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Structural characterization of annealed $\text{Si}_{1-x}\text{C}_x/\text{SiC}$ multilayers targeting formation of Si nanocrystals in a SiC matrix

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Amorphous $\text{Si}_{1-x}\text{C}_x/\text{SiC}$ multilayer films were prepared by alternating deposition of Si-rich $\text{Si}_{1-x}\text{C}_x$ and near-stoichiometric SiC layers by using magnetron sputtering. The as-deposited films were annealed at different temperatures (T_a) from 800 to 1100 °C. The influence of T_a and Si content in the Si-rich layer on the layered structural stability and on the formation of Si and/or SiC nanocrystals (NCs) is investigated by a variety of analytical techniques, including x-ray reflectivity (XRR), x-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, and Fourier transform infrared spectrometry (FTIR). XRR showed that $\text{Si}_{1-x}\text{C}_x/\text{SiC}$ multilayers annealed at temperatures of up to 800 °C retain their layered structure. XRD revealed that Si NCs were formed in samples with a high Si content in the Si-rich layer for $T_a \geq 800$ °C. At annealing temperatures of 900 °C or greater, the formation of Si NCs was accompanied by the formation of β -SiC NCs. Additionally, the formation of Si and SiC NCs was confirmed by TEM imaging and Raman spectroscopy. The Si-NC size obtained from the TEM micrographs is within the range of 3–5 nm. The β -SiC NCs are smaller (2–3 nm) than Si NCs. Raman analysis identified an $\sim 9 \text{ cm}^{-1}$ Raman peak shift in the Si-NC peak to a lower energy with respect to that for bulk Si. FTIR Si–C bond absorption spectra exhibited narrowing of the full width at half maximum and a peak shift toward a higher wave number with increasing T_a . This behavior can be explained by an increase in order as well as an increase in the number of Si–C bonds. © 2008 American Institute of Physics. [DOI: 10.1063/1.2909913]

I. INTRODUCTION

Self-organized silicon nanocrystals (Si NCs) embedded in a dielectric matrix are widely considered as a promising material for potential applications in the fields of optoelectronics,^{1,2} data storage,³ and single electron devices.⁴ Most previous studies of Si-NC materials involved deposition of a single Si-rich oxide layer or alternating layers of Si-rich oxide and SiO_2 , followed by thermal annealing in an inert atmosphere. Si NCs are produced by means of excess Si precipitation from the supersaturated Si-rich oxide.⁵ Many investigations also focused on the use of Si-rich nitride, which ran parallel to the work on Si NCs in oxide.^{6,7} It was demonstrated that materials consisting of self-organized Si NCs in oxide or nitride exhibit an increasing optical band gap with decreasing Si-NC size.^{8–10} This phenomenon is explained by quantum confinement of carriers within Si NCs.^{8,9} Carrier confinement in Si NCs causes an enlargement of the effective band gap and efficient emission in the visible range at room temperature.

Recently, interest in Si-NC materials has been stimulated by the potential application in third generation photovoltaic devices.^{11–13} Si-NC nanostructures in SiO_2 or Si_3N_4 can be used to engineer materials with a wider band gap.¹² Such materials may be employed in “all-Si” tandem cells with a wide range of design flexibility. The concept of all-Si tandem solar cells based on Si-NC nanostructure involves the use of

several solar cells of different band gaps stacked on top of one another, with the highest band gap cell uppermost.^{11,14} Each cell absorbs a slice of the solar spectrum, with below band gap photons passing through to underlying cells.¹¹ Si-NC materials are considered to be promising candidates for solar cell applications since their band gaps can be fine tuned by adjusting the NC-Si size. However, the tunneling probability of carriers between quantum dots (Si-NC size $< \sim 7$ nm in diameter) strongly depends on the barrier height of the host material. The barrier between Si NCs in SiO_2 or Si_3N_4 is large because of the wide band gaps of SiO_2 (~ 9 eV) and Si_3N_4 (~ 5.3 eV).¹⁵ A lower barrier height exponentially enhances the tunneling probability of carriers between adjacent NCs. SiC is an attractive alternative Si-NC host material for solar cell applications due to its low band gap (~ 2.5 eV) relative to SiO_2 and Si_3N_4 . The relatively low band gap of SiC leads to a higher effective carrier mobility.¹⁶

