

Research Letter

Room-Temperature Growth of SiC Thin Films by Dual-Ion-Beam Sputtering Deposition

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Received 16 January 2008; Accepted 7 March 2008

Recommended by Igor Murin

Silicon carbide (SiC) films were prepared by single and dual-ion-beam sputtering deposition at room temperature. An assisted Ar⁺ ion beam (ion energy $E_i = 150$ eV) was directed to bombard the substrate surface to be helpful for forming SiC films. The microstructure and optical properties of nonirradiated and assisted ion-beam irradiated films have been characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and Raman spectra. TEM result shows that the films are amorphous. The films exposed to a low-energy assisted ion-beam irradiated during sputtering from *a*-SiC target have exhibited smoother and compacter surface topography than which deposited with non-irradiated. The ion-beam irradiated improves the adhesion between film and substrate and releases the stress between film and substrate. With assisted ion-beam irradiated, the density of the Si–C bond in the film has increased. At the same time, the excess C atoms or the size of the sp^2 bonded clusters reduces, and the *a*-Si phase decreases. These results indicate that the composition of the film is mainly Si–C bond.

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1. INTRODUCTION

Amorphous semiconductor alloys are of technological importance for electronic and optoelectronic device application. Amorphous silicon carbide (*a*-SiC) has been recognized as a semiconductor material with outstanding physical and chemical characteristics. Silicon carbide exhibits a large bandgap, a higher breakdown field, a higher thermal conductivity, and a higher saturation velocity, compared to widely used silicon. On the other hand, amorphous SiC films have interest related to their high hardness and optical properties and have potential applications as hard, wear resistant coatings, masking material in Si micromachining technology as well as for the formation of optical windows, filters, and color sensors [1, 2]. Recently, plasma-assisted deposition methods such as plasma enhanced CVD [3, 4], electron cyclotron resonance (ECR) [5, 6], the conventional physical vapour deposition methods (magnetron sputtering [7, 8], pulsed laser deposition [9, 10]), ion implantation [11], and molecular beam epitaxy [12] methods have been used to grow SiC films on Si substrate. However, these methods need high grown tem-

perature, which process defect creation, resulting from high tensile stress generated from a temperature dependent difference in the thermal expansion coefficient between SiC and Si, and involve many pollutions of impurity in the films such as H element.

This letter reports the growth of SiC thin films at room temperature using dual-ion-beam sputtering deposition (DIBSD), a method that has been used to grow many different types of films. Recently, it has also been shown that ion-assisted techniques can greatly improve the adhesion by minimizing the total stress at the interface and compactness of the coatings despite the higher optical absorption near the bandgap of the material [13, 14]. By proper adjustment of dual-ion-beam parameters, the method permits a precise control of film composition, which is almost independent of deposition rate. The microstructural, optical, and electrical properties may also be tailored significantly by ion bombardment during film deposition [15]. The energy given by the ion-beam system is high enough to reduce the temperature needed for the formation of the SiC phase [16, 17]. In the paper, the microstructure and morphology of the films have

been measured by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and Raman spectra. The effect of a low-energy assisted-ion bombardment during deposition on the film properties has been investigated.

2. EXPERIMENT

SiC films were deposited by employing a DIBSD system at room temperature. A DIBSD system consists of a focused Kaufman ion source (main ion source) and a broad-beam Kaufman ion source (assisted-ion source). The Ar gas as pure as 99.999% was used for source gas and for ion-beam generation. Main ion source of 10 cm diameter with the incident angle of 45° served as a sputtering ion source. Normal sintered high-purity SiC target was used as a sputtering target. The sputtering chamber was evacuated to 2×10^{-4} Pa before argon was introduced through a mass flow controller. The working pressure of argon was 4×10^{-2} Pa. Before deposition, the substrates of KBr, Suprasil quartz, and *p*-type (100) Si wafer (resistivity, $5 \Omega\text{-cm}$) after standard cleaning sequence to remove organic and inorganic surface contaminants were cleaned again with an argon ion beam for 15 minutes using the assisted source (200 eV energy and 10 mA beam intensity). During deposition, the beam energy and beam current of the main ion source which was used to sputter the SiC target were 800 eV and 40 mA, respectively. An assisted-ion source of 10 cm diameter with the incident angle of 60° was used. The beam current of the assisted-ion source which was used to bombardment the substrate was 10 mA, and beam energy was variable parameter 0–150 eV. No intentional heating was applied on substrate during deposition. SiC films were deposited for 2 hours on the substrate. All of the thicknesses of the SiC films were range of 150–260 nm, which were measured with an ET350 surface profilometer (Kosaka Laboratory Ltd.).

