thermal data obtained from the TGA/DSC analysis. The TGA data of pristine $C_{60}(en)_6$ heated in either air or nitrogen show an initial weight loss probably due to elimination of water, hydrogen chloride, or excess en molecules followed by a multistep decomposition of the coordinated en ligands (Figure 4).[26] More specifically, the weight decrease between 100 and 450 °C, which is attributed to en decomposition, is consistent with the presence of six en ligands per C_{60} cluster.[21c] Further weight decrease at approximately 450 °C in air and 675 °C in nitrogen is attributed to the decomposition and sublimation of C_{60} clusters, respectively. These temperatures agree well with those recently reported for unfunctionalized C_{60}.[7] In contrast, the onset of decomposition/sublimation for the intercalated carbon clusters does not commence until 800 °C in air and 900 °C in nitrogen. The observed initial weight loss is attributed to the elimination of five water molecules per unit cell, followed by the decomposition of six en ligands, consistent with the elemental analysis[24] and the observed decrease in the *d* spacing. The TGA data provide further support to the X-ray and spectroscopic data, which indicate that the clusters remain intact upon intercalation.

The remarkable enhancement of the thermal and oxidative stability of the intercalated carbon clusters is attributed to their confinement in the silicate galleries. Using TGA data, Milliken et al. concluded that C_{60} is thermally less stable than graphite.[7] In similar experiments, we find that intercalation increases the thermal and oxidative stability of C_{60} to at least that of graphite. This agrees well with our earlier observations on the enhanced thermal stability of intercalated polymers.[27a] In the case of intercalated small organic molecules or polymers, however, pyrolysis results in the formation of alternating carbon and silicate layers followed by complete delamination of the multilayer at $\sim$1000 °C, which is attributed to the reaction of the intercalated carbon layers with the silicate matrix.[27a,b] Eventually, a mixture of SiC and mullite is produced at even higher temperatures as a result of the carbothermal reduction of the silicate network. In contrast, the intercalated C_{60} clusters appear to be unreactive and thermally stable at comparable temperatures with no evidence for delamination or the formation of other ceramic phases.

In summary, intercalation is used to obtain two-dimensional, molecular arrays of functionalized buckminsterfullerene. Preliminary experiments show that the en ligands can be eliminated by heat treatment in oxygen at intermediate temperatures. To that end, films heated to 750 °C in air for 12 h exhibit a gallery height of 7 Å, in excellent agreement with the size of C_{60}. The intercalated $C_{60}(en)_6$ clusters exhibit a higher thermal stability compared to pristine $C_{60}(en)_6$ and C_{60} with no evidence for reaction with the silicate host. This behavior is in sharp contrast to that of amorphous and graphitic carbon layers obtained through pyrolysis of intercalated organic molecules or polymers. Complete elimination and removal of the en ligands could result in two-dimensional microporous materials analogous to pillared layered silicates wherein the C_{60} clusters constitute the gallery pillars. Current work is being directed toward further characterization of the intercalated carbon clusters.

Acknowledgment. This work was sponsored in part by the National Science Foundation (DMR-8818558) through the Materials Science Center at Cornell. We are grateful to R. J. Gruber for his continuous support and encouragement. We thank F. Wudl for a preprint of his work on C_{60} amine derivatives and for many helpful discussions regarding the preparation and properties of the water soluble forms. We thank F. J. DiSalvo for the use of the TGA equipment. J. W. Otto and E. Rodeghiero are gratefully acknowledged for experimental assistance.

---

(26) Mass spectral analysis using a solids probe with the sample gradually heated from ambient to 350 °C at 20 °C/min showed the evolution of a component, tentatively identified as en, at approximately 200 °C.

(27) (a) Mehrotra, V.; Giannelis, E. P. 91st American Ceramic Society Annual Meeting; Indianapolis, IN, Apr 23–27, 1989. (b) Sugahara, Y.; Sugimoto, K.; Kuroda, K.; Kato, C. *Yogyo-Kyokai-Shi* 1986, *94*, 38.

