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$SiCl_3CCl_3$ as a novel precursor for chemical vapor deposition of amorphous carbon films

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Abstract

Amorphous carbon films, characterized by XRD, AFM, SEM and Raman, were deposited from $SiCl_3CCl_3$ on quartz substrates at 773–1273 K by low pressure chemical vapor deposition using a hot-wall reactor. XPS studies showed that the films grown at 773 K contained 90% C and 10% Cl, while the films grown at 1273 K contained 100% C. $SiCl_4$, CCl_4 and Cl_2C=CCl_2 were detected by on-line FT-IR studies. The extrusion of dichlorocarbene, :CCl_2, from $SiCl_3CCl_3$ should provide the source of carbon in the reaction. On Si substrates, an etching process at the film-substrate interface assisted the lift-off of the films from the substrates. The C films curled and formed rolls.
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Keywords: A. Carbon films; B. Chemical vapor deposition

1. Introduction

The field of disordered carbon materials is important and covers a wide range, including carbon fiber [1], glassy carbon [2], microcrystalline carbon [3], amorphous carbon [4], and hydrogenated amorphous carbon [5]. Recently, there has been considerable interest in applying carbon thin films to photovoltaic cells [6,7], cold cathode devices and flat panel displays [8–10]. Chemical vapor deposition (CVD) methods [11–15], including hot-filament CVD, plasma-enhanced CVD and laser-assisted CVD, have been employed to deposit carbon thin films using various hydrocarbons as the precursors.

It has been shown that thin films and wires of Group IV, such as Si and Ge, can be deposited using divalent precursors SiF_2 [16], SiO [17] and GeI_2 [18], respectively. We would like to demonstrate that the strategy can be extended to deposit carbon thin films. According to literature reports [19,20], extrusion of :CCl_2, dichlorocarbene, from $SiCl_3CCl_3$ can be performed by pyrolyzing the silane in vacuum. Disproportionation of gaseous :CCl_2 into solid carbon and gaseous CCl_4 is calculated to be an exothermic reaction. The estimated H_{reaction} is -139 kcal/mol [19,21]. Since the divalent species is highly reactive, we predict that carbon materials can be produced from $SiCl_3CCl_3$. In this report, we demonstrate the deposition of amorphous carbon thin films using this strategy.

2. Experimental

$SiCl_3CCl_3$ (Aldrich, 97%) was used as the precursor to deposit thin films. The deposition experiments were carried out using a hot-wall reactor with a base pressure of 10^{-1} Pa. $SiCl_3CCl_3$ was evaporated at 273 K without carrier gas. The typical deposition pressure was at ~10 Pa. Silica-glass and *n*-Si(100) substrates, approximately 10 mm^2, were used. The deposition temperatures were between 773 and 1273 K.

X-ray diffraction (XRD) studies were carried out using a diffractometer with CuKα radiation. Images of the films were taken using a scanning electron microscope (SEM) equipped with an energy-dispersive spectra (EDS) attachment and an atomic force microscope (AFM). The growth rates were calculated from the SEM cross-section views. X-ray photoelectron spectra (XPS) were measured using a

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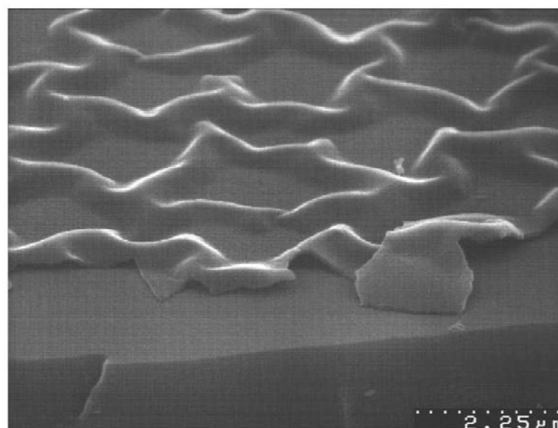
spectrometer with MgKα (1253.6 eV) radiation equipped with an Ar^+ sputter gun. Raman data were collected using a Renishaw-1000 microscope powered by a He–Ne laser. The volatile products were analyzed on-line by an infrared spectrometer (FT-IR). They were also collected at 77 K and characterized by gas chromatography–mass spectrometry (GC–MS).

