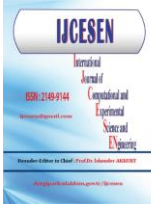
TITLE: Study of Luminescence Properties of PVA Capped Porous Silicon Carbide Microparticles Thin Films Deposited by Spin Coating Method

AUTHORS: Samira KACI

PAGES: 15-19

International Journal of Computationaland ExperimentalScienceandEngineering (IJCESEN)
Vol. 3-No.2 (2017)pp. 15-19
http://iakkurt.dergipark.gov.tr/ijcesen



ISSN:2149-9144

ResearchArticle

Study of Luminescence Properties of PVA Capped Porous Silicon Carbide Microparticles Thin Films Deposited by Spin Coating Method[#]

Samira KACI[*], Isma BOZETINE, Aissa KEFFOUS

Research Center on Semiconductor Technology for Energetic, Thin Films/Surface and Interface Division, CMSI, CRTSE, 2 B^d Frantz Fanon, PB 140 7M, Algiers, Algeria

* Corresponding Author : k_samira05@yahoo.fr

(First received 30 June 2017 and in final form 01 July 2017)

[#] Presented in ”3rd International Conference on Computational and Experimental Science and Engineering (ICCESEN-2016)”

Keywords
SiC micropowder
Electroless etching process
UV irradiation

Abstract: In order to be used in an optical device, thin films of pure Poly Vinyl Alcohol and PVA mixed with porous SiC microparticles were prepared by spin coating technique. The average size of SiC microparticles were 7µm. An electroless method was used for producing porous silicon carbide powder under UV irradiation was investigated. The electroless process was chosen because it does not require electrical contact during etching like in anodic one. Silver nanolayer coated SiC particles was formed by polyol process prior the etching and served both as an anode, catalyst and mask for the reduction of a chemical oxidant. The etchant was composed of HF and different oxidants in water. Various porous morphologies are presented and studied as a function of etchant concentration, oxidant type, etching time, and wavelength of irradiation. Morphological, optical and photoluminescence characterizations of SiC micropowder embedded in PVA matrix and deposited as thin films on glass substrates are reported. We concluded that the chemical etching conditions of SiC powder seems to have a large impact on the resulting properties. We noticed that SiC powder etched under UV light of 254 nm using $K_2S_2O_8$ as oxidant, at reaction temperature of 80°C for t=40min exhibited the best photoluminescence property.

1. Introduction

Growth of silicon carbide thin films is of importance for potential optoelectronic applications. Most of the SiC based devices require specific properties of the SiC thin films that meet the applications in sight. The most common methods used for SiC thin films elaboration are physical vapour deposition (PVT) [1, 2], chemical vapour deposition (CVD) [3], liquid phase sintering (LPS) or mechanical alloying (MA) which were well detailled previously [4]. Generally, elaboration of SiC thin films destined for photodevices, such as light emetting diodes, requires in part, good crystallinity and low defect density, and in another part, having particular porous morphologies [5]. This requires to establish suitable processes to respond to such conditions. Several woks [6-8] have been previously reported for the porous SiC thin films formation. Nevertheless, these processes were hampered by numerous impediments such as SiC polytypes nature and the structural imperfection of the elaborated thin films which provided often limited optical performances. These limitations were assigned to the depth of the porous layer which still difficult to control (presence of dislocations, micropipes, stacking faults, etc. appearing across the depth). Other results indicated that the structural perfection of the SiC thin films plays a major role in how deep the pores propagate. However, dislocations, micropipes, stacking faults, etc. affect greatly the porous morphology [9].

We dealt, thus, to study one of the properties of the SiC material, which is the photoluminescence, at it micronic powder shape. A nanostructuring of the latter, by formation of pores on the surface of the SiC microparticles was unavoidable step, following the overview of litterarture. We have carried out the production of porous silicon carbide via an electroless process. Results in the literature have shown a variety of porous morphologies of SiC produced on it thin film form using electroless process [10, 6]. The electroless process was chosen because it does not require electrical contact during etching like in anodic one.

