Growth of 3C-SiC Films on Si (111) and Sapphire (0001) Substrates by MOCVD

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Abstract
Thick silicon carbide films were grown on sapphire (0001) and silicon (111) substrates using metal organic chemical vapor deposition (MOCVD). Diethylmethylsilane (DEMS) has been used as a single precursor, which contain Si and C atoms in the same molecule, without any carrier or bubbler gas. Atomic structure, surface composition and morphology have been investigated by XRD, AES, SEM and AFM analysis. SiC films of 5-7 micron thickness were grown at a rate of ~ 40 nm/min on sapphire (0001) and Si (111) substrates. The films grown at low temperature (850 ºC and 900 ºC) on both substrates show crystalline 3C-SiC in the (111) orientation. XRD results show that the orientation of the crystal structure does not depend of the substrate orientation AFM pictures of SiC films grown on sapphire (0001) exhibit more crystalline order as compared to films grown on the Si (111) substrates. AES of the grown films shows that in both cases the Si peak intensity is greater than that of carbon. This work shows promise for the development of alternative processes for developing low cost, large area substrates for application to III-nitrides LED and UV photodetector fabrication and also for gas detector application.

Introduction
The motivation for the development of SiC based heterostructures is mainly supported and justified by the need for a new generation of devices which can work in very extreme conditions. Silicon carbide (SiC) is a wide bandgap semiconductor material with a high breakdown electric field, high saturated electron drift velocity, and high thermal conductivity that make the material suitable for electronic devices operating in extreme conditions of temperature and power [1-5]. In the field of high power devices, including high-speed electronics the greatest interest is for epitaxial structures based on silicon carbide. Microwave electronics applications focus on GaN/AlN/SiC structural compositions, whereas for optoelectronics the specific structure GaAlN/SiC, is of interests as it providing radiation in the UV region of the spectrum [6]. Recent work [7] has shown a new application for nanocrystalline 3C-SiC films as electrode material for electrochemistry and bioelectrochemistry. SiC wafer production on a commercial basis has led to the realization of many types of electronic and optoelectronic devices such as high brightness blue LEDs made from III-nitrides grown on SiC, and UV sensors and gas sensors for use in high-temperature environment. The benefits of SiC substrates for growth of group III-nitrides is the close lattice match of III-nitrides and SiC (Lebedev [8]); however, the main disadvantages of using SiC single crystal substrates are high cost and small wafer size. A possible solution of this problem is to grow heteroepitaxial silicon carbide thin films on low-cost substrates.

The more common method of SiC film growth is a chemical vapor deposition process (CVD) [9-11], with the source of silicon and carbon supplied by silane gas for silicon, and methane, propane, etc. as a carbon source. However, use of the noted separate gases not only involves toxicity of the silane, but also requires separate flow control of each, and the high decomposition temperatures of the gases makes this an energy-consuming method.
In this work SiC films were synthesized by metalorganic chemical vapor deposition (MOCVD) using a nontoxic single precursor. This method is quite direct as the transition from a complex organic molecule to a SiC film involves the decomposition of a single organometallic at low temperature on a heated substrate surface yielding layer by layer thin film growth, and under optimal conditions resulting in the growth of crystalline silicon carbide films.

**Experimental**

SiC thick films were grown on both sapphire (0001) and Si (111) substrates in a custom made vertical stainless-steel MOCVD chamber (Fig. 1). Films were synthesized using diethylmethylsilane (DEMS) as a single precursor without any carrier or bubbler gas. Use of a single precursor that contains directly bonded Si and C atoms in a ratio of 1:1, and that decomposes at low temperatures may be effective for SiC growth [12]. Si (111) and sapphire (0001) substrates 1.5 x 1.5 cm in size were prepared by chemical cleaning. The sapphire substrate was cleaned for 12 hours in xylene, and the Si (111) substrate was cleaned by immersing in n 80% KOH solution to remove the top oxide layer. After the cleaning, both substrates were washed in an ultrasonic cleaner in DI water, acetone and methanol, and blown dry with nitrogen gas to remove any remaining surface contaminants. The stainless-steel chamber was pumped by mechanical pump with a liquid nitrogen cooled trap. A high temperature boron nitride cup heater was mounted inside of the chamber for substrate heating. The DEMS precursor was loaded into a stainless steel bubbler, and was connected to the chamber by a stainless steel tube wrapped with heating tapes so as to eliminate precursor condensation on the walls of the tube. The temperature of heating tapes was controlled by a variable autotransformer, and was set at the precursor boiling point of 78 °C. Precursor gas flow was directed inside of the growth chamber to the hot substrate (850 and 900 °C) by a quartz nozzle shower head yielding near perpendicular flow of precursor toward the substrate. Precursor flow was controlled by needle valve so as to maintain a constant chamber pressure of 10-2 Torr. SiC films of 5-7 micron thickness were grown at a rate of ~ 40 nm/min on sapphire (0001) and Si (111) substrates.