3. Results and discussion

The experimental conditions and results are summarized in Table 1. The color of the film prepared at 773 K on quartz was gray and opaque while the film produced at 1273 K was dark and transparent. None of the films showed XRD patterns, suggesting that the films were amorphous. The surface morphology of the films was characterized by SEM and AFM. Fig. 1a and b are the SEM micrographs of the films deposited on quartz at substrate temperatures of 773 and 1173 K, respectively. The deposition rate, 0.35–1.16 nm/min, was estimated from the cross-sectional SEM images. For a deposition temperature of 773 K, the film did not adhere well to the substrates and formed a rough and fluffy surface. When deposition occurred above 973 K, smooth films with good adhesion to the substrates were prepared. A selected AFM image of the film grown at 1173 K is shown in Fig. 2. From the images, the R_{rms} (root mean square roughness) of the surface was estimated to be 3–21 nm. The film deposited at 773 K showed an R_{rms} value of 21 nm since the film curved and lifted from the substrate.

The surface composition of the films was characterized by XPS (Fig. 3). The surface contains more than 90% C (Fig. 3a). The film deposited at 1073 K contains more than 97% C on the surface. For the films grown at temperature above 1073 K, the Cl concentration is near the detection limit of XPS. The Cl concentration increased with decreasing the temperature of deposition. For the deposition temperature of 773 K, the Cl concentration on the surface is 10%. As shown in Fig. 3b, the high-resolution signals of C 1s electron are observed at 284.5 eV, which is close to the value of a graphite-like environment [22]. The bulge at 286 eV can be assigned to a C–Cl bonding environment on the surface. The Cl $2p_{3/2}$ and Cl $2p_{5/2}$ peaks of the high-resolution spectra (Fig. 3c) are observed at 200.2 and 201.8 eV, respectively. These values correspond to the C–Cl bonds linkage, as reported in the literature [22]. The oxygen concentration is low on the surface. After Ar^+

(a)



(b)

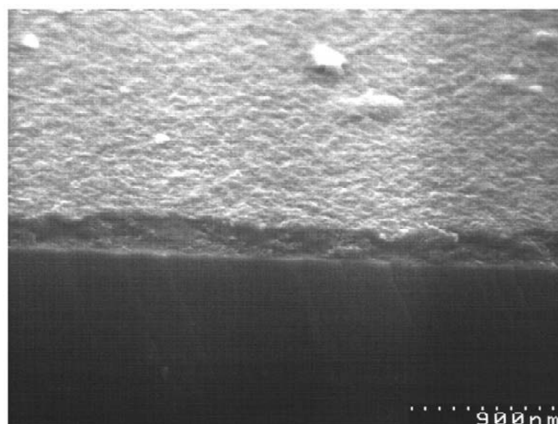


Fig. 1. SEM images of film prepared at (a) 773 K and (b) 1173 K.

Table 1
Summary of the deposition conditions and characteristics of the deposits on silica glass

Deposition temperature (K)	Deposition time (h)	Growth rate (nm/min)	Roughness R_{rms} (nm)	Composition by XPS (w/o Ar^+ etching)	Resistivity (μΩ cm)
773	3	0.35	21	C 90% Cl 10%	$1.25 \cdot 10^6$
973	3	0.29	3	C 92% Cl 2% O 6%	4920
1073	3	0.64	10	C 97% Cl<1% O 2%	3800
1173	3	0.69	6	C 99% Cl<1%	2470
1273	2	1.16	7	C 100%	1970

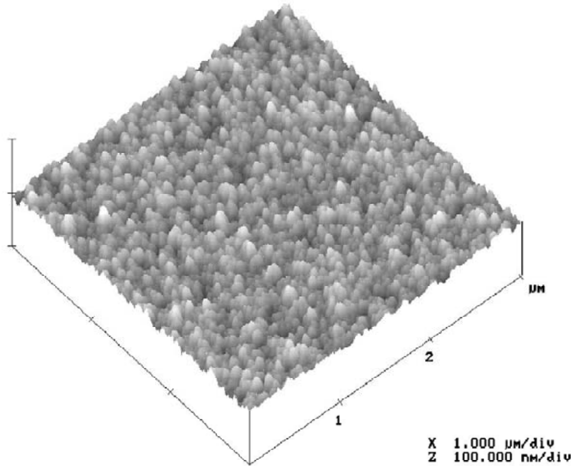


Fig. 2. AFM image of an amorphous carbon film deposited on quartz at 1173 K, R_{rms}=6 nm.

sputtering for 30 s, the O concentration decreased below the XPS detection limit. This suggests that the oxygen atoms were adsorbed on the surface as the films were exposed to air, which is a classical contamination.

