

Bias enhanced deposition of highly oriented β -SiC thin films using low pressure hot filament chemical vapour deposition technique

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Abstract

Highly oriented cubic silicon carbide (β -SiC) thin films are deposited on Si(111) substrates using bias assisted low-pressure hot filament chemical vapour deposition technique. Methane (CH_4) is used as the source for carbon, while the substrate itself acts as the source for silicon. The technique is quite simple, cheap, has one step, and requires no stringent reaction conditions; the substrate temperature used being in the range of $\sim 750^\circ\text{C}$ and the chamber pressure ~ 1 torr. The films have been characterised by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and Raman spectroscopy. Bombardment of negatively biased substrate by high-energy positive ions under relatively low chamber pressure is believed to facilitate the growth of highly oriented SiC films.

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1. Introduction

Because of its numerous outstanding properties [1–3], crystalline silicon carbide (SiC) is being considered as a promising wide band gap semiconductor material. It is potentially suitable to be used for electronic devices, capable of operation at high power levels, high temperatures and hostile environments where the efficiency of the conventional Si-based devices is seriously limited. Of more than 130 polytypes of SiC, differing only in the stacking sequence of tetrahedrally bonded SiC bilayers [4], β -SiC, with the energy gap of 2.2 eV and relatively high electron mobility, in particular, appears very promising. The material is required in the form of thin films for certain specific purposes. For instance the SiC layer on Si has proved to be a much better substrate material for hetero-epitaxial growth of GaN [5] and it has helped to grow smooth and continuous diamond film of thickness less than $6\ \mu\text{m}$, which is the smallest reported value in hetero-epitaxial diamond [6]. On oxi-

dation, the film is covered with a silicon dioxide (SiO_2) passivating layer and this is an important consideration for device fabrication. However, certain technological problems need to be addressed. The greatest hurdle in controlling the epitaxy of SiC on Si wafers has been the large mismatch ($\sim 20\%$) between the lattice constants for β -SiC ($4.359\ \text{\AA}$ at room temperature) and Si ($5.430\ \text{\AA}$ at room temperature). There are several reports on the successful deposition of amorphous/polycrystalline Si-C films by a variety of techniques, e.g. RF glow discharge decomposition [7], electron beam evaporation, thermal/plasma-assisted chemical vapour deposition [8–12], pulsed laser ablation and ion beam reactions [13]. The techniques used so far are generally expensive, involve complicated equipment and require very stringent reaction conditions such as high temperatures, ultra high vacuum, single/multiple precursors and multi step processing. In contrast, we report here a fairly simple, cheap, easy to operate and single step process for the preparation of highly oriented β -SiC thin films on silicon single crystal substrates using a bias-assisted low-pressure chemical vapour deposition (BALPCVD) technique. Our method has CH_4 as the carbon source, a

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substrate temperature of ~ 750 °C and a chamber pressure of ~ 1 torr.

2. Experimental details

Single crystal silicon wafers with crystal orientation (111) obtained from Wacker-Chemitronic GmbH are used as substrates. These are sonicated in tri-chloroethylene, acetone and isopropyl alcohol, then subjected to etching for 2 min in 40% HF and finally a rinse in de-ionised water. A BALPHFCVD facility [14] is used for film deposition directly on the above substrates without any further treatment. CH_4 and hydrogen (H_2) are used as feed gases, while the substrate itself acts as the source for silicon. The optimised deposition parameters are given in Table 1. After deposition the samples have been taken out of the coating system and characterised *ex situ*.

XRD patterns are recorded in a Philips X-ray diffractometer PW 1710 using $\text{CuK}\alpha$ line from an X-ray generator operated at 30 kV and 20 mA. For AFM topography, a Park Digital Instrument is used in contact mode employing silicon nitride tips. FTIR measurements are done in a Bomem model DA-8 instrument with resolution of 2 cm^{-1} . Raman spectra are recorded using LABRAM-1 spectrometer (ISA make) in a back scattering geometry and a spectral resolution of 2 cm^{-1} .