**Characterization of SiC Thick Films**

SiC films grown on both Si (111) and sapphire (0001) substrates were characterized using several techniques. The surface morphology, thickness and interface structure of the grown films were studied by scanning electron microscopy (JEOL JSM 5410) and atomic force microscopy (PSIO XE-100). The crystallinity and orientation of the films was measured using a SIEMENS «D5000» X-ray diffractometer, with Cu Kα (λ = 1.5418 Å) radiation. Elemental analysis and the ratio of the chemical components of the grown films were investigated by Auger Electron Spectroscopy (AES).
Results and Discussions

SEM cross section images of SiC films were obtained by fracturing the samples grown on sapphire and Si (111) substrates and observing the fracture surface. The samples grown at 900 ºC temperature for a 90 min. deposition time are shown in Fig. 2. Figure 2(a) shows an SEM micrograph of a 5 micron thick-SiC film grown on the sapphire (0001) substrate where it can be seen that the SiC film has oriented structure (striations), and has a smooth surface morphology. Figure 2(b) shows a SEM micrograph of a SiC film deposited on Si (111) at the same parameters as the film deposited on sapphire. The film is 7 microns thick with a smooth surface and well delineated interfaces with no cracks or voids.

The surface morphologies of the grown 3C-SiC films were also studied by AFM. AFM scans of the SiC films grown on Si (111) (Fig. 3 (a)) and grown on sapphire (0001) (Fig. 3(b)) show that the SiC film on sapphire exhibits increased grain size as compared to the SiC film grown on Si. The surface roughness of the grown films is also shown in Fig. 3, and is approximately 25 nm for the SiC grown on sapphire and 45 nm for the SiC grown on Si (111).

The XRD technique was employed to verify the phase and the orientation of deposited SiC films as well as to their lattice parameter. Figures 4 and 5 show XRD spectra for SiC films deposited at 850 ºC and 900 ºC on Si (111) and on sapphire (0001) substrates respectively. An intense reflection peak of 3C-SiC (111) was observed at 2θ = 35.7º, indicating that the deposited β-SiC film has a single phase cubic structure on both Si 111 and sapphire 0001 substrates. Figures 4 and 5 clearly show the dependence
of the SiC peak intensity on deposition temperature with the higher deposition temperature (900 °C) growth exhibiting a stronger peak, and hence a more crystalline structure of the 3C-SiC film.

![XRD spectra of SiC thin films deposited (a) at 850 °C, and (b) at 900 °C on Si (111).](image1)

Fig. 4. XRD spectra of SiC thin films deposited (a) at 850 °C, and (b) at 900 °C on Si (111).

![XRD spectra of SiC thin films deposited at (a) 850 °C, and (b) at 900 °C on sapphire (0001).](image2)

Fig. 5. XRD spectra of SiC thin films deposited at (a) 850 °C, and (b) at 900 °C on sapphire (0001).

SiC thin films grown on Si and sapphire substrates were investigated by Auger electron spectroscopy to confirm the elemental composition and bonding states of the grown films. The surface of the samples was first cleaned by a 5 min, 3 kV energy argon ion bombardment since an air-exposed SiC surface has been shown to consist mainly of carbon and oxygen [13]. Figures 6 (a, b) and 7 (a, b) show the Auger spectra after ion bombardment cleaning of SiC films grown on sapphire and on silicon at 850 °C and 900 °C. It can be seen that in both cases the Si peak intensity is greater than that of carbon, as has been reported by Matsunami [3].

