SiC Thin Film Growth on Different Substrates using Pulsed Nd^{3+}:YAG Laser Deposition

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Synthesis of SiC thin film on different substrates, namely crystalline silicon substrate and a-cut sapphire substrate is studied using a Q-switched pulsed Nd^{3+}:YAG laser. The morphological and structural properties of SiC layers on the substrates were investigated by scanning electronic microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy. The results shows polycrystalline (combined 3C-SiC and 4H-SiC) nature of SiC films on Si(100) substrates and a-cut sapphire substrates, respectively. The droplet formation on the deposited film was reduced significantly by selecting the grit count of SiC powder 500 and the pressure of 2×10^{-2} Pa for thin film grown on Si(100) substrate and grit count of SiC powder 800 and the pressure of 2×10^{-3} Pa for thin film grown on sapphire substrate respectively. n-Si/SiC heterostructures exhibit diode characteristics: current–voltage measurements showed a typical rectifying characteristic of a p–n junction.
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1. Introduction

Silicon carbide (SiC) thin films are useful in optoelectronics and high-temperature semiconductor related applications. SiC possesses good physical, chemical, and mechanical properties similar to that of diamond. SiC has high hardness (30-50 GPa), wear resistance, resistance to thermal shock, high thermal conductivity (3.2–4.9 W/cm°C), low thermal coefficient of expansion, wide band gap (2.4 to 3.3 eV), high breakdown field strength (2.1–2.5 MV/cm), and high electron mobility (1000 $cm^2/V{\cdot}s$).

The growth of bulk single crystals of SiC is difficult, because it has numerous prototypes. The polytypes have the same chemical composition but exhibit different crystallographic structures and stacking sequences along the principal crystal axis. All SiC prototypes consist of carbon atoms covalently bonded with equal numbers of Si atoms. However all SiC polytype has its own distinct set of electrical semiconductor properties. Several important polytypes of SiC are hexagonal (4H-SiC and 6H-SiC) (α-SiC) and cubic (3C-SiC or β-SiC) ploytypes. The hexagonal polytype 4H-SiC exhibits large band gap energy of ≈3.2 eV, while possessing a large critical breakdown field and high thermal conductivity. However, the 4H-SiC and 6H-SiC based metal-oxide-semiconductor field-effect-transistor (MOSEFT) devices have exhibited low channel mobility, which is attributed to the high density of interface traps. In contrast, 3C-SiC possesses high effective channel mobility (165-229 $cm^2/V{\cdot}s$). In comparison with 4H-SiC, the 3C-SiC (β-SiC) prototype has the advantages, such as isotropic properties (cubic structure), isotropic electron mobility of 1000 $cm^2/V{\cdot}s$, low mass density and thermal expansion, high thermal conductivity and flexural strength, thermal shock resistance, oxidation and wear resistance potential. An application of an p-type 3C-SiC thin film on an n-type Si wafer has been considered for a hetero-junction solar cell where 3C-SiC is used as an emitter [1,2].

SiC possesses a wide-band gap from 2.4 to 3.3 eV and p-type SiC thin film is easy to grow using several techniques, such as chemical vapor deposition (CVD), electron beam CVD (EB-CVD), pulsed laser deposition (PLD). Chemical vapor deposition (CVD) technique is commonly used for SiC thin film synthesis, which forms epitaxial SiC layers. However the process temperature is above 1400 °C.

Alternatively, the PLD technique allows deposition of amorphous and crystalline SiC films on various substrates. It offers several advantages over other techniques, such as simple experimental setup with flexibility and control, stoichiometric film deposition [3], wide deposition parameter control, such as temperature, ambient pressure; multiple layer deposition with different target material is possible. In PLD, both neutral and ionized species within the vapor plume (or) plasma can have kinetic energies in the range from 10 to 100 eV, which is several orders of magnitude larger than other methods, such as the molecular beam epitaxy technique. As a result, a smoother surface morphology at low substrate temperatures is expected by PLD, in comparison to other thin film deposition techniques. Different research groups have demonstrated the PLD technique for SiC thin film deposition [4-6].

