

