In previous works, we demonstrated that Si NCs embedded in a SiC matrix can be formed by high temperature annealing of a single Si-rich SiC precursor layer.^{17,18} In this work, Si NCs embedded in a SiC matrix were prepared by alternating deposition of Si-rich and near-stoichiometric silicon carbide ($\text{Si}_{1-x}\text{C}_x/\text{SiC}$) multilayers by using magnetron cosputtering, followed by postdeposition annealing. The use of $\text{Si}_{1-x}\text{C}_x/\text{SiC}$ multilayers instead of a single precursor layer is expected to give a better control over Si-NC size as the Si-NC size is constrained by the thickness of the Si-rich

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layer. This was found to be the case for the analogs of Si NCs in SiO₂ and Si₃N₄ that were reported elsewhere.^{5,12} We present the influence of annealing temperature (T_a) and the Si content in Si-rich layers on the structural evolution of Si_{1-x}C_x/SiC multilayers and the formation of Si NCs by using a variety of structural characterization techniques. The results from these characterization methods are discussed and compared.

II. EXPERIMENTAL PROCEDURE

Substrates consisting of $\langle 100 \rangle$ -oriented Si wafers and quartz plates were subjected to standard RCA cleaning, rinsing in de-ionized water, and drying by a nitrogen (N₂) gas flow. The Si wafers were additionally dipped in a 5% HF solution for 10 s to remove the surface native oxide. The Si wafer substrates were used for structural characterization, and the quartz plates were used for optical characterization. Si_{1-x}C_x/SiC multilayers were deposited by magnetron cosputtering (AJA International, Inc., model ATC-2200) of Si and SiC targets. None of the samples were intentionally heated during the deposition process. The Si target consisted of a single crystalline disk (diameter of 100 mm, thickness of 3 mm), and the SiC target consisted of a powder pressed disk (diameter of 50 mm, thickness of 3 mm, density of 3.01 g/cm³). The near-stoichiometric SiC layer was prepared by direct-current (dc) sputtering of the SiC target, while the Si-rich SiC layer was deposited by simultaneously sputtering from Si and SiC targets employing radio-frequency (rf, 13.56 MHz) and dc sources, respectively. Various Si contents in the Si-rich layer were obtained by varying the ratio of sputtering power supplied to the two targets. To investigate the effect of Si content on structural evolution, two Si-rich layer compositional fractions x (0.1 and 0.04) were used. The samples consisted of 20 Si_{1-x}C_x/SiC bilayers. The average layer thicknesses were estimated by transmission electron microscopy (TEM) and x-ray reflectivity (XRR) measurements to be 5.5 ± 1 nm (Si_{1-x}C_x layer) and 2.5 ± 0.5 nm (SiC layer). Prior to film deposition, the sputtering system vacuum chamber was evacuated down to a pressure of about 5×10^{-7} Torr. The chamber was then supplied with pure Ar gas to a working gas pressure of 2 mTorr. The Ar flow was maintained at 20 SCCM (SCCM denotes cubic centimeter per minute at STP) during deposition. The targets were sputtered for 10 min before film deposition to remove surface contamination and oxides on the targets to ensure stable sputtering conditions. As-deposited samples were cut into several pieces then annealed within the temperature range of 800–1100 °C in a conventional quartz tube furnace in ambient N₂ for 9–25 min. The specific temperature-time combinations were 800–900 °C for 25 min, 1000 °C for 12 min, and 1100 °C for 9 min.

X-ray photoelectron spectroscopy (XPS) was used to determine the chemical composition of the layers. The XPS apparatus comprised a Fisons ESCALAB 220i-XL with a monochromatic Al $K\alpha$ (1486.5 eV) x-ray source and a hemispherical energy analyzer. Single layer films were prepared for compositional analysis. The single films were deposited under the same conditions as the multilayer samples. The