In this work, influence of the grit size of SiC and sintering temperature of the target, ambient pressure of deposition was studied for an improved minimized droplet formation on SiC thin film during the PLD process using a nanosecond-pulsed Nd^{3+}:YAG laser. Based on I-V measur-

Table 1 Parameters and specification of PLD

Parameters	Specifications
Laser used	Nd^{3+}:YAG (λ = 355 nm)
Pulse duration (frequency)	8 ns (10 Hz)
Pulse energy (fluence)	54 mJ (≈1.7 J/cm^2)
SiC pellet size	30 mm diameter and 5 mm thickness
SiC grit count (grit size in μm)	36 (530), 60 (265), 120 (115), 400 (23), 500 (20),600 (17), 800 (13)
Target density	≈1.6 g/cm^3(500 grit count),1.8 g/cm^3(800 grit count)
Chamber Pressure	2×10^{-3} to 2 Pa (He)
Substrates	c-Si (100) wafer, a-cut sapphire 10 mm^2
Distance between target and substrate	40 mm
Substrate temperature	400 to 800 °C
Duration of deposition	30, 60, 90 min
Sintering temperature	1,000, 1,200, 1,400, 1,600, 2100 °C

-ements, SiC/n-Si hetero-structure showed the rectifying characteristic of a p–n diode. Second, SiC thin film grown on the a-cut sapphire substrate and the influence of a grit size (grit count) of SiC and sintering temperature of the target, ambient pressure of deposition was studied for minimized droplet formation. Further studies are proposed to deposit 3C-SiC and ZnO films on a-cut sapphire substrates. The estimated lattice mismatch values for a-cut sapphire substrates and 3C-SiC films are ≈0.5%, ≈5.2% in different directions and the value for 3C-SiC and ZnO is ≈5%. Nevertheless thermal expansion values are comparable and hence films with less defect densities are expected.

2. Experimental Procedure

SiC powder (Carborundum Universal Limited, India) with grit counts (grit size) ranging from 36 (530 μm) to 800 (13 μm) was used. Green pellets were made by mixing SiC powder with binder (polyvinyl alcohol) and compressing the mixture with a hydraulic press (100kN capacity, SAS Chennai). The hard steel HS13 die plunger setup was used for the pellet preparation of 30 mm diameter and 5 mm thickness. Green pellets were sintered by soaking at a high temperature in a controlled Ar atmosphere. The rate of the sintering was 5 °C/min. After reaching the soaking temperature of 1400 °C, pellets were maintained for about 7 hour as shown sintering cycle in Fig. 1.

The experimental setup for the PLD process was similar to that reported elsewhere [7]. A pulsed Nd^{3+}:YAG laser with a repetition rate of 10 Hz and pulse width of 8 ns was used for the laser ablation of the target. The output wavelength and the energy were 355 nm and around 54 mJ, respectively. Nd^{3+}:YAG laser was focused on a SiC target, using a plano-convex lens with a focal length of 300 mm, in a vacuum chamber. The laser fluence was estimated to be approximately 1.7 J/cm^2, considering a laser-focused spot size of 2 mm. The target was rotated at 10 rpm to attain uniform ablation. Thin film deposition was performed in He ambience with different ambient pressure values. n-type crystalline Si (c-Si) wafer of 10 mm × 10 mm in size was used as a substrate. The target to the substrate distance of 40 mm was maintained.

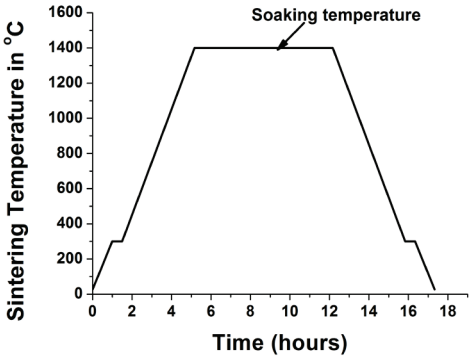

Fig. 1 Sintering Cycle for preparing SiC Pellets in argon gas environment.

Experimental parameters used for the PLD of SiC thin films on different substrates are described in Table 1. Influence of grit count and sintering temperature during the target preparation and ambient pressures and substrate temperatures during the PLD process were investigated by characterizing pulsed laser-deposited SiC thin films on crystalline Si and a-cut sapphire substrates. Surface profile of as deposited SiC thin films was measured using a non-contact type optical surface profilometer (TMS-1200 TopMap μ.Lab, Polytech North America). Crystalline characteristics were studied using the X-ray diffraction (XRD) technique (PAN Analytical 2830 ZT, X'pert Pro) with CuKα line emission mode. Crystalline characteristics of SiC thin film were also studied by using the Raman spectroscopy technique. Raman scattering frequency spectra was obtained using the confocal Raman spectroscopic

(ALPHA300, WITec, Germany) method. Surface morphol--ogy studies were performed by using a scanning electron microscope (Quanta FEG 200, FEI). Electrical I-V characteristics of SiC thin film on n-type crystalline Si film were also studied.