We proceeded to deposit the porous SiC micropowder-based thin films by employing a modified sol-gel method using polyvinyl alcohol (PVA) as the gel-phase by mean of spin coater apparatus. The photoluminescence property of the as-deposited PVA capped porous SiC powder-based thin films were investigated.

2. Experimental details

A 7µm SiC powder was used in our investigations. The powder was washed fistly, in HNO_3, then in acetone, followed by rinsing several times with deionised water after eash wash, in order to eliminate native SiO_2 and/or any organic impurities whish could exist on the SiC microparticles surfaces. The cleaned powder was dried and subjected for various characterizations in order to identify the SiC polytype and morphology. Proposal states that no surface sensitization was carried out on the SiC microparticles, like it used to be done, before the electroless plating [11].

An electroless etching method for producing porous silicon carbide powder under UV irradiation was investigated. Unlike in thin films form, depositing electrical contact on microparticles is more difficult to realize. To do it, Silver nanolayer coated SiC microparticles was formed by polyol process prior the etching process using $AgNO_3$/NaOH and Ethylene glycol mixture.

The electroless etching of SiC was made possible by using Ag metal to catalyze the reduction of a chemical oxidant in the presence of HF, which combined with UV illumination, injects holes into the valence band, the holes subsequently participating in the oxidation and dissolution of the substrate. The Ag nanoparticles will serve both as an anode, catalyst and mask for the reduction of a chemical oxidant.

Unlike in the case of the SiC thin film form, in which the deposition of metallic coating can be achieved by simple vacuum evaporation of the metal or by chemical reduction of it on the top of the thin film, the metallization of SiC microparticles, with different shapes, could be more difficult to realize since the microparticles can't be immobilized on a support like the thin films. Thus, the chemical reduction of the metal is the unique route metallizing the SiC microparticles, by direct reduction of the metallic particles on the different faces of the microparticles.

The precursors used in the reduction of Ag by using polyol process are 0.1 M of $AgNO_3$ salt and NaOH. In a typical reaction, the precursors were introduced in boiling ethylene glycol (EG), containing SiC micrpowder, with an $[OH^-]/[Ag^+]$ molar ratio as high as 40 to enable reduction. The reaction temperature and duration were 373K and 15 min, respectively. The Ag-coated SiC particles thus obtained were washed with deionised water for several times and the dried powder was used for various characterizations.

An etchant composed of a mixture of HF and an oxidant was found to produce porous PSiC consistently. Two different oxidants, $Na_2Cr_2O_7$ and $K_2S_2O_8$ were used in order to select which one will yield the best porous morphologies. In concentrated HF etchant, a mixture of 14 M of HF and 0.075 M of oxidant was used. The electroless etching process was carried out in the presence of ultraviolet illumination using a LED lamp which works in both wavelengths λ=254 nm and λ=365nm. The resulting porous morphology of SiC microparticles was studied as function of oxidant nature.

SiC micropartciles-based Thin films were prepared on clean glass slides by spin coating method. Polyvinyl alcohol (PVA) with molecular weight of 17.000 g/mol served to cap the SiC microparticles and preparing the thin films in sight. The PVA solution was prepared by adding 50 ml of deionized water to 0.5g of PVA powder. The solution was stirred for 3 hours at the temperature of 353 K using a hot plate with magnetic stirrer. It was kept overnight in an air tight container to increase its viscosity. At the end of the preparation, a clear solution of PVA was obtained.

The porous SiC microparticles were kept in water suspension to prevent their agglomeration. Before adding SiC particles to PVA solution, the suspension was sonicated for 30 minutes in bath Sonicator at room temperature. The PVA/ porous SiC microparticles solution was further sonicated for 1 hour to improve dispersion of SiC particles in PVA matrix. The obtained solution was used for spin coating. Thin films of pure PVA, PVA mixed with 10 % by weight of porous SiC microparticles were prepared by spin coating at 1000 rpm for 120 seconds.The prepared samples were dried in Oven at 363K and kept in air tight container. Finaly, the obtained thin films were subjected to photoluminescence investigations.

