Temperature dependence of silicon carbide interface formation: A photoelectron spectroscopy study

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The formation of a carbide interface layer between the Si(100) surface and hydrogen-free sp^2 amorphous carbon films is investigated at different substrate temperatures in the range from ambient to 1040 °C. The analysis of the interface and film is performed with photoelectron spectroscopy in the ultraviolet and x-ray regime. A carbon beam is created by electron-beam evaporation of graphite and the stepwise *in situ* deposition of carbon (0.3 monolayer/min) allows to follow the evolution of the carbide surface layer and interface. At temperatures at and below 750 °C a thin carbide layer ($\leqslant$0.4 nm) is rapidly formed, followed by the growth of a pure carbon overlayer. The valence band (VB) as well as the core-level spectra reflect the rapid formation of a SiC interface and subsequent carbon overlayer growth. If a substrate temperature above 900 °C is chosen, the carbon overlayer growth is completely suppressed, and a pure carbide layer is present. The VB spectra of the carbide layer are identical to those of the bulk SiC phases. The continued carbide layer formation and absence of a carbon overlayer is attributable to the enhanced outdiffusion of silicon, which leads at the same time to the formation of a Si-rich surface. For temperatures below 900 °C the carbidic interface is carbon-rich, which is attributed to carbon enrichment at the carbon-overlayer–carbide contact area. A comparison with experiments described in the literature allows to evaluate the influence of processing parameters such as ion irradiation on the interface formation.

INTRODUCTION

In the deposition of thin films the formation of an interfacial layer at the contact area between substrate and overlayer can determine the functionality of the whole structure. Investigations on the electronic, mechanical, and other properties of interfaces have been numerous in recent years and illustrate the importance of controlling and tailoring the properties of these thin intermediate layers. Since carbonaceous thin films have found widespread application, the study of interface formation has become important and often involves the formation of a carbidic interface layer. In the beginning, interest was focused on understanding and solving questions related to film adhesion,[1,2] whereas recent experiments are concerned with the electronic properties of *a*-C:H/silicon structures and the nucleation of diamond.[3–6] Questions related to the nucleation of diamond have triggered a renewed interest in the formation of thin silicon carbide (SiC) layers as a primary reaction step in the growth of polycrystalline diamond films. The investigation of interface formation, however, poses a number of experimental problems related to the usually small interface thickness and the continuously and rapidly changing surface composition early on in the deposition process. The combination of photoelectron spectroscopy as a highly surface sensitive analytical tool, and the *in situ* deposition of thin films has been particularly fruitful in the investigation of the early stages of film growth and interface formation.[1,4,7,8]

Interface formation is an inherently complex process, and since the deposition conditions are often far from thermodynamic equilibrium, the relations between the different parameters and the final interface properties are mostly difficult to understand. In choosing electron-beam evaporation of graphite as the deposition technique, only particles with thermal energies are involved and erosion of the interface due to chemical reactions with a highly reactive gas phase is avoided. A similar process using either gaseous or solid carbon precursors is also frequently employed to deposit thin SiC layers on Si with applications in electronic devices in mind.[9–12]

In the present study the interaction between carbon and a silicon (100) surface is investigated for temperatures ranging from ambient to 1040 °C. The changes in surface composition and structure are monitored subsequent to each deposition step by photoelectron spectroscopy in the ultraviolet (UPS) and x-ray photoelectron spectroscopy regime (XPS).

EXPERIMENT

The substrates were silicon wafers of (100) orientation, which were subjected to repeated sputter-anealing cycles prior to the experiment in order to remove surface contaminants such as carbon and oxygen. As endpoint for the substrate preparation we used the emergence of the surface state located at 0.7 eV binding energy in the UPS spectra (see Fig. 1, bottom spectra), which is characteristic for a dimer reconstructed Si(100) surface. The oxygen concentration was below 2% for all deposition steps. The substrate temperature was adjusted between ambient and 1040 °C and measured by a thermocouple at the back side of the heater. Subsequent to the cleaning procedure, the substrates were exposed to a carbon beam produced by evaporation of graphite using an electron-beam evaporation source (Omicron EFM3). The deposition rate was adjusted at about 0.3 ML carbon/minute [a monolayer of amorphous carbon (*a*-C) corresponds to 2.0 Å for a film density of 1.8 g/cm^3] and controlled by means of a quartz-crystal monitor. We will henceforth use the term

