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Novel Synthetic Routes to Carbon–Nitrogen Thin Films

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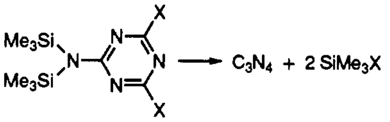
New unimolecular carbon-nitride precursors such as $C_3N_3F_2N(SiMe_3)_2$ and $C_3N_3Cl_2N(SiMe_3)_2$ were synthesized and used to deposit thin films of composition C_3N_4–$C_{3.2}N_4$, the highest nitrogen content observed in C–N solids. The films were formed by the thermal decomposition of the precursors via elimination of $SiMe_3F$ and $SiMe_3Cl$ at 400–500 °C. Film thicknesses between 1200 and 4000 Å were deposited on (100) Si, graphite, beryllium, and SiO_2, and were extensively characterized for composition and chemical purity using RBS, energy-dispersive X-ray analysis, and SIMS. The material was amorphous as indicated by X-ray diffraction. IR, EELS, and ^{13}C NMR reveal substantial sp^2 hybridization in both the carbon and the nitrogen. This material should be an excellent precursor for the high-pressure synthesis of C_3N_4, the highly sought structural and compositional analog of Si_3N_4.

Introduction

The possibility of an ultrahard carbon nitride phase with composition C_3N_4 that exceeds the hardness of cubic BN and diamond has been of considerable interest in recent years. It has been suggested that a tetrahedral carbon nitride will have a bulk modulus significantly larger than diamond.[1] Previous attempts to prepare cubic C_3N_4 include high-pressure thermal decomposition of C–H–N precursors,[2,3] ion and vapor deposition (IVD) of nitrogen ions and carbon vapor,[4] plasma decomposition of methane and N_2,[5] shock-wave compression of organic molecules,[6] and sputtering experiments.[7–9] More recently, hard carbon–nitrogen materials containing 60% C and 40% N have been deposited by pulsed laser ablation of graphite in combination with an atomic nitrogen source.[10] Unfortunately all these methods resulted in materials with bulk nitrogen contents much lower than the expected 57 at. % for C_3N_4.

The high-pressure synthesis of diamond and cubic boron nitride normally utilizes graphitic carbon and hexagonal BN as precursors. A corresponding layered carbon nitride of stoichiometry C_3N_4 should therefore be an ideal precursor for the high-pressure synthesis of a three-dimensional carbon nitride. Our research has been directed toward the preparation of low-dimensional non-hydrogen-containing carbon–nitrogen solids of composition C_3N_4 to use as precursors for the high-pressure synthesis of tetrahedral carbon nitride. We have developed novel chemical vapor deposition methods for depositing sp^2 carbon nitrides with an average composition corresponding to nearly stoichiometric C_3N_4. The carbon content in our films ranges reproducibly from 43–45% and the nitrogen content ranges from 55 to 57%, the highest observed in C–N solids. The synthetic route to these materials involves deposition temperatures of 400–500 °C and the use of inorganic, unimolecular precursors which incorporate the correct stoichiometry. To keep the deposition temperature low, it is important that the carbon and nitrogen atoms of the precursors do not contain any strong CH and NH bonds. Examples of precursors possessing the correct stoichiometry and lacking NH and CH bonds (except for the trimethylsilyl leaving groups) are $C_3N_3F_2N(SiMe_{32}$ (**1**) and $C_3N_3Cl_2N(SiMe_3)_2$ (**2**). In this paper we report the syntheses of **1** and **2**, and we describe their decomposition via elimination of $SiMe_3F$ and $SiMe_3Cl$ (reaction 1)to form carbon–nitrogen solids



(1)

X = F, Cl; Me = CH_3

of composition C_3N_4. A crystalline C_3N_4 in which both the carbon atoms and the nitrogen atoms are 3-fold coordinated and form dense layers like the carbon atoms in graphite is not possible for symmetry reasons. We propose a model layered structure for which the $(CN)_3N$ framework of molecules **1** and **2** is both the compositional and structural building block. In this structure the layers are not as dense as in graphite, but contain periodic holes. Furthermore, they have two types of nitrogen atoms: two-thirds are two-fold coordinated and one-third is three-fold coordinated (Figure 1). We envisioned the synthesis of **1** and **2** with this structure in mind.