Morphology analysis was carried out with a scanning electron microscope (SEM) (PHILIPS SEM505). Optical measurements were carried out using an UV–VIS-NIR spectrophotometer (Cary

500 Version 8, 01) in the wavelength range of 250–2500 nm. The X-ray diffraction (XRD) patterns were obtainedby D8 Advance Bruker AXS diffractometer with a Ni filter and CuKα radiation (λ = 1.54056 Å). Photoluminescence spectra of samples excited under a wavelength of 325 nm were measured using a PERKIN-ELMER LS 50B luminescence spectrometer.

3. Results and discussion

The SEM micrograph of the as-analyzed SiC/Ag microparticles is shown in Fig. 1. It clearly shows that the coating surface is covered by a compact thin film and approximately spherical Ag nanoparticles.

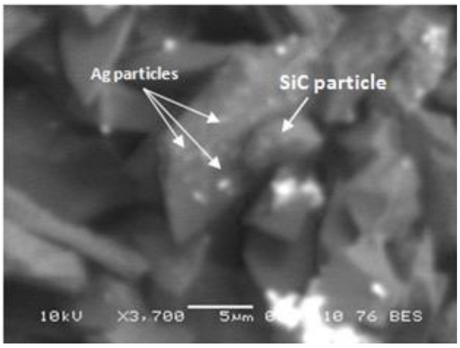


Figure 1. *Scanning electronic microscopy of and Ag-coated SiC microparticle.*

The XRD patterns of SiC/Ag powder is shown in Fig. 2. All the as prepared SiC/Ag microparticles show two set of diffraction peaks. The diffraction peaks marked with “#” indicate peaks due to 6H-SiC. The peaks marked with “*”at 2θ values of 38.12, 44.32, 64.46, 77.47, and 81.53 correspond to (111), (200), (220), (311), and (222) planes of face centered cubic Ag (JCPDS file no. 04-0783), respectively.

In the SiC/Ag samples, the presence of the Ag peaks compared to that of pure SiC is attributed to the deposition of silver nanoparticles on its surface.

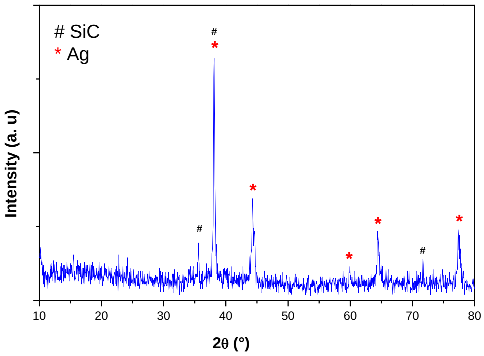


Figure 2. *XRD pattern of Ag-coated SiC microparticles*

As can be observed, the XRD pattern of SiC/Ag core-shell microparticles consist mainly of the four intense and broad peaks of FCC Ag in the 2θ range of 20-80° along with the most distinct peaks of hexagonal type SiC. The Ag peaks are more intense in comparison to those of SiC. No trace of Ag_2O can be seen in these formed SiC/Ag microparticles. Herein, the use of EG as the polyols, in presence of Ag ions, has avoided the formation of silver oxide (Ag_2O) particles, highlighting it reducibility power. Thus, the reduction of Ag by EG leads the formation of oxide free Ag-coated SiC powder.

İn our investigations, various operational conditions were carried out for producing porous SiC powder. The most interesting one was that where two type of wet etchants were used. The SEM analysis of SiC powder, before and after being etched in $HF/Na_2Cr_2O_7$, are given in Fig. 3 (a) and (b) respectively. We specify that the surface of the UV-etched SiC micropowder was treated in aquea regia to remove the Ag-coated region.