3. Results and discussion

Fig. 1 shows the XRD pattern of a typical SiC film grown on Si(111) substrate. The pattern normally contains a sharp and intense peak of Si(111) occurring at $2\theta = 28.5^\circ$ together with rather weak peaks of β -SiC. The former arises since the thickness of the deposited film is not large enough to block the signal from the substrate. To give a better representation to the signals from thin β -SiC film, the silicon region has been purposefully excluded in Fig. 1. Occurrence of peaks at $2\theta = 35.6^\circ$ and 76° , respectively, correspond to (111)

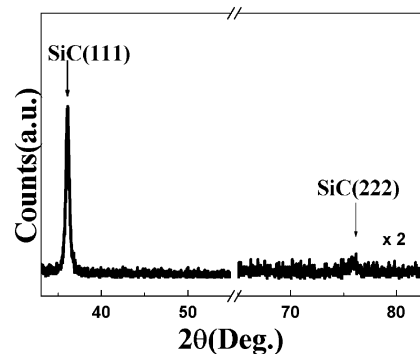


Fig. 1. Typical X-ray diffraction pattern of the deposit on Si(111) substrate excluding the Si(111) region. SiC(222) region is shown after multiplying by 2 for a better presentation.

and (222) planes of cubic SiC. The absence of diffraction lines, from planes other than (111) or its higher orders, clearly indicates that SiC crystallites are oriented along the (111) planes. To confirm the presence of SiC, FTIR transmission spectra are recorded in the wave number region of $400\text{--}4000\text{ cm}^{-1}$. The spectrum was duly corrected to eliminate lines originating from the silicon substrate itself. The corrected spectrum (Fig. 2) clearly exhibits a very intense peak at $\sim 800\text{ cm}^{-1}$, attributed to the TO (Γ) phonon modes of Si–C bonds in $-\text{SiC}$ [9]. The absence of Si–H and C–H stretching vibrations, reported to occur at 2100 cm^{-1} and 2900 cm^{-1} , respectively, is worth noting. The Raman spectrum of the sample has also been recorded in the range of $400\text{--}2000\text{ cm}^{-1}$ (Fig. 3). It shows two distinct peaks at $\sim 790\text{ cm}^{-1}$ and 970 cm^{-1} . These peaks correspond, respectively, to the transverse and longitudinal optical phonons of cubic silicon carbide [9], thereby confirming its presence. Fig. 4 shows a set of main core level Si2p, C1s and O1s XPS spectra for a typical film. The spectra are neither normalised nor compensated for atomic

Table 1
Deposition parameters used for sample preparation

Parameters	Optimised values	Measuring probe
Base pressure	10^{-5} torr	Discharge gauge
Working pressure	0.8 torr	Strain gauge
CH_4 flow rate	1 sccm	Mass flow controller
H_2 flow rate	50 sccm	Mass flow controller
Filament	W coil (wire diameter: 0.5 mm)	
Filament temperature	1950 °C	2C Optical pyrometer
Substrate	Si(111) wafer	
Substrate temperature	~ 750 °C	Pt, Pt-14% Rh thermocouple
Filament–substrate distance	~ 6 mm	
Substrate bias	-350 V	
Bias current	~ 4 mA	
Deposition time	20 min	
Deposition rate	~ 20 nm/min	

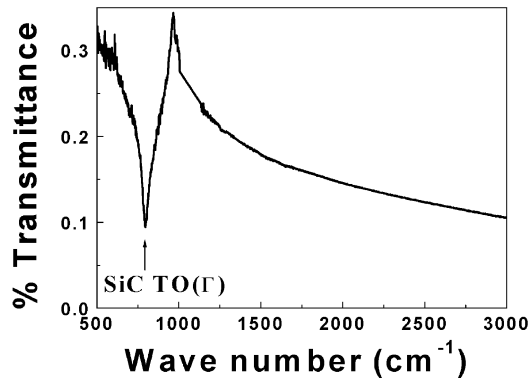


Fig. 2. Transmission FTIR spectrum of a typical coating on Si(111) substrate.

