



Morphological and Optical Properties Study of ZnO/Porous Silicon(PS) Nano composites Prepared by Electrodeposition Technique

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Abstract

ZnO nano particles deposited on silicon porous substrates (PS) were prepared by electro-deposition anodization on n type (100) silicon wafer. This ZnO/PS structure combines substrates having specific structural and optical properties (IR emission), with nano-composites of ZnO potentially interesting due to their functional properties (UV emission) to be integrated as constitutive elements of devices in various optoelectronic applications mainly in blue light emitters. The blue shift in the photoluminescence PL peak is possible and easy to obtain (467nm) in this combined structure. The structural properties are characterized by X-ray diffraction (XRD) and scanning electronic microscopy (SEM).

Key-words : *Nano composites ZnO; Electrochemical deposition; Porous silicon.*

Résumé

Des nano particules de ZnO déposés sur des substrats du silicium poreux (PS) ont été préparées par anodisation par dépôt électrochimique sur une plaquette de silicium de type n (100). Cette structure ZnO / PS combine des substrats ayant des propriétés structurales et optiques spécifiques (émission IR), avec des nano-composites de ZnO potentiellement intéressants en raison de leurs propriétés fonctionnelles (émission UV) à intégrer comme éléments constitutifs des dispositifs dans diverses applications optoélectroniques, principalement en l'émission de la lumière bleu, avec cette structure combinée, le décalage bleu dans le PL (photoluminescence) est possible et facile à obtenir (467nm). Les propriétés structurales ont été caractérisées par diffraction des rayons X (DRX) et microscopie électronique à balayage (MEB).

Mots-clés : *ZnO nano composites ; dépôt électrochimique ; silicium poreux .*

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1. Introduction

ZnO is an important binary compound semiconductor of the II-VI group. It currently grows in the hexagonal wurtzite crystal structure. It has a large free excitation binding energy of 60 meV, at room temperature and a direct wide band gap ranging between 3 and 3.7 eV depending of the elaboration process. Zinc oxide has received considerable attention for a long time due to its many attracting applications such as piezoelectric [1], photovoltaic devices [2-3], gas sensors [4,5], optical catalysis[8], and solar cells [7-9]. Due to its large direct band gap; this compound is also interesting for the production of blue and UV light emitters used in the optoelectronic devices, such as UV lasers [10], blue to UV light-emitting diodes [10-13] and UV sensors [10]. Several methods are used for preparing ZnO films, such as magnetron sputtering [14-15], pulsed laser deposition (PLD) [16], spray pyrolysis [17-20], sol-gel process [21-23]; chemical bath deposition (CBD) [24-27] and chemical vapor deposition (CVD) [28,29],...etc. However, these methods are not well suited for large area coating, low temperature processing, and low cost. The electro-deposition technique has been proved to be one of the simplest and most effective way to prepare nicely crystallized ZnO at relatively low temperatures. This technique is widely used in order to growth and functionalizes oxide materials with specific chemical and physical properties. The advantages offer by the electro-deposition technique for oxide films [30-34] are numerous as the easy preparation, rapid and simple, low cost, possibility of large-scale deposition, low temperature processing and direct control of film thickness, in comparison with other deposition techniques [14-23]. Generally, in literature [30, 33], the aqueous deposition was performed using either zinc chloride or zinc nitrate on a variety of substrates. In this work, the nano composites of ZnO have been deposited on n type porous silicon (PS) substrates. This later has been intensively studied since the discovery of its efficient photoluminescence at room temperature in the visible light region with the possibility to adjust its emitting wavelength from red to blue by managing the erosion process. In the present work, the electro-deposition technique was

successfully used for the preparation of ZnO on nanoporous silicon substrates with high porosity. Within this device topology, we expect to combine the particular properties of PS with the potential applications of ZnO. For this reason, structural, optical and electrical properties of the structure ZnO /PS were investigated using X-ray diffraction (XRD), Scanning Electro Microscopy (SEM) spectroscopy and FTIR

2. Experimental Set up

2.1 Preparation of the porous silicon substrate

The silicon samples used in this study were cut into 5 x 5mm² squares, from single crystal silicon wafer. The porous silicon (PS) layers are formed on n type (100) c-wafers with resistivity of 1-10 Ω .cm and thickness of 500-550 μ m using the electrochemical anodization. For that, silicon wafers are initially prepared with a bath in Trichloro heated at 50 $^{\circ}$ C for 10 min followed by bath in acetone. The cleaning was performed in a bath of ethanol followed by a final rinsed with deionised water. After a drying phase, samples are placed in the N₂ nozzle, and the ohmic contacts are deposited by application of InGa on the non polished face of the substrates mounted on copper support.

