Ω.cm, the resistivity of NiO:Li layers grown at RT was more than two orders of magnitude less than that for undoped NiO layers. SEM images revealed a continuous NiO:Li coating with a relatively rough topology and no sign of cracking. There were also particulate features on the surface ranging from about 20 to 500 nm in diameter. The sample morphology did not show any sign of the porosity necessary for p-DSSC applications, however.

In order to obtain a nanoporous morphology in the NiO a new method was developed based on (a) coating a sacrificial nano ZnO template with NiO and (b) preferential chemical etching away of the ZnO nanotemplate and thus leave an imprinted nanoporosity in the NiO. Figure 7 shows a schematic of a potential process flow employing the above approach and the use of a gold contact plus wire bonding so as to illustrate one method for obtaining a nanoporous NiO photocathode for p-DSSC applications.

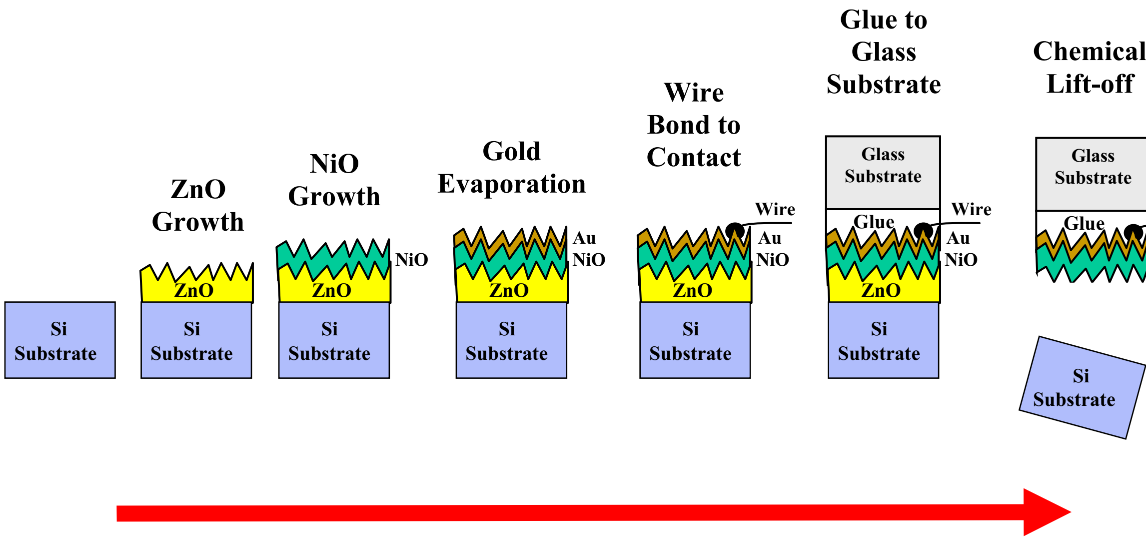


Figure 7. Schematic of the proposed process flow for device fabrication using the templating and lift-off approach

Beyond the specific fabrication of nanoporous NiO for use as p-DSSC photocathodes by PLD, such a lift-off process could represent a more general new paradigm for imprinting a tailored nanoporosity.

ACKNOWLEDGEMENTS

The authors would like to thank the French Agence Nationale de la Recherche "POSITIF" program for their financial support.

REFERENCES

[1] S. Chakrabarty, K. Chatterjee, **J. Phys. Sci.** 13 (2009) 245-250.
[2] P.S. Patil, L.D. Kadam, **Appl. Surf. Sci.**, 199 (2002) 211-221.
[3] V.M.L. Figueireido, **PhD. thesis**, FCT, Universidade Nova de Lisboa (2012).
[4] F. A. Kröger, **J. Phys. Chem. Solids** 29 (1968) 1889-1899.
[5] Z. Zhai, X. Yang, L. Xu, C. Hu, L. Zhang, W. Hou, Yining Fan, **Nanoscale** 4 (2012) 547-556.
[6] X. Li, S. Xiong, J. Li, J. Bai, Y. Qian, **J. Mater. Chem.** 22 (2012) 14276-14283.
[7] A. Azens, L. Kullman, G. Vaivars, H. Nordborg, C.G. Granqvist, **Solid State Ionics** 113/115 (1998) 449-456.
[8] H. Ohta, M. Kamiya, T. Kamiya, M. Hirano, H. Hosono, **Thin Solid Films** 445, 2 (2003) 317-321.
[9] W. Shin, N. Maruyama, **Mater. Lett.** 45, 6 (2000) 302-306. on NiO.
[10] A. Dirksen, K. Duval, T.A. Ring, **Sens. Actuators B** 80 (2001) 106-115.
[11] S. Bai, M. Cao, Y. Jin, X. Dai, X. Liang, Z. Ye, M. Li, J. Cheng, X. Xiao, Z. Wu, Z. Xia, B. Sun, E. Wang, Y. Mo, F. Gao, F. Zhang, **Adv. Energy Mater.** 4 (2014) 1301460.
[12] A. Vu, Y. Qian, A. Stein, **Adv. Energy Mater.** 2 (2012) 1056-1085.
[13] P. I. Cowin, C.T.G. Petit, R. Lan, J.T.S. Irvine, S. Tao, **Adv. Energy Mater.** 1 (2011) 314-332.
[14] H. Shimotani, H. Suzuki, K. Ueno, M. Kawasaki, Y. Iwasa, **Appl. Phys. Lett.** 92 (2008) 242107.
[15] S. Zhang, X. Yang, Y. Numata, L. Han, **Energ. Environ. Sci.** 6 (2013) 1443-1464.
[16] W. Chia-Ching, Y. Cheng-Fu, **Nanoscale Res Lett.** 8, 1 (2013) 33.
[17] D. J. Rogersa, F. Hosseini Teherani, A. Ougazzaden, S. Gautier, L. Divay, A. Lusson,O. Durand, F. Wyczisk, G. Garry, T. Monteiro, M. R. Correira, M. Peres, and A. Neves ,D. McGrouther and J. N. Chapman, M. Razeghi, **Appl. Phys. Lett.** 91 (2007) 071120.

[18] D.J. Rogers, V.E. Sandana, S. Gautier, T. Moudakir, M. Abid, A. Ougazzaden, F. Hosseini Teherani, P. Bove, M. Molinari, M. Troyon, M. Peres, Manuel J. Soares, A.J. Neves, T. Monteiro, D. McGrouther, J.N. Chapman, H.-J. Drouhin, R. McClintock, M. Razeghi, **Photo. and Nano. - Fund. and Appl.** 15 (2015) 53-58.
[19] D. J. Rogers, D. C. Look, F. Hosseini Teherani, K.Minder, M. Razeghi, A. Largeteau, G. Demazeau, J. Morrod, K. A. Prior, A. Lusson, and S. Hassani, **Phys. Status Solidi C** 5, (2008) 3084.
[20] V. E. Sandana, D. J. Rogers, F. Hosseini Teherani, R. McClintock, C. Bayram, M. Razeghi, H.-J. Drouhin, M. C. Clochard, V. Sallet, G. Garry, and F. Falyouni, **J. Vac. Sci. Technol. B** 27, (2009) 1678.
[21] D. J. Rogers, V. E. Sandana, F. Hosseini Teherani, M. Razeghi, and H.-J. Drouhin, **Proc. SPIE** 7217, (2009) 721708.
[22] V. E. Sandana, D. J. Rogers, F. Hosseini Teherani, P. Bove, R. McClintock, M. Razeghi, **Proc. of SPIE** Vol. 8987, (2014) 89872P-7.