

Chemically active plasmas for deterministic assembly of nanocrystalline SiC film

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Abstract

Silicon carbide thin films are self-assembled onto crystalline silicon substrate from a sintered SiC target at low substrate temperature of 400 °C in Ar + H₂ discharge using inductively coupled plasma (ICP) assisted RF magnetron sputtering system. Surface morphology and structural properties of SiC films are investigated by SEM, XRD, FTIR and EDX. SEM, XRD and FTIR results show that the SiC film deposited at an ICP power of 800 W is 3C-SiC nanocrystalline film while the film deposited without ICP power exhibits an amorphous structure. At ICP power of 800 W, there exists a large amount of dissociated H in the plasma, leading to the structural relaxation of the amorphous network towards the crystalline state. The EDX result shows that elemental compositions of Si and C atoms in both the films are almost stoichiometric.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

During the past decades, nanostructured semiconductor materials have been extensively studied due to their unique physical and optical properties that pave the way for promising applications in microelectronic and optoelectronic devices [1–3]. With its wide band gap (3 eV), excellent thermal conductivity (2.5 times that of Si), highly breakdown field strength (10 times that of Si), high saturated electron drift velocity (2 times that of Si) and large bonding energy (451.5 KJ mol⁻¹), SiC offers great applications in electronics and optoelectronics operating at high temperatures, high voltage, high frequency and high power levels, chemically hostile environment.

It is well known that high-quality SiC has so far been prepared at high substrate temperature, i.e. above 1000 °C [4]. Owing to the lattice mismatch (20%) and the difference in the thermal expansion coefficient (8%) between SiC and

Si, it is quite possible that high density of defects may be formed at the SiC/Si interface particularly when the processing temperatures are very high. Therefore, a low temperature deposition technique is desirable from the view point of widening its application to devices such as solar cells and thin film transistors. In this work, we report on the role of chemically active plasmas for deterministic assembly [5] of nanocrystalline SiC film at a low substrate temperature of 400 °C.

2. Experimental details

SiC films are deposited by a low frequency inductively coupled plasma (ICP) assisted RF magnetron sputtering in Ar + H₂ discharges [6, 7]. The schematic diagram of the system in this experiment is shown in figure 1. In this unconventional magnetron sputtering process, the plasma production and the sputtering processes can be controlled separately so that the deterministic assembly of nanostructures

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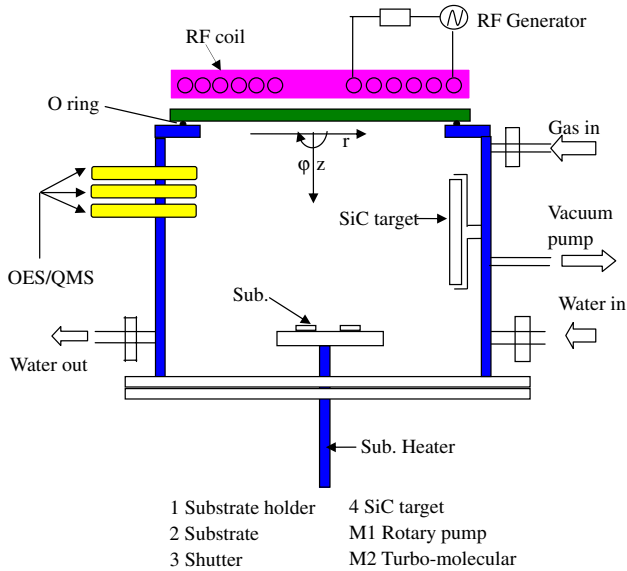


Figure 1. Schematic of ICP assisted RF magnetron sputtering deposition system.

is realized by manipulating plasma parameters and processing conditions.