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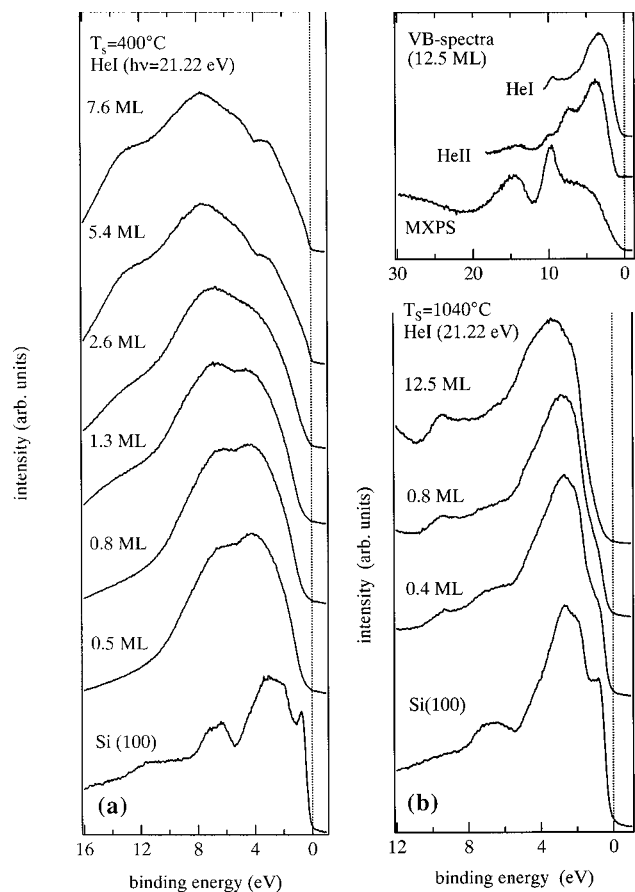

FIG. 1. On the left-hand side (a) the UPS VB spectra recorded during the carbon deposition on Si(100) at a substrate temperature of 400 °C are shown. The bottommost spectrum corresponds to the clean Si(100) substrate. The figure in the right-hand side (b) contains the VB spectra measured for the carbon deposition performed at 1040 °C substrate temperature. The VB spectra obtained with different excitation energies ranging from He *I* to MXPS (Al $K\alpha$), for the deposition step with a carbon coverage of 12.5 ML, are included at the top of the figure. Note the different scaling as compared to the main body of the figure.

carbon coverage to refer to the amount of carbon deposited on the sample according to the measurement of the quartz-crystal monitor. Subsequent to each carbon deposition step the substrate was transferred from the preparation to the analysis chamber (base pressures around 5×10^{-10} mbar). A series of deposition steps covering the range from 0.2 to a maximum of 50 ML carbon were performed.

The photoelectron spectra were measured on a Leybold-SPECS EA11/100MCD system. A helium-gas discharge lamp emitting light in the ultraviolet region (UPS, He I, $h\nu=21.22$ eV and He II, $h\nu=40.82$ eV) was used to determine the valence-band spectra (VB spectra), and the typical resolution is 0.1–0.2 eV. The x-ray photoelectron spectroscopy was performed with an excitation energy of 1253.6 eV (Mg $K\alpha$, XPS), and for the series at 1040 and 950 °C substrate temperature an excitation energy of 1486.6 eV (Al$K\alpha$,MXPS) was used. The spectra have been recorded using constant retardation ratio for the UPS, and constant pass energy for the XPS measurements and are presented without background or satellite subtraction. The energies of the discussed spectral features are given with respect to the Fermi level (E_F) and the Au$4f_{7/2}$ core-level line (positioned at 84.0 eV binding energy) of a clean gold sample.

RESULTS AND DISCUSSION

In Fig. 1 the VB spectra recorded in the course of carbon deposition for the substrate temperatures of 400 °C [Fig. 1(a)] and 1040 °C [Fig. 1(b)] are shown. The bottom spectrum is in each case the VB spectrum of the Si(100) substrate and the surface state at 0.7 eV can clearly be distinguished. The surface state is characteristic for the presence of a (2×1) dimer-reconstructed surface, while the other spectral features up to a binding energy of 6 eV are linked to the bulk band structure of silicon. A detailed discussion of the Si(100) VB spectra is given in Refs. 13 and 14. The smaller peaks at binding energies of about 6 and 7 eV are related to residual oxygen[13] (<2% according to XPS) and are enhanced in the UPS spectra due to the relatively large photoionization cross section of oxygen[15] as compared to the *s*-symmetric states of Si. The rapid disappearance of the surface state, e.g., after the deposition of about 0.5 ML at ambient temperature, attests to the strong interaction between the Si surface and carbon: it can be related to a breaking of the Si-Si dimer bond in favor of the formation of a Si-C bond.[12]

