Effects of plasma hydrogenation on low temperature growth of nanocrystalline cubic SiC thin films

M. Wang, A.P. Huang, Paul K. Chu, B. Wang, H. Yan

Abstract

The effects of plasma hydrogenation on the fabrication of nanocrystalline cubic silicon carbide (SiC) thin films on Si (100) are investigated. Our results indicate that plasma hydrogenation is an effective method to reduce the deposition temperature and to improve the composition and microstructure of the cubic SiC (β-SiC) thin films. In particular, the crystal particle size and the oxygen diffusion can be controlled. The mechanism is discussed.

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PACS: 81.05.Hd; 68.55.-a; 81.15.Gh

Keywords: SiC; PECVD; Plasma hydrogenation; Film

1. Introduction

Silicon carbide (SiC) is considered one of the alternative power semiconductor materials due to its excellent properties such as wide bandgap, high breakdown field, and high thermal conductivity [1,2]. Another property of SiC is its poly-types. 3C–SiC (β-SiC), which has cubic crystal structure, is suitable for high-frequency power devices on account of its high electron mobility and electron saturation velocity. The limited leakage current as a result of the larger bandgap of β-SiC than Si is an important property in bipolar transistors, solar cells, photodiodes and phototransistors [3,4]. Various techniques have been utilized to deposit β-SiC thin films, and chemical vapor deposition (CVD) is one of the simple methods that may produce high-quality β-SiC thin films [5]. Plasma-enhanced chemical vapor deposition (PECVD) is a versatile and well-established technology. The technique offers the possibility to fabricate new structures and to change the properties associated with the microstructure of the thin films by altering the synthesis parameters [6]. However, SiC thin films are typically synthesized by PECVD at high temperature, and the high deposition temperature may cause autodoping, redistribution of dopants in the Si substrate, high tensile stress, and lattice defects [7]. Generally, enhancing the activity of the precursors is a possible way to reduce the substrate temperature.

In the work reported here, β-SiC thin films were fabricated by plasma hydrogenation on Si (100) substrates at lower substrate temperature in a PECVD system, and the effects of plasma hydrogenation on the growth of nanocrystalline cubic SiC thin films were investigated in details. Our results indicate that plasma hydrogenation can reduce the deposition temperature while improving the composition and microstructure of the β-SiC thin films, particularly the crystal particle size and the oxygen diffusion.

2. Experimental details

SiC thin films were fabricated on n-type, 100 mm Si (100) wafers with resistivity of 4–7 Ω cm using a plasma-enhanced chemical vapor deposition (PECVD) system equipped with a radio frequency (RF) source operated at a frequency of 13.56 MHz and power of 200 W. Prior to deposition, the wafers were etched in situ using hydrogen plasma for 10 min at 900 °C to eliminate surface oxygen. CH₄ (99.999%) and SiH₄ (99.999%) were used as the precursors and H₂ (99.999%) was used as the carrier gas. The substrate temperature was...
500 °C, which is rather low compared to that used in conventional PECVD to deposit polycrystalline SiC thin films PECVD [7]. The substrate temperature that was controlled by means of a heater assembly mounted below the stainless steel substrate holder was measured by a chromel–alumel thermocouple attached to the backside of Si substrates. The important instrumental conditions are summarized in Table 1.

Rutherford backscattering spectrometry (RBS) was carried out using a 2 MeV 4He++ beam and a backscattering angle of 170° to determine the composition as well as the thickness of the thin films. Microstructural analyses were carried out using a Xian Fourier transform infrared (FTIR) spectrometer and Philips X-ray diffractometer in a θ − 2θ configuration and Cu Kα radiation. The thickness of the as-deposited SiC thin films was measured by a Seimitzu Surfcom 480A profiler and the surface morphology was evaluated by contact-mode atomic force microscopy (AFM). Si, C and O bonding information was acquired using X-ray photoelectron spectroscopy (XPS) employing monochromatic Al Kα radiation. Prior to the XPS analyses, the sample surface was cleaned by 4 keV Ar ion bombardment for 1 min to remove atmospheric contaminants.

