Silicon carbide film formation by pulsed laser ablation and its characterisation study

Pratima. K. Mishra* and Bijayalaxmi Sahoo

Advanced Materials Technology Department

Institute of Minerals and Materials Technology (CSIR)

Bhubaneswar-751013, Orissa, India

Abstract

This paper presents a study on preparation of transparent and crystalline silicon carbide thin films on Si(100) substrates by pulse laser ablation technique using high density silicon carbide targets as the source material. A KrF excimer laser (λ = 248nm, pulse width- 20ns) was used for this purpose. The films were deposited at a temperature of 800^{o}C under vacuum (2 X10^{-5} bar) and then further annealed at 800^{o}C for 3h and etched to obtain transparent and crystalline SiC film suitable for MEMs applications. Phase and microstructural studies of the same were carried out by glancing angle X-ray diffraction, X-ray Reflectivity, micro-Raman techniques, FESEM and Nanoindentation etc. and silicon carbide films of hardness of 18-19GPa, with high elastic modulus has been prepared. This study can contribute in understanding the radiation effect on SiC wall materials used in thermonuclear reactors.

*Corresponding author. Tel.:+919439584412; fax: (0674)-2581637
Email address: pmimmt10@gmail.com (Dr. P. K. Mishra)

1. Introduction

Thin film of silicon carbide has excellent physical and chemical properties such as high thermal conductivity (5-7W cm^{-1} K^{-1}), wide band gap energy (2.3-3.2eV), high refractive index, high breakdown field (>20×10^5V/cm), high saturation velocity (2.2×10^7cm/s), high mobility (1000cm^2/Vs), high resistance to oxidation and corrosion, low expansion coefficient, high thermoelectric power, high thermal and chemical stability, higher hardness and elastic modulus etc [1-5]. All these properties make it suitable for the fabrication of devices that can operate under extreme conditions of temperature, frequency and power where silicon (Si) based devices would fail resulting in smaller, lighter and simpler electrical systems especially benefit for hybrid and electric vehicles. Besides, these films have application as VUV reflectors and radiation detector application and this study contribute in understanding the laser radiation effect on SiC wall materials used in thermonuclear reactors.

Silicon carbide films are prepared by different chemical and physical methods such as Hot filament CVD [6], Plasma enhanced chemical vapor deposition [7], Metal organic chemical vapor deposition [8], APCVD [9], EBPVD [10], Molecular beam epitaxy[11], RF and magnetron sputtering [12]. CVD and MBE are shown to result in device grade films but usually require very high temperature i.e, in between 1300-1600^{o}C during deposition.

Pulsed laser deposition is a technique which can be used to deposit both crystalline, polycrystalline and amorphous films at relatively lower temperature depending on the process parameters. In this process both neutral and ionized species within the vapour plume can have kinetic energies in the range of 10-100eV which is several orders of magnitude larger than other methods. Besides it has an ability to transfer complicated target stoichiometries to the composition of the film with good adhesion and high deposition rate. Silicon carbide deposition by PLD has been attempted by many authors and both beta and alpha SiC have been prepared depending on process variables such as substrate temperature, laser fluence, target to substrate distance, gas atmosphere etc. In most of the paper crystalline SiC film has been obtained by annealing only above 950^{o}C.

This paper presents systematic studies on preparation of thin, hard and smooth silicon carbide thin films using a pulse laser ablation technique and their detailed characterization studies using GAXRD, XRR, FTIR, Microraman, FESEM and Nanoindentation studies etc. SiC films with thickness varying from 200-500 nm, roughness 0.3-1.5 nm, and hardness around 18GPa have been prepared. The results are described below.

2. Experimental:

SiC films were deposited by PLD from a SiC target (stoichiometric, 99.9% purity). A KrF excimer laser (λ= 248 nm, pulse width=25 ns) was focused to a spot size of 4 mm^2 on rotating SiC target at a pulse frequency of 10 Hz and pulse energy of 470 mJ, yielding an energy density of about 10 J/cm^2 on the target. The target to substrate separation was kept at 4 cm. A p-type 1 inch dia. Si (100) wafer (1-10 Ω cm) was used as the substrate and was cleaned using strandard Si cleaning procedure and passivated in 5% HF solution. Laser light irradiated at an angle of 45^0 to the target and the substrate was placed parallel to the target with a provision to heat the target up to 850^{o}C. The chamber pressure was maintained at a vacuum level of 7x 10^{-6} mbar. During the process of deposition, 99.99% pure argon gas at a flow rate of 30 sccm was introduced into the chamber by lowering chamber pressure to about 2 x 10^{-3} mbar. The depositions were carried out at different temperatures (800^0 C to 830^{o}C)

for 30 min. After deposition the films were annealed in vacuum (10^{-5} mbar) at 800^0 C for 1- 3 h and here we have reported the results of the film deposited and annealed at 800^oC.