The chamber is made of stainless steel in the shape of a cylinder with a diameter of 450 mm and a height of 300 mm. The top cover is a quartz plate with a thickness of 1.25 cm. ICP power (460 KHz) is transferred across the quartz into the chamber to generate and maintain the discharge. A 12 cm in diameter, high purity sintered SiC target (Si:C = 1:1) is located on the RF powered (13.56 MHz) electrode. A circular substrate holder is located at 20 cm horizontally from the target. A heater is attached to the bottom of the substrate holder to provide a suitable temperature for film growth. A series of rotary and turbo-molecular pumps are used to achieve a base pressure of $\sim 10^{-4}$ Pa. Thereafter, high purity argon (30 sccm) and hydrogen (30 sccm) gas mixtures that can act as both reactive and sputtering gases were introduced into the chamber via a D08-2C/ZM mass flow controller. A p-type silicon wafer with resistivity of 8–12 Ω cm and (1 0 0) orientation is used as the substrate for the deposition of SiC films. Prior to deposition, RCA cleaning was used to remove impurities from the silicon surface, and a 10% hydrofluoric acid was used to remove the native oxide on the wafer surface. The wafer was then rinsed in deionized water and dried in a nitrogen ambient.

A comprehensive study of the plasma production and growth process was undertaken. By connecting *in situ* parametric measurement of the radical and none radicals as well as ionized and excited species and *ex situ* film property analysis, two growth conditions were selected to verify the influence of radicals via application of an ICP power. Both samples were deposited onto silicon substrate with target power of 160 W, Ar flow rate 30 sccm, H₂ flow rate 30 sccm, working pressure 1.2 Pa, substrate temperature 400 °C and deposition time 60 min. The first sample was deposited with no ICP power while the second sample was with ICP power of 800 W. The two ICP powers represent quite different radical production processes. On the application of ICP power, a high density electromagnetic mode plasma was

generated. The quadruple mass spectrometer and optical emission spectroscopy showed that energetic plasma electrons impacting on hydrogen molecules created a remarkable amount of hydrogen radicals. The electrons followed a Druyvesteyn-like distribution. The non-neutral radicals, on the other hand, were mainly singly ionized ions.

The surface morphology of SiC QDs is observed using a JEOL JSM-6700F field emission scanning electron microscope (FESEM). X-ray diffraction is performed using the vertical Siemens D5005 x-ray diffractometer. The diffraction is excited by Cu K α radiation (wavelength of 1.54 Å) at 40 kV and 40 mA. The angle between the incident x-ray and the surface of the film is fixed at 1°, and the diffraction pattern is obtained by changing the position of the counter. The infrared (IR) absorption spectra have been investigated by a Perkin-Elmer FTIR 1725X spectrometer in the mid-IR from 400 to 4000 cm⁻¹. The spectrometer has a resolution of 4 cm⁻¹. The elemental compositional study is carried out using an Oxford Instruments EDX INCA spectrometer coupled to a JEOL JSM-6700F FESEM.

3. Results and discussion

Figure 2 shows the surface morphology of two typical samples synthesized at different ICP powers. Figure 2(a) depicts the morphology of a sample fabricated without ICP power. It is seen that the film consists of uniform SiC nanodots with the average size of particle around 18 nm. The structural analysis reveals that this film is amorphous. However, for a sample deposited at an ICP power of 800 W shown in figure 2(b), the film features uniform nanocrystalline SiC particles with the average size of around 3 nm. High concentration of atomic hydrogen dissociated via electron impacting on hydrogen molecules effectively removed the amorphous phase and passivated the surface of the film.

In order to confirm that SiC nanocrystal is indeed successfully deposited onto silicon substrate at low substrate temperature with the help of ICP power (800 W), XRD and FTIR measurements were undertaken on these two samples. Figure 3 shows the XRD spectra of sample 1 and sample 2. For sample 1, no XRD peak is observed, revealing that the film deposited at an ICP power of 0 W is amorphous. On the other hand, the film deposited at an ICP power of 800 W shows one diffraction peak at $2\theta = 35.7^\circ$, which corresponds to (1 1 1) of 3C-SiC [8,9]. This indicates that the film deposited at ICP power of 800 W includes 3C-SiC nanocrystallites. The mean crystallite size, estimated from Scherrer's formula ($B = 0.9\lambda/d \cos\theta$) is about 3 nm, which is consistent with the average nanoparticle size measured by SEM. Figure 4 shows the IR absorption spectra of the two samples. From the inset of figure 4, we can see obviously that the absorption peak due to Si-C bond shifts from 784 cm⁻¹ to 800 cm⁻¹ and the band shape evolves from a Gaussian to Lorentzian with the increase in ICP power from 0 to 800 W. While the Gaussian peak signifies a broad distribution of the bond lengths and bond angles characterizing the amorphous state, the Lorentzian peak represents a narrow spreading of the bond length and low distortion of the bond angle corresponding to a crystalline state. Si-C bond peak shift and further evolution confirms that SiC crystalline grains are deposited at low substrate temperature