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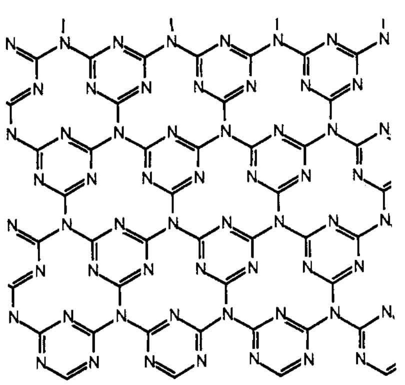

Figure 1. Model layered structure of C_3N_4. The synthesis of precursors 1 and 2 was developed with this structure in mind.

Results and Discussion

Precursor Synthesis. We prepared 1 by the reaction of 2,4,6-trifluoro-1,3,5-triazine with lithium bis(trimethylsilyl)amide in 40% yield. Compound 1 is a colorless, air-stable, and fairly volatile liquid (bp 65 °C at 2 Torr). The ^{13}C spectrum in deuteriochloroform shows the expected resonances corresponding to the ring carbons and the methyl carbons of the trimethylsilyl groups. The FTIR spectrum reveals the characteristic C–H stretches of the trimethylsilyl group at 2966–2905 cm^{-1} and the strong absorptions of the aromatic ring at 1500–1632 cm^{-1}. Mass spectroscopic analysis indicates the molecular ion minus CH_3 as the most intense peak at m/e = 261 and a fragmentation pattern which is consistent with the monosubstituted ring structure.

We also prepared compound 2 by the reaction of 2,4,6-trichloro-1,3,5-triazine with bis(trimethylsilyl)amide as a colorless, air–stable liquid (bp 67 °C at 0.1 Torr) in 75% yield. The compound was characterized by FTIR, NMR, GC/MS, and elemental analysis. The spectroscopic data and elemental analyses, presented in the Experimental Section, are consistent with the monosubstituted ring structure.

Film Deposition. Compound 1 was decomposed in a low-pressure reactor at temperatures as low as 350 °C to give thin films. Most depositions, however, were carried out at 450–500 °C due to low growth rate below 450 °C. Typical run times were 1–2 h, resulting in films 1200–4000 Å thick. All films adhered well to silicon, SiO_2, HOPG (highly oriented pyrolytic graphite), and beryllium substrates and were smooth and continuous when examined with optical and scanning electron microscopes. The mirrorlike appearance and bright coloration due to interference effects remarkably resembled those of aluminum nitride, gallium nitride, and boron nitride thin films.[11]

The decomposition byproducts for each deposition were collected in a liquid nitrogen trap and subsequently examined by NMR, FTIR,[12] and vapor pressure measurements. The main component of the byproduct mixture was identified as $SiMe_3F$ and the remainder as starting material 1. The total mass of the mixture corresponded approximately to the weight loss of the precursor indicating no substantial loss due to noncondensibles.

The decomposition of compound 2 was carried out in the same CVD reactor setup at temperatures of 400–450 °C and nitrogen pressures of 0.1–0.5 Torr. Film growth rates and appearance were similar to those observed in the decomposition of 1. The byproducts of the decomposition reaction consisted almost exclusively of $SiMe_3Cl$ and traces of a volatile solid which was not collected in sufficient quantities to permit proper identification. No starting material 2 was collected in the cold trap.

Film Composition. The ratio of nitrogen to carbon in the films was established by Rutherford backscattering (RBS) analysis. In addition to the carbon and nitrogen analyses, the experiments routinely included channeling through the silicon substrate to enhance the C and N signals, oxygen resonance reactions, and He forward scattering to determine levels of oxygen and hydrogen impurities. RBS was also used to estimate film thicknesses. Figure 2a illustrates a 2-MeV aligned spectrum for a 1200-Å film resulting from the decomposition of precursor 1 and deposited on (100) silicon. The film contains only carbon and nitrogen in a ratio of 3C to 4N and an oxygen impurity on the order of 2–3 at. % as indicated by oxygen resonance. Thin films were also deposited on graphite and beryllium metal in order to avoid the silicon background. Rutherford backscattering spectra of the deposited films and energy-dispersive X-ray analysis (EDX) of free-standing films both confirmed only trace amounts of silicon and fluorine. Figure 2b shows the RBS spectrum of a 3000-Å thin-film sample (on graphite) with composition $C_3N_4O_{0.3}Si_{0.02}F_{0.05}$. In most depositions, however, Si and F are not observed even in trace quantities. RBS and EDX analysis of films obtained using precursor 2 also indicated C_3N_4 compositions and noise levels of silicon and chlorine.

