The chemisorption of $H_2C[Si(CH_3)_3]_2$ and $Si_6(CH_3)_{12}$ on Si(100) surfaces

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(Received 28 June 1996; accepted for publication 12 May 1997)

The chemisorption of bis(trimethylsilyl)methane (BTM, $CH_2[Si(CH_3)_3]_2$) and dodecamethylcyclohexasilane (DCS, $Si_6(CH_3)_{12}$) on clean Si(100) surfaces has been studied by C 1*s* core-level and valence-band photoemission spectroscopy. Our model for the deposition of carbon by BTM involves decomposition into a $-CH_2Si(CH_3)_3$ surface moiety for room-temperature adsorption, which further decomposes upon annealing to 550 °C to form a surface terminated primarily by CH_x units. DCS deposits almost three times as much C on the surface as BTM. The data are consistent with DCS undergoing a ring opening and bonding to the surface as polydimethylsilane chains. Annealing both adsorbates to 950 °C causes a large decrease in the C 1*s* signal due to the fact that Si segregates to the surface at temperatures above 900 °C. The valence-band photoemission of Si(100) dosed with DCS at 950 °C is in good agreement with that of β-SiC, whereas the analogous BTM spectrum deviates significantly.

[S0021-8979(97)02716-3]

INTRODUCTION

Silicon carbide (SiC) has attracted the attention of researchers for two principal reasons: first, because it is a semiconductor that can be used at high temperatures and in high radiation fields, and second for its tribological importance as a wear-resistant material in the tool industry. SiC's resistance to radiation and thermal breakdown, and its hardness are all manifestations of the high silicon–carbon bond energy (5 eV). SiC exists in the cubic β phase, as well as in approximately 170 hexagonal polytypes, each with a slightly different band gap and carrier mobility.[1] This allows for band-gap-engineering structures using different polytypes or stoichiometries.[2] In order to realize such structures, it is necessary to achieve layer-by-layer control of the epitaxial growth of SiC via atomic layer epitaxy (ALE). This technique consists of a series of two step cycles: self-limiting adsorption of a monolayer followed by reactivation of the surface.[3]

Up to now, chemical vapor deposition of SiC has been performed by pyrolysis of hydrocarbons at high temperatures, typically, above 900 °C. Although useful for some applications, there is little hope of achieving layer-by-layer control of the growth process at such high temperatures. However, there is a major problem with low-temperature deposition; specifically, the comparatively small amount of C that is deposited onto the surface, as has been demonstrated in exploratory work of ALE of SiC. CCl_4 has a low sticking coefficient on Si and is, thus, a poor candidate for ALE. Dimethylsilane and diethylsilane (DES) can both be adsorbed as monolayers in a self-limiting fashion, but most of the alkyl groups desorb[4] at temperatures of 500–600 °C, which are required to desorb the hydrogen passivation layer from the Si surface. This led to the idea of connecting a C atom between two Si atoms as in bis(trimethylsilyl)methane (BTM, $CH_2[Si(CH_3)_3]_2$) to prevent it from desorbing as an alkyl group. Indeed, the uptake of C from BTM was increased by a factor of 2 over DES and the C deposited was carbidic without the graphitic component found with DES. We have found that a cyclic compound, dodecamethylcyclohexasilane (DCS, $Si_6(CH_3)_{12}$), has almost three times again as much C uptake as BTM and gives surfaces with a valence-band structure very similar to that of single-crystal SiC.

