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Deposition of Silicon Carbonitride Films Using Methylsilazane

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In recent years there has been an increasing interest in the conversion of organometallic precursors into inorganic materials via pyrolysis.[1-4] One advantage of this process is that the organometallic compound already contains the bond structure necessary for the pyrolytic product, and the conversion can thus take place at moderate temperatures.

Silicon carbide[5] and silicon nitride[6] are two important candidate materials for both structural and electronic applications due to their high thermal and chemical stability, hardness, high strength, and a variety of other properties. Much work has been done on the synthesis of these materials by pyrolysis of suitable organometallic precursors.[1-3,7,8] Silicon carbonitride, a ternary phase in the Si–C–N system, has properties between silicon carbide and silicon nitride. The capability to tailor the structure and composition and ultimately the properties should make silicon carbonitride an important material for many applications. A few studies have been reported on the deposition of silicon carbonitride.[9-12] However, the deposition has mostly been carried out at temperatures above 1273 K, which may be too high for many practical applications. We report in this paper the low-temperature synthesis of silicon carbonitride films from a gas mixture of methylsilazane and hydrogen by chemical vapor deposition.

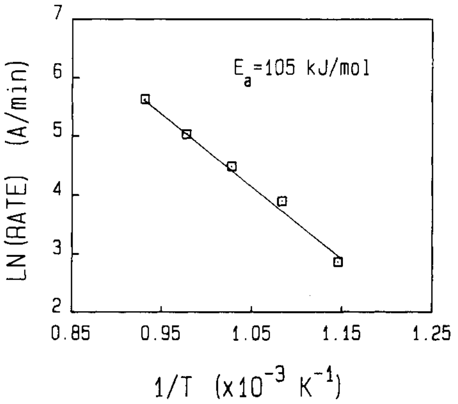

Figure 1. Logarithm of the deposition rate versus the reciprocal temperature for the deposition of silicon carbonitride films at 873–1073 K.

The liquid methylsilazane compound was prepared following a procedure described in a previous study.[2] It consists mainly of $[CH_3SiHNH]_n$ cyclics, with the major component being $n = 4$ (cyclic) and the average molecular weight being about 290 g/mol. The deposition was carried out in a resistance-heated cold-wall quartz reactor at 760 Torr at 873–1073 K. Single-crystal silicon (100) was used

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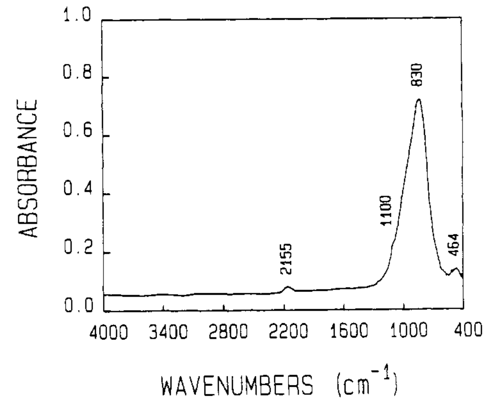

Figure 2. Typical infrared absorption spectrum of a 2830-Å silicon carbonitride film deposited at 1073 K.

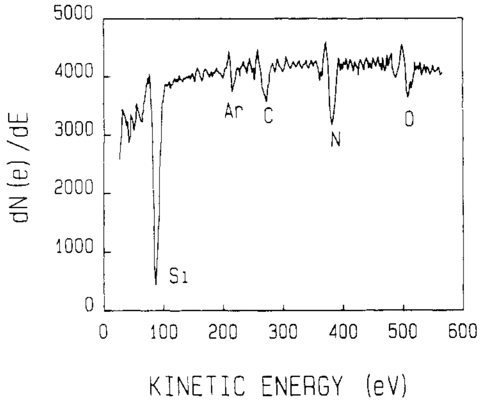

Figure 3. AES spectrum of a 2830-Å silicon carbonitride film deposited at 1073 K.

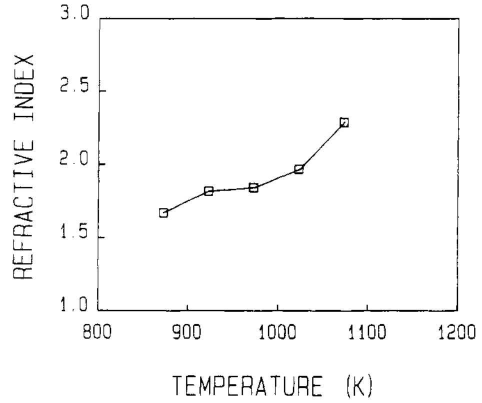

Figure 4. Refractive index of the silicon carbonitride films as a function of the deposition temperature.

as the substrate. The compound was injected by a vacuum-tight motorized syringe into a stainless steel container maintained at 323 K. Hydrogen gas at a flow rate of 200 SCCM was passed through the container and entrained the vaporized compound. The methylsilazane-saturated hydrogen and 300 SCCM of additional hydrogen were mixed and introduced into the reactor. The films deposited were characterized by ellipsometry, Fourier transform infrared spectrometry (FTIR), and Auger electron spectroscopy (AES).