sensitivity factor of the respective elements. On deconvolution of Si2p spectra, two main components corresponding respectively, to a Si–C bond in SiC at ~ 101.2 eV and a Si–O bond in silicon oxide/silicon oxy carbide at ~ 102.5 eV are observed [13]. The oxide/oxy carbide phase might have been formed on the surface of the film on being exposed to the atmosphere before analysis [15]. The C1s spectra could be resolved into three major components related to a C–Si bond in SiC at ~ 283.2 eV, C–C at ~ 284.7 eV and a C–O bond at 286.4 eV. The peak at ~ 284.7 eV might have originated from adventitious carbon or from the carbonaceous impurities co-deposited along with SiC phase. The O1s spectrum comprises of an intense peak at ~ 532.6 eV corresponding to a O–Si bond in silicon oxide/silicon oxy carbide and a small feature at ~ 533.8 eV due to an O–C bond.

Fig. 5 shows the AFM topography of a typical ~ 3 – 4 - μm -thick SiC film wherein highly oriented, crystals with well-delineated edges and faces and having an average size of 0.5 μm are clearly visible. Their number

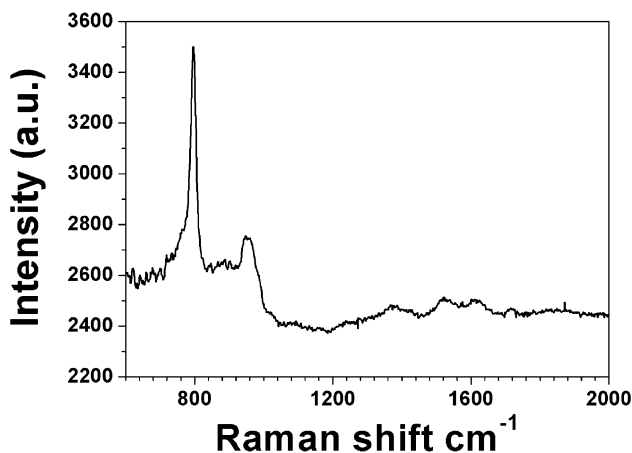


Fig. 3. Raman spectrum of a typical coating on Si(111) substrate.

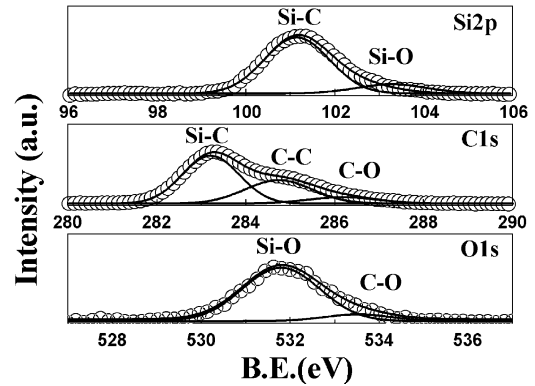


Fig. 4. Main core levels Si2p, C1s, and O1s XPS spectra, along with its deconvolution, of a typical film grown on Si(111) substrate.

density is $\sim 10^8/\text{cm}^2$. The average roughness of the films is ~ 30 nm.

Thus, it is clear that BALPHFCVD technique is able to deposit, under appropriate conditions, highly oriented β -SiC films on a Si single crystal substrate. Application of bias results in the bombardment of the substrate and the growing film by high-energy positive ions. This in turn results in the increase in kinetic energy as well as mobility of the adsorbed atoms and/or their aggregates and possibly leading to their sub-implantation into the substrate. It has indeed been predicted from theoretical calculations involving ion beam analysis using TRIM software [16] that the penetration depth of carbon atom with an energy of ~ 0.35 keV in silicon substrate can be as large as 4 nm. Moreover, due to temperature effect carbon can diffuse even more. However, the low pressure (~ 1 torr) used in the present experiment, corresponds to the mean free path of the precursor species that is comparable with the distance between the filament and the substrate. This ensures that a larger number