Raman scattering spectra, shown in Fig. 4, were collected for the films deposited at 773, 1073 and 1273 K on quartz substrates. They were dominated by peaks at 1600 and 1327 cm^{-1} which are assigned to the G and D bands of graphitic carbon materials [23]. For each sample, both peaks are broad and the D peak is stronger than the G peak. This observation is consistent with the phenomenon observed for amorphous carbon films [23–25]. For the films deposited at 1273 K, as shown in Fig. 4c, the signals are sharper than for lower deposition temperature. This suggests that the film structure is more graphite-like at higher deposition temperatures.

A four-point probe was employed to measure the resistivity of the films prepared at various temperatures (Fig. 5). For the film deposited at 773 K, the resistivity is high, $1.25 \cdot 10^{6}$ μΩ cm. This probably reflects the high Cl concentration in the film. As the temperature of deposition increases, the resistivity decreases significantly. At 1273 K, the resistivity is 1970 μΩ cm, close to the value of a-C film prepared by CVD (1000 μΩ cm) [7]. Compared to the reported data of other carbon materials, the value of 1970 μΩ cm is higher than graphite (40 μΩ cm) [26] and nanocrystalline diamond film (200 μΩ cm) [8], but much lower than evaporated a-C (~10^{9} μΩ cm) or a-C:H (~10^{13} μΩ cm) films [27].

We also studied the deposition process from $SiCl_3CCl_3$ on Si substrates. The SEM image of the film that was deposited at 1073 K for 25 min is shown in Fig. 6. It does not adhere to the substrate. It curled into a roll of C film. We speculate that the Cl atoms from the precursor etched the thin film–substrate interface and lifted the film from the substrate. The uneven distribution of the thermal expansion property, probably originated from the difference in the elemental composition within the film, might cause the film to curl into a roll-like structure. EDS analysis indicated that the composition was 76% C, 20% Si and 4% O.