x-ray source power was 10 kV $\times$ 12 mA, and the analyzed sample area was ~ 0.3 mm². Detailed XPS spectra data were collected for the C 1s and Si 2p photoelectron peaks. The data were then processed by the ECLIPSE software package (VG Scientific) for a quantitative compositional analysis. The recorded XPS spectra were fitted by Gaussian functions and the background was removed by the Shirley subtraction method. XRR measurements were performed by using a Philips X'Pert MRD system, which employs Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) and operates at a system voltage of 45 kV with a current of 40 mA. The primary beam was defined by a front slit and a parabolic mirror. The resolution of the reflected beam was provided by a long-plate collimator, a slit in the horizontal plane, and a Soller slit in the vertical plane inserted in front of the detector. The information obtained was from a sample area of $\sim 20 \times 15$ mm². The crystalline structure was investigated by grazing incidence x-ray diffraction (GI-XRD). The GI-XRD measurements were carried out on the same apparatus that was used for the XRR measurements. The glancing angle between the incident x-ray and the sample surface was fixed at 0.3°. The detector (2θ) axis was scanned within the range of 20°–80° to cover the main intense diffraction peaks of crystalline Si and SiC. The NC size (g) was estimated by using Scherrer's formula¹⁹ $g = k\lambda / \Delta(2\theta)\cos\theta$, where λ is the wavelength of the x rays, θ is the Bragg diffraction angle at the peak position in degrees, $\Delta(2\theta)$ is the full width at half maximum (FWHM) in radians, and k is a correction factor. The value of k is usually chosen to be 0.9.²⁰ Raman spectra were measured by micro-Raman spectroscopy (Renishaw, RM2000) in the backscattering configuration, with a 50 $\times$ optical microscope objective. The optical source consisted of an Ar⁺ ion laser with a wavelength of 514.4 nm. Cross-sectional TEM observations were performed with a JEOL-3000F operated at 300 kV. The TEM samples were prepared by a standard mechanical thinning technique followed by Ar⁺ ion milling at 3 kV. Fourier transform infrared spectrometry (FTIR) absorption spectra were measured by a Nicolet 5700 spectrometer within the 400–4000 cm⁻¹ spectral region, with the resolution set at 4 cm⁻¹. An uncoated Si substrate was used to measure the background signal, which was subtracted from the measured IR absorption spectra.

III. RESULTS AND DISCUSSION

A. X-ray reflectivity

Specular XRR is a powerful tool for investigating the internal properties of multilayer structures.^{21–23} The technique is nondestructive and can provide statistical information averaged over a large sample area. XRR probes the sample density with a depth resolution as high as one-tenth of a nanometer. Figure 1 shows the XRR patterns of two samples on Si substrates: (a) Si_{0.9}C_{0.1}/SiC and (b) Si_{0.96}C_{0.04}/SiC multilayer films annealed at various temperatures from 800 to 1100 °C. The reflected x-ray intensity was recorded as a function of the x-ray incidence angle θ from 0.1° to 3°. For a very small incidence angle that is less than some critical angle θ_c ($< \sim 0.25^\circ$), the reflection intensity is almost constant because the incident x ray is totally reflected

FIG. 1. (Color online) X-ray reflectivity spectra obtained from 20-period multilayer films on a Si substrate: (a) $\text{Si}_{0.9}\text{C}_{0.1}/\text{SiC}$ and (b) $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayers with annealing temperature as a parameter.

at the air/film interface, whereas above θ_c , the intensity rapidly drops by several orders of magnitude and many high frequency oscillations (Kiessig fringes) appear in the spectrum. The total thickness of the sample can be determined by the position of the Kiessig fringes. The low-frequency and high-intensity periodic maxima correspond to Bragg peaks that are due to x-ray waves being reflected at different interfaces within the multilayer film, giving rise to constructive/destructive interference effects. The Bragg peak spacing directly depends upon the multilayer periodicity, while their number is an indication of layer thickness uniformity throughout the entire multilayer film.

From Figs. 1(a) and 1(b), it is clear that the films show significant structural variations with changes in T_a and Si concentration in Si-rich layers. As-deposited samples exhibit four similar Bragg peaks ($m=1, 2, 3$, and 4) with the Kiessig oscillations between the successive Bragg peaks, indicating a low variation in layer thickness throughout the multilayer films and low roughness at the interface of successive layers. The layered structure remains almost unchanged upon annealing at 800°C . With increasing T_a above 800°C , the effect of annealing on the layered structure depends on the compositional fraction x in the $\text{Si}_{1-x}\text{C}_x$ layers. For the sample

FIG. 2. (Color online) X-ray diffraction spectra obtained from 20-period multilayer films on a Si substrate: (a) $\text{Si}_{0.9}\text{C}_{0.1}/\text{SiC}$ and (b) $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayers with annealing temperature as a parameter.