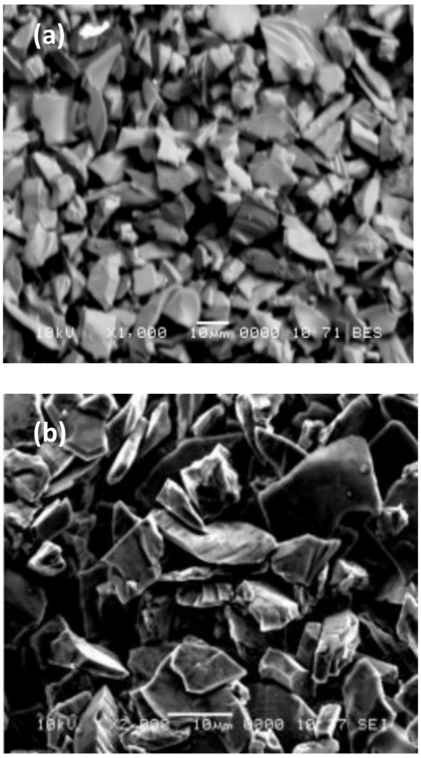


Figure 3. *SEM pictures of SiC powder (a) before etching process and (b) after etching process*

The Micrograph 3(b) indicates that the etchant affected the SiC microparticles morphologies. UV irradiation is required during etching to form the porous morphology, because the energy of the holes available from oxidant reduction is not sufficient for direct injection into the valence band of SiC. In addition, the presence of metallic coating is necessary to catalyze the oxidant reduction and to act as a local cathode. İt seems that the Ag areas have the benefit of acting as a masking agent.

Figure 4 depicts the photoluminescence spectra of PVA-capped Porous SiC (PSiC) powder based thin films and PVA-capped SiC micropowder based thin film excited at 325 nm demonstrating the change in emission of Porous SiC (PSiC) based thin films compared to the unetched based one. The etched powder (PSiC) have been electrolessly etched in HF/oxidant ($K_2S_2O_8$ or $Na_2Cr_2O_7$) etchant for 40 min, at different temperatures, resulting in different morphologies.

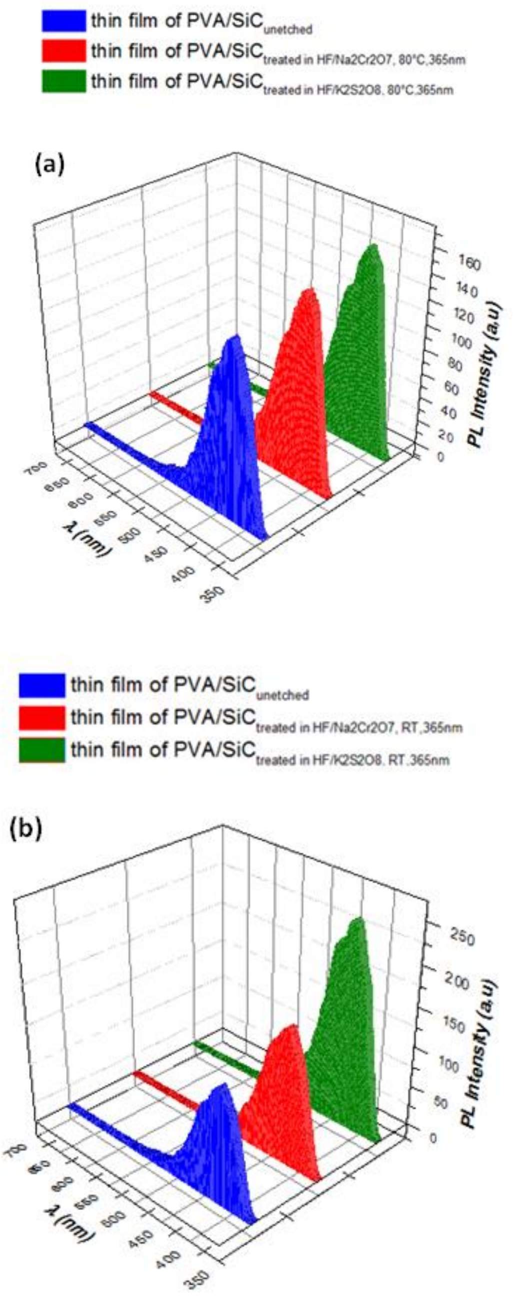


Figure 4. *Photoluminescence spectra of four PVA-capped etched SiC powder based thin films and PVA-capped unetched SiC powder based thin film, at two different temperatures; (a) at T=80°C and (b) at room temperature.*