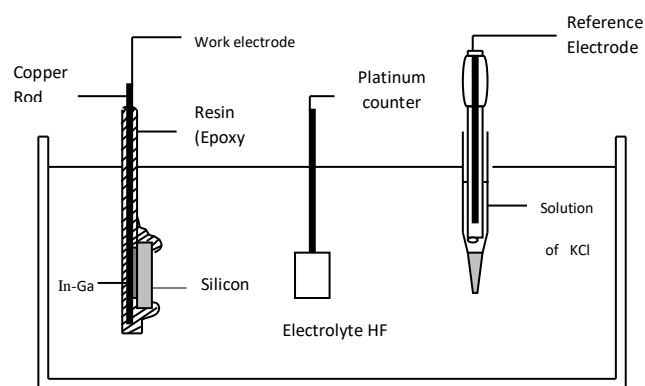


Fig 1: Descriptive schematic of anodization cell

he electrochemical anodisation is carried out at room temperature with HF(50%) C₂H₅OH (99%) for 2 min at a constant current density of 100 mA/cm². Because the samples are n type, a back illumination from a 50W lamp mounted at a distance of 10 cm was used during etching process. "Fig.1" shows the anodisation cell

with three electrodes. i.e. The working electrode on the silicon substrate (cathode), a platinum wire as a counter electrode and a reference electrode.

2.2 Deposition of ZnO layer

The ZnO layers were deposited on PS substrates using electrochemical anodization. This technique has been chosen because it gives a non blocking electrode for cathodic reactions in the silicon pores compared with others techniques as spray pyrolysis, vacuum evaporation. The electrolytic solutions were prepared using aqueous solution of 5mM ZnCl₂ with a PH about 6. To ensure a good conductivity of the solution allowing optimal conditions for the deposition of ZnO, the samples were introduced at 65°C during time between 10 and 15min 0.1 M KCl, controlled by a cyclic voltammetry driving the voltage of the potentiationstat. The important aim of the cyclic voltammetry of our experiment approach is to give the optimal condition to achieve ZnO deposition on silicon substrate using this technique. It is thus possible to know the potential that may be applied at the potentiationstat to obtain good ZnO composites quality. ZnO nanocomposites were electrodeposited from an aqueous solution of ZnCl₂ and KCl, used as supporting electrolyte, and flowing air as precursors. The electrodeposition conditions were optimized in order to obtain uniform and stoichiometric thin films. The deposition was carried out by adjusting the bath temperature at 65°C, and the pH of electrolyte at 6.5 and the applied potentials from -0.3 to -1.6V /SCE.

“Fig.2” shows the voltammogram on copper substrate obtained from acidic solution (pH 6.5) containing 5mM ZnCl₂ and 0.1M KCl at temperature 65°C. Good quality films of ZnO were obtained at the cathodic potential of -1.3 V/SCE. This value corresponds to the good reduction of the Zn⁺² ions. The reduction of Zn⁺² ions leads to a metallic Zn that reacts chemically with ZnO. Therefore, it is observed that there is no current at E= -1.3 V/SCE corresponding to the reduction of Zn⁺² into metallic Zn, while the value E= -1.3 V/SCE found for the potential is consistent with the literatures [27,34]. All samples reported in this work were prepared at

potential -1.3V/SC. All electrochemical experiments were carried using a potentiostat/galvanometer.

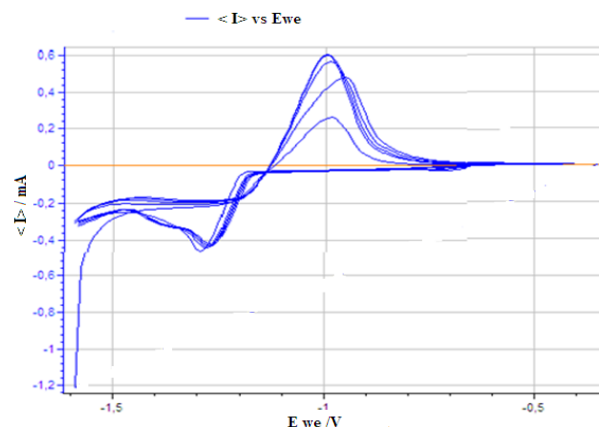


Fig 2: Cyclic voltammograms measured on ZnO/PS at 0.005 m ZnCl₂+ 0.1 kCl T=65°C scan rate=20mV/S