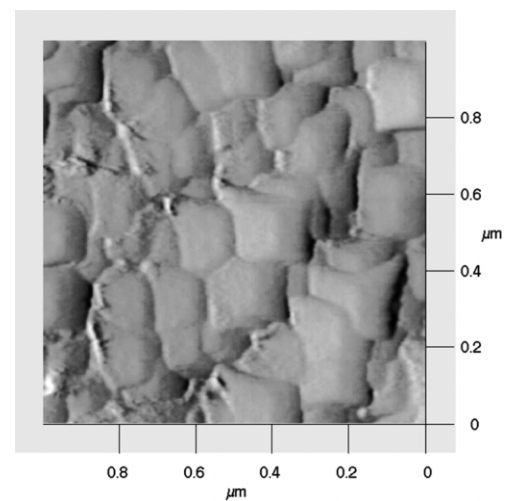


Fig. 5. AFM topography of a typical film. Its RMS roughness value is ~ 26 nm.

of high-energy precursor species reach the substrate before actually getting lost by collision and thus increasing the chance of their aggregation which in turn improves nucleation, facilitating the formation of the highly oriented SiC layer. However, it should be borne in mind, that films of very large thickness could not be made using this technique because of the strain developed due to large lattice mismatch. Nevertheless, it is possible to deposit films of $\sim 3\text{--}4\ \mu\text{m}$ without their getting delaminated. Further, it may be very interesting to note that the crystallites are oriented along (111) planes, which is similar to that of the substrate.

It is worthwhile to compare the results of the present investigation with other reports which describe successful deposition of amorphous/polycrystalline SiC films. Most of the CVD techniques invariably used a separate Si-bearing precursor either in the form of silane or chlorosilane, which are both toxic and pyrophoric [12]. However, a modified synthetic route has been suggested by Madapura and the group using a single source organosilane precursors, such as trimethylsilane [11] and silacyclobutane [12]. The substrate temperatures used in the former case were $1000\text{--}1200\ ^\circ\text{C}$ and in the latter case $\sim 900\ ^\circ\text{C}$ and they obtained high growth rates. However, mostly the substrates used by them have been precarbonised silicon thereby making the method, overall, a multi-step process involving carbonisation of the substrate at $\sim 1300\ ^\circ\text{C}$ as a separate step. Henke et al. [17], however, have reported the synthesis of epitaxial $\beta\text{-SiC}$ films by depositing C_{60} in ultrahigh vacuum on silicon at $800\text{--}900\ ^\circ\text{C}$. They could obtain films up to $1\ \mu\text{m}$ thick with a deposition time varying from 5 to 15 h. Similarly, there is a report by Elchhorn et al. [18], who have tried to form SiC by carbon ion implantation in to silicon. However, in their case, depending on the choice of implantation conditions and/or annealing temperature, they get three groups of crystallites with different orientation relative to the silicon matrix. In contrast to all these methods, our procedure is rather simple, involves a single step and the substrate temperature used is rather low, $\sim 750\ ^\circ\text{C}$, being amongst the lowest reported values. Further, to the best of our knowledge, there is no report on the use of bias exclusively for the deposition of SiC as is done in the present case.

4. Conclusions

We have described a rather simple, cheap, and easy to operate single step process for preparation of highly oriented $\beta\text{-SiC}$ films on silicon single crystal substrate.

It neither uses any toxic Si-bearing precursor gas nor requires stringent reaction conditions; the substrate temperature is $\sim 750\ ^\circ\text{C}$ with a chamber pressure ~ 1 torr. Bombardment of negatively biased substrate and/or the growing film by high energy positive ions, under relatively low chamber pressure, is believed to facilitate the growth of highly oriented $\beta\text{-SiC}$ films by a combination of surface and sub-surface processes.

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