Silicon carbonitride films of thicknesses between 1000 and 3000 Å were deposited in the temperature range 873–1073 K. The deposition rate increased from 18 to 283 Å/min, values much higher than those reported.[12] Figure 1 shows the Arrhenius relation between the deposition rate and the temperature. The apparent activation energy is about 105 kJ/mol. This value as well as the low deposition temperatures suggest that the process is rate-limited by reaction kinetics at the film surface. The low activation energy, compared with the dissociation energies (typically above 340 kJ/mol) of C–H, N–H, and Si–H bonds in polymer compounds,[13] indicates that the decomposition of the methylsilazane compound takes place via a lower energy transition state, which may be assisted by the presence of hydrogen.

FTIR studies indicate that all silicon carbonitride films exhibited similar IR absorption spectra, without apparent dependence on the deposition temperature. Shown in Figure 2 is a typical IR spectrum of a 2830-Å film deposited at 1073 K. As shown, the IR maximum absorption appears at 830 cm^{-1}, with additional features at 464, 1100, and 2155 cm^{-1}. The symmetrical absorption band centered at around 830 cm^{-1} is attributed to the formation of amorphous silicon carbonitride, and arises from the fundamental vibration of the [SiC_xN_{4-x}] tetrahedra.[12,14,15] The band at 464 cm^{-1} and the shoulder at 1100 cm^{-1} in the spectrum are characteristic of the Si–O bond bending and stretching, respectively,[15] which indicate oxygen incorporation in the film. While a band at 2155 cm^{-1} is apparent in Figure 2, which is characteristic of the Si–H bond stretching, there exist no bands characteristic of N–H and C–H bonds.[3,12] The FTIR analysis indicates that the N–H and C–H bonds in the methylsilazane compound can be effectively cleaved on pyrolysis to form a network structure based on the [SiC_xN_{4-x}] tetrahedra, with a fraction of the Si–H bonds remaining.

The silicon carbonitride films were further studied by using AES at a base pressure of 10^{-10} Torr. Prior to the analysis, the film surface was sputter-cleaned by using a low-energy (0.2 keV) argon ion beam to remove surface contaminants. Shown in Figure 3 is the AES spectrum of a 2830-Å film deposited at 1073 K. Peaks corresponding to Si, C, N, O, and Ar are detected. The argon peak comes from the argon ions implanted into the film during sputtering. The compositional analysis shows that the film has an approximate atomic composition of Si, 48%; C, 22%; N, 21%; and O, 9% (ignoring H, which is not detectable by AES). The AES analysis also indicates that the silicon carbonitride films are uniform in composition, independent of the deposition temperature. Note that the Si/C/N atomic ratio in the methylsilazane compound is unity. The higher Si atomic concentration in the silicon carbonitride films may be contributed to the partial loss of carbon and nitrogen due to the formation and evolution of CH_4 and NH_3 byproducts on pyrolysis.[2] Oxygen substitution for the carbon and nitrogen atoms may also be a reason for the high silicon content. The oxygen incorporation in the silicon carbonitride films may be due to water and/or oxygen residues in the gas stream or a small leak in the system. The presence of even a trace amount of water and oxygen can result in the incorporation of a significant amount of oxygen atoms in silicon based films, as often encountered in the CVD processing of silicon nitride for integrated circuits applications, because of the high thermodynamic stability of silicon dioxide.[16]

The ellipsometry measurement indicates that the refractive index of the silicon carbonitride films increases with the deposition temperature, as seen in Figure 4. The

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refractive index is indicative of the atomic composition and structural density. The AES studies have shown that the atomic composition of the silicon carbonitride films does not depend on temperature. Therefore, the temperature dependence of the refractive index must be attributed to the increase in the structural density. We postulate that as temperature increases, the rupture of the cyclic structure of the methylsilazane compound is enhanced, which leads to a denser packing of the film network structure.

In conclusion, we have demonstrated the ability to deposit silicon carbonitride films using a gas mixture of methylsilazane and hydrogen in the relatively low temperature range 873–1073 K. The apparent activation energy for the film deposition is 105 kJ/mol, far lower than the dissociation energies of individual bonds in the methylsilazane compound. While the change in temperature causes no change in the composition of the film, it has a significant effect on the structural density of the film. The increase in the structural density with temperature may be attributed to the enhanced rupture of the cyclic structure of the methylsilazane compound, which results in a denser packing of the silicon carbonitride network structure.