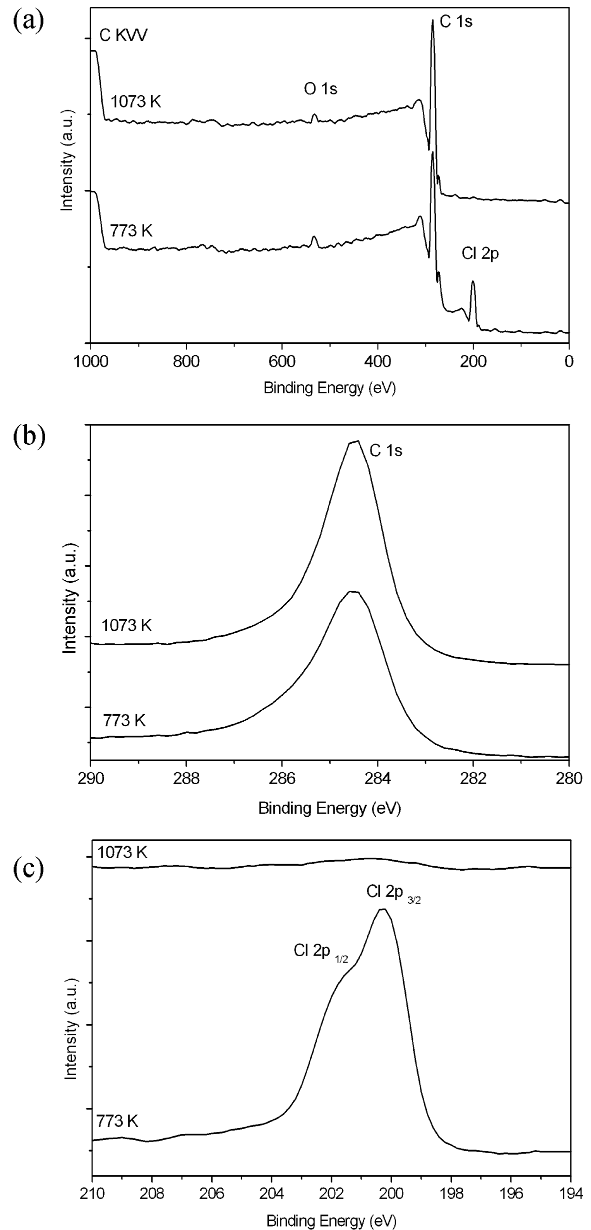


Fig. 3. XPS spectra of films grown on quartz at 773 and 1073 K: (a) survey, (b) high-resolution C 1s electrons and (c) high-resolution Cl $2p_{3/2}$ and Cl $2p_{5/2}$ electrons.

In order to understand the reaction pathway of the precursor $SiCl_3CCl_3$, an on-line FT-IR experiment was performed to identify the volatile products generated at different temperatures. The spectra are shown in Fig. 7.

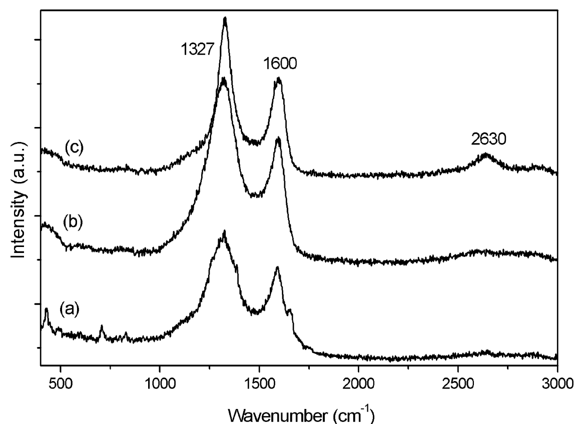


Fig. 4. Raman spectra of films deposited on quartz substrates at (a) 773, (b) 1073 and (c) 1273 K.

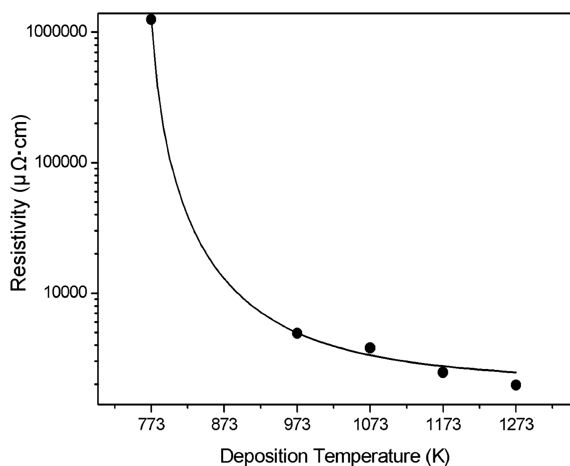


Fig. 5. Resistivity of the films prepared at 773–1273 K.

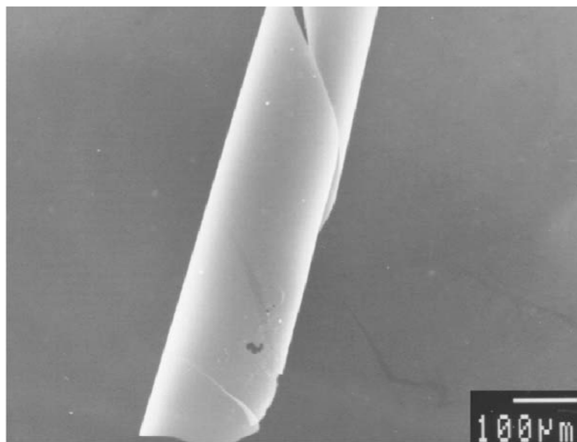


Fig. 6. SEM image of a carbon roll deposited on n-Si(100) substrate at 1073 K.