The crystal structure and phase composition of the films were identified by the glancing angle of 1^0. The thickness and roughness of the films have been determined by analysing the X-ray reflectivity data using the globalfit software. To identifying the bonding between the different elements in the film, Fourier transform infrared (FTIR) measurements were performed using a perkin Elmer model based FTIR system working in the wavenumber region 400-4000 cm^{-1}. Microstructural studies were carried out by Field Emission Scanning Electron Microscope (Supra 55, Carlzeiss, Germany). Raman spectra were carried out by micro-Raman spectrometer (In Via Renishaw, U.K) equipped with confocal microscope and a CCD camera detector and samples were excited using 514 nm Ar^+ laser. Elastic modulus and hardness of the films were determined using a Nano-Indenter (UMIS, Fisher-cripps, Austrelia). In nanoindentation , the depth of penetration of a diamond indentor is measured alongwith the prescribed load. The resulting load-displacement response typically shows an elastic-plastic loading followed by an elastic unloading. The elastic equations of contact are then used in conjuction with the unloading data to determine the elastic modulus and hardness of the specimen materials. Here a continuous stiffness method was used for this analysis. A load of 1mN was applied on the surface of the films with an interval of 10μm between each indent. Oliver-Pharr method was used for evaluation of elastic modulus and hardness of the film. The poisson's ratio of the films was taken to be 0.17.

Results and Discussions

Films were deposited at various temperatures with a deposition rate of 18nm/min for 10 to 30mins. Films with varying thickness and crystallinity were obtained but here the results of detailed characterization data of SiC deposited and annealed at 800^oC are reported.

X-ray diffraction data of 800^oC deposited film without annealing showed amorphous carbon peaks with minor peaks due to 4H-SiC only whereas peaks intensity at 2θ= 33.09 and 61.7 pertaining to <100> and <110> increased due to 4H-SiC in the vacuum annealed film [Fig 1]. Presence of DLC types carbon crystallites make the film harder and suitable for micro fabrication work.

FTIR spectra of annealed SiC films sample show strong vibration bands in lorenzian form $804cm^{-1}$ along with other minor dips at 675 cm^{-1}, 1080 cm^{-1} whereas there occur absorption bands at 674 cm^{-1}, 796 cm^{-1},$1055cm^{-1}$ for annealed film. The band around $804cm^{-1}$ with lorenzian form reflects minimal bond angle distortion and bond length dispersion characterizing the crystalline phase. With increase in the annealing time, there is a red shift of all the bands thus improving the Si –C bond formation. This result suggests that vacuum annealing results in formation of Si-C bonds and in improvement of the distribution of bond angle and bond length. IR signals get affected by change in the local dielectric constant and total number of vibration bands. The dip at $674cm^{-1}$ may be attributed to Si-C stretching mode and 1080 cm^{-1} probably due to Si-O stretching vibration absorption and also could be due to presence of interstitial oxygen impurities dissolved in the Silicon substrates. Formation and enhancement of the SiC structures can also be found by Raman measurements (vide infra).

Microraman studies (shown in Fig 3) of typical annealed SiC films show major peaks at 778 cm^{-1}, 965 cm^{-1} and minor peaks at 1349 cm^{-1} and 1512 cm^{-1} which are attributed to transverse optical and longitudinal optical modes of nanocrystalline SiC. The raman peaks at 1349 cm^{-1} may be due to D band and 1512 cm^{-1} due to G band of amorphous carbon phase.

Detailed microstrutural studies by FESEM show amorphous nature for unannealed film and crystalline form for annealed film showing SiC crystallites of size within 10-20nm.

Surface roughness and thickness data of the films were determined by both XRR and specular reflectivity data. In x-ray reflectivity measurements one can measure film thicknesses of a few hundred angstroms. This is an extremely effective, accurate, and nondestructive technique for measuring the thickness, density, and microscopic surface roughness. These properties are difficult to accurately measure using other methods. However, since they affect the functional performance of these films and are dependent on preparation conditions, their determination is particularly important.