3. Results and discussion

3.1 Structure and morphology of the ZnO samples

“Fig.3” shows SEM images of the PS samples at different magnifications. SEM micrographies of deposited ZnO layers on PS are presented in Fig. 4. It is clear that crystalline ZnO is deposited along the outer walls of the pores of PS either partially by filling or completely covering them, Fig (4) . Few pores of PS were not covered completely by the ZnO particles.

Fig 4 shows the particles of ZnO in the pores of PS. This technique of deposition is better than others physical techniques for many reasons. The first reason is that these methods of deposition as the vacuum evaporation and sputtering show a blocking of the particles at the entered pores of PS. The second reason is due to the difficulty to obtain the porous silicon n-type. Because, this type of silicon needs an illumination for increasing the probability of the ionised impurities. We assume the diameter of the pores between 10-40 nm, and the size of ZnO between 4 – 13 nm.

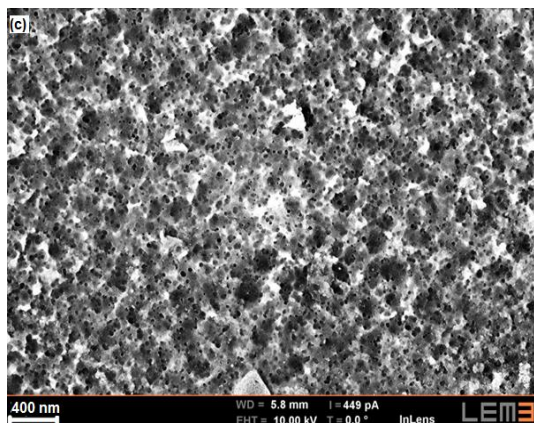
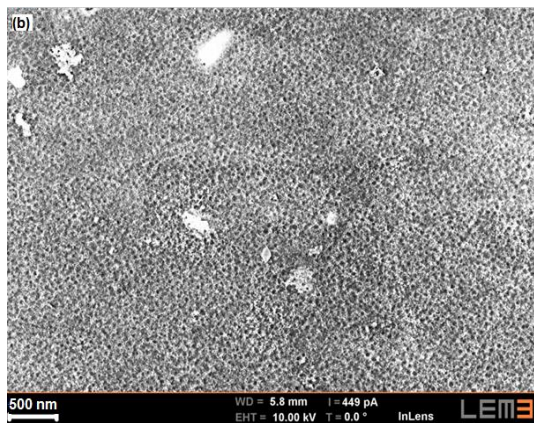
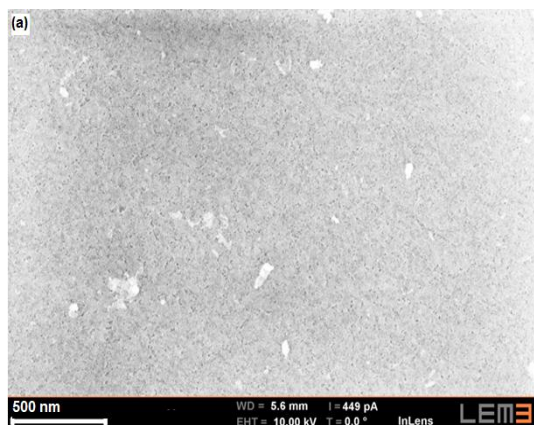


Fig 3: SEM images of porous silicon layer for different magnifications (a,b,c,d)