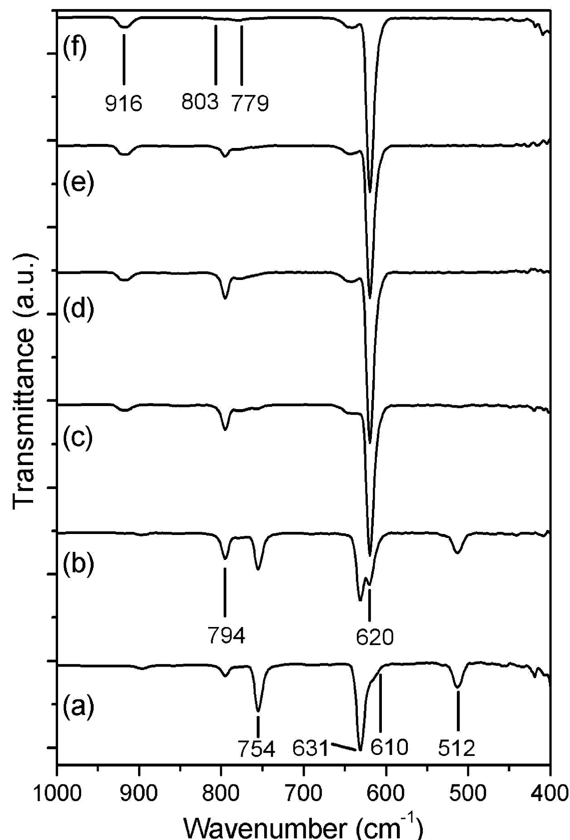


Fig. 7. On-line FT-IR spectra of the vapor phase products obtained at (a) 300 K, (b) 473 K, (c) 573 K, (d) 773 K, (e) 973 K and (f) 1173 K.

The absorptions of the precursor, at 512, 610, 631and 754 cm^{-1} [28], are shown in Fig. 7a. The precursor starts to decompose above 473 K (Fig. 7b). Above 573 K, as shown in Fig. 7c–f, the signals of the precursor become negligible while the signals of $SiCl_4$ (620 cm^{-1}) [29], CCl_4 (794 cm^{-1}) [30] and $Cl_2C{=}CCl_2$ (916, 803 and 779 cm^{-1}) [30] dominate the spectra. As the deposition temperature increases, the signal of CCl_4 decreases while the signals of $Cl_2C{=}CCl_2$ increase. The volatile byproducts were also collected in a U-trap at liquid nitrogen temperature and studied by GC–MS. The generation of $SiCl_4$, CCl_4 and $Cl_2C{=}CCl_2$ were confirmed. This agrees with the literature reports [19,20,31,32]. In Fig. 8, a reaction pathway is proposed to summarize and rationalize the experimental observation. Based on the formation of $SiCl_4$ and $Cl_2C{=}CCl_2$, it is proposed that a carbene, $:CCl_2$, was extruded from the precursor above 473 K. The divalent species may undergo a disproportionation reaction to deposit carbon films and to release CCl_4. Between 773 and 1073 K, the stripping of Cl atoms from the solid appeared to be incomplete, leaving excess Cl atoms in the film.

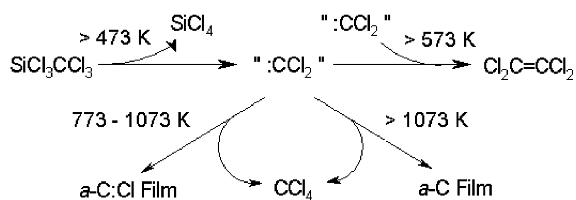


Fig. 8. Reaction pathway for the deposition of a-C:Cl and a-C thin films.

High-purity amorphous carbon films were grown at temperatures above 1073 K.

4. Conclusion

A simple LPCVD method, using $SiCl_3CCl_3$ as the precursor to grow a-C films and a-C:Cl films at 773–1273 K, was developed. The film grown at a low temperature, 773 K, reveals a rough morphology with 10% Cl content by XPS. As the deposition temperature increases above 973 K, the film is smooth and transparent, and the composition determined by XPS is nearly pure carbon. Unlike other CVD methods used to grow amorphous carbon thin films, the process developed here does not require plasma as a source of energy to activate the gaseous carbon source. Thermolysis of the precursor extrudes an active divalent intermediate, $:CCl_2$, from the silane precursor. The carbene disproportionates to deposit amorphous carbon films and to form CCl_4 as a byproduct. This observation parallels other reports using the divalent molecules of Group IV to deposit thin films by CVD.

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