Longitudinal specular and off-specular data were collected for GIXR using the X-ray wavelength of 1.54Å. Fig show typical x-ray reflectivity data of the annealed silicon carbide thin film. Recursive formalism has been used for data analysis and the roughness and thickness of the typical annealed film were found to be 0.3 nm and 82nm respectively.Other films were also analysed and thickness value corroborated with the results obtained from different methods i.e, specular reflection(not shown here), XRR and cross section FESEM image data.

Elastic modulus and hardness studies of these films obtained by nanoindentation technique revealed the hardness and elastic modulus to be 18 Gpa and 250 Gpa which further increase with annealing temperature.

Conclusions

Studies on hard, smooth SiC thin film with roughness of 0.3 to 1.5 nm and thickness 200-500 nm have been prepared by pulse laser ablation studies and characterised in detail using various sophisticated physical characterisation techniques. These films have application as VUV reflectors and radiation detector application and may contribute in understanding the laser radiation effect on SiC wall materials used in thermonuclear reactors.

Acknowledgements

The authors would like to thank the Director, Prof. B. K. Mishra, Institute of Minerals and Materials Technology, Bhubaneswar, India for kindly permitting to present and publish this paper. They would like to specially thank Council of Scientific Industrial Research, New Delhi, for financial assistance to carry out this work

References

[1] M. Tabbal, A. Said, E. Hannoun, T. Christidis, Appl. Surf. Sci. 253 (2007) 7050.

[2] A. Keffous, K. Bourenane, M. Kechouane, N. Gabouze, T. Kerdja, Vacuum 81(2007) 632.

[3] Y.S. Katharria, S. Kumar, R.J. Choudhary, F. Singh, N.P. Lalla, D.M. Phase, E. Kanjilal, Thin Solid Films 516 (2007) 6083.

[4] S.Takao, H. Kohno, S. Ichikawa, S. Takeda, Appl. Surf. Sci. 254 (2008) 7630.

[5] J. B. Casady, R.W. Johnson, Solid-State Electron. 39 (10) (1996) 1409.

[6] T. Chen, Y. Yang, D. Yang, R. Carius, F. Finger, Phys. Stat. Sol. (a) 4 (2010) 61.

[7] H. Zhang, H. Guo, Z. Chen, G. Zhang, Z. Li, J. Micromech. Microeng. 17 (2007) 775.

[8] S-H Nam, M-H Kim, J-S Hyun, J-H Boo, Nanotech 1 (2009) 452.

[9] K.-S. Kim, G.-S.Chung, Sensor Actuat A- phys 155 (2009)125.

[10] J. Yi, X. D. He, Y. Sun, J. Vac. Sci. Tech 461(2008) L11.

[11] J. Chen, A. J. Steckl, M. J. Loboda, J. Vac. Sci. Technol., B 16(1998) 1305.

[12] C. K. Chung, B. H. Wu, J. Nanosci. Nanotechnol 10 (2010) 4679.

Figure caption

Fig.1 X-ray diffraction patterns of the SiC film annealed at 800^0C

Fig.2 FTIR spectra of SiC thin film annealed at 800^0C

Fig.3 Raman spectrum of SiC film

Fig.4 (a) FESEM image of SiC film without annealing deposited on Si substrate

(b) FESEM image of SiC film with annealing at 800^0C

(c) Crosssection image of SiC film showing thickness of about 200 nm

(d) EDAX spectrum of SIC film showing presence of Si and C

Fig.5 XRR graph of SiC film

Fig.6 Nanoindentation study of SiC film

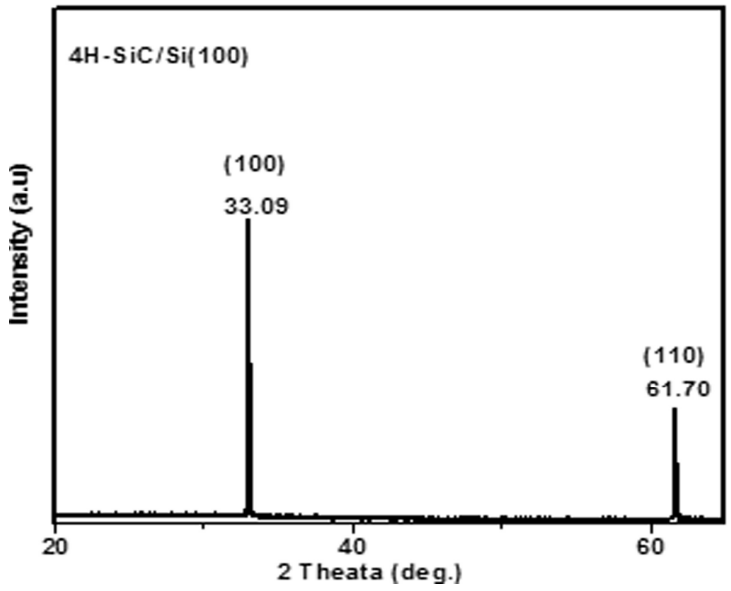
4H-SiC/Si(100)
(100)
33.09
(110)
61.70
Intensity (a.u)
20
40
60
2 Theata (deg.)