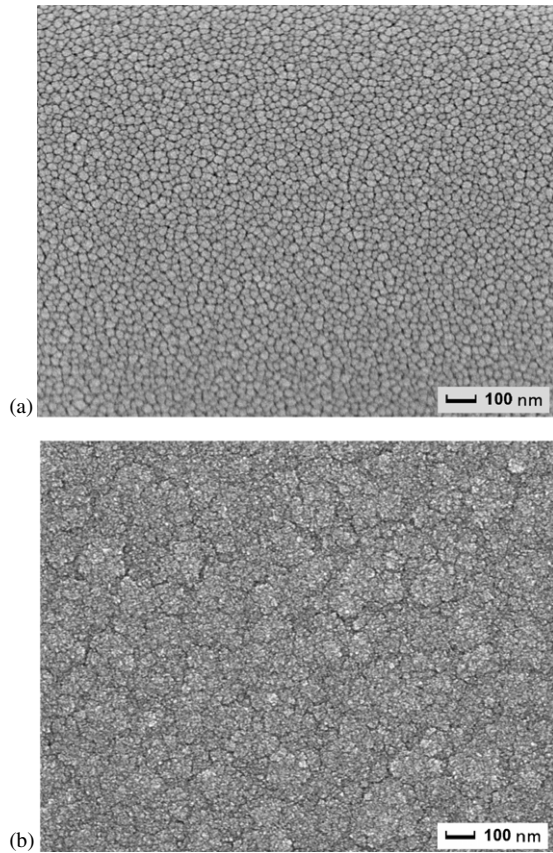


Figure 2. SEM images of SiC film deposited at ICP power of 0 W and 800 W, respectively. (a) ICP power = 0 W, average size of particle = 18 nm; (b) ICP power = 800 W, average size of particle = 3 nm.

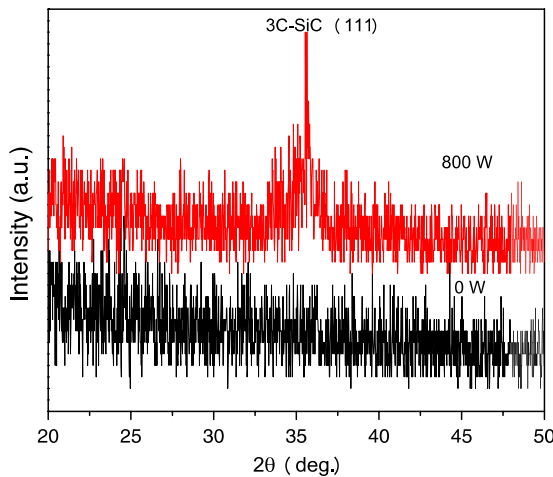


Figure 3. XRD spectra of sample 1 and 2 deposited at ICP power of 0 W and 800 W, respectively.

of 400 °C at the ICP power of 800 W [10, 11]. Additionally, the peaks at around 2090 cm⁻¹ are attributed to Si–H bonds (a shift of the Si–H stretching mode from 2000 to 2090 cm⁻¹ is caused by the electronegativity difference between the nearest neighbouring atoms in the network structure, which results from the substitution of silicon by carbon in the nearest