Chemical Vapor Deposition of Silicon Carbide from 1,3-Disilacyclobutane

D. J. Larkin*

NASA Lewis Research Center
Cleveland, Ohio 44135

L. V. Interrante*

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180-3590

Received September 19, 1991
Revised Manuscript Received December 10, 1991

Silicon carbide is becoming widely recognized as the semiconducting material of choice for use in high-power, high-temperature electronic devices.[1] Now that single-crystal 1-in. SiC wafers are commercially available,[2] the research pace is quickening.[3] These single-crystal SiC wafers are currently the most promising substrate for SiC epitaxy which is generally accomplished by using a mixture of separate Si and C sources, such as silane or chlorosilanes and various hydrocarbons, at temperatures in excess of 1000 °C.[4] The use of specially designed single-source precursors offer, in principle, the opportunity for improved control of the Si/C stoichiometry as well as lower deposition temperatures.[5] However, the simple carbosilanes usually employed for this purpose, such as CH_3SiCl_3,[6] afford little advantage in terms of either improved stoichiometry control or lowered deposition temperatures.

We have been exploring the use of substituted 1,3-disilacyclobutanes as potential single-source precursors for SiC and have previously reported on the use of 1,3-dimethyl-3-methylsilamethylene-1,3-disilacyclobutane (I) for this purpose.[7] This class of compounds offers the prospect of lower deposition temperatures by virtue of the significant strain energy present in the four-membered $-(SiC)_2-$ ring.[8] Moreover, the parent compound, 1,3-disilacyclobutane $[SiH_2CH_2]_2$ (II), has the additional attractive features of a built-in 1:1 ratio of Si and C and relatively weak Si–H bonds. In this case, dissociation into the highly reactive $H_2Si{=}CH_2$ species remains a possibility; although prior gas-phase studies have suggested that ring opening

---

(1) Shenai, K.; Scott, R. S.; Baliga, B. J. *IEEE Trans. Electron. Dev.* 1989, *36*, 1811. Baliga, B. J. *IEEE Electron. Dev. Lett.* 1989, *10*, 455.

(2) Cree Research, Inc., Durham, NC 27713.

(3) Davis, R. F.; Kelner, G.; Shur, M.; Palmour, J. W.; Edmond, J. A. *Proc. IEEE* 1991, *79*, 677.

(4) Powell, J. A.; Larkin, D. J.; Matus, L. G.; Choyke, W. J.; Bradshaw, J. L.; Henderson, L.; Yaganathan, M.; Yang, J.; Pirouz, P. *Appl. Phys. Lett.* 1990, *56*, 1442.

(5) Brown, D. M.; Parsons, J. D.; U.S. Patent 4,923,716 May, 1990.

(6) Schlichting, J. *Powder Met. Int.* 1980, *12*, 141.

(7) Larkin, D. J.; Interrante, L. V.; Hudson, J. B.; Han, B. *Proc. M.R.S. Meeting*; *Chem. Perspec. Microelectr. Mater. II*, Dubois, L. H., Interrante, L. V., Gross, M. E., Jensen, K. F., Eds.; *Mater. Res. Soc. Symp. Proc.*, 204; Pittsburgh, PA, 1991; p 141.

(8) O'Neal, H. E.; Ring M. A. *J. Organomet. Chem.* 1981, *213*, 419.

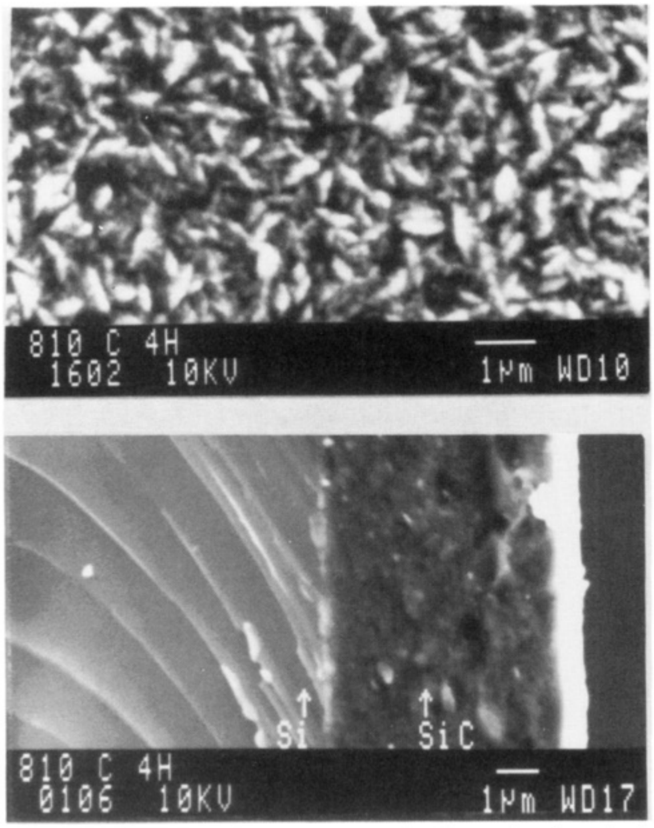

Figure 1. Scanning electron micrograph of a coating deposited on Si(100) at 810 °C. Top: surface view of the coating showing the elongated surface features. Bottom: cross-sectional view of the SiC coating/Si(100) interface.