For the experiment performed at a substrate temperature of 400 °C the deposition of 0.5 ML carbon leads to the disappearance of the surface state, and the spectrum is dominated by two peaks located at binding energies of 4.0 and 6.6 eV. With increasing carbon coverage the peak at 6.6 eV is shifted to slightly higher binding energies and gains in intensity with respect to the 4.0-eV peak. An additional rather narrow peak is observed at 3.0 eV for coverages exceeding 2.6 ML. After the deposition of 2.6 ML carbon, the VB spectra are dominated by the amorphous carbon film (*a*-C), and any further changes are attributable to the rapidly diminishing contribution from the substrate/interface. The valence band of *a*-C is composed of the *p*-π band situated close to the Fermi energy (corresponding to the peak at 3.0 eV in the spectra) and the *p*-σ band at larger binding energies (8.0 eV for this film); the presence of the *p*-π band also attests to the dominance of sp^2 hybridized carbon in these layers. *a*-C films deposited at elevated substrate temperatures already possess graphitic inclusions, and their VB spectra as a function of deposition temperature have been described in detail elsewhere.[16] The assignment of the other spectral features is, however, not as straightforward. A comparison with the VB spectra of SiC (described in detail in the next paragraph) indicates that the peak that appears at 4.0 eV is linked to the SiC interfacial layer, but it cannot be unequivocally separated from the signal of the Si substrate. The presence of a thin SiC layer is also confirmed by the XPS analysis.

The observations made at the higher substrate temperature of 1040 °C differ markedly from the results obtained for the lower temperature. The VB spectra are summarized in Fig. 1(b), and the intensity of the surface state at 0.7 eV is diminished after the deposition of the first 0.4 ML carbon, but more than 1 ML has to be deposited for a complete disappearance. The most intense peak is shifted from 2.7 eV in Si(100) to a binding energy of 3.4 eV, while an additional small peak located at 9.5 eV gains in intensity. The position of the valence-band maximum is shifted to 0.5 eV, quite in

contrast to the a-C film [Fig. 1(a)] where the valence-band maximum coincides with the Fermi energy. After the deposition of 3.2 ML no further changes are observed in the VB spectra. The spectra do not resemble those of a-C films or graphite[17] but are in good agreement with the VB spectra of SiC.[7,14,18] The XPS analysis supports this assignment and shows the absence of a pure carbon phase and the formation of a SiC layer at the surface. The graph included at the top of the figure contains the VB spectra obtained after the deposition of 12.5 ML carbon measured with different excitation energies, namely He I, He II, and Al $K\alpha$. The energy dependence of the photoionization cross section leads to a dominance of excitation from p-symmetric bands in the UPS and of s-symmetric bands in the XPS VB spectra,[15,19] which explains the difference in relative spectral intensities. The peak located at 3.4 eV, close to the Fermi energy, is related to the Si $3p-C\,2p$ band, while for higher binding energies the contribution from s states increases. The peak around 9.5 eV is related to excitation from a band derived from the Si $3s$ and C $2s$ states, and the peak at the highest binding energy which for energetic reasons is only visible in the MXPS VB spectrum, stems from a band dominated by C $2s$ states.[18] The VB spectra are indeed in good agreement with the SiC spectra described in the literature. Since the general features of the density of states (DOS) in a covalently bonded semiconductor such as SiC are determined by the short-range chemical order, the differences in the VB spectra for different polytypes are rather small. We are therefore reluctant to draw any conclusions on the presence of a specific SiC structure in the surface layer, although other investigations have shown that β-SiC is frequently formed on Si(100) substrates.[9,11,20]