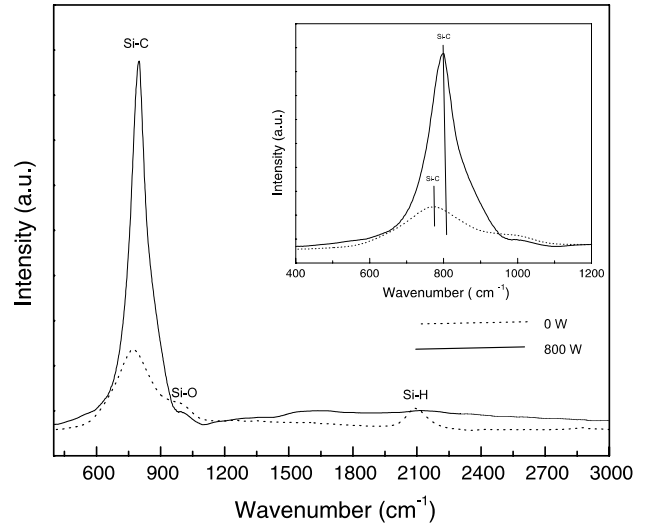


Figure 4. FTIR absorption spectra of sample 1 and 2 deposited at ICP power of 0 W and 800 W, respectively.

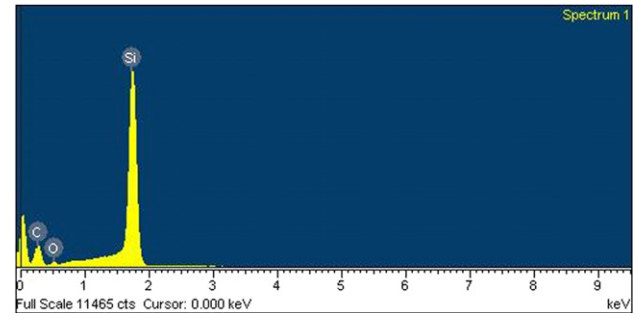


Figure 5. EDX spectra of sample 2 deposited at ICP power of 800 W.

environment of the Si–H bond [12]) and a shoulder peak observed at around 1025 cm⁻¹ is most probably corresponding to the asymmetric stretching mode of O in Si–O–Si due to amorphous silicon dioxide (SiO₂).

Figure 5 shows the EDX spectra of sample 2 deposited at ICP power of 800 W. The spectra shown in figure 5 indicate three distinctive peaks confirming the presence of Si, C and O in the SiC film. Elemental compositions obtained from the spectra are 51.97% silicon, 45.50% carbon and 2.53% oxygen. The existence of oxygen in the sample could come from two sources: the environmental O₂ in the air and the residual O in the growth chamber. It should be pointed out, however, there is only a small shoulder Si–O peak in the FTIR spectra in figure 4. The elemental compositions for sample 1 deposited without ICP power have almost the same atomic percentage.

Now we discuss the mechanism of fabricating 3C–SiC nanocrystallites at low substrate temperature of 400 °C in our ICP assisted RF magnetron sputtering deposition system. It is generally believed that there exist two competing processes in RF sputtering synthesis of hydrogenated silicon carbide in argon plus hydrogen plasma: (i) the sticking and surface diffusion of highly reactive Si-based and C-based radicals ; and (ii) the selective etching of weak or strained near-surface bonds (such as sp² C and stressed sp³ C or Si bonds) by

hydrogen [10, 13]. ICP is an ideal source for production of high density plasma, which can obtain a factor of 10–100 times higher than that for capacitive discharge [14]. High plasma density characteristic of ICP in argon plus hydrogen at an ICP power of 800 W for sample 2 results in a large amount of dissociated H existing in the plasma [15, 16], compared with sample 1 without ICP power. A large amount of dissociated H in the plasma makes the etching role of hydrogen obvious, which leads to the structural relaxation of the amorphous network towards the crystalline state for sample 2.

4. Conclusion

In this work, we have proposed an innovative deposition system to fabricate nanocrystalline silicon carbide at low substrate temperature of 400 °C. Using two selected samples, we have convincingly demonstrated that the high plasma density characteristic of ICP in argon plus hydrogen is responsible for obtaining 3C–SiC nanocrystallites at low substrate temperature. The elemental compositions of SiC film are almost stoichiometric. Finally, SEM, FTIR and XRD analysis confirmed our finding.

Acknowledgments

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