Fig- 1

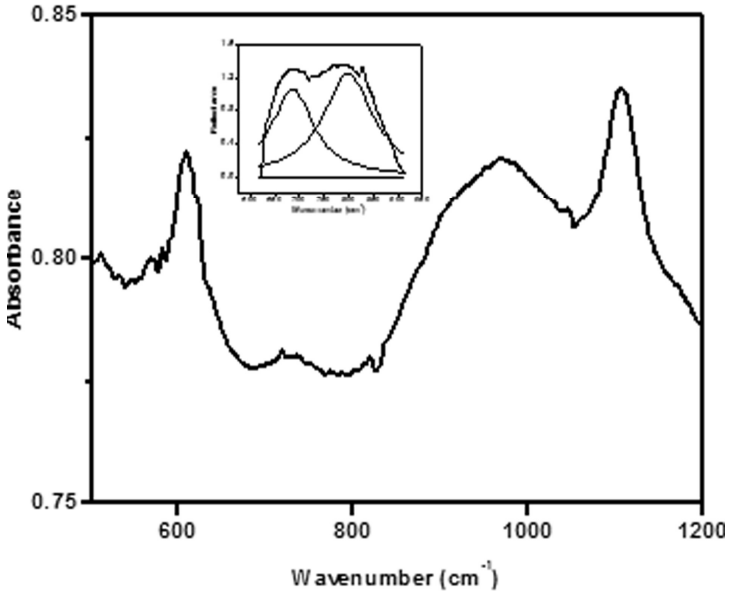
0.85
0.80
0.75
Absorbance
600
800
1000
1200
Wavenumber (cm-1)

Fig-2

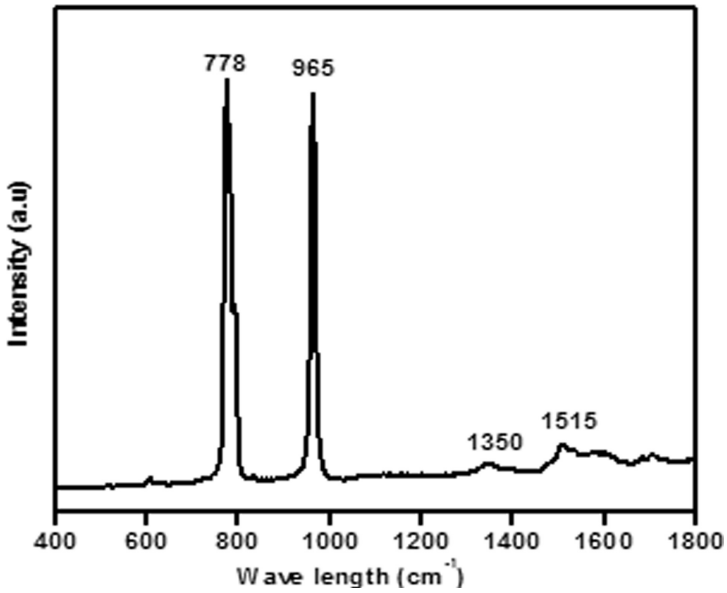
778
965
1350
1515
Intensity (a.u)
400
600
800
1000
1200
1400
1600
1800
Wave length (cm-1)