The films were studied by scanning electron microscopy (SEM) using Hitachi S-4700 equipped with energy dispersive spectroscopy (EDS), for their morphology and composition, respectively. The bonding configurations and the structure were measured by TEM (Hitachi H600A-II), FTIR (Niolot AVATAR 360), and Raman spectra which were obtained in the backscattering configuration between 200 cm^{-1} and 1800 cm^{-1} by JY-HR800 using an argon ion laser at a wavelength of 514 nm. All the measurements were conducted at room temperature.

3. RESULTS AND DISCUSSION

3.1. Structure analysis

During DIBSD, the assisted ion beam has been utilized to significantly enhance and control the properties of the film. In order to compare the characteristics of films prepared by DIBSD, IBSD, which did not use assisted ion beam to irradiate the substrate, was used to form SiC film. Figure 1 shows our TEM result from which only halos are observed in the selection electron diffraction picture, the samples regarded to be amorphous.

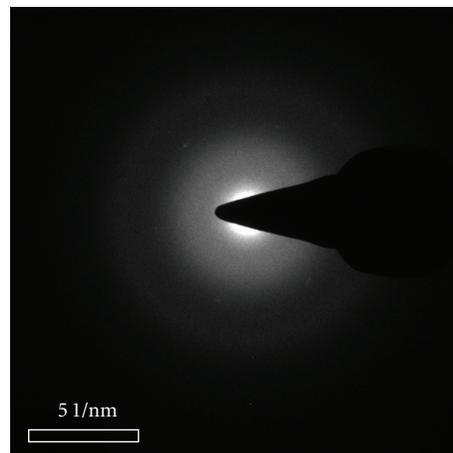


FIGURE 1: The TEM micrographs of the sample with 150 eV ion-beam irradiated.

At low resolution, the top SEM micrograph of a film prepared on Si substrate nonirradiated (sample a) and irradiated by 150 eV ion beam (sample b) is shown in Figures 2(a) and 2(c), respectively. Compared to Figure 2(a), the average grain size increases, and the surface is found to be denser with ion-beam irradiated in Figure 2(c). The cross-sectional SEM micrographs of sample a and sample b are shown in Figures 2(b) and 2(d), respectively. As shown in Figure 2(b), we see that the film/substrate interface is quite smooth and clear. Moreover, in region A, there are many obvious cracks on both film and substrate, which might originate from the inter-stress between film and substrate. As shown in Figure 2(d), sample b is more compact than sample a. The film/substrate interface is roughness and dark. Nevertheless the quantity of the cracks decreases in region C. There is a buffer layer between SiC film and Si substrate in region B, which releases the stress caused by the large lattice mismatch, around 20%, and indicates very good coating to substrate adhesion. It found that the ion-beam-assisted bombarding enhanced the coating to substrate adhesion. These results indicate that low-energy ion-assisted growth improves the adatom mobility, which is attributed to the distribution of nonequilibrium phonon on surface. At the same time, the ion-beam irradiated is the densification of film, increases the average of the cluster, improves the adhesion between SiC and Si substrate, and releases the stress between SiC and Si substrate.

The EDS was only used to measure the proportion of Si and C in our films grown on KBr substrates. The composition uniformity in the film was studied by analyzing several points (with 1 mm^2 analysis area) over the surface of the sample. EDS analyses indeed showed that all the films consist of Si and C. The proportion in sample a is Si:C = 9:11 (at.% ratio), nevertheless it decreases to 2:3 with ion-beam irradiated in sample b. It indicates that all the films are C excess. The main source ion beam sputters the SiC target, then the sputtering particles deposit on the substrate, which include Si, C, and SiC atoms. At the same time, the assisted-source ion beam sputters the deposition, and the secondary