Finally, secondary ion mass spectroscopy (SIMS) depth profile experiments revealed that carbon and nitrogen are fairly homogeneous throughout the sample. They also confirmed the absence of hydrogen and silicon and showed that the oxygen impurities are mostly concentrated on film surfaces. A representative SIMS profile of a carbon-nitrogen film in which we monitored $^{12}C^-$, $^{18}O^-$, $^{30}Si^-$, and $^{26}CN^-$ (nitrogen does not make a stable elemental negative ion) is presented in Figure 3.

In conclusion, C–N materials with a carbon content ranging reproducibly from 43–45 at. % and a nitrogen content ranging from 55–57 at. % were generated from the decomposition of compounds 1 and 2. The absence of fluorine (only traces of fluorine have been observed in some samples), chlorine, and silicon in the films clearly demonstrates that the trimethylsilyl leaving groups are completely eliminated as TMS fluoride and TMS chloride as indicated in reaction 1. Although, the decomposition of 1 and 2 produced nearly identical compositions, compound 1 was used more frequently for sample preparation because it is considerably more volatile and therefore more suitable for CVD experiments.

Film Structure and Bonding. The morphologies and bonding characteristics of the films were studied by a variety of techniques. X-ray diffraction experiments indicated that the material is amorphous. The X-ray spectrum showed a broad reflection at d = 3.6 Å. This is reminiscent of amorphous carbon diffraction patterns. Scanning electron micrographs (obtained on a ISI 440 microscope operated at 30 keV) revealed that the C–N films are smooth and featureless.

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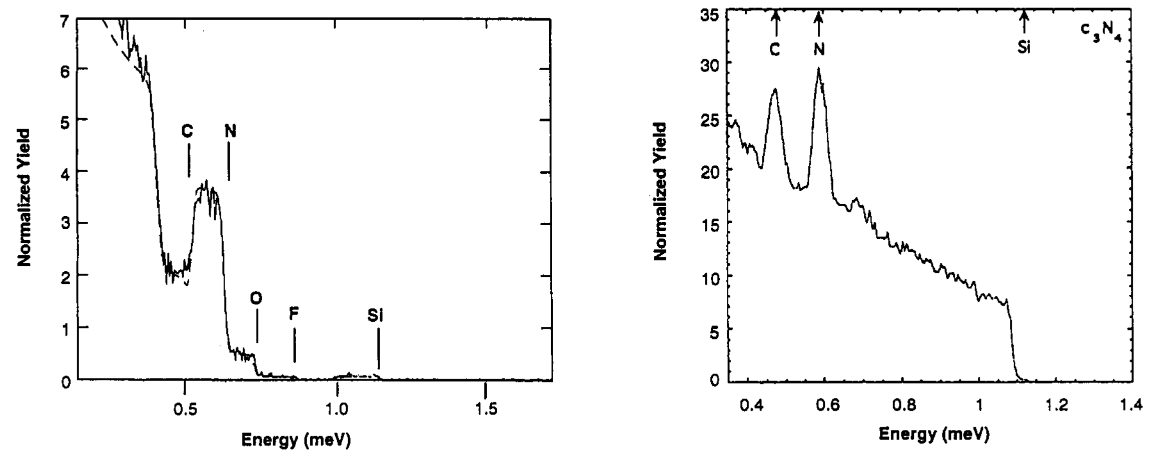

Figure 2. (a, right) Backscattering aligned spectrum of a carbon–nitride phase deposited at 500 °C on (100) Si. A simulation of the composition using the program RUMP indicates a composition of C_3N_4 and a film thickness of 1200 Å. (b, left) Backscattering spectrum of a carbon–nitride phase deposited at 450 °C on HOPG. A simulation of the composition using the program RUMP (as shown by dotted line) indicates a composition of $C_3N_4O_{0.3}Si_{0.02}F_{0.05}$ and a film thickness of approximately 3000 Å.

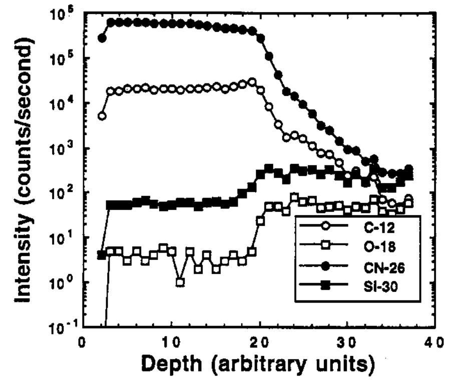

Figure 3. Secondary ion mass spectrometer (SIMS) depth profile of a C_3N_4 sample. An $^{16}O_2^+$ primary ion beam was used to sputter $^{12}C^-$, $^{18}O^-$ (avoiding interference from the $^{16}O^-$ primary beam), $^{30}Si^-$, and $^{26}CN^-$.