For the use of SiC in the manufacture of integrated circuits, it is desirable to deposit it epitaxially over a large-area substrate such as a Si wafer. However, the 20% difference in lattice constants between Si (5.4301 Å) and SiC (4.3596 Å) has made the epitaxial growth of SiC on Si substrates difficult to perform.[1] Chemical vapor deposition (CVD) using separate precursors for Si and C [such as SiH_4 and methane (Ref. 5) or propane (Ref. 6)] has been attempted and, recently, reports of single-precursor CVD [methylsilane,[1] diethylsilane,[4] dimethylisopropylsilane,[7] silacyclobutane,[8] disilacyclobutane,[9] methyltrichlorosilane,[10] hexamethyldisilane,[11] C_{60} (Ref. 12)] have been cited. In addition to the obvious simplification of the experimental apparatus, the other principal advantage of using a single precursor is that they are often more stable under ambient conditions than the pyrophoric SiH_4. Ideally, the precursor should be noninflammable and nontoxic; to reduce the thermal budget it should decompose to form SiC at low temperature, and it should contain as few extraneous elements (i.e., hydrogen) as possible. As yet, there is no obvious correlation between the stoichiometry or bonding configuration of the precursor gas and the quality of the resultant SiC film.

The general goal of this report is to identify the chemical species that are present on a Si surface following a saturation coverage of a precursor gas at a range of different temperatures. Particularly interesting is the nature of the passivation layer that terminates the broken bonds at the Si surface (the first step in an ALE cycle). Understanding the thermal decomposition, desorption, or chemical reaction of this layer is necessary for the second step of the ALE cycle, and has consequences for attaching self-assembling monolayers to Si surfaces.[13] We report the results of a high-resolution C 1*s* and valence-band photoemission investigation of the chemical species that are present on a Si(100) surface following the chemisorption of bis(trimethylsilyl)methane (BTM, $H_2C[Si(CH_3)_3]_2$) and dodecamethylcyclohexasilane (DCS, $Si_6(CH_3)_{12}$). Upon ring cleavage, DCS is known to undergo a thermal decomposition to form polycarbosilane,[14,15] which upon further heating, is known to form high-purity SiC fibers,[14–17] thus, making it an obvious candidate for CVD of SiC films.

EXPERIMENT

The C 1*s* and valence-band photoelectron spectra were recorded on the IBM display spectrometer in angle-integrated mode on the IBM/LLNL/Tulane/Tennessee/Wisconsin/LBNL undulator beamline (8.0) at the Advanced Light Source at Lawrence Berkeley National Laboratory (LBNL). C 1*s* photoemission and valence-band photoemission spectra were recorded with photon energies of 320 and 140 eV, respectively. We also recorded Si 2*p* core-level spectra (not shown). Because of the small chemical shifts in these spectra, they turned out to be less informative.

CVD experiments were performed in a sample preparation chamber adjacent to the IBM display spectrometer allowing samples to be prepared and transferred to the spectrometer *in vacuo*. Clean Si(100) substrates were prepared by direct Ohmic heating to 1000 °C in the preparation chamber, which is maintained at a base pressure of 5×10^{-10} Torr. Exposures were carried out by introducing into the chamber, through a sapphire leak valve, either BTM or DCS at 1×10^{-4} Torr for 100 s (10 000 L). DCS is a solid at room temperature and needed to be heated to 60 °C to increase the vapor pressure. These samples were then annealed at various temperatures, which were recorded using a Minolta Cyclops 152 optical pyrometer with emissivity set at 0.4. The BTM was purchased from Petrarch Systems and used without further purification and the DCS was synthesized by one of the authors (K.M.B.), according to a previously published procedure.[18]

RESULTS AND DISCUSSION

Figure 1 shows the C 1*s* photoemission spectra of a Si(100) surface after room-temperature exposure to 10 000 L of BTM and after annealing the exposed sample to 550, 750, and 950 °C. The room-temperature curve is broader than the spectra at higher annealing temperatures, suggesting some type of chemical inhomogeneity. It is known that diethylsilane spontaneously decomposes upon exposure to Si(100) leaving $-CH_2-CH_3$ moieties on the surface.[4] Thus, it is reasonable to assume that BTM similarly decomposes leaving behind $-CH_2-Si(CH_3)_3$. The CH_3 groups would give rise to the main peak at 284.6 eV (commensurate with the binding energy of adsorbed alkylsilanes) and the $-CH_2-$ group (bound between two Si atoms) could give rise to an asymmetric tail at lower binding energy. This is also commensurate with the fact that the integrated area of the top curve in Fig. 1 is greater than that of identical experiments (not shown) done with dimethylsilane and diethylsilane, which are believed to deposit one and two carbon atoms on the surface, respectively.[4]