The analysis of the C $1s$ and Si $2p$ core level also shows the evolution of a carbide interface and, for temperature below 900 °C, the growth of the carbon overlayer as already described in the previous paragraph. In addition, the analysis of the XPS core-level spectra enables us now to separate the contributions from the carbide interface, the substrate, and the overlayer. Thus we can evaluate in a more quantitative manner the evolution of the interface in the course of the deposition experiment. In order to separate the carbide and Si substrate components of the Si $2p$ peak, a deconvolution procedure using Doniach-Sunjic functions[21] and a Shirley[22] background is used. The Si $2p$ peak is composed of two components due to the spin-orbit splitting, and the Si $2p_{3/2}$ substrate peak is located at a binding energy of 99.4 ± 0.1 eV, while the chemically shifted carbide peak is positioned at 100.4 ± 0.1 eV. During the deconvolution procedure the spin-orbit splitting was fixed at 0.6 eV and the branching ratio $2p_{3/2}/2p_{1/2}$ was set at 2.0. An example for a deconvolution of the Si $2p$ and C $1s$ core-level peaks is given in Fig. 2(b) for a substrate temperature of 1040 °C after the deposition of 6.4 ML carbon. Figure 2(a) contains the results of the deconvolution procedure applied to all Si $2p$ peaks recorded at 400, 750, 900, and 1040 °C as a function of carbon coverage. The SiC concentration is below 5% throughout the complete deposition cycle at ambient temperature, which corresponds to a SiC interface ''thickness'' of less than a monolayer.

The thickness of the carbide layer can be calculated from the exponential attenuation of the signal from the underlying Si substrate by the SiC layer.[4,23] In this calculation the presence of a homogenous, flat carbide layer is implicitely assumed and the mean free path of the electrons is set at 1.8 nm for the XPS and 2.0 nm for the MXPS measurements. It should be mentioned at this point that the slow disappearance of the surface state at the 1040 °C deposition cycle (see Fig. 1) indicates a deviation from the ideal layer-by-layer growth and the formation of SiC islands and crystallites. Similar observations have been made for the oxidation of Si(100).[13] The extension of the SiC interface is clearly quite small for 400 and even 750 °C: 0.19 and 0.4 nm, respectively, which corresponds to only 1–3 ML of SiC. The onset of carbon film growth is observed for carbon coverages below 1 ML, and a steady-state thickness of the carbide layer is rapidly reached. However, raising the temperature by another 150 °C to 900 °C completely changes the situation, and a continuous growth of the SiC layer takes place, while the carbon over-

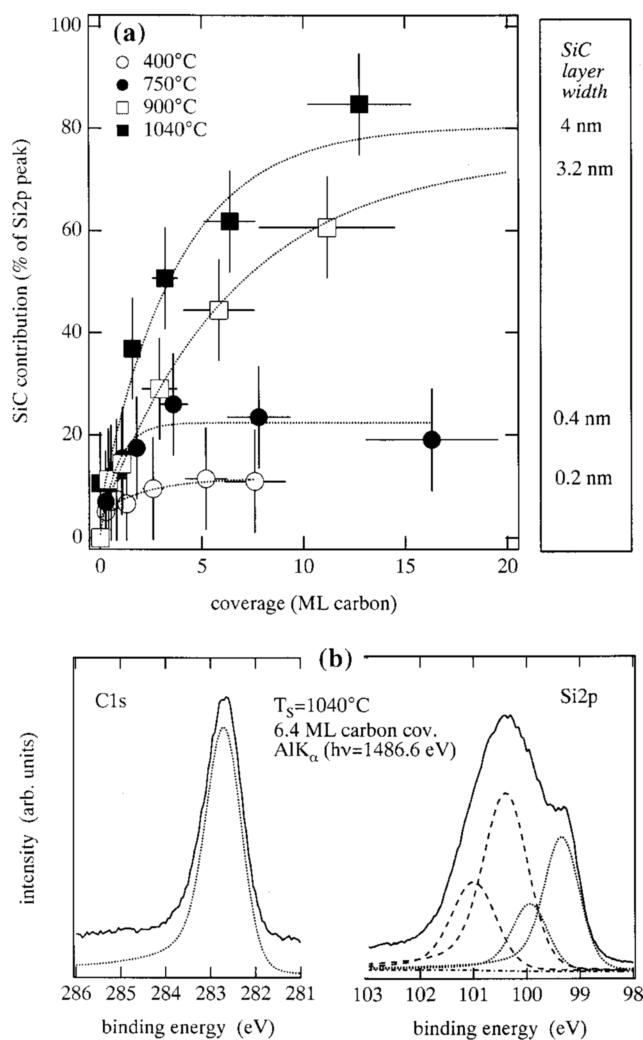

FIG. 2. (a) Contribution of SiC to the Si $2p$ peak as a function of carbon coverage for the temperature range between 400 and 1040 °C. The results for ambient temperature are given in the text. An estimate for the SiC film thickness is included at the right-hand side of the figure, and the bottom graph (b) illustrates the fit procedure applied to determine the SiC contributions to the Si $2p$ and the C $1s$ peak. The spectra measured after the deposition of 6.4 ML carbon at a substrate temperature of 1040 °C are shown and yield a Si/SiC ratio of 61% to 49%, and the C $1s$ peak contains only a SiC contribution.