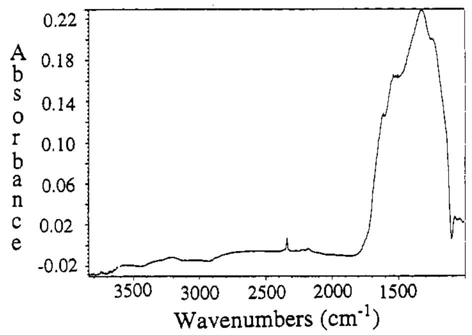

Figure 4. Infrared spectrum of carbon–nitride films deposited at 450 °C on (100) Si.

Transmission infrared spectra of films deposited on single-crystal silicon wedges, polished slightly off axis to suppress interference effects, were obtained routinely. Figure 4 shows the spectrum of a film 24-h after it was deposited at 450 °C. The strong bands between 1650 and 1150 cm^{-1} represent the $(CN)_3$ ring and C–N stretching modes. The small peak at 2300 cm^{-1} indicates the presence of a triple bonded C–N stretching mode and the broad peak at 3200 cm^{-1} corresponds to O–H contamination. The oxygen due to the O–H was also observed by RBS resonance and SIMS depth profile experiments primarily as surface contamination.

Carbon (^{13}C) NMR spectra of free-standing films showed a strong, sharp resonance at 104 ppm and a weak, broad shoulder at 115 ppm indicating sp^2 hybridized carbon. There is no evidence of the presence of sp^3 hybridized carbon. Electron energy loss spectra (EELS) of the same films supported on a carbon coated grid clearly demonstrate that the material contains only carbon and nitrogen. The nitrogen K-edge fine structure contains a broad π-to-π^* transition indicating strong sp^2 character. The EELS experiments couldn't be used to differentiate between the sp^2 nitrogen and any sp^3 nitrogen that may be present in this C_3N_4 amorphous material as indicated by the model structure we suggest in Figure 1.

Conclusion

We have demonstrated that the thermal decomposition reaction of the new $C_3N_3F_2N(SiMe_3)_2$ and $C_3N_3Cl_2N(SiMe_3)_2$ precursors results in C–N thin films with the elimination of the stable gaseous species $SiMe_3F$ and $SiMe_3Cl$, respectively. RBS and EDX analyses indicate virtually complete elimination of silicon- and halide-containing species. The film stoichiometries range from C_3N_4 to $C_{3.2}N_4$, the highest nitrogen contents ever observed in C–N solids. Solid-state NMR, transmission infrared spectra, and electron energy loss spectra reveal that the carbon and nitrogen atoms are primarily sp^2 hybridized. However, a very small concentration of sp hybridization, presumably terminal CN, is also observed. Our data thus far are consistent with the proposed model structure.

Experimental Section

General Procedures. All reagents and precursors were handled in a nitrogen-filled glovebox (Vacuum Atmospheres Model HE493 MO20-40) or using standard schlenk and vacuum-line techniques. Infrared spectra were obtained on a Nicolet Magna 550 spectrometer from liquid samples between KBr salt plates or gas samples in a 10-cm path-length glass cell with KBr windows. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Varian Gemini 300 NMR spectrometer. Mass spectra were obtained by GC/MS on a HP 5995 spectrometer. Elemental analyses were performed at Galbraith Laboratories in Knoxville, TN. Hexamethyldisilazane and 1,3,5-trichloro-2,4,6-triazine (purchased from Aldrich Chemical Co.) and 1,3,5-trifluoro-2,4,6-triazine (purchased from Alfa Chemicals) were used without further purification.

The decompositions were carried out in a horizontal, hot-wall, low-pressure CVD quartz reactor. The precursor was loaded into a fritted glass bubbler and carried into the reactor in a flow of dry nitrogen. During deposition the bubbler and the lines into the reactor, were maintained at 40–60 °C to facilitate transport of the precursor. At the exhaust side of the reactor a glass trap cooled to −196 °C was used to collect the reaction byproducts. The base pressure in the deposition system prior to the start of the experiment was typically 10^{-4} Torr.

RBS spectra were collected on a General Ionics Model 4117 instrument using 2-MeV helium ions. The signal in oxygen resonance experiments is generated by a $^{16}O(\alpha,\alpha)^{16}O$ resonance reaction that enhances the oxygen signal by 10 times, thus making it possible to quantify oxygen contents as low as 1%.