All PL spectra (Fig 4 (a) and (b)) of the PVA-capped PSiC powder based thin films showed evidence of an increased PL emission below 500 nm. This increased emission is pronounced with an emission band peaking in the 400–420 nm region. Our results shift from some reports in the literature where an increase in photoluminescence intensity was observed in the 460–500 nm region of the spectrum upon etching. İn other studies, there were reports of changes in the PL of the wide visible band attributed to defects and $N–B^+$ recombination in anodically-produced PSiC [6]. There is no indication of a peak in PL emission in the 460–500 nm range for the electrolessly etched PSiC produced in this work.

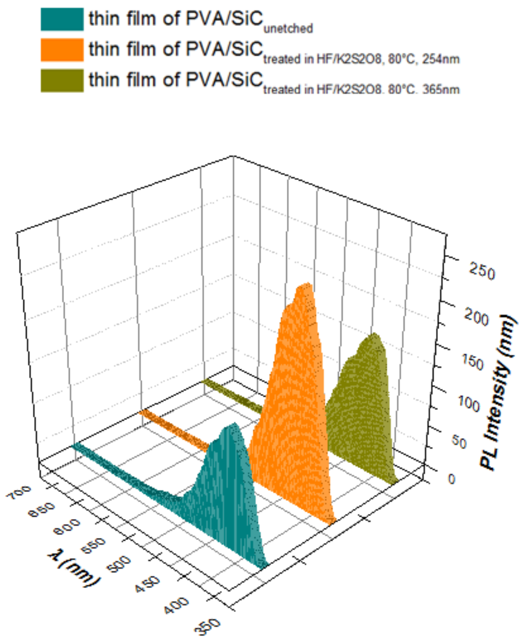


Figure 5. *Comparaison of the photoluminescence spectra of PVA-capped etched SiC powder based thin films at two different working wavelength.*

As shown in Fig. 4 the wavelength of maximum emission in PL increase in the porous SiC based thin films obtained in the case of etchant HF/$K_2S_2O_8$ for both temperatures. The PL peak is more intense for PVA-capped PSiC thin films which powder was etched at room temperature. Because the emission in this spectral region muches with the bandgap energy, the most likely source of luminescence is band-to-band, the variation upon etching signifying a variation in the bandgap. For the fourth etched SiC powders, we noted that thin film obtained basing on PVA-coated SiC powder etched under UV light of 254 nm using $K_2S_2O_8$ as oxidant, at reaction temperature of 80°C for t=40min led the best photoluminescence property (Fig. 5).

4. Conclusion

We have described in this part of the study the deposition of SiC based composite thin films formed by passivating a porous SiC microparticles via a polymer, the polyvinyl alcohol (PVA), using the spin coating method. Photoluminescence investigations have shown that it depended a lot on the surface state of the studied material and that, a porous surface, could exhibit a significant enhancement of it. The SiC microparticles were electrolessly etched using a wet etchant composed of HF and two different oxidants, $Na_2Cr_2O_7$ and $K_2S_2O_8$ which, under an UV illumination and in the presence of a metal, led to the formation of more or less porous surface. This later varied as function of the oxidant, the working temperature and the wavelength of the UV light. Our study revealed that thin film based on PVA-coated SiC powder etched under UV light of 254 nm using $K_2S_2O_8$ as oxidant, at reaction temperature of 80°C for t=40min has led to the best photoluminescence property.