3. Results and discussion

Fig. 1 shows the Fourier transform infrared (FTIR) spectra of the SiC thin films deposited using different hydrogen ratios. An absorption peak at about 800 cm⁻¹ can be readily observed. It is well known that the characteristic vibration frequency of Si–C bonds for the TO mode is around 796 cm⁻¹ in cubic silicon carbide (β-SiC) [8]. The formation of Si–C bonds in the thin films is thus revealed in spite of a small shift toward a higher wavenumber. This can be attributed to a decrease in the length of the Si–C bonds as there is compressive strain possibly associated with the formation of nano-structures in the thin films. At a lower hydrogen ratio or no hydrogen addition, another salient absorption peak can be observed at about 1020 cm⁻¹, which corresponds to the characteristic vibration frequency of Si–O [9]. As the hydrogen content increases in the plasma, the Si–O absorption peak intensity diminishes abruptly, and when the gas ratio reaches 3:3:100, the Si–O absorption peak almost disappears as shown in Fig. 1. It clearly indicates that plasma hydrogenation suppresses the formation of Si–O during the fabrication of SiC thin films. However, as the hydrogen ratio further increases, a weak absorption peak at the 670 cm⁻¹ which originates from amorphous SiC [10] can be observed as shown in Fig. 1(e). It is believed to be due to increased H adsorption onto the surface at a higher H₂ gas ratio thereby influencing the continuous growth and inducing the amorphous SiC phase in the thin films. Hence, suitable plasma hydrogenation conditions are necessary to suppress oxygen diffusion and formation of the amorphous phase during the growth of SiC.

Fig. 2 displays the RBS spectra that contain both the experimental and fitted results acquired from the samples produced by different hydrogen ratios corresponding to the FTIR spectra (a) and (d) in Fig. 1. Only Si and C are observed in the thin film fabricated using condition (d) and that the composition of the thin film is basically uniform throughout the thickness. Furthermore, the Si to C ratio is close to 1 suggesting the formation of SiC as shown in Fig. 2(d). On the other hand, very little O can be detected and the Si to C ratio is smaller than 1 in the sample deposited without hydrogen, which is consistent with the FTIR results. It further corroborates that plasma hydrogenation can suppress oxygen diffusion during the deposition of SiC by PECVD. According to the deconvoluted RBS data of Fig. 2(a), excessive carbon is detected which may

<table>
<thead>
<tr>
<th>Sample</th>
<th>Base vacuum (Pa)</th>
<th>Working pressure (Pa)</th>
<th>Temperature (°C)</th>
<th>RF power (W)</th>
<th>Deposited time (h)</th>
<th>Gas ratio (CH₄:SiH₄:H₂)</th>
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<tr>
<td>(a)</td>
<td>3.0 × 10⁻³</td>
<td>20</td>
<td>500</td>
<td>200</td>
<td>2</td>
<td>3:3:0</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>3:3:30</td>
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<tr>
<td>(c)</td>
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<td>3:3:50</td>
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<tr>
<td>(d)</td>
<td></td>
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<td>(e)</td>
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<td>3:3:150</td>
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Fig. 1. FTIR spectra of SiC thin films prepared with different hydrogen ratios.

Fig. 2. RBS spectra acquired from the SiC thin films deposited at 500° C with different hydrogen ratios: (a) without H₂ and (d) CH₄:SiH₄: H₂=3:3:100.
be due to the different diffusion rates of Si and C in the absence of hydrogen. A small amount of C–C can form leading to amorphous carbon in the thin films. To further fathom the effects of plasma hydrogenation on the composition of the SiC thin films, the elemental concentrations and Si and C bonding information were determined by XPS. Prior to the analysis, the sample surface was cleaned by 4 keV Ar ion bombardment for 1 min to remove atmospheric contaminants. The XPS results show that the Si to C ratio in the thin film produced under suitable plasma hydrogenation conditions is nearly stoichiometric. It is in agreement with the RBS results. However, the thin film has excessive carbon and a small amount of oxygen can be detected from the sample prepared without hydrogen. Fig. 3 depicts the Si2p and C1s core level XPS spectra which exhibit apparent asymmetry. The best Gaussian fit of the Si2p spectrum acquired from the sample without plasma hydrogenation shows two peaks located around 100.8 eV and 101.9 eV. The former corresponds to the Si2p binding energy of SiC and the latter is that of SiO\(_x\) [11]. The formation of SiO\(_x\) arises from residual oxygen in the vacuum chamber. As hydrogen is introduced, the Si2p peak becomes more symmetrical and the SiO\(_x\) concentration diminishes. It means that plasma hydrogenation can mitigate the formation of SiO\(_x\) during deposition. The Gaussian fits of the C1s spectra under different hydrogenation conditions disclose two peaks centered at 283.4 eV and 284.9 eV. The former peak is assigned to C–Si in SiC and the latter one is C–C in amorphous carbon [12]. It can be clearly seen that C\(_{C-C}\) decreases significantly after plasma hydrogenation as shown in Fig. 3, in agreement with the RBS results. Our results show that plasma hydrogenation is an effective method to improve the composition of the thin films and stoichiometric SiC thin films can be fabricated by PECVD at lower substrate temperature.