corresponding to Fig. 1(a), there exist very weak Bragg peaks at the positions of $m=1, 2$, and 3 following annealing at 900°C , however, the fourth-order Bragg peak is absent. For $T_a \geq 1000^\circ\text{C}$, the Bragg peaks are barely distinguishable. The absence of clear Bragg peaks suggests that no true layering exists in the films for $T_a \geq 1000^\circ\text{C}$. This is most probably due to complete interdiffusion of C and Si atoms through the thin $\text{Si}_{1-x}\text{C}_x/\text{SiC}$ bilayers during annealing. In contrast, Fig. 1(b) features Bragg peaks ($m=1$ and 2) for all T_a values although higher order Bragg peaks ($m=3$ and 4) disappear within the range of $T_a=900$ – 1100°C . This shows that a higher Si content in the Si-rich layers results in preservation of the layered structure, even after annealing at 1100°C . The broad modulation in the 900 and 1000°C XRR curves is attributed to the growth of a very thin oxide layer on the surface during annealing.^{24,25} The broad modulation disappears after the oxide layer is removed with a dilute HF solution (see the curves for $T_a=1100^\circ\text{C}$).

B. X-ray diffraction

The formation of Si NCs and/or SiC NCs after annealing was confirmed by XRD measurements. Figure 2 shows the

FIG. 3. (Color online) Si and β -SiC NC size as a function of T_a and Si content in the Si-rich layers obtained by Scherrer's equation. Sample (a) represents $\text{Si}_{0.9}\text{C}_{0.1}/\text{SiC}$ multilayer films, and sample (b) represents $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayer films.

XRD spectra of two samples on Si substrates with T_a as a parameter: (a) $\text{Si}_{0.9}\text{C}_{0.1}/\text{SiC}$ and (b) $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayer films. The penetration depth of the incident x-ray source is larger than the thickness of the samples (~ 160 nm), so crystallinity information is averaged over the total thickness of the films. From Figs. 2(a) and 2(b), the as-deposited multilayers are in an amorphous state as the XRD spectra do not contain any crystalline peaks. Furthermore, from Fig. 2(a), it is clear that the $\text{Si}_{0.9}\text{C}_{0.1}/\text{SiC}$ multilayer film remained amorphous after annealing at 800 °C. In contrast, when the $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayer film was annealed at 800 °C, Si-NC formation occurred, as the 800 °C XRD pattern of Fig. 2(b) reveals the presence of a crystalline phase that can be assigned to the Si structure according to the data from the Joint Committee on Powder Diffraction Standards (JCPDS).²⁶ The three major diffraction peaks appearing at around $2\theta=28.4^\circ$, 47.3° , and 56.2° are from the Si{111}, Si{220}, and Si{311} planes. This suggests that at low annealing temperatures, Si NCs can be obtained by using a high Si content in the Si-rich layers. As the annealing temperature is increased further ($T_a \geq 900$ °C), several additional peaks appear in the XRD patterns. The peak intensities increase with increasing T_a . An analysis of these additional peaks shows that they can be matched to β -SiC according to Ref. 43. The peaks correspond to the β -SiC {111}, β -SiC {220}, and β -SiC {311} planes. The formation of Si NCs accompanied by the presence of β -SiC NCs was observed in annealed single Si-rich layer films in our previous work.¹⁷ By comparing the XRD spectra of Figs. 2(a) and 2(b), it is evident that the ratio of the Si NC peak intensity to the β -SiC NC peak intensity depends on the Si content of the Si-rich layers. An increase in Si concentration results in an increase in the ratio $I_{\text{Si}\{111\}}/I_{\beta\text{-SiC}\{111\}}$. This indicates that the dominant type of nanocrystals (Si or SiC) in annealed films can be controlled by changing the Si concentration in the Si-rich layer.