Fig-3

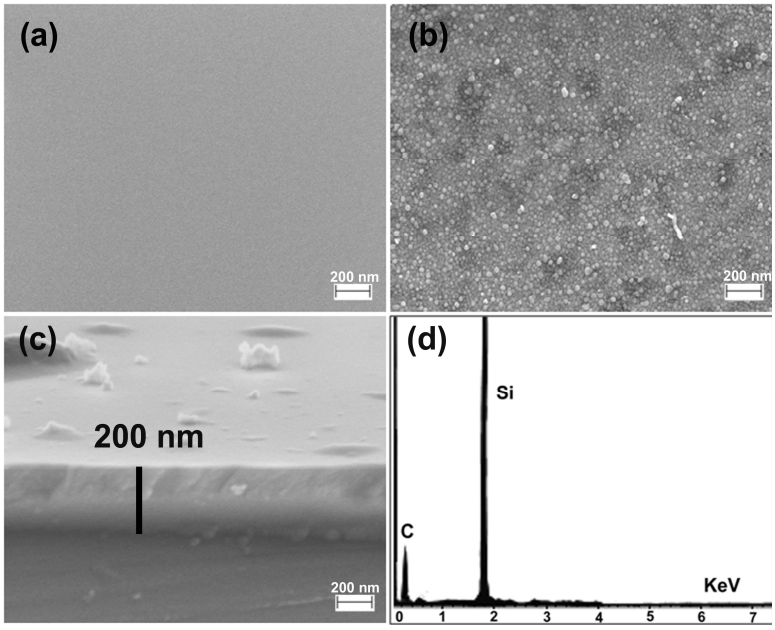
(a)
200 nm
(b)
200 nm
(c)
200 nm
200 nm
(d)
Si
C
KeV
0
1
2
3
4
5
6
7

Fig.4

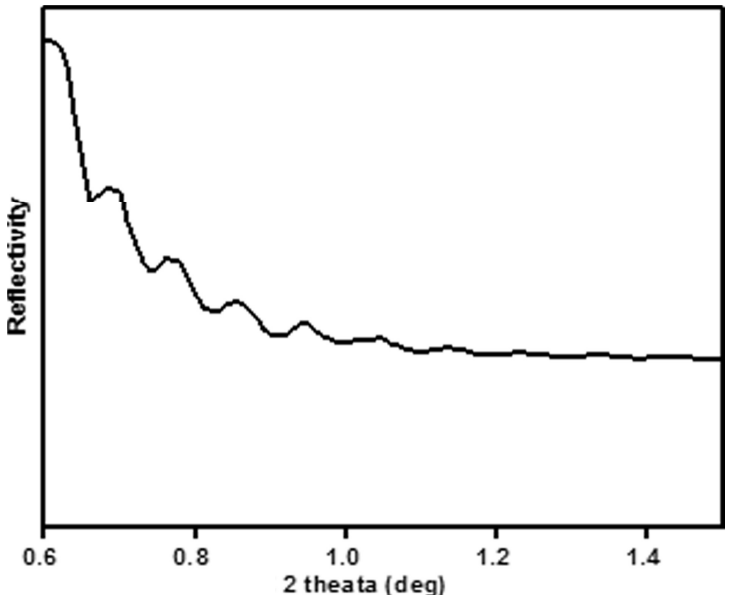
Reflectivity
0.6
0.8
1.0
1.2
1.4
2 theata (deg)

Fig-5

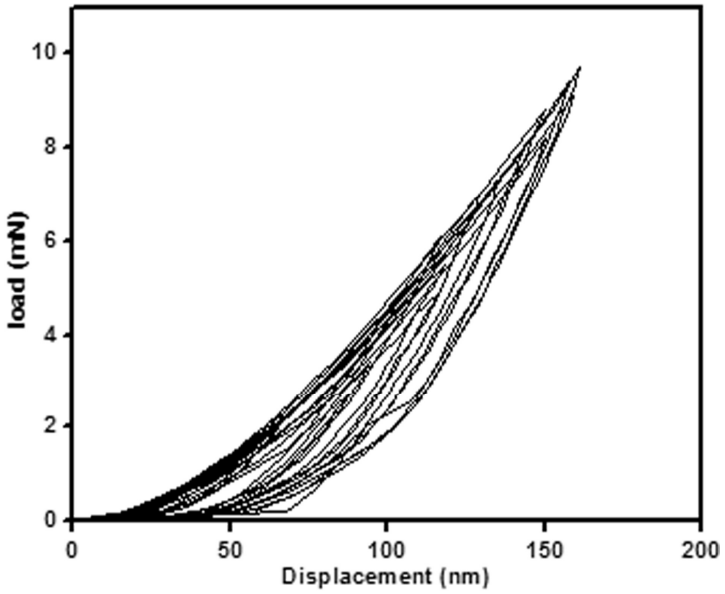
load (mN)
0
2
4
6
8
10
0
50
100
150
200
Displacement (nm)

Fig-6