In order to further investigate the effects of plasma hydrogenation, SiC thin films were fabricated at different temperatures from 300 °C to 700 °C at a constant ratio of CH\(_4\):SiH\(_4\):H\(_2\) = 3:3:100. The corresponding FTIR spectra are shown in Fig. 4. All the spectra show absorption bands at about 800 cm\(^{-1}\) indicative of Si–C bands in the thin films. Furthermore, as the substrate temperature increases, the peak position shifts slightly to higher wavenumbers and the full-width at half maximum
(FWHM) values of the Si–C stretching band decrease as shown in Fig. 5. According to Sun et al., the frequency and width of the absorption peak vary significantly with changes in the Si–C composition and bond such as the bond length, bond angle, and other distortions [13]. The peak shift observed here suggests an increase in the force of the Si–C stretching mode, that is, compressive strain in the SiC films. Decrease in the length of the Si–C bond leads to compressive strain and is possibly associated with the formation of nano-structures in the thin films. The FWHM values correspond with the order degrees of SiC thin films. Basa et al. have studied the variation in the FWHM values of the Si–C stretching band in amorphous SiC films with annealing temperatures from 650 °C to 1200 °C and pointed out that the decrease in the FWHM results from a microstructural change from an amorphous to a crystalline phase [14]. Thus, the decrease of the FWHM value here can mean the formation of crystalline SiC thin films.

Fig. 6 shows the X-ray diffraction patterns of the SiC thin films as shown in Fig. 4. There are three diffraction peaks when the substrate temperature is higher than 500 °C at 2θ = 35.7, 60.0 and 71.58° corresponding to the (111), (220), and (311) planes of the cubic phase of SiC, respectively [15]. Among the three peaks, the (111) plane dominates. The results reveal that the films are polycrystalline and it agrees well with the FWHM values in the FTIR spectra. Hence, plasma hydrogenation promotes the formation of the crystalline phase of SiC at lower substrate temperatures. Furthermore, as shown in Fig. 6, the FWHM of the (111) peak becomes slightly narrower as the substrate temperature increases, possibly because of the grains size effects. Using the Debye–Scherrer formula, the crystalline sizes of the samples are calculated to be about 16 nm for 500 °C and 52 nm at 700 °C, respectively. Our FTIR and XRD results indicate that plasma hydrogenation spurs the formation nanocrystalline β-SiC thin films at lower substrate temperatures.

The surface morphology determined by atomic force microscopy (AFM) in the contact mode from representative samples is displayed in Fig. 7. Uniform crystalline particles with nano-size are observed on the thin films prepared at the lower substrate temperature of 500 °C as shown in Fig. 7(a). As the substrate temperature increases to 700 °C, the average particles size increases and uneven surface grains are observed as shown in Fig. 7(b). The data agree with the blue shift of the FTIR peak and the FWHM value change observed in the XRD patterns. It further corroborates that plasma hydrogenation in conjunction with PECVD is an effective method to improve the composition and microstructure of SiC.

Plasma hydrogenation is believed to promote the interactions between the reactive precursors in the plasma and deposited clusters on the growing surface giving rise to faster diffusion of the deposited particles and relaxation of the growing surface. Meanwhile, the weak bond and radicals on the growing surface can be etched by plasma hydrogenation thereby reducing the disorder and improving the crystallization of SiC at lower substrate temperatures [16]. In the reaction between atomic H and the growing surface, very little energy can be released to increase the effective surface temperature. However, it can improve the mobility of the absorbed chemical
radicals on the surface which is similar to the annealing effects from a chemical perspective [11]. Coper et al. have studied the role of surface-active species (surfactants) in CVD and concluded that atomic H on the growing surface exhibits the surfactant effects and decreases the surface reaction energies. The dangling bonds between the saturated β-SiC thin films and atomic H can induce negative effective surface energies which can match the surface wetting conditions [17]. Besides, a large amount of atomic H in the plasma gas can saturate the dangling bonds on the growing surface which can further suppress the formation of sp² bonds [18].

4. Conclusion

Stoichiometric SiC thin films have been fabricated on Si (100) substrates by plasma hydrogenation at substrate temperatures lower than that in conventional CVD. Our results suggest that plasma hydrogenation effectively decreases the deposition temperature and improves the composition and microstructure of the cubic SiC (β-SiC) thin films, particularly the crystal particle size. It also retards the growth of amorphous carbon and oxides.

Acknowledgements

This work is partially supported by the project of the National Natural Science Foundation [No. 90305026], and Hong Kong Research Grants Council (RGC) Competitive Earmarked Research Grant (CERG) No. CityU 1120/04E.

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