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Registry No. Silicon carbonitride, 64477-28-7.

Effect of Oxygen Stoichiometry on the Superconductivity of $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$

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The new superconducting system $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ has recently been investigated.[1-3] In order to ascertain whether the observed properties are optimized with respect to the oxygen content, we have systematically varied δ and characterized the following superconducting properties: critical temperature (T_c), flux exclusion (diamagnetism), and flux expulsion (Meissner effect). In addition, for one sample, with $x = 0.4$ and $\delta = 0.22$, the critical current density (J_c), as determined by magnetic measurements, was obtained as a function of temperature.

Ceramic samples of $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ with $x = 0$, 0.2, and 0.4 were prepared by sintering at 900 °C, annealing at 860 °C, and cooling in a low oxygen atmosphere to preserve the orthorhombic phase and $\delta \approx 0$. Subsequently, the samples were reheated in a thermobalance in an oxygen atmosphere so that δ increased to various values between $\delta = 0$ and 1.5. Each sample was then quenched to preserve its value of δ. Quenched samples were examined by X-ray diffraction (XRD) to ascertain the phase content and by magnetic measurements to determine T_c and qualitatively the percentage of the superconducting phase present. The XRD indicated each sample was essentially single phase. However, this examination does not directly confirm that the oxygen content is uniform throughout the sample since previous work has shown that single phase exists over a wide range of oxygen content.[3]

Table I. Summary of Magnetic Measurements

			fraction	
x^a	δ^b	T_c, K	diamagnetic (5 K)	Meissner (5 K)
0.4	0.22	67	0.71	0.16
	0.06	78	0.84	0.25
	0.22	77	0.74	0.18
	0.39	77	0.58	0.15
	0.64	75	0.44	0.11
0.2	0.16	61	0.35	0.08
	0.08	71	0.80	0.18
	0.31	66	0.27	0.06

[a] x is the Ca content per formula unit. [b] δ is the 0 excess over 8 per formula unit.

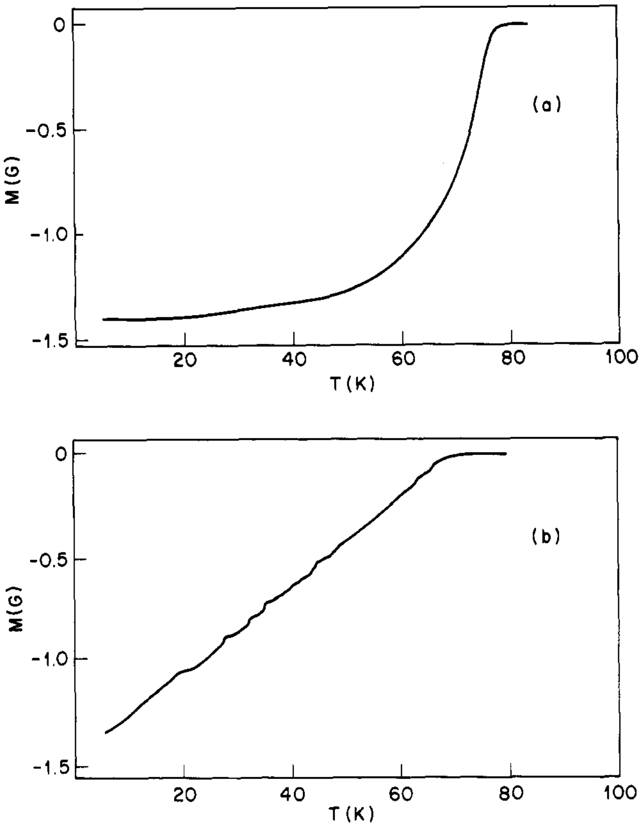

Figure 1. Magnetic moment as a function of temperature for samples cooled in zero field ($H < 0.1$ G) and then measured in a field of 20 G as the temperature is increased. (a) $x = 0.4$; $\delta = 0.06$; (b) $x = 0.2$, $\delta = 0.08$.

The magnetic measurements were carried out by using a vibrating sample magnetometer, VSM. Samples nominally 2 × 2 × 10 mm^3 were cut from $^1/_4$-in. pellets. The field was applied along the long axis. The magnetic results are summarized in Table I where we give T_c, the diamagnetic fraction, and the Meissner fraction as a function of x (the Ca content) and δ (the oxygen excess over eight oxygen atoms per formula unit).

To obtain the diamagnetic fraction, the sample is cooled to 5 K in zero field (<0.1 G). Then the applied field is increased to 20 G, and the effective magnetization is obtained as a function of increasing temperature. The Meissner fraction is measured by decreasing the temperature from above T_c in the field of 20 G. It is interesting

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