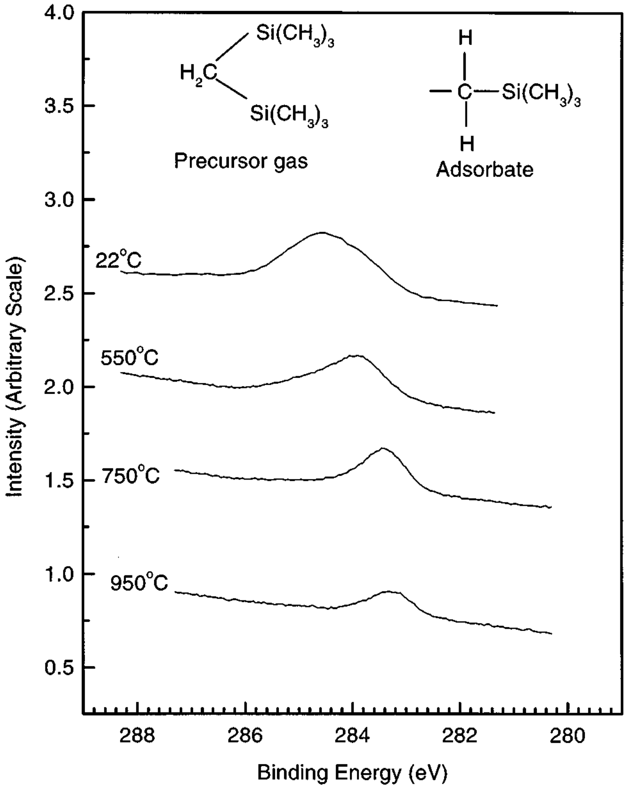

FIG. 1. The C 1*s* photoemission spectra of Si(100) exposed to 10 000 L of $CH_2[Si(CH_3)_3]_2$ (BTM) at 22 °C and after annealing at 550, 750, and 950 °C. The shift to lower binding energy after annealing indicates increasing dehydrogenation and the eventual formation of SiC.

After annealing at 550 °C for 10 s, the peak has become narrower and has shifted to lower binding energy, indicating that most of the methyl groups (or trimethylsilyl groups) have desorbed leaving a surface that is terminated primarily by CH_x groups. After the sample is annealed for 10 s at 750 °C, the Si, because it has a lower surface energy than C, has started to segregate to the surface and has begun to form SiC.[19] This is evidenced by three changes in the spectrum: a further shift in the peak position towards lower binding energy, the narrowing of the linewidth (indicative of more homogeneous chemical environment), and a decrease in the overall C 1*s* intensity. A further anneal to 950 °C causes yet another small shift in the binding energy and a further reduction in the intensity due to surface segregation of the Si. The final peak position (283.3 eV) is commensurate with that of C in SiC (283.25 eV).[4]