3. Results and Discussion

3.1 Film Thickness Measurement

The Surface profiles of as deposited SiC thin film along with Si(100) substrate edge were measured by using an optical surface profilometer (TMS-1200 TopMap μ.Lab, Polytech North America], North America) which is a non-contact type profilometer. The average film thickness for 60 minutes deposition was observed as 100 nm, 90 minutes deposition was 130 nm respectively. It is observed that the deposition rate was reduced to 1 nm/minute with increase in deposition time after 60 minutes [8].

3.2 X-ray Diffraction Analysis

Figure 2 shows the X-ray diffraction patterns of n-Si/SiC hetrostructure corresponding to deposition time of (a) 30 minutes and (b) 60 minutes. The films were deposited with the substrate temperature ranging from 600 °C to

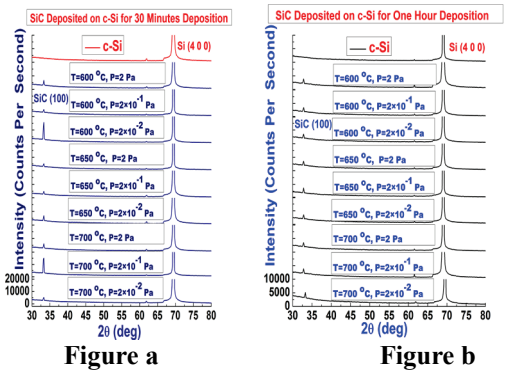

Fig. 2 X-ray diffraction pattern of SiC film on c-Si substrate.

700 °C and the ambient pressure ranging from 2 Pa to 2×10^{-2} Pa. In both cases, distinct diffraction peak of SiC

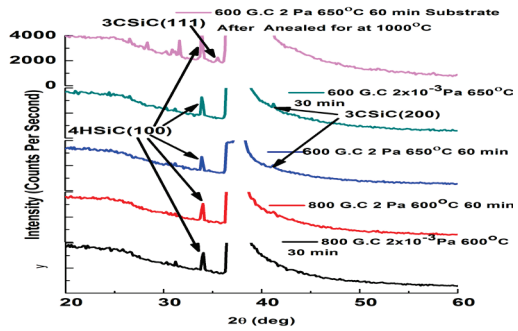

Fig. 3 X-ray diffraction pattern of SiC film on a-cut sapphire substrate.

(100) at 2θ value of 33.46° which corresponds to the 4H-SiC was observed.

Figure 3 shows the X-ray diffraction patterns of SiC film on a-cut sapphire substrate with different substrate temperatures (600 °C and 650 °C) and ambient pressures (2 Pa, and 2×10^{-3} Pa). In the case of SiC film deposited with the target made with the grit count of 800 and with the substrate temperature of 600 °C, the diffraction peak at 2θ value of 33.46° corresponding to 4H-SiC(100) was observed. In the case of SiC film deposited with the target made with the grit count of 600 and with the substrate temperature of 600 °C, two diffraction peaks at 2θ values of

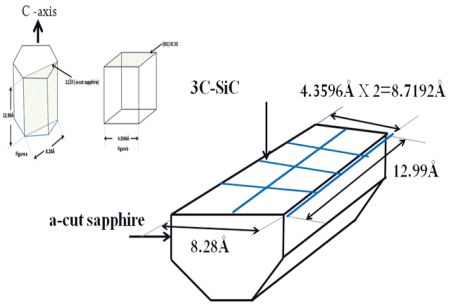

Fig. 4 Schematic illustration of SiC thin film on a-cut sapphire substrate.

33.46°, 41.4° corresponding to 4H-SiC(100) and 3C-SiC(200) were observed.

Figure 4 shows the schematic of the growth of 3C-SiC on a-cut sapphire substrate. The lattice parameters of sapphire substrate is a = 4.785Å, c = 12.99Å and 3C-SiC is a = 4.3596Å. Based on the lattice size, the lattice mismatch between the a-cut sapphire and 3C- SiC is expected to be ≈5.2% as compared to the ≈24% between the Si(100) substrate and 3C-SiC. It was reported elsewhere that the crystallinity of the thin film was improved by increasing the substrate temperature near 1100 °C during the PLD [9].