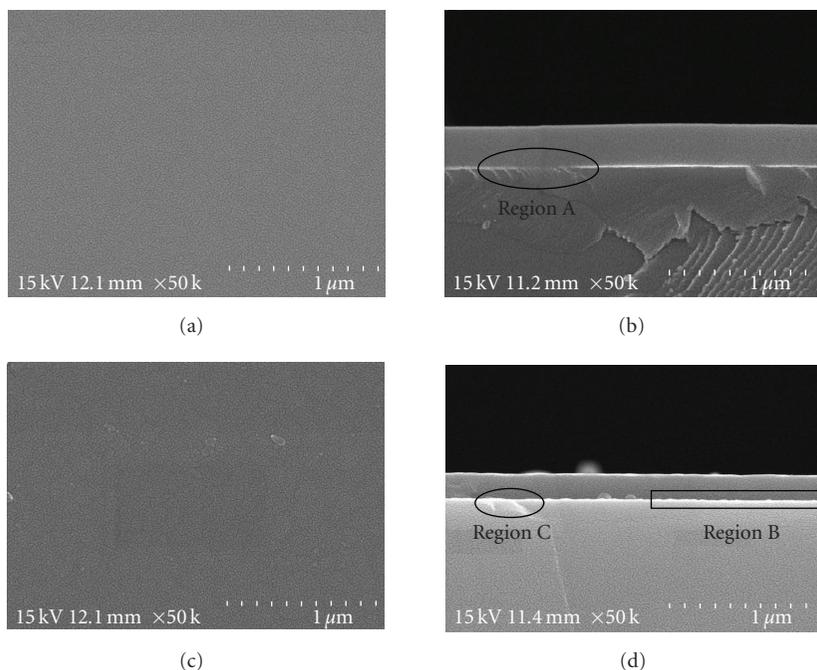


FIGURE 2: (a) Top- and (b) cross-sectional SEM micrographs of the sample prepared on Si with nonirradiated, (c) top-, and (d) cross-sectional SEM micrographs of the sample irradiated by 150 eV ion beam.

ion sputtering rate of Si ion is higher than that of C ion in the films. The increasing of the proportion of C atom might be attributed to resputter on as-deposition film, which maybe due to the sputtering rate of Si ion is higher than that of C ion.

The FTIR is a powerful tool to investigate the bonding structure in *a*-SiC films. The IR spectra for sample a and the sample b which are deposited on KBr substrates are shown in Figures 3(a) and 3(b), respectively. As can be seen, almost all the measured spectra are characterized by the absorption peak related to the Si-C bond, which is around 800 cm^{-1} , except the weak peaks around 1018 cm^{-1} , 1090 cm^{-1} , 1260 cm^{-1} , and 2950 cm^{-1} . The bands corresponding to 1018 cm^{-1} , 1090 cm^{-1} , and 1260 cm^{-1} are due to oxygen adsorption on the film surface in air or the O atoms at the film/substrate interface [18], while the band corresponding to 2950 cm^{-1} is attributed to the stretching vibration of C-H_n groups in sp^3 configurations [19], which may be due to H₂O from the atmosphere adsorbed on the film surface [20]. The 740 cm^{-1} band as a broad absorption maybe related to these results, just as (a) the high concentration of substitutional C, (b) the appearances of the C-C bonds, and (c) the nonsubstitutional C in the Si substrate [21, 22]. Compared to Figure 3(a), the shape of the 800 cm^{-1} peak progressively changes and becomes narrow in Figure 3(b). The full width at half maximum (FWHM) of 800 cm^{-1} peak is smaller than that of other spectra, indicating that the stoichiometric proportion of the SiC films after assisted ion-beam irradiated is improved [23]. It demonstrates a better quality of the SiC film grown with assisted ion-beam irradiated. The full width at half maximum (FWHM) of 800 cm^{-1} peak is narrower than that of other

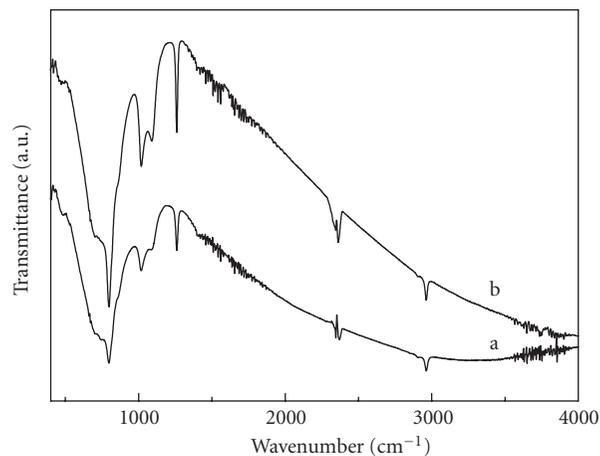


FIGURE 3: The FTIR spectra of the films on KBr substrates (a) with nonirradiated (b) with 150 eV ion-beam irradiated.

spectra, indicating that the Si-C band is a majority of the film.