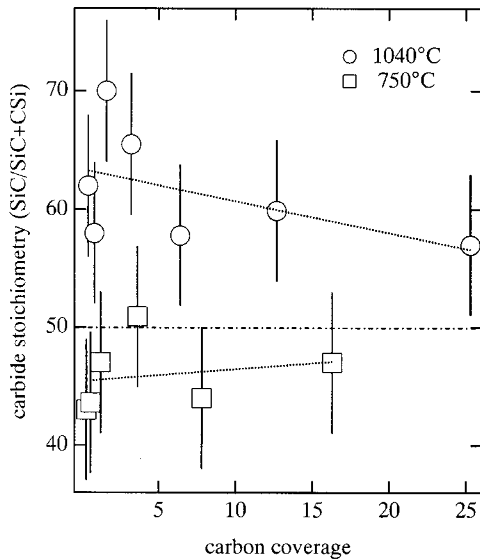

FIG. 3. Stoichiometry of the carbide surface layer for a substrate temperature of 750 and 1040 °C. The lines are included as a guidance for the eye.

layer formation is completely suppressed. The different nature of the surfaces is reflected in micrographs taken with a scanning electron microscope: while for the deposition cycles performed below 900 °C an essentially featureless surface is observed, the 1040 °C films exhibit a granular structure that is characteristic of polycrystalline material with a small size of the individual crystallites.

The deconvolution of the C 1s and Si 2p peaks also allows to determine the stoichiometry of the carbide layer. For this purpose the integrals of the carbide peaks are corrected for the photoionization cross section[24] of the respective core level (C 1s and Si 2p) and the analyzer transmission function. The percentage of carbide that stems from the Si 2p peak (SiC) as a function of carbon coverage is shown in Fig. 3 for 750 and 1040 °C. The denominator (SiC+CSi) is the sum of the corrected carbide integral from the Si 2p (SiC) and C 1s (CSi) peaks. The values obtained for the other temperatures are omitted from the figure for the sake of clarity, but the general behavior for depositions at and below 750 °C is equivalent, and the same holds true for the second group at temperatures at and above 900 °C. The SiC surface is enriched in carbon for the lower temperature, and a carbon-deficient and therefore silicon-rich surface is present at 1040 °C. Since no significant chemical shift in the C 1s (282.6 eV) or Si 2p carbide peak occurs, it can be assumed that the short-range order around the carbon atoms remains essentially unchanged and corresponds to that of SiC.[7] It seems most likely that the excess silicon is indeed accumulated at the surface of an otherwise stoichiometric SiC layer. In addition, the low solubility of carbon in SiC supports the model that the enrichment in one element indeed takes place at the surface rather than in the bulk. The graphitization of SiC surfaces due to the loss of Si by sublimation usually occurs at still higher temperatures with a threshold for sublimation above 1100 °C (Refs. 14 and 25) and is not expected to be of importance here. A carbon-rich SiC layer is, on the other hand, only observed in the presence of a carbon overlayer, and the SiC-carbon boundary can be likened to a carbon-terminated SiC surface.

The formation of an SiC layer exhibits a strong temperature dependence: while at temperatures at and below 750 °C only a thin SiC layer is formed, which subsequently functions indeed as an interfacial layer, higher temperatures exceeding 900 °C favor the buildup of SiC surface layers, and the a-C overlayer formation is completely suppressed. In general, the thickness of a surface/interface layer formed by chemical reactions between a solid material and an atom beam is limited by the mass transport or diffusion of the reactants through the emerging surface layer. In a rather simple view of the process the fluxes of the reactants to the site of interaction are considered. In our case the incoming carbon atoms readily interact with the Si surface, leading immediately to the formation of a SiC layer: if the flux of carbon atoms can now be equilibrated either by the diffusion of carbon or Si through the carbide barrier, the carbide layer continues to grow. If, on the other hand, the carbon flux exceeds the reactant transport flux through the barrier (the SiC layer in our case), the carbon overlayer begins to grow. The reaction required to continue SiC formation would now involve the liberation of carbon atoms from a binding environment in the a-C layer, and thus constitutes a solid-state reaction among a-C, SiC, and Si.