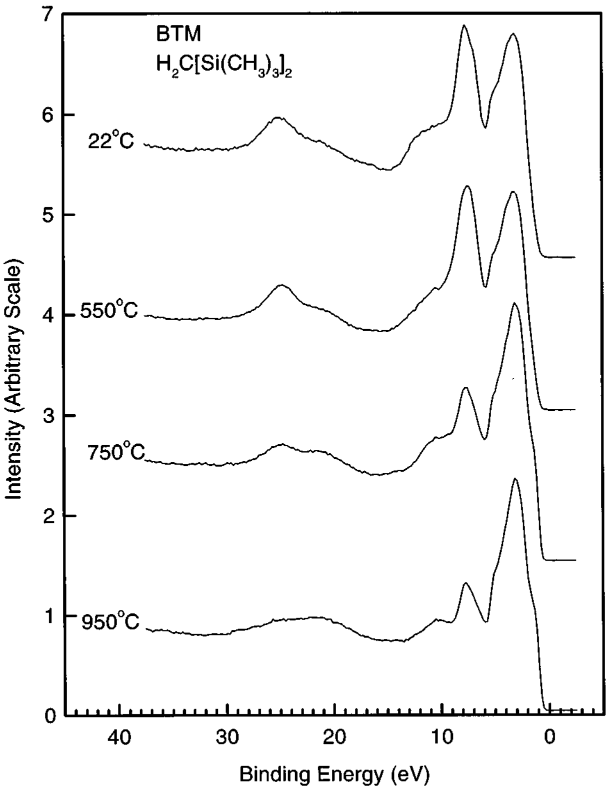

FIG. 2. The valence-band photoemission spectra of Si(100) exposed to 10 000 L of BTM at 22 °C and after annealing at 550, 750, and 950 °C. The decrease in the peak at 7.7 eV after annealing to 750 °C is indicative of the loss of C–H bonds in the film. The spectrum after the 950 °C anneal is nearly identical to that of clean Si(100), indicating Si segregation.

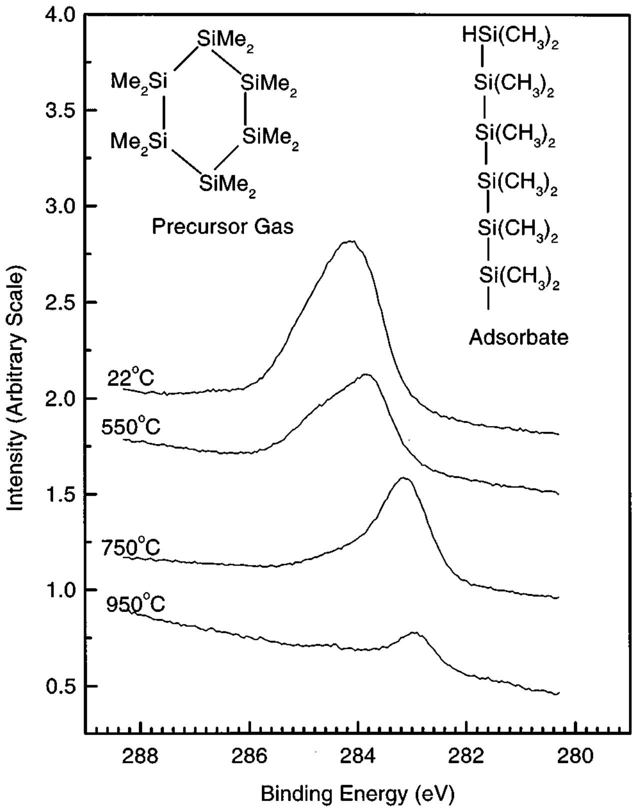

FIG. 3. The C 1s photoemission spectra of Si(100) exposed to 10 000 L of $Si_6(CH_3)_{12}$ (DCS) at 22 °C and after annealing at 550, 750, and 950 °C. The carbon signal remains very strong up to 750 °C, demonstrating effective carbon deposition by DCS. Me stands for methyl groups (CH_3).

Figure 2 shows the valence-band photoemission spectra of the same samples presented in Fig. 1. Comparing these spectra with the spectra of molecules[20] such as $Si(CH_3)_3$–$Si(CH_3)_3$, which contain similar bonds (Si–Si, Si–C, and C–H), we can assign the sharp feature at 7.7 eV binding energy to the presence of C–H bonds. We know from the core-level spectra in Fig. 1 that, upon annealing the sample to 550 °C, the C species with the higher binding energy desorbs. However, the first two valence-band spectra in Fig. 2 (before and after annealing to 550 °C) are essentially identical. Thus, we know that there must still be a significant number of C–H bonds at the surface after the first anneal, which is further evidence that the surface is now terminated by moieties consisting primarily of CH_x units.

After annealing to 750 °C, we see that the peak at 7.7 eV decreases significantly, indicating the removal of H from the film.

Further annealing to 950 °C causes only small changes in the spectra, as expected from the C 1s core-level spectra in Fig. 1. The spectrum is very similar to that of a clean Si(100) surface, with the remnant of the 7.7 eV feature characteristic of the Si valence band and the broad feature around 20 eV due to plasmon losses. This suggests segregation of Si to the surface.

Figure 3 shows the results of an experiment identical to that presented in Fig. 1, except the adsorbate gas is now the cyclic molecule $Si_6(CH_3)_{12}$ (DCS). The C 1s photoemission spectrum of the Si(100) surface exposed to 10 000 L of DCS at 22 °C is shown, together with spectra after annealing at 550, 750, and 950 °C. The most significant difference between the two precursors shows up in the area under the C 1s peak. For example, the C 1s area after room-temperature adsorption of DCS in Fig. 3 is fully 2.65 times as great as that in Fig. 1 for BTM, which is indicative of a proportionately greater amount of C deposited on the surface. If, as suggested, the surface moiety for BTM adsorption is $-CH_2-Si(CH_3)_3$, containing four C atoms, then DCS must contribute 10.6 C atoms to equally as many sites on the surface. Within experimental error, it is reasonable to assume that DCS undergoes a ring opening upon exposure to the clean Si(100) surface and attaches lengthwise as a polydimethylsilane chain ($[Si(CH_3)_2]_n$) contributing nearly all 12 of its C atoms to the surface (i.e., $n=6$). This would explain the increased intensity. The room-temperature C 1s spectrum of DCS is 13% narrower than that of BTM, which is reasonable in view of the fact that BTM has two inequivalent C atoms in the $-CH_2-Si(CH_3)_3$ surface species, whereas DCS contains only one type of C in the $Si(CH_3)_2$ groups. However, the extra width of the room-temperature spectra compared to the annealed surfaces suggests some additional chemical in both cases.

The second curve in Fig. 3 shows the C 1s spectrum after annealing the sample at 550 °C for 10 s. Here, the peak has taken on an asymmetry and shifted to lower binding

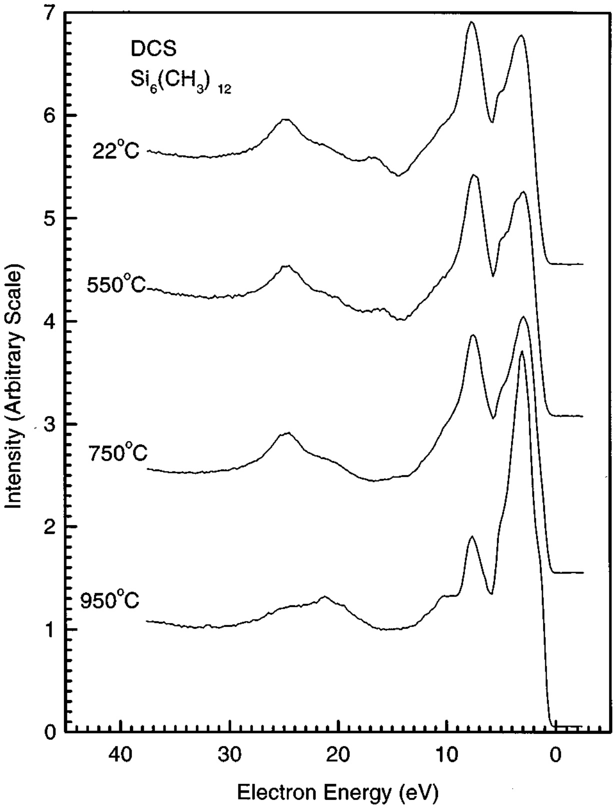

FIG. 4. The valence-band photoemission spectra of Si(100) exposed to 10 000 L of DCS at 22 °C and after annealing at 550, 750, and 950 °C. The presence of a well-defined C 2*s* feature at 16.5 eV suggests C atoms in a uniform chemical environment (such as that in polydimethylsilane). There is still a large number of C–H bonds in the film even after annealing to 750 °C, as indicated by the strength of the peak at 7.7 eV.

energy. This can be explained by the fact that polydimethylsilane is known to undergo thermal decomposition to form polycarbosilane,[14–17] which is an amorphous cross-linked material consisting primarily of C and Si. The second curve in Fig. 3 shows an intermediate stage of this decomposition, where some of the C is still in the form of CH_3 groups (high binding energy shoulder at 284.2 eV) and some is now cross-linked between two Si atoms in neighboring chains (low binding energy peak at 283.7 eV).

After annealing at 750 °C, the peak shifts dramatically to lower binding energy (283.1 eV), but there is still a weak shoulder at about 284 eV, the peak position for lower annealing temperatures. Further annealing removes this shoulder and also causes a dramatic decrease in intensity. The general trend in decreasing intensity as a function of annealing temperature is due to two causes: first, there is probably some desorption of methyl groups from the sample surface, and second, there is segregation of the Si to the surface. The small decrease in intensity between the first and third spectrum is probably due primarily to the desorption process, while the large final decrease is almost certainly due to Si segregation.

Figure 4 shows the valence-band photoemission spectra of the samples shown in Fig. 3. This series of spectra is essentially the same as those shown in Fig. 2 but with two important differences. First, the sample annealed to 750 °C still has a very strong peak corresponding to C–H bonds,[20] as might be expected from the fact that the polydimethylsilane adsorbates contain much more H and their bulkiness makes it more difficult for H to escape. Second, there is a well-defined C 2*s* peak[4] at 16.5 eV in the top two spectra of Fig. 4, which is washed out in the spectra of BTM in Fig. 2.

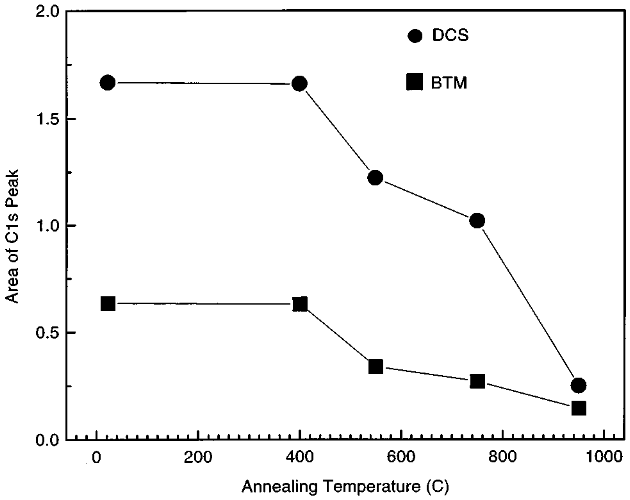

FIG. 5. The area under the C 1*s* photoemission peak vs annealing temperature for the spectra shown in Figs. 1 and 3. DCS deposits more than twice as much C at the Si(100) surface. The sharp drop in C 1*s* intensity at 950 °C is due to Si surface segregation.

Figure 5 shows a plot of the integrated areas under the C 1*s* photoemission peaks from Figs. 1 and 3 as a function of annealing temperature from 22 to 950 °C. Initially, the C 1*s* intensity of the DCS sample compared to that of the BTM sample has a ratio of 2.65:1. Although data between 22 and 550 °C has not been shown in any of the previous figures, there is essentially no change in the spectra of either sample up to 400 °C. Between 400 and 550 °C, there is a sharp drop in the C 1*s* intensity for samples dosed with BTM or DCS, but the DCS sample retains a greater percentage of its C with the peak intensity ratio now being 3.6:1. At 750 °C, the ratio increases slightly to 3.8:1, but at 950 °C, the two samples show almost identical C coverages. The sharp drop in the C 1*s* intensity for the DCS sample between 750 and 950 °C is due to surface segregation of the Si atoms at temperatures above 900 °C.[19]

Figure 6 shows a comparison of the valence-band photoemission spectra of β-SiC and that of two Si(100) samples dosed with 1×10^{-4} Torr of DCS or BTM. Unlike previous dosing experiments, which were done at room temperature, the samples prepared for Fig. 6 were dosed at 950 °C. Comparison of the SiC spectrum with that of the film grown with DCS shows excellent agreement, demonstrating that the film is composed of a material consisting primarily of C–Si bonds. The long tail at higher binding energies suggests that the film is not of entirely uniform composition. Both of the top two spectra are in excellent agreement with previously published valence-band spectra of SiC.[21] The spectrum of the film grown with BTM (bottom curve) does not show as good an agreement and may still contain C–H, Si–H, or SiC in a silicon-rich stoichiometry.

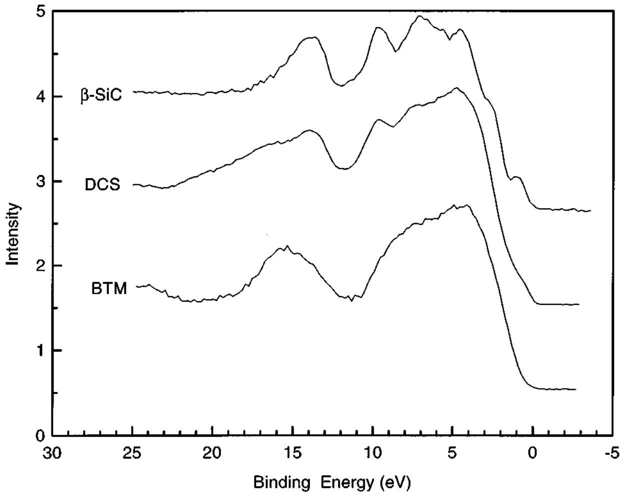

FIG. 6. The valence-band photoemission spectrum of β-SiC and two samples of Si(100) dosed with 10^{-4} Torr of DCS or BTM at 950 °C. The spectrum of the DCS sample is in good agreement with that of β-SiC.

SUMMARY

In summary, we have developed models for the C surface species deposited on a Si(100) surface by bis(trimethylsilyl)methane (BTM, $CH_2[Si(CH_3)_3]_2$) and dodecamethylcyclohexasilane (DCS, $Si_6(CH_3)_{12}$), based on surface-sensitive C 1*s* spectra.

BTM deposits $-CH_2Si(CH_3)_3$ moieties at the surface at room temperature, which contain two inequivalent C atoms. Upon annealing to 550 °C, the C atoms with higher binding energy, the methyl groups, or perhaps the whole trimethylsilyl group, desorb, and/or decompose, yielding a surface that is terminated primarily by $-CH_x$ where $0 \leqslant \times \leqslant 3$. At 750 °C, the valence-band peak corresponding to C–H bonds shows a dramatic decrease in intensity and the C 1*s* peak shows a large shift in the peak position towards lower binding energy as well as a decrease in the linewidth and intensity. All of these phenomenon are indicative of C atoms that are bonded almost exclusively to Si. Further annealing to 950 °C completes the process and causes Si to segregate to the surface driven by the lower surface energy of Si compared to C.

Repeating the experiment with DCS shows 2.65 times as much C on the surface at room temperature (compared with BTM) with a somewhat narrower linewidth, which is consistent with the fact that this molecule has all of its C atoms in the same chemical environment. Further evidence for this comes from the well-defined C 2*s* feature in the corresponding valence-band spectrum. From this evidence, it is postulated that DCS undergoes a ring opening and bonds to the Si surface as a polydimethylsilane chain. Upon annealing to 550 °C, an asymmetry appears in the C 1*s* spectrum as the polydimethylsilane side chains begin to polymerize into polycarbosilane. At 750 °C, there is still a large percentage of C–H bonds, as evidenced by the valence band and from the high binding energy tail in the C 1*s* spectrum. At 950 °C, most of the C atoms have been absorbed into the sample due to surface segregation of the Si to the surface, causing a large drop in the C 1*s* intensity.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research and by The Division of Materials Science, Office of Basic Energy Sciences. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48 and the NSF under Contract No. DMR-9632527. The work was performed at the Advanced Light Source at Lawrence Berkeley National Laboratory, which is also supported by the Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

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