Acknowledgement

This work was completed thanks to the National Funds of Research, DGRSDT/MESRS (Algeria).

References

[1] A. Keffous, A. Chriet, Y. Belkacem, A. Mansri, N. Gabouze, M. Kechouane, A. Brighet, A. Boukezzata, S. Kaci, I. Menous, G. Nezzal, L. Guerbous, H. Menari, Investigation properties of a-$Si_{1-x}C_x$:H films elaborated by Co-sputtering of Si and 6H-SiC, Mod. Phys. Lett. B, 24 (2010) 2101-2112.
DOI:10.1142/S0217984910024262.

[2] S. Kaci, A. Keffous, S. Hakoum, N. Makrani, M. Kechouane, L. Guerbous, Investigation of nc-PbS/a-$Si_{1-x}C_x$:H/pSi(100) heterostructures for LED applications, Opt. Mater. 35 (2012) 1-4.
DOI: 10.1016/j.optmat.2012.05.031.

[3] M. Chubarov, H. Pedersen, H. Högberg, Zs. Czigany, A. Henry, Chemical vapour deposition of epitaxial rhombohedral BN thin films on SiC substrates, Cryst. Eng. Comm. 16 (2014) 5430-5436.
DOI:10.1039/c4ce00381k.

[4] H. Abderrazak, E. Selmane Bel Hadj Hmida, Silicon carbide: synthesis and properties, Book edited by Rosario Gerhardt, ISBN 978-953-307-201-2, (2001).
DOI:10.5772/15736.

[5] J. Y. Fan, X.L. Wu, P. K. Chu, Low-dimensional SiC nanostructures: Fabrication, luminescence, and electrical properties, Progr. Mater. Sci. 51 (2006) 983–1031.
DOI:10.1016/j.pmatsci.2006.02.001

[6] L. T. Rittenhouse, P. W. Bohn, I. Adesida, Structural and spectroscopic characterization of porous silicon carbide formed by Pt-assisted electroless chemical etching, Sol. Stat. Comm. 126 (2003) 245–250.
DOI:10.1016/S0038-1098(03)00130-3

[7] A. Boukezzata, G. Nezzal, L. Guerbous, A. Keffous, N. Gabouze, Y. Belkacem, A. Manseri, A. Brighet, M. Kechouane, H. Menari, Comparative study of porous amorphous a-$Si_{1-x}C_x$ films and a-$Si_{1-x}C_x$ membranes on structural and luminescence properties, J. Lumin. 131 (2011) 1184–1188.
DOI:10.1016/j.jlumin.2011.02.029.

[8] A. Keffous, N. Gabouze, A. Cheriet, Y. Belkacem, A. Boukezzata, Investigation of porous silicon carbide as a new material for environmental and optoelectronic applications, Appl. Surf. Sci**.** 256 (2010) 5629–5639.
DOI:10.1016/j.apsusc.2010.03.029.

[9] T. Hossain, F. Khan, I. Adesida, P. Bohn, and T. RittenhouseNanoporous Silicon Carbide For Nanoelectromechanical Systems Applications, NASA/CR-2003-212198.
http://gltrs.grc.nasa.gov.

[10] A. Boukezzata, A. Keffous, A. Cheriet, Y. Belkacem, N. Gabouze, A. Manseri, G. Nezzal, M. Kechouane, A. Bright, L. Guerbous, H. Menari, Structural and optical properties of thin films porous amorphous silicon carbide formed by Ag-assisted photochemical etching, Appl. Surf. Sci. 256 (2010) 5592-5595.
DOI:10.1016/j.apsusc.2010.03.037.

[11] N. B. Khosroshahi, R. A. Khosroshahi, R. T. Mousavian, D. Brabazon, Effect of electroless coating parameters and ceramic particle size on fabrication of a uniform Ni–P coating on SiC particles, Ceram. Int.40 (2014) 12149-12159.
DOI:10.1016/j.ceramint.2014.04.055.