The influence of furnace annealing after thin film deposition was also studied. A SiC thin film deposited a-cut sapphire substrate was furnace annealed at 1000 °C for the duration of 60 minutes in the argon ambient. Thin film was deposited on the substrate heated to a temperature of 650 °C using the SiC target of 600 grit count at the chamber pressure of 2 Pa. XRD peaks corresponding to 4H-SiC(100), 3C-SiC(111) were observed at 2θ values of 33.46° and 35.5°, respectively. Furnace annealing resulted into a polycrystalline formation. In the case of SiC, polytypes have close energy levels resulting into multi-crystalline formation. Hence, critical temperature and pressure control is essential to allow an epitaxial growth of the film.

3.3 Raman Spectroscopy Analysis

Crystalline characteristics of SiC thin film were also

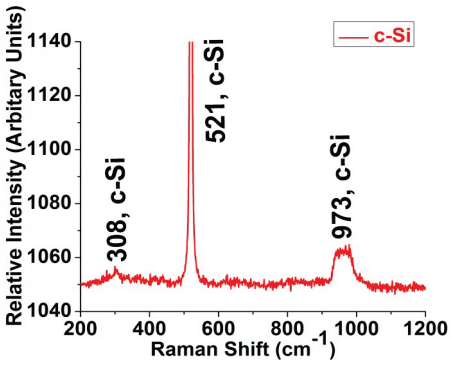

Fig. 5 Raman spectroscopy of c-Si substrate.

studied by using the Raman spectroscopy technique. Raman scattering spectra obtained using an Nd^{3+}: YAG laser from the c-Si substrate and the SiC deposited film at the substrate temperature of 650 °C and the ambient gas pressure of 2×10^{-1} Pa, respectively. Fig. 5 shows the Raman spectra of c-Si substrate. The Raman scattering peaks at 308, 521 and 973 cm^{-1} were observed. Fig. 6 shows the

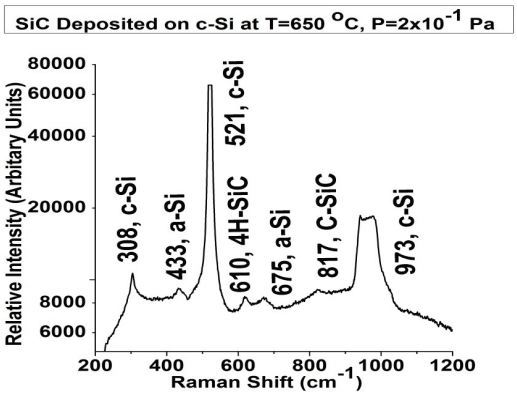

Fig. 6 Raman spectroscopy of SiC deposited on c-Si substrate at the temperature of 650 °C.

Raman spectra of SiC deposited c-Si Substrate. The Raman scattering peaks at 610 and 817 cm^{-1} were observed corresponding to 4H-SiC and 3C-SiC, respectively.

3.4 SEM Analysis

Previously, SEM studies of SiC deposited on the c-Si substrates at the chamber pressure of 2 Pa had clearly

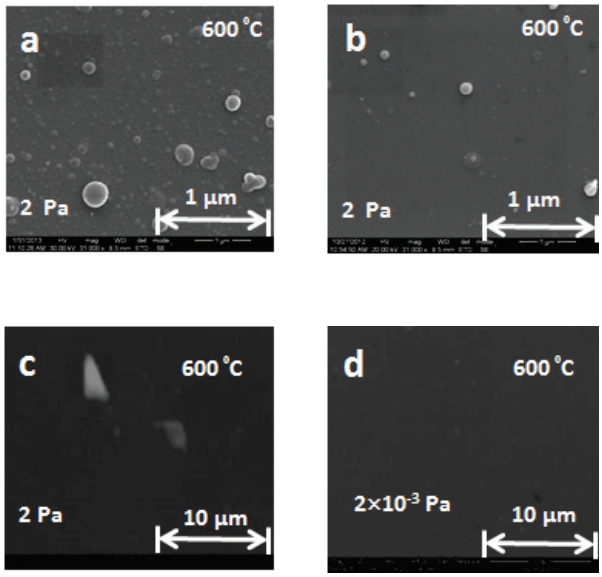

Fig. 7 SEM images of SiC deposited on different substrates at the substrate temperature of 600 °C with different grit count and ambient pressure. (a) G.C 36 sintered at 1600 °C, chamber pressure of 2 Pa on Si substrate; (b) G.C 500 sintered at 1600 °C, chamber pressure of 2 Pa on Si substrate; (c) G.C 800 sintered at 2100 °C, chamber pressure of 2 Pa on a-cut sapphire substrate; (d) G.C 800 sintered at 2100 °C, chamber pressure of 2 Pa on a-cut sapphire substrate.