The NC size is estimated from the broadening of Bragg peaks in the XRD spectra by using Scherrer's equation. Figure 3 shows the calculated sizes of Si NCs and β -SiC NCs as

FIG. 4. (Color online) Raman spectra of (a) $\text{Si}_{0.9}\text{C}_{0.1}/\text{SiC}$ and (b) $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayer films with annealing temperature as a parameter. The films were deposited on quartz substrates. The origins of major peaks are indicated.

a function of T_a and Si content in the Si-rich layers. For the Si NCs, the general trend is that the size increases with increasing T_a . The Si-NC size increases from ~ 3.4 to ~ 5 nm for $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayer films when T_a increases from 800 to 1100 °C. At high temperature $T_a=1100$ °C, Si-NC size is close to the thickness of the Si-rich layer. While at low $T_a=800$ °C, a small Si-NC size (~ 3.4 nm) is likely due to the short annealing time, resulting in an Si-NC size that is not well developed. Compared to the size of Si NCs, the β -SiC NC size increases only slightly when T_a increases from 900 to 1100 °C (3.2–3.4 nm for $\text{Si}_{0.9}\text{C}_{0.1}/\text{SiC}$ multilayers and 3.0–3.3 nm for $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayers). Since the majority of β -SiC NCs would be formed in the near-stoichiometric SiC layers, the nearly constant β -SiC NC size appears to be a result of constraining the thickness of the SiC layers.

C. Raman measurements

Figure 4 shows the T_a dependence of Raman spectra for (a) $\text{Si}_{0.9}\text{C}_{0.1}/\text{SiC}$ multilayer films and (b) $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$

multilayer films together with the spectra of as-deposited films. The samples subjected to spectroscopy were prepared on quartz plates to prevent Si-NC signal from being masked by that from a Si substrate. An asymmetric hump centered at about 470 cm^{-1} is a characteristic of as-deposited samples. A feature of this nature may be attributed to the transverse optical mode of amorphous Si (*a*-Si).²⁷ After annealing at $800\text{ }^{\circ}\text{C}$, the $\text{Si}_{0.9}\text{C}_{0.1}/\text{SiC}$ multilayer sample [Fig. 4(a)] still features *a*-Si, as shown by a band centered at about 470 cm^{-1} . This result is consistent with the XRD measurements [see Fig. 2(a)]. In contrast, the $T_a=800\text{ }^{\circ}\text{C}$ Raman spectrum of the $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayer sample [Fig. 4(b)] features a small thin peak at $\sim 511\text{ cm}^{-1}$, which can be attributed to Si NCs.²⁸

For $T_a \geq 900\text{ }^{\circ}\text{C}$, Si NCs were formed in all samples as shown by the pronounced Raman peak at $\sim 511\text{ cm}^{-1}$. Salient features of these Raman peaks are the frequency downshift with respect to $\sim 520\text{ cm}^{-1}$ of bulk Si and asymmetric broadening at low wave numbers. This behavior is considered to be caused by grain size related effects in a small-grained nanostructure as well as compressive stress in the films.^{29,30} The correspondence between Si-NC size and Raman peak shift was previously investigated by theoretical and experimental methods.^{28,31} The Raman peak shift to a lower wave number by a value of $\Delta\omega \sim 9\text{ cm}^{-1}$ may be caused by a Si-NC size of around 3-4 nm.³¹ The Si-NC size indicated by Raman measurements is in reasonable agreement with the Si-NC size determined from XRD and TEM observations (see later discussion). Also evident in Figs. 4(a) and 4(b) is the peak intensity increase with increasing T_a and Si content in the Si-rich layers. This can be explained by the increase in the volume fraction and size of Si NCs with increasing T_a and Si content.

In addition to the Raman peak from Si NCs, a very weak band centered at $\sim 940\text{ cm}^{-1}$ was also observed when the samples were annealed at temperatures above $900\text{ }^{\circ}\text{C}$. The origin of this Raman peak may be attributed mainly to SiC but not to Si (two-phonon process), as we observed that the Raman peak intensity increases with increasing β -SiC NC volume fraction in the film.¹⁷ Considering that the amorphous SiC vibrational density of states in Raman spectra is up to $\sim 900\text{ cm}^{-1}$ (Ref. 32) and that the maximum optical phonon energy of any of the crystalline polytypes of SiC is 972 cm^{-1} ,³³ the Raman bands at $\sim 940\text{ cm}^{-1}$ can be explained by changes in the SiC bonding states from amorphous to crystalline with increasing annealing temperature. This view is supported by the XRD results that show the presence of the β -SiC phase in annealed films. It should be noted that the Raman bands at $\sim 940\text{ cm}^{-1}$ that were reported in Ref. 34 for a SiC film showed features very similar to those observed in this work. In the cited reference, they were attributed to the longitudinal optical phonon band of microcrystalline SiC.