![Auger spectra of SiC films deposited at 850 °C (a) on sapphire and (b) on Si substrates after 5 min of sputtering.](image3)

Fig. 6. Auger spectra of SiC films deposited at 850 °C (a) on sapphire and (b) on Si substrates after 5 min of sputtering.
Conclusion

Good-quality crystalline 5-7 micron thick films of 3C-SiC were grown on Si (111) and sapphire (0001) substrates using DEMS as the single precursor without any carrier gas. Optimal growth parameters were found for the MOCVD chamber at 900 °C, growth pressure of 10-2 Torr, and growth rate of 40 nm/min. XRD indicated the films were grown along the [111] direction as crystalline 3C-SiC. SEM and AFM scans show that the grown films have a smooth surface with no voids or cracks at the interface. However, the films grown on sapphire show a larger grain size than those grown on silicon implying improved crystalline quality of the films grown on sapphire. AES showed that after removal of surface contaminants by ion bombardment the silicon to carbon peak ratio is higher than that for stoichiometric SiC indicating that under MOCVD at high substrate temperatures, some loss of carbon may occur.

References

1. H. Abderrazak and E. Selmane B.H. Hmida. Silicon Carbide: Synthesis and Properties, Properties and Applications of Silicon Carbide, edited by Prof. Rosario Gerhardt, pp. 361-388.
2. Masri P. Silicon carbide and silicon carbide-based structures, the physics of epitaxy. Surface Science Reports 48 (2002), pp. 1-51.
3. J.A. Cooper, Jr. Silicon Carbide, edited by W. J. Choyke H. Matsunami, and G. Pensl (Akademie, Berlin, 1997), Vol. II, p. 305.
4. Matsunami H. Progress in epitaxial growth of SiC and its electronic devices. J. of the Korean physical society. Vol. 30, pp. S186 - S190.
5. Park K.S., Kimoto T., Matsunami H. High quantum-efficiency 4H-SiC UV photodiode. J. of the Korean physical society. 1997, Vol. 30, Issue 1, pp. 123-130.
6. B. Luchinin, Yu. Tairov. Silicon Carbide - Diamond-like material. NANOINDUSTRY 2010, Issue 1, pp. 36.
7. N. Yang, H. Zhuang, R. Hoffmann, W. Smirnov, J. Hees, X. Jiang, C.E. Nebel. Electrochemistry of Nanocrystalline 3C Silicon Carbide Films. Chemistry - A European Journal (2012), Vol. 18, Issue 21, pp. 6514-6519.
8. Lebedev A.A. Evergreen semiconductor. Chemistry and Life, № 4, 2006, pp. 14-19.
9. F. Shariatmadar Tehrani, M.R. Badaruddin, R.G. Rahbari, M.R. Muhamad, S.A. Rahman. Low-pressure synthesis and characterization of multiphase SiC by HWCVD using CH4/SiH4. Vacuum, Vol. 86, 2012, pp. 1150-1154.
10. Okui Y., Jacob C., Ohshima S., Nishino, S. Selective epitaxial growth of pyramidal 3C-SiC on patterned Si substrate. Silicon carbide and related materials 2001, pts 1 and 2, proceedings, 2002, MATERIALS SCIENCE FORUM, Vol. 389-3, pp. 331-334.
11. S. Nishino, J.A. Powell and H.A. Will. Production of large-area single-crystal wafers of cubic SiC for semiconductor devices. Appl. Phys. Lett., 1983, Vol. 42, pp. 460.
12. J.-S. Hyun, S.-H. Nam, B.-C. Kang, J.-H. Park, and J.-H. Boo. Growth of 3C-SiC nanowires on nickel coated Si (100) substrate using dichloromethylvinylsilane and diethylmethylsilane by MOCVD method. J. of Nanoscience and Nanotechnology, 2008, Vol. 8, 5581-5585.
13. Y.M. Lei, Y.H. Yu, L.L. Cheng, C.X. Ren, S.C. Zou. Auger electron spectroscopy study of SiC thin films deposited on silicon. Vacuum, Vol. 58, 2000, pp. 602-608.

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