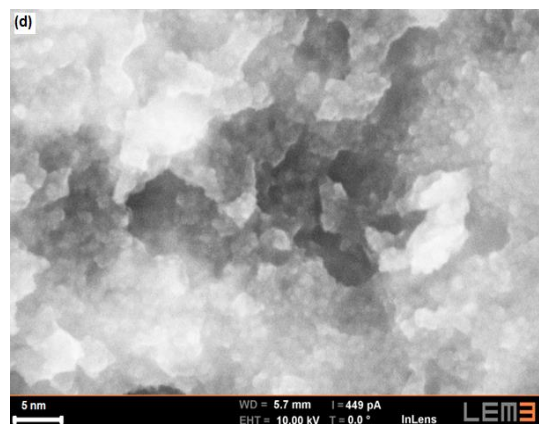
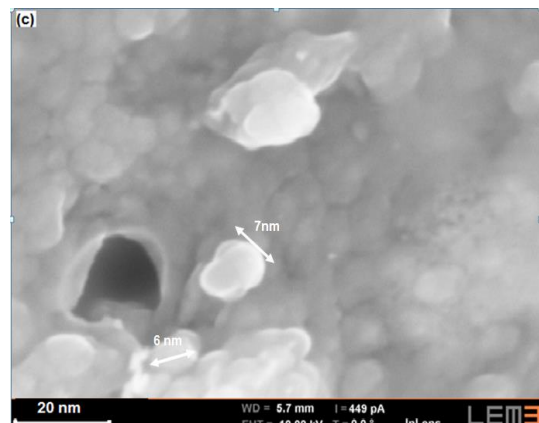
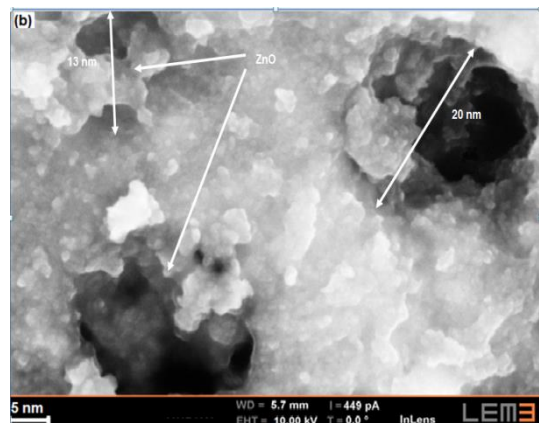
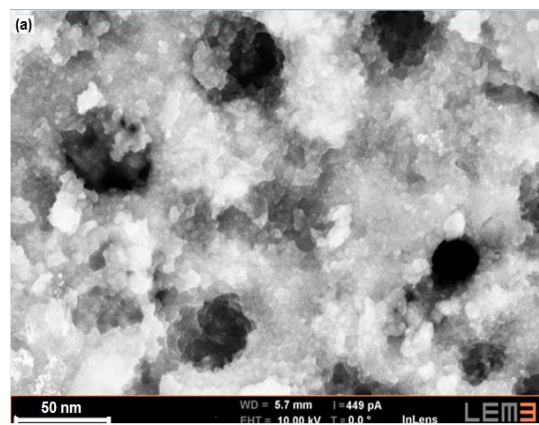
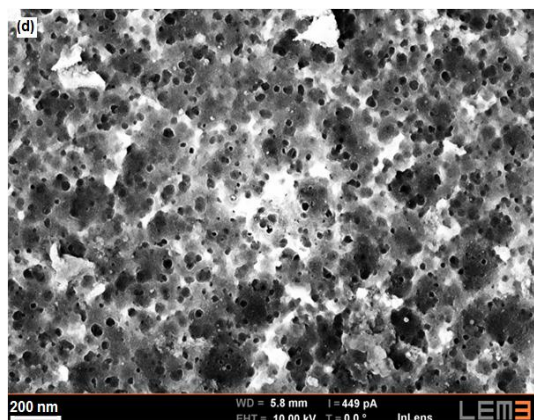


Fig 4: SEM images of ZnO deposited on PS from 0.005M ZnCl_2 +0.1M KCl at 65^o C for E=-1.3 V/SCE (a,b,c,d)

The XRD of ZnO films prepared on PS substrate is displayed in "Fig.5" The most intensive peak diffraction observed at 63° , can be indexed to n-Si (1 0 0) diffraction. The strong peak intensity of the nanocomposites ZnO is located at 34.22° . Also, others peaks displayed for the ZnO peaks having intensity weaker than the first, located at 31.21° , 38.17° and 45.32° their intensities are (100),(101) and (102) respectively. The XRD analysis indicates that the nanocomposites of ZnO presents a preferential orientation along the n-Si (1 0 0) substrate. It is similar with a strong (0 0 2) peak which located at 34.12° and a number of weaker peaks with (1 0 0), (1 0 2), (1 1 2), which indicates that the nanoparticles on Si wafer are of perfect c-axis orientation.

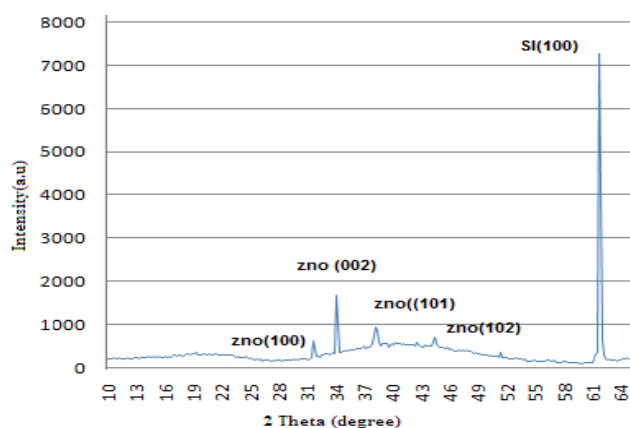


Fig.5. X-ray diffraction patterns of ZnO films prepared on PS substrates at a potential $E = -1.3$ for 10 min

3.2 Optical properties

Fig.6 Shows FT IR spectrum of the silicon after anodization (silicon porous). The porous silicon is evidenced by different vibrations modes. The stretching vibrations bonds of the Si-H; SiH₂; SiH₃; at 2083, 2118, 2140 cm⁻¹, respectively. The peaks at 2150-2400 cm⁻¹ can be attributed to the composite O_xSiH_y compounds (O₂SiH at 2305 cm⁻¹, O₃SiH at 2366 cm⁻¹), these vibrations result firstly by the oxidation of Si-H bonds in the solution, secondly, the contact with the atmosphere. Others peaks were appeared at the region 900-1150 cm⁻¹, attributed of the stretching vibrations of Si-O-Si and Si-O_x[27],

which confirming the formation of an oxide on the surface.

The prepared samples of ZnO/PS were also characterized by FTIR. Fig7 shows the FT-IR spectrum of the ZnO/PS. We observed a presence of different vibration modes; the stretching vibration of the OH bond at the region 2800-3400 cm⁻¹ due to the presence of traces of water. There is also the presence of traces of CO₂ (2370 cm⁻¹). Asymmetric stretching vibration, and the symmetric stretching vibration of deformation of the C = O bond were observed at 1582 cm⁻¹ and 1437 cm⁻¹ respectively and 1094 cm⁻¹. Bands mentioned above are due to the facts that the development is carried out with air ambient. The vibration of the Zn-O bond is observed at 473.7 cm⁻¹ which confirmed the ZnO training (formation).

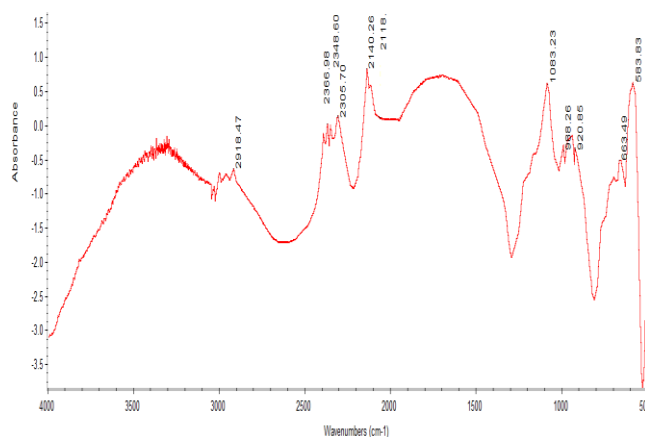


Fig 6: FTIR spectra of porous silicon layer after oxidation.

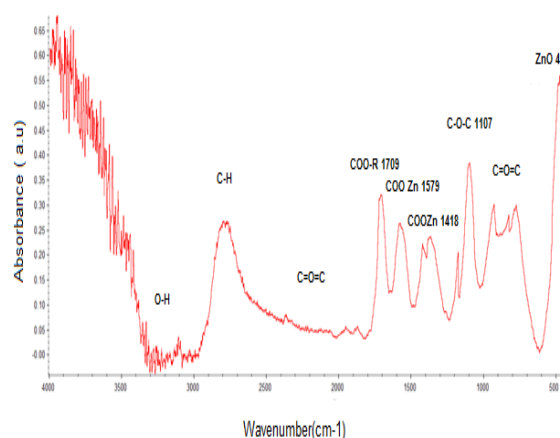


Fig 7: FTIR spectra of ZnO nano deposited on PS

Fig. 8 shows Photoluminescence spectra of ZnO/PS nanocomposites measured by Cary 500 (Varian). ZnO/PS nanocomposites exhibits large band luminescence across most visible spectrum (400-700 nm), this refers to the good quality (002) axis orientation of ZnO (Fig. 5) and the high quality of PS substrate in which we combined the PS optical properties (IR emission) with the ZnO which has a large gap in UV emission (3.37eV), the UV emission due to the direct recombination of the photo generated charge carriers [29, 31],

In PL spectra of ZnO/PS, we can observe an intense PL peak located at (374 nm) caused by wide emission of ZnO (3.37 eV), and the peak located at 623 nm from PS revealing the high porosity of PS.

Red shift in PL peak of ZnO from the original PL emission 367.5nm [32] toward the longer wavelength of 374 nm was attributed to Zn vacancies in ZnO energy band, the peak located at 462 nm correspond to the bleu emission caused by the combine by the high quality of the porosity of PS and ZnO optical properties and its UV emission [31].

According to the previous results, the photoluminescence of PS is commonly attributed to the oxidation of PS surface and the quantum confinement of electrons in n anodized particles of C-Si presents in PS. This can be observed clearly in Fig.6 revealing to the different stretching mode of PS, we know that the surface of PS influenced easy by ambience and the PL properties are very sensibly by the surface structure, the entire PS surface is recovered by hydrogen, such as SiH_x species Fig.6 which unstable and easy to break. The Si-O and Si-H bonds break and form some defects, which may decrease the Photoluminescence intensity. Fig .4.b shows that a few pores of PS didn't covered completely by the ZnO particles, this refers to many deposition parameters of the electro-deposition technique as: the deposition time, type and nature of PS substrate (orientation and resistivity), concentration of ZnCl₂, bath temperature ...etc. and the high porosity of PS layer, the blue shift in the PL peak is possible and easy to obtain [30, 33, 34]. The low dimension of the PS structure may be increase the probability of the

recombination of electrons and holes leading to the increasing of photoluminescence of ZnO/PS films leading to used in much optoelectronics devices as the blue and red emitters.

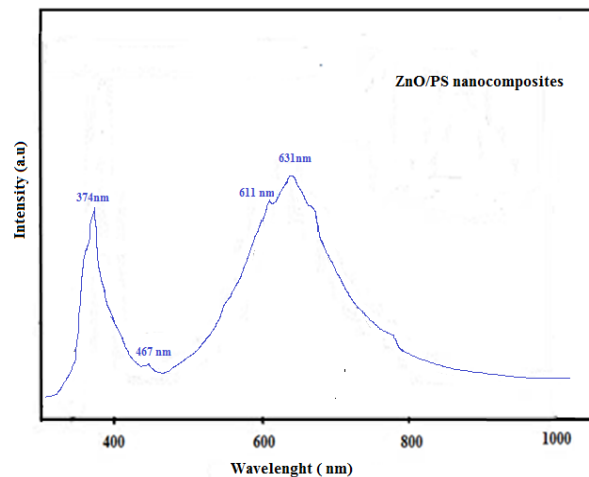


Fig 8: Spectroscopy spectra of ZnO/PS layers

4. Conclusion

To combine the optical properties of porous silicon with those of zinc oxide “which has a wide applications for example as UV and blue emitters”; ZnO nanocomposites were successfully deposited on PS substrates. These nanostructures were prepared by electro-deposition technique using ZnCl₂ and the KCl under optimized conditions. This technique has some advantages compared to the physical deposition techniques. The photoluminescence (PL) of ZnO/PS increased and covered the most of the visible spectra. SEM images show clearly that the ZnO particles entered in the pores of porous silicon despite the fact that few pores of PS were not covered completely by the ZnO particles. In other words, with the high porosity and the low dimension of the PS layer structure may be increase the photoluminescence (PL), the blue shift in the PL peak is possible and easy to obtain. RDX measurements had been interpreted.

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References

- [1] M.H. Zhao, Z.L. Wang, S.X. Mao, Nano Lett.. 587–590,4 (2004).
- [2] L. Stolt, J. Hedström, J. Kessler, et al., J.Appl. Phys. Lett. 62 597,3 (1993).
- [3] K. Keis, E. Magnusson, H. Lindström, SE. Lindquist, A.Hagfeldt, Sol. Energ. Mat. Sol. Cells . 73:51–58 ,1 (2002)
- [4] L. Stolt, J. Hedström, J. Kessler, M. Ruckh, K.-O. Velthaus, and H.-W.J. Appl Phys Lett, vol. 62, no. 6, pp. 597–599, (1993).
- [5] Changhui Ye, Xiaosheng Fang, Guanghai Li and Lide Zhang, , Appl. Phys. Lett. 85 (15) 3035–3037 (2004).
- [6] Jian Feng Yan, Hong Wei Liang, You, J. Infrared Millim.Waves 23 (2) 103–106(2004).
- [7] H. Jacobs, W. Mokawa, D. Kohl, G. Heiland, Surf. Sci.160, 217(1985).
- [8] S. Yano, R. Schroeder, H. Sakai, Appl. Phys. Lett. 82 (13) 2026–2028(2003).
- [9] Xiu-hua Fu, Yu-lin Sun, Cai-mei He, Infrared Laser Eng. 38 (5) 803–806(2009).
- [10] Guo Gang Qin, J. Infrared Millim.Waves 24 165–173 ,3 (2005)
- [11] R.T. Girard, O. Tjernberg, G. Chiaia, S. Söderholm, U.O. Karlsson, C. Wigren, H. Nylén, I. Lindau, Surf. Sci. 373 (1997) 409.
- [12] Paraguay FD, Estrada WL, Acasta DRN, Andrade A, Miki-Yoshida M. Thin Solid Films;350:192(1999).
- [13] P. Nunes, E. Fortunato, R. Martins, Thin Solid Films 383 277(2001).
- [14] X.W. Sun, R.F. Xaio, H.S. Kwok, , J. Appl Phys 5776.84 (1998).
- [15] P. Nunes, E. Fortunato, R. Martins, Int. J. Inorg. Mater 1125, 3 (2001).
- [16] A. Bedia, F.Z. Bedia, M. Aillerie, N. Maloufi, B. Benyoucef, Energy Procedia, 603 -609,50(2014)
- [17] Y. Natsume, H. Sakata, Thin Solid Films 30.372 (2000).
- [18] W. Tang, D.C. Cameron, , Thin Solid Films 238 .83(1994)
- [19] Q. Zhang, C.S. Dandeneau, X. Zhou, G. Cao, Adv. Mater. 4087.21 (2009).
- [20] K. Kakiuchi, Saito M, Fujihara S. Thin Solid Films 516:2026–30(2008).
- [21] Y. Kashiwaba, F. Katahira, K. Haga, T. Sekiguchi, H. Watanabe, J. Cryst. Growth 221 431(2000).
- [22] V. Sallet, C. Thaindoume, J.F. Rommeluere, A. Kusson, A. Riviere, J.P. Riviere, O.Gorochoy, Materials Letters 126 .53 (2002)
- [23] N.Ait Ahmed, G.Fortas, H.Hammache, S.Sam, A.Keffous, A.Manseri, L.Guerbous, N.Gabouze, Appl.Surf. Sci 7442.256(2010)
- [24] Mane RS, Nguyen H-M, Ganesh T, Kim N, Ambade SB, Han S-H. ElectrochemCommun;11:752–5(2009).
- [25] Li G, Dawa C, Bu Q, Lu X, Ke Z, Hong H . J Phys.Chem C;111:1919–23(2007).
- [26] Yoshida T, Zhang J, Komatsu D, Sawatani S, Minoura H, Pauporté T, . Adv Funct Mater, 19, 17–43(2009).
- [27] Y. Zhao et al. / Current Applied Physics 10 (2010) 930–933.
- [28] Kyeong-Won Park, Jong Hwa Jung, J. Power Sources 379– 385. 199 (2012)
- [29] Y. He, B. Yang, G. Cheng, Catal. Today 595.98 (2004).
- [30] Khaldun A, Salman, Khalid Omar,Z.Hassan, Sol. energy 541-547.86(2012).
- [31] Prabakaran,Rperes,M,Monteiro,T,Fortunato,E,Martin,R, Ferreira,I, . U.Non –Cryst.Solids 354,2181-2185(2008).
- [32] T.Steinner.Artech House . Inc,Norwood (2004).
- [33] Liu ,Y.L Liu.Y.C,yang .HW.BMa.JG, 2003, J.Phys.D Appl.Phys.36,2705-2708.
- [34] Umar ,A.karunagaran,B,BSuh, E.K,Hahn.Y.B, Nanotechnology 17,4072-4077. (2006)