D. TEM investigations

As a complementary technique to XRR and XRD, TEM yields local structural information with atomic resolution. To provide a direct view of the structural evolution and forma-

FIG. 5. Cross-sectional TEM images of $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayer samples. The samples were [(a) and (b)] as deposited, annealed at [(c) and (d)] $900\text{ }^{\circ}\text{C}$, and at [(e) and (f)] $1100\text{ }^{\circ}\text{C}$. Each horizontal pair of plots correspond to the same processing conditions. The left plot is a bright field image and the right plot is a high resolution image. The visible Si NCs (dashed-line circles) and β -SiC NCs (solid-line circles) are indicated in the high resolution images [plots (d) and (f)].

tion of NCs, several samples were characterized by TEM. Figure 5 shows cross-sectional TEM views of $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayer films. Plots (a) and (b) depict the as-deposited films, plots (c) and (d) show the films annealed at $900\text{ }^{\circ}\text{C}$, whereas plots (e) and (f) show the films annealed at $1100\text{ }^{\circ}\text{C}$. Each horizontal pair of images corresponds to the same processing condition. In each case, the left plot is a bright field image and the right plot is a high resolution image. Figure 5 shows that T_a has a strong influence on the physical structure of the films. The as-deposited sample [plot (a)] features a clear layered structure with sharp interfaces. The individual layers comprise uniform amorphous phases. The Si-rich layers and near-stoichiometric SiC layers appear light and dark, respectively, due to the density difference between $\text{Si}_{1-x}\text{C}_x$ and SiC. No lattice planes were observed in a high resolution image [see plot (b)], which indicates that the as-deposited sample is amorphous. For $T_a=900\text{ }^{\circ}\text{C}$, the layered structure is recognizable [see plot (c)], although the interfaces of adjacent layers are somewhat rougher.

The associated high resolution image [plot (d)] features clear lattice fringes (labeled by dashed-line circles), indicating the formation of NCs. It should be noted that only NCs that have the correct orientation with respect to the incident electron beam can be seen by their lattice images. A measurement of the lattice fringes in plot (d) demonstrates that the NCs are composed of Si atoms because the lattice spacing is $\sim 3.1\text{ }\text{\AA}$, matching well with Si {111} lattice planes. After annealing at $1100\text{ }^{\circ}\text{C}$, the layers have broken down and become discontinuous [see plot (e)] due to atomic diffusion during annealing. At the same time, more lattice fringes of NCs emerged (dashed-line and solid-line circles), indicating a higher density of NC. Besides Si NCs, SiC NCs (la-

FIG. 6. (Color online) (a) FTIR absorption spectra obtained from Si_{0.96}C_{0.04}/SiC multilayer films with annealing temperature as a parameter. (b) The peak position and FWHM of the Si-C absorption peak vs annealing temperature. The dashed lines are guides for the eye.

beled by solid-line circles) were found with lattice fringes (~ 2.5 Å) matching β -SiC {111} lattice planes. The Si-NC size obtained from the TEM micrographs is in the range of 3–5 nm, whereas the β -SiC NC size is in the range of 2–3 nm.

E. Infrared absorption

Bonding configurations were investigated by IR absorption spectroscopy. To minimize the effect of substrates on IR absorption measurements, the multilayer films were deposited on intrinsic Si wafers (400 μ m thickness, double sides polished, resistivity of ~ 2500 Ω cm). Figure 6(a) shows the dependence of the IR absorption spectra of Si_{0.96}C_{0.04}/SiC multilayer films on various annealing temperatures. For comparison, the spectrum of the as-deposited film is also shown. Similar IR spectra (not shown) were observed for the Si_{0.9}C_{0.1}/SiC multilayer films. Also shown in Fig. 6(b) is the peak position (ν_0) and FWHM of the Si-C absorption peak versus T_a , which were extracted from Fig. 6(a). A well-defined peak centered at 734–810 cm⁻¹ [see plot (a)] corresponds to stretching vibrations of Si-C bonds.^{35,36} The IR spectra of the as-deposited film and the film annealed at 800 °C consist of broad bands centered at ~ 734 and ~ 772 cm⁻¹, respectively, which can be fitted well by a Gaussian function. The Gaussian shape reflects a Gaussian distribution of the Si-C bond length and angle that is char-