shown in-homogeneously dispersed droplet formation on the film surface [10]. Figure 7 shows the SEM images of SiC thin deposited on Si and a-cut sapphire substrates at the substrate temperature of 600 °C with different grit count and ambient pressure. As shown in Figs. 7(a) and (b), the droplet formation, while depositing SiC on n-Si substrate, was reduced with the increase in the SiC-target grit count. The decrease in droplet formation was partly attributed to the increase in target densification and cohesive agglomeration resulting in less number of voids and the materials ablation without dislodging of partially melted SiC particles. As the grit size was increased from 36 to 500, the density of the target formed by the powder compacting and subsequent sintering process was increased from 1.5 gm/cm^3 to 1.7 gm/cm^3 at the sintering temperature of 1600 °C. With the grit sizes of 600 and 800, the density was further increased from 1.7 gm/cm^3 to 1.8 gm/cm^3. Target densification and SiC agglomeration was also confirmed by SEM studies on sintered targets. Figs. 7(c) and 7(d) show SEM microphotographs of SiC thin deposited on a-cut sapphire substrates at different ambient pressure values of 2 Pa and 2×10^{-3} Pa. The droplet size was decreased with decrease in the ambient pressure. The film morphology was at 2×10^{-1} Pa was almost comparable to that when the ambient pressure was 2×10^{-3} Pa.

3.5 I-V Characteristics of P-N Diode

Forward and reverse I–V characteristic of the n-Si/SiC hetero-structure at room temperature is shown in Fig. 8. The Ohmic contacts were established in SiC with an Au electrode. Based on Fig. 8, a rectifying diode-like behavior with the cut-in voltage of 1.2 V was observed for SiC grit count of 400. However the film resistance was quite high (of MΩ order) and consistent Hall mobility depicting P-type characteristics was difficult to observe. This rectifying diode-like behaviour was attributed to the impurities in SiC

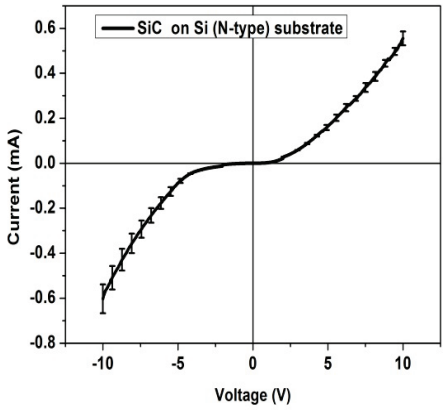

Fig. 8 Forward and reverse I-V characteristics are measured with SiC thin film on n-Si with the SiC grit count of 400.

films. Although from these data it can be seen that I–V characteristics of the structure was comparable to those of many other high-quality, wide-bandgap homojunction and hetero-junction devices [11–13], further improvements in terms of improved mobility and consistent I-V characteris-

tics are expected with appropriate doping and improving crystalline characteristics of SiC film.

4 Conclusion

Pulsed Nd^{3+}:YAG (355 nm) laser-assisted pulsed laser deposition technique was used for SiC thin film deposition of n-type c-Si substrate and a-cut sapphire substrate respectively. The XRD and Raman spectroscopy results showed the polycrystalline (combined 3C-SiC and 4H-SiC) nature of SiC thin film on different substrates. The XRD results of SiC grown on a-cut sapphire substrate show that with 800 Grit count, substrate temperature at 600 °C, chamber pressure of $2x10^{-3}$ Pa, polycrystalline nature of the film with a prominent crystalline peak corresponding to 4H-SiC(100) was attained. After furnace annealing the SiC thin film on a-cut sapphire substrate, the growth 3C-SiC(111) was also observed. The average SiC film deposition rate based on 60 minute duration was observed as 1.5 nm/min on c-Si substrate. With increase in the grit count of SiC the droplet formation was reduced significantly. Further, the number of droplets deposited on SiC thin film decreased with the decrease in the chamber pressure from 2 Pa to $2x10^{-2}$ Pa. The I-V characteristic of the SiC thin film on Si was similar to p-n diode characteristics. It is challenging to grow epitaxial layer of n-type ZnO on p-type SiC grown on a-cut sapphire substrate.

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