It is, however, not required that the atoms diffuse through the dense SiC network, but they might move along pores and grain boundaries. Such a mechanism for Si diffusion through a SiC barrier layer has been described in Ref. 11 and the out-diffusion of Si leads consequently to the formation of etch pits underneath the SiC layer. The presence of a Si-rich surface for the high-temperature regime also indicates that Si is now transported in significant amounts through the SiC layer. It can be assumed that the incoming carbon atoms react immediately with any unreacted Si atom thus depleting the surface of Si, rather than diffuse through the SiC layer and react with the underlying Si substrate. The rapid disappearance of the surface state in the VB spectra also attests to a strong interaction between C and the Si surface, while the somewhat slower intensity reduction at elevated temperatures indicates a change in the carbide growth mode in the direction of an island or ''patch'' growth mode.

A comparison with other experiments illustrates the influence of processing parameters such as ion irradiation or the presence of atomic hydrogen on the carbide interface formation. The deposition of amorphous hydrogenated carbon (a-C:H) requires the use of energetic ions, and the carbide formation has been reported in detail in several publications.[1–4] In contrast to the thermally activated process observed in our experiment, the additional energy input by the irradiation of the sample in the plasma-assisted deposition process for a-C:H leads to an increased thickness of the carbide interface. Schäfer *et al.*[4] observed an interface thickness of 1.8 nm for a maximum ion energy of 200 eV, while Kawasaki *et al.*[3] give values of 0.7 nm for ion energies around 350 eV and are unable to detect a carbide interlayer if ion energies as low as 15 eV are used. The connection between energy input by ion irradiation and interface thickness is evident, the microscopic mechanisms which contribute to interface growth in the presence of energetic particles, however, remain uncertain.

The role of a SiC interface has also been controversially

discussed in the bias-enhanced nucleation of diamond. It has been shown in our experiment that the formation of an SiC layer is unavoidable, as is expected for an exothermic reaction such as C with Si, albeit the thickness of the SiC layer is strongly temperature dependent. The temperature range of the bias-enhanced nucleation falls indeed in the regime of rapidly changing interface thickness between 750 and 900 °C. In addition to the primary interface-forming reaction the SiC layer can be thinned by interaction with atomic hydrogen,[23] present in large concentrations in the plasma employed for diamond growth. The interface observed at the end of the deposition process therefore does not necessarily reflect the surface composition or structure present at the beginning of the nucleation process, and slightly different processing conditions might finally yield quite substantial deviations in the observed interface characteristics. In order to study the dynamic changes in a carbide interface induced by reactive species or ion irradiation, the experiment described in the present publication can be easily extended and will afford a better understanding and control of the deposition of thin carbide and other surface or interfacial layers.

CONCLUSIONS

The formation of SiC layers on Si(100) substrates was observed step-by-step with photoelectron spectroscopy for various substrate temperatures spanning the range from ambient to 1040 °C. The surface was exposed to a low-energy carbon beam created by electron-beam evaporation of graphite. It is indeed possible to roughly divide the investigated temperature range in two regimes. At and below 750 °C a thin SiC layer is formed, but immediately followed by the growth an *a*-C overlayer. The SiC layer thickness is only about 1 ML at 400 °C and is about doubled at 750 °C. Although the lack of well-defined peaks related to crystalline SiC in the VB spectra might indicate the presence of an amorphous rather than crystalline interface, the evidence is insufficient for a final conclusion. Going to higher substrate temperatures beyond about 900 °C, the formation of a carbide surface layer is observed, while the *a*-C layer growth is completely suppressed. The SiC layer is clearly crystalline in nature, and the VB spectra correspond well to published data on SiC. In the lower-temperature regime the surface is carbon terminated, while for higher temperatures a Si-rich surface layer is observed. These results are commensurate with a thermally activated process, and the diffusion of Si through the SiC surface layer fuels the continuation of SiC growth at higher temperatures, while C atoms tend to react immediately with surplus surface Si. The results of the present study can be used to estimate the influence of other processing parameters, such as ion irradiation or reactive species common to plasma chemical vapor deposition processes.

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