acteristic of an amorphous SiC structure.³⁷ As T_a increases within the range of 900–1100 °C, narrow and nearly symmetric absorption peaks emerge at about 800–810 cm⁻¹. These peaks cannot be fitted by a Gaussian distribution and are best fitted by a combination of Lorentzian ($\sim 60\%$) and Gaussian ($\sim 40\%$) distributions. The Lorentzian shape is characteristic of low bond angle distortion and narrow bond length dispersion. An increasing Lorentzian component suggests the production of more uniform Si-C bond environments³⁸ and/or crystalline structure,³⁹ with which a higher number of Si-C bonds are associated. The FWHM [see plot (b)], on the other hand, significantly decreases with T_a . It is 245 cm⁻¹ for the as-deposited sample and then reduces to 119 and 88 cm⁻¹ after annealing at 900 and 1100 °C, respectively.

In summary, with increasing T_a , the IR absorption spectra of Si-C bonds have the following features: (i) the absorption band becomes more pronounced and ν_0 is shifted to a higher wave number, (ii) the FWHM decreases as ν_0 increases, and (iii) the line shape changes from a Gaussian distribution to a Lorentzian distribution. These phenomena combined with XRD and Raman data demonstrate that simultaneous Si and SiC phase separation takes place upon annealing at $T_a \geq 900$ °C. The following chemical equation describes the reaction:

Due to decomposition of Si_{1-x}C_x into SiC and elemental Si, the observed evolution of IR spectra with increasing T_a can be assigned to temperature activated breaking and rearrangement of Si-C and Si-Si bonds in the amorphous matrix.¹⁸ The band shifts toward higher wave numbers and the FWHM narrowing indicate an increase in order as well as an increase in the number of Si-C bonds in the annealed films.^{38,40} However, it should be noted that IR spectroscopy does not allow direct information on Si NCs.

The concentration of Si-C bonds ($N_{\text{Si-C}}$) can be determined from the integrated IR absorption peak according to the following equation:^{41,42}

$$N_{\text{Si-C}} = A_s \int \frac{\alpha(\omega)}{\omega} d\omega, \quad (2)$$

where $\alpha(\omega)$ is the absorption coefficient, ω is the vibration frequency of the corresponding absorption band, and A_s is the inverse absorption cross section of the considered mode. For the stretching vibration mode of a Si-C bond, A_s is 2.13×10^{19} cm⁻².^{37,42} The calculated Si-C bond density is shown in Fig. 7. $N_{\text{Si-C}}$ density progressively increases from 5.2×10^{22} cm⁻³ (as deposited) to 9.8×10^{22} cm⁻³ (annealed at 1100 °C).

IV. CONCLUSIONS

Sputter-deposited Si_{1-x}C_x/SiC multilayer films were prepared by depositing alternating layers of Si-rich and near-stoichiometric SiC. The Si_{1-x}C_x/SiC layers act as a starting material for the formation of Si NCs during postdeposition annealing. The influence of the annealing temperature on the structural evolution and formation of Si and SiC NCs was

FIG. 7. (Color online) Evolution of the $N_{\text{Si-C}}$ density vs annealing temperature. The dashed lines are guides for the eye.

investigated. As-deposited films exhibited an amorphous structure. Annealing induced changes in the layered structure and formation of Si and SiC NCs. XRR measurement revealed that the $\text{Si}_{1-x}\text{C}_x/\text{SiC}$ layered structure is well developed and stable for an annealing temperature of up to 800 °C. XRD analysis shows that the formation of Si NCs occurs at 800 °C in the $\text{Si}_{0.96}\text{C}_{0.04}/\text{SiC}$ multilayer films. The $\text{Si}_{0.9}\text{C}_{0.1}/\text{SiC}$ multilayer films, on the other hand, remain amorphous at 800 °C. At temperatures ≥ 900 °C, the formation of Si NCs is accompanied by the formation of β -SiC NCs in all samples. At the same time, interfaces between adjacent layers become less well defined. The NC sizes estimated from XRD and Raman shift data were found to be in reasonable agreement with TEM results. The changes in IR absorption spectra observed with annealing suggest an increasing Si-C bond density with increasing temperature.

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