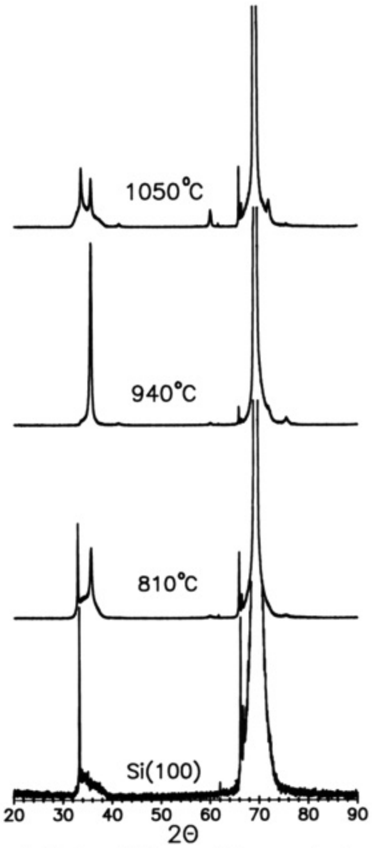

Figure 2. Stacked plot of the resulting graphs from the powder XRD of the coatings deposited from the pyrolysis of compound II at various Si(100) surface temperatures. A piece of the uncoated, unheated Si(100) substrate is shown for comparison.

accompanied by 1,2-H transfer from Si-to-C is a more likely occurrence.[9] We report here the preliminary results of our studies of this compound (II) as a potential single-component, low-pressure, thermal CVD route to silicon carbide.

The title compound (II) was synthesized according to methods described in the literature, starting from 1,1-dichloro-1-silacyclobutane (III).[10-12] The flow pyrolysis of (III) was used to prepare the intermediate 1,1,3,3-tetrachloro-1,3-disilacyclobutane[11] which was then reduced to the desired $(SiH_2CH_2)_2$ (II) with $LiAlH_4$.[10] The product was purified by distillation under 1 atm of N_2 pressure (bp = 60–65 °C) and characterized by ^{29}Si, ^{13}C, and ^{1}H 200-MHz NMR spectroscopy as well as quadrupole mass spectrometry (QMS).[13]

The details of the turbo-pumped, cold-wall, hot-stage LPCVD system are described separately.[7,14] The series of CVD experiments performed using the LPCVD system were all carried out using a mass flow controlled argon carrier gas (10.0 sccm) while maintaining a constant reactor pressure of 1.0 ± 0.1 Torr. The Si(100) substrates (Wacker Siltronic Co.; thickness = 525 μm; resistivity = 1.1 Ω cm; phosphorous doped) were loaded into the reactor after scoring by using a metal carbide scribe on the unpolished face and then cleaving into ca. 1.4 cm × 6.5 cm rectangular sections. Two or three substrates were then connected in a series circuit using tungsten clips with copper leads and resistively heated, between 600 and 1100 °C, by using a current-limited dc power supply. The precursor II was loaded into a stainless steel bubbler while inside a N_2 drybox. Once the bubbler was attached to the CVD system, the precursor was subsequently freeze–thaw degassed (backfilling with argon to remove the $N_2(g)$) before the start of the CVD experiment. In a set of separate experiments, a temperature-controlled capacitance manometer was used to measure the vapor pressure of II as a function of temperature, which was determined to be 305 Torr at 25 °C ($\Delta H_v = 10 \pm 0.9$ kcal/mol). During each LPCVD experiment, the partial pressure of the precursor was maintained at ca. 2.0 Torr by cooling the bubbler to ca. −42 °C with an appropriate slush bath.