Although FTIR is high efficiency of Si-C band, it is low efficiency of Si-Si and C-C bonds. However, Raman spectra are optimum for researching identical atomic polar bonds, such as Si-Si and C-C bands. So, we used Raman spectra to analyze the changes of Si-Si and C-C bands. The Raman spectra from these samples are characterized by the presence of bonds characteristic of amorphous material, in the $200\text{--}600\text{ cm}^{-1}$ and $1300\text{--}1600\text{ cm}^{-1}$ spectral regions. This can be seen in Figure 4(a), where the spectra measured in these regions from the sample a. These bands are similar to those

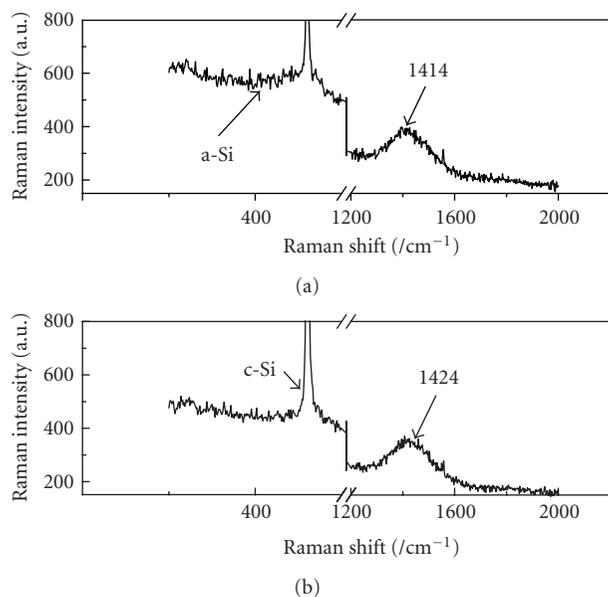


FIGURE 4: The Raman spectra of the films on Si substrates (a) with nonirradiated (b) with 150 eV ion-beam irradiated.

reported for amorphous $\text{Si}_{1-x}\text{C}_x$ films obtained by different techniques [24–26] and have been interpreted according to a two-mode behavior, related to the different Si–Si and C–C vibrational modes. So, the first band are similar to the Si–Si TO mode one from amorphous Si (at about 480 cm^{-1}). The band appearing in the 1300–1600 spectra region is related to C–C vibrational modes. This C–C signature already observed in Si–C alloys with carbon excess [24, 27–30] corresponds certainly to a specific structure which could be described like a random covalent network of tetrahedral-trigonal bonding carbons with distorted bond angles and bond lengths [31–35]. As a matter of fact, it shows that in mixed sp^2 – sp^3 bonded carbon layer, the overall Raman spectrum is dominated by the G component (E_{2g} Raman mode of perfect graphite crystal), because the cross section of the graphite stretching mode is much higher than that of the 1332 cm^{-1} diamond mode.

After assisted ion-beam irradiated, the *a*-Si contribution in the spectra decreases, the first-order peak from *c*-Si is restored, and the peak of C–C bond shifts toward to high-frequency while the intensity of the peak decreases as shown in Figure 4(b). It indicates that the sp^3/sp^2 ratio decreases while the excess C atoms or the size of the sp^2 bonded clusters reduces. The lack of C–C bands suggests that part of excess carbon atoms are bonded to *a*-Si instead of forming the graphite-like structure. And that the residual excess C can be present in solid solution.

4. CONCLUSION

SiC films were prepared by single and dual-ion-beam sputtering deposition at room temperature. The microstructure and optical properties of nonirradiated and assisted ion-beam irradiated films have been characterized by TEM,

EDS, SEM, FTIR, and Raman spectra. The films exposed to a low-energy assisted ion-beam irradiated during sputtering from a SiC target have exhibited smoother and compacter surface topography and different optical behavior than the films deposited with nonirradiated. With assisted ion-beam irradiated, the density of the Si–C bonding in the film has increased. At the same time, the excess C atoms or the size of the sp^2 bonded clusters reduces, and the *a*-Si phase decreases. These results indicate that the composition of the film is mainly Si–C bond. These data suggest the high stability of *a*-SiC to be related to the absence of a complete chemical order, which can be attributed to the ion-assisted irradiated at 150 eV during deposition.

ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (No. 10275047 and No.10575073) and the Natural Science Foundation of Jiangsu Province of China (No.03KJB140116). This work is also partially supported by Hubei Key Laboratory of Plasma Chemistries and Advanced Materials (Wuhan Institute of Technology).

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