The SIMS experiments were performed using a CAMECA IMS 3F spectrometer. For the depth profiles, a mass-filtered primary ion beam of $^{16}O^{2+}$ at 50 nA was rastered over a 250 × 250 μm sample surface. Negative secondary ions with 0–40 eV excess kinetic energy from a circular area of 60 μm diameter in the center of the sputtered crater were admitted into the mass spectrometer. We monitored $^{12}C^-$, $^{18}O^-$ (avoiding interference from the $^{18}O^-$ primary beam), $^{30}Si^-$, and $^{26}CN^-$. Minor sample charging was corrected by adjusting the sample voltage to maximize the $^{12}C^-$ intensity prior to each cycle of measurements. The EELS spectra were obtained on a JEOL-2000FX electron microscope equipped with a Gatan Model 666 parallel EELS spectrometer.

Synthesis of 2,4-Difluoro-6-bis(trimethylsilyl)imido-1,3,5-triazine (2). Lithium bis(trimethylsilyl)amide ($LiN\{SiMe_3\}_2$) **3** was prepared by slowly treating hexamethyldisilazane with 1.6 M *n*-butyllithium in hexane at 0 °C and was isolated as a white solid by removal of the solvent in vacuo. The white solid was purified by sublimation at −55 °C and 10^{-4} Torr. A suspension of **3** (5.56 g, 33 mmol) in dry, degassed hexane was added dropwise to a solution of 2,4,6-trifluoro-1,3,4-triazine (5 g, 37 mmol) in hexane at 0 °C. The mixture was stirred under nitrogen for 12 h at ambient temperature. The reaction mixture was filtered to separate the insoluble lithium fluoride and the solvent in the filtrate was removed in vacuo. The resulting liquid (4.0 g, 14.5 mmol) was purified by low-pressure distillation at 65 °C and 1.1 Torr to obtain **1** in 40% yield.

IR (liquid thin film): 2966.3 m, 2905.2 w, 1734.1 sh, 1632.2 v st, 1530.4 st, 1494.8 st, 1392.9 v st, 1260.5 st, 1118.0 st, 1082.3 st, 919.4 m, 863.4 st, 781.9 w, 756.4 m, 700.4 w, 654.6 w. ^{13}C NMR ($CDCl_3$) 2.3705, 2.7618 and 1.9801 (weak ^{29}Si satellite peaks), 170 [dd, $^1J(CF) = 228.6$ Hz, $^3J(CF) = 20.25$ Hz C-2, C-4)], and 176.31 (t, $^3J(CF) = 16.5$ Hz, C-6]. MS (most intense peaks): $(M - CH_3)^+$ 261, $[M - (CH_3 + CNF)^+]$ 216 $(SiMe_3F - CH_3)^+$ 77, $SiMe_3^+$ 73. Elemental Anal. Found (%): C, 39.09; H, 6.61; N, 20.20; F, 13.11. Calcd (%): C, 39.13; H, 6.52; N, 20.29; F, 13.77; Si, 20.29.

Synthesis of 2,4-Dichloro-6-bis(trimethylsilyl)imido-1,3,5-triazine, 2. A suspension of **3** (5.5 g, 32.9 mmol) in dry, degassed hexane was added dropwise to a hexane solution of 2,4,6-trichloro-1,3,5-triazine (6.08 g, 32.9 mmol) at 0 °C. The mixture was stirred under nitrogen for 12 h at ambient temperature. The reaction mixture was filtered to separate the insoluble lithium chloride and the solvent in the filtrate was removed in vacuo. The resulting liquid (6.5 g, 21 mmol) was purified by low-pressure distillation at 70 °C and 0.100 Torr yielding 60% of compound **2**.

IR (liquid thin film): 2961.2 m, 2905.2 w, 1734.1 sh, 1545.7 v st, 1479.5 st, 1454.0 st, 1316.5 m, 1250.4 st, 1036.5 st, 929.6 st, 863.4 st, 700.4 w, 639.3 m. ^{13}C NMR ($CDCl_3$) 2.66, 169.79, 172.2 ppm (3 peaks). ^1H NMR ($CDCl_3$) 0.3178, 0.5164 and 0.1162 (satellite peaks). MS (most intense peaks): M^+ 308, $(M - CH_3)^+$ 293, $(SiMe_3Cl - CH_3)^+$ 93, $SiMe_3^+$ 73. Elemental Anal. Found (%): C, 35.03; H, 5.82; N, 18.00; Cl, 24.21. Calcd (%): C, 35.06; H, 5.84; N, 18.18; Cl, 22.73.

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