Scanning electron microscopy (SEM) was used to examine the surface and cross-sectional morphologies of the coatings. The coating deposited at 810 °C displayed randomly orientated, elongated surface features having a width of ≤0.1 μm and length of ca. 0.5 μm (see Figure 1). In comparison, the coatings deposited from DSCB in subsequent experiments at substrate temperatures of 945 and 1055 °C exhibited surface features which were spherical and larger in size. The SEM micrographs of the SiC/Si(100) cross sections were also used to determine the coating deposition rate from DSCB at each substrate temperature. The LPCVD experiments that were performed using Si(100) substrate temperatures of 810, 945,

---

[9] Auner, N.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Lawrence, F. T. *Organometallics* **1986**, *431*, 5. Genchel', V. G.; Demidova, N. V.; Nametkin, N. S.; Gusel'nikov, L. E.; Volnina, E. A.; Burdasov, E. N.; Vdovin, V. M. *Izv. Akad. Ser. Khim.* **1976**, *10*, 2337.

[10] Irwin, R. M.; Cooke, J. M.; Laane, J. *J. Am. Chem. Soc.* **1977**, *99*, 3273.

[11] Auner, N.; Grobe, J. *J. Organomet. Chem.* **1981**, *222*, 33.

[12] Nametkin, N. S.; Vdovin, V. M.; Zav'yalov, V. I.; Grinberg, P. L. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1965**, *5*, 929.

[13] The characterization of compound II was carried out by means of ^{29}Si, ^{13}C, and ^{1}H 200-MHz NMR and quadrupole mass spectrometry (QMS). The following chemical shifts (ppm) in benzene-d_6 were observed: ^{1}H $\delta = 0.173$ (5), $\delta = 4.63$ (5); ^{29}Si $\delta = 27.88$ (3); ^{13}C $\delta = 8.28$ (3 of 5). The major *m/e* peaks and intensity values from the QMS were 88 ($I = 45$), 86 (100), 69 (40), 43 (50).

[14] Larkin, D. J.; Interrante, L. V.; Knorr, D. B.; Tracy, D. P., paper in preparation.

24 *Chem. Mater.* **1992,** *4,* 24-27

and 1055 °C resulted in deposition rates of ca. 6.0, 7.0, and 13 μm/h, respectively.

Specular reflectance FTIR of the SiC coatings deposited on Si(100), from DSCB, revealed only one strong absorption at ca. 790–800 cm^{-1}, which is indicative of the Si–C stretch.[15] No adsorption was observed between 1900 and 2200 cm^{-1} or 2800 and 3100 cm^{-1}, which is characteristic of the Si–H and C–H infrared stretching frequencies, respectively.

Powder X-ray diffraction (XRD) was used to determine the relative crystallinity of the coatings. The powder XRD spectra of the coatings deposited from DSCB at 810, 945, and 1055 °C are shown relative to a piece of the "as-received" Si(100) substrate (see Figure 2). The crystallization onset temperature is presumed to be <810 °C, since the β-SiC coating deposited at 810 °C exhibited a relatively intense SiC(111) peak (at a 2θ value of ca. 36°).[16] In comparison, the powder XRD of the SiC films produced in previous studies, from the pyrolysis of I on Si(100), indicated a crystallization onset of >900 °C.[7]

The decomposition onset temperature of II was determined, on Si(100), by using a quadrupole mass spectrometer attached to the LPCVD system, as described previously.[7] The mass peak intensity for $H_2(g)$ ($m/e = 2$), which is the initial decomposition byproduct of II, was monitored as a function of increasing substrate temperature. The results of this experiment indicated that II has a decomposition onset temperature of 680 °C on a Si(100) surface. This decomposition onset temperature of 680 °C for II is ca. 80 °C lower than that previously determined for I (ca. 760 °C)[7] in a similar experiment.

