

Experimental study of optical and electrical properties of ZnO nano composites electrodeposited on n-porous silicon substrate for photovoltaic applications

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Abstract. ZnO films 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. With this combined structure, the blue shift in the PL peak is possible and easy to obtain (467nm). The vibration modes of PS and ZnO films on PS substrates (ZnO /PS) were investigated by infrared (FTIR) measurements and their behaviors were analyzed and discussed by considering the structural properties characterized by X-ray diffraction (DRX) and scanning electronic microscopy (MEB).

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 [2-4], gas sensors [5,6], optical catalysis[8], and solar cells [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[10-11] and UV sensors [10]. Several methods are used for preparing ZnO films, such as magnetron sputtering [12-13], pulsed laser deposition(PLD)[14], spray pyrolysis [15,16], sol-gel process [17,18] chemical bath deposition (CBD) [19,20] and

chemical vapor deposition (CVD) [21,22],...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 ways to prepare nicely crystallized ZnO at relatively low temperatures. This technique is widely used in order to growth and functionalize oxide materials with specific chemical and physical properties. The advantages offer by the electro-deposition technique for oxide films [23-25] 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 [12-18]. Generally, in literature [23], the aqueous deposition was performed using either zinc chloride or zinc nitrate on a variety of seeded or seedless 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 [26].

In the present work, the electro-deposition technique was successfully used for the preparation of ZnO on nano-porous 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 (DRX), Scanning Electro Microscopy (SEM) spectroscopy and FTIR measurements.

2. Experimental set up

2.1 Preparation of the porous silicon substrate

The silicon samples used in this study were cut into 5 x 5 mm² 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 500-550μm using the electrochemical anodization. For that, silicon wafers are initially prepared with a bath in Trichloro heated at 50 °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.

The electrochemical anodization 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 anodization cell with three electrodes.i.e. The working electrode on the silicon substrate (cathode), a platinumium 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 15 min 0.1 M KCl, controlled by a cyclic voltammetry.

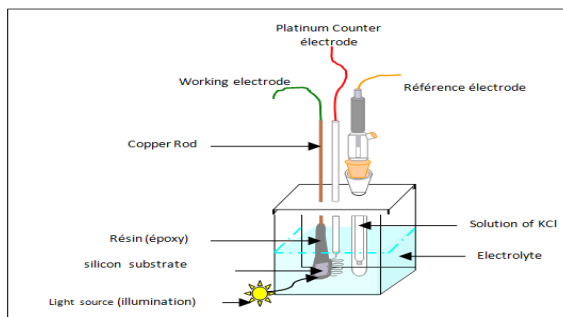


Fig.1. Descriptive schematic of anodization cell.

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 potentiostat to obtain good ZnO composites quality. ZnO nanocomposites were electrodeposited from an aqueous solution of $ZnCl_2$ 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 $65^\circ C$, and the pH of electrolyte at 6.5 and the applied potentials from -0.3 to -1.6V /SCE. Fig.2 shows the voltamogram on copper substrate obtained from acidic solution (pH 6.5) containing 5mM $ZnCl_2$ and 0.1M KCl at temperature $65^\circ C$. 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 [29,36]. All samples reported in this work were prepared at potential -1.3V/SC. All electrochemical experiments were carried using a potentiostat/galvanometer.

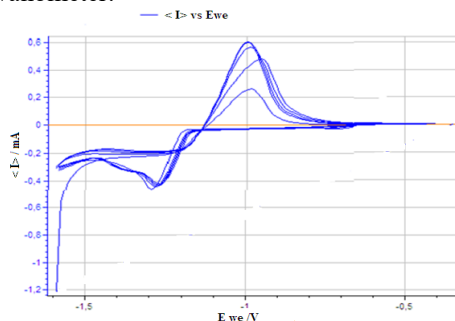


Fig.2. Cyclic voltamograms measured on ZnO/PS at 0.005 M $ZnCl_2$ +0.1 M kCl, $T=65^\circ C$, Scan rate=20mV/S

3. Results and discussion

3.1 Structure and morphology of the ZnO samples

Fig.3 (a,b) shows SEM images of the PS samples at different magnifications. SEM micrographies of deposited ZnO layers on PS are presented in Fig. 4 (a,b). 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 (a). Few pores of PS were not covered completely by the ZnO particles. Fig (4-b) 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. And 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.

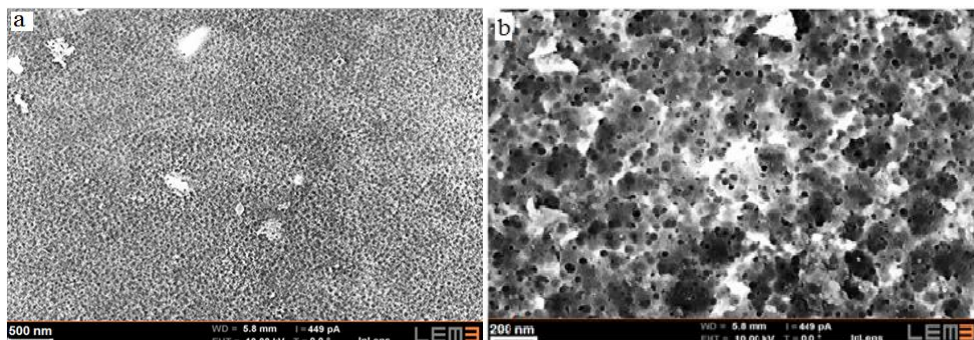


Fig.3. SEM images of n porous silicon layer for different dimensions (a,b)

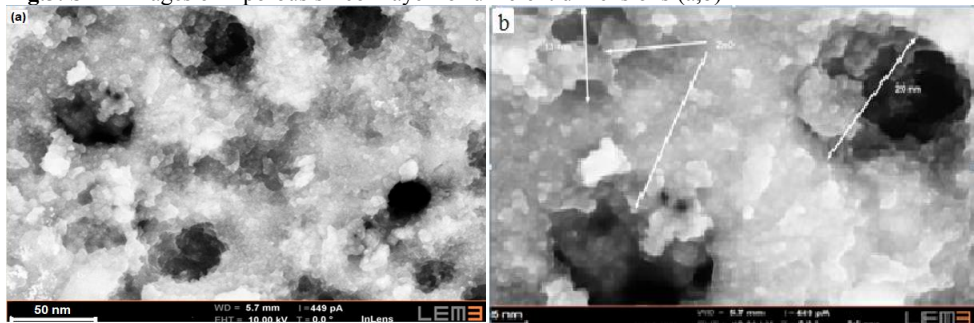


Fig.4. SEM images of ZnO deposited on PS from 0.005M ZnCl₂ +0.1M KCl at 65° C for E=-1.3 V/SCE (a,b)

The DRX 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 nano-composites 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° corresponding to the (100),(101) and (102) planes of ZnO, 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 0 1), which indicates that the nanoparticles on Si wafer are of perfect c-axis orientation.

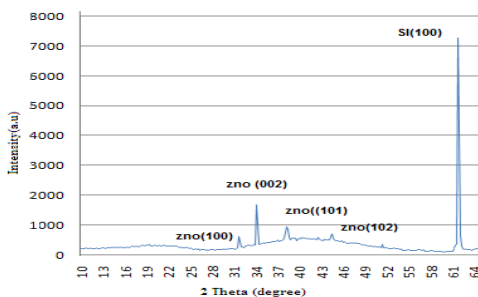


Fig.5. X-ray diffraction patterns of ZnO films prepared on PS substrates at a potential E=-1.3V/SCE for 10min

3.2 Electrical properties:

The solution using to preparing the ZnO, either zinc chloride ZnCl₂ or zinc nitrate (Zn(NO₃)) and their concentrations are important parameters because they affect the electrical properties and all films properties that have been influenced by some parameters as by the proposed technique as: the time of deposition, substrate type, concentration of the solutions, current density or potential, bath temperature. We are interested in this present work by the electrical resistivity of these films because they give us an idea for the application of our thin films.

The carriers are electrons in our samples of ZnO /PS. The electrical Resistivity ρ ($\Omega.cm$) is a function of the concentration N and mobility μ ,

$$\rho = 1/Nq\mu \tag{1}$$

With q: electron charge (1.6×10^{-19} Coulomb).

The relationship between resistance by unit area (square resistance) and resistivity of a thin layer of a thickness d is by the relation (2)

$$P=R_s d \tag{2}$$

We found that the value of square resistance changed vs. the time of deposition of the ZnO films deposited on porous silicon substrate .For the films deposited at 15 min, the square resistance was 385k Ω /* ; and it is 442 k Ω /* at 10min. Another effect was observed concerning of the films prepared using zinc nitrate Zn(NO₃) deposited at 10min where the resistance was 849 k Ω /* , and the films prepared using zinc chloride ZnCl₂ the resistance became 384 k Ω /* at the same time. We can conclude that the time of deposition is an important parameter when using the electrodeposition technique. We know that there is a net dependence between the time of deposition, the concentration and the resistivity. The resistivity of a semiconductor is inversely proportional to the concentration of impurities. If we increase the deposition time, the concentration also increases; because the probability of the ionized impurities will increase.

This electrical resistance was calculated by the technique of four points. It uses two pairs of electrodes, a pair injecting the current (I) and the second pair measuring the voltage (V). This method reduces the error due to resistances of contact between the electrodes

3.3 Optical properties

Fig.6 shows the 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, 2140cm⁻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 2366cm⁻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 an oxide on the surface.

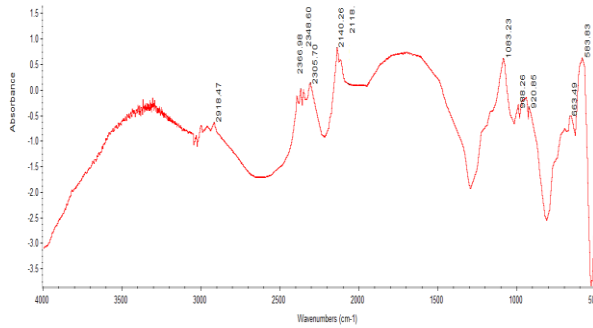


Fig.6. FTIR spectra of porous silicon layer

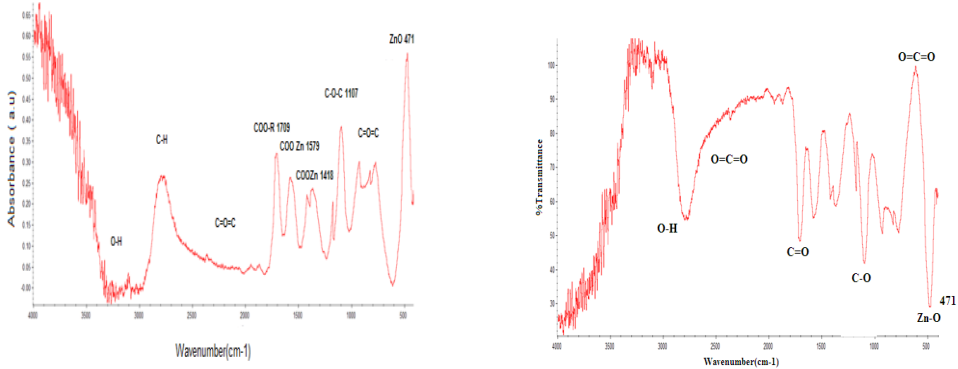


Fig. 7. FTIR spectra of ZnO nano deposited on PS : (a) absorbance, (b) transmittance composites

Fig. 8 shows PL 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 blue 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 studies the photoluminescence of PS is commonly attributed to the oxidation of PS surface and the quantum confinement of electrons in nanosized particles of C-Si presents in PS. This can be observed clearly in Fig.7 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 covered by hydrogen, such as SiH_x species Fig.7 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... . The blue shift in the PL peak is possible and easy to obtain [30, 33, 34] Fig. 8. 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.

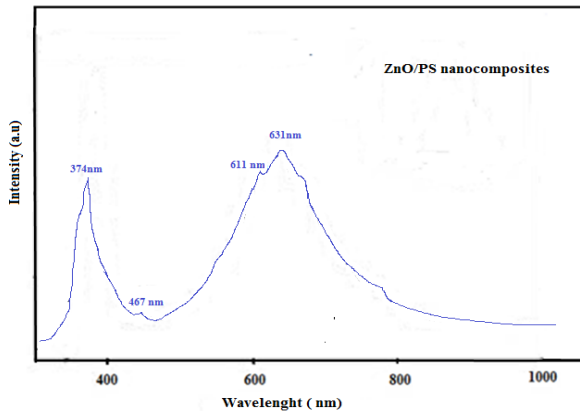


Fig. 8. Spectroscopy spectra of ZnO/PS layers

4. Conclusions

To combine the optical properties of porous silicon with those of zinc oxide which has wide applications for example UV and blue emitters. ZnO nanocomposites were successfully deposited on PS substrates. These nanostructures were prepared by electrodeposition technique using ZnCl₂ and the KCl under optimized conditions. This technique has some advantages compared to the physical deposition techniques. By this combine the photoluminescence (PL) of ZnO/PS increased and covered the most of the visible spectra. MEB images shows 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. The electrical properties had been investigated, and the FTIR and 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. Nylen, 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.Gorochov, 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 ,R peres,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)