Pyrolysis byproducts produced from the decomposition of II at a maximum Si(100) surface temperature of ca. 850 °C were collected in a series of three liquid N_2 cooled traps for later identification. A minimum of four experiments were performed, at different substrate temperatures, to ensure an ample supply of gases for GCFTIR. The only noncondensable (at 77 K) byproduct detected from II was $H_2(g)$, which is in contrast to both $H_2(g)$ and $CH_4(g)$ detected in previous studies of the pyrolysis of I.[7] Information concerning the pyrolysis chemistry of compound II was obtained by systematically analyzing these trapped byproducts by using the quadrupole mass spectrometer attached to the LPCVD system. The series of cold traps were separately allowed to slowly warm to room temperature while continuously monitoring the m/e peak intensities from 1 to 200 amu. The first series of m/e peaks detected were determined to be a mixture of $C_2H_x(g)$ hydrocarbons followed by a small amount of methylsilane. As the third and final trap approached room temperature, a series of m/e peaks of much greater intensities emerged corresponding to a significant amount of dimethylsilane. These m/e peaks were followed by the final series of mass peaks detected which were attributed to II. In contrast to the results from the previous pyrolysis studies of I,[7] no trimethylsilane or tetramethylsilane was detected. This suggests that the byproducts, from the pyrolysis of II, are not derived from simple recombination of radical species but rather the result of discrete mechanistic decomposition routes, involving H transfer from Si to the adjacent $-(CH_2)-$ group as suggested by previous mechanistic studies.[17,18]

Auger electron spectroscopy (AES) was used to determine the elemental composition of the coatings that were deposited from II at various Si(100) substrate temperatures. The Si and C peak intensities (peak-to-peak heights) were averaged over the SiC(0001) and SiC(000$\bar{1}$) faces of the single-crystal SiC Lely[19] standard, which was used as a reference during each AES determination. The coatings deposited from II at 810 °C contained ca. 2% (atomic) excess silicon, which is consistent with a significant amount of dimethylsilane that was detected from the pyrolysis of II at $\leq$850 °C. Subsequent coatings deposited at ca. 945 and 1055 °C resulted in stoichiometric silicon carbide.

This is in contrast to the AES results of coatings produced using the derivative I of compound II.[7] The films deposited from I in this previous study contained as much as 10% (atomic) excess carbon, as determined by AES.

Further investigations of II, and derivatives thereof, as potential single-source CVD precursors to polycrystalline and single-crystal silicon carbide are currently underway. These investigations include electrical characterization of the films and also a detailed, quantitative evaluation of the pyrolysis byproducts produced as a function of varying both the substrate temperature and substrate material.

Acknowledgment. This work was supported by the Chemistry Division of the Office of Naval Research.

---

(15) Smith, A. L. *Spectrochim. Acta* **1960,** *16,* 87.

(16) *JCPDS Powder Diffraction Files*; Card No. 29-1129.

(17) Davidson, I. M. T.; Fenton, A.; Ijadi-Maghsoodi, S.; Scampton, R. J.; Auner, N.; Grobe, J.; Tillman, N.; Barton, T. J. *Organometallics* **1984,** *3,* 1593.

(18) Auner, N.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Lawrence, F. T. *Organometallics* **1986,** *5,* 431.

(19) Lely, J. A. *Ber. Dtsch. Keram. Ges.* **1955,** *32,* 229.

Synthesis of Silver and Gold Nanoclusters within Microphase-Separated Diblock Copolymers

Y. Ng Cheong Chan and R. R. Schrock*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

R. E. Cohen

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received November 4, 1991

Diblock copolymers are known to self-assemble in films to yield microdomains (lamellae, cylinders, or spheres) whose sizes and spacings are typically in the range 100–1000 Å.[1] The geometry of the microdomains and the domain sizes usually can be varied in a predictable manner by adjusting the length of each block and the total molecular weight[2] or by blending with homopolymer.[3] To date, studies largely have concerned purely organic polymers, and the phase behavior of such materials is relatively well-understood. In this communication, we report the

---

(1) (a) Quirk, P. R.; Kinning, D. J.; Fetters, L. J. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Aggarval, S. L., Eds.; Pergamon Press: New York, 1989; Vol. 7. (b) Bates, F. S. *Science* **1991,** *251,* 898. (c) Liebler, L. *Macromolecules* **1980,** *13,* 1602.

(2) (a) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1976,** *9,* 879. (b) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1978,** *11,* 960. (c) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1980,** *13,* 994. (d) Hadziioannou, G.; Skoulios, A. *Macromolecules* **1982,** *15,* 258. (e) Hashimoto, T.; Tanaka, H.; Hasegawa, H. *Macromolecules* **1985,** *18,* 1864.

(3) (a) Kinning, D. J.; Thomas, E. L.; Fetters, L. J. *J. Chem. Phys.* **1989,** *90,* 5806. (b) Thomas, E. L.; Winey, K. I. *Polym. Mater. Sci. Eng.* **1990,** *62,* 686.

0897-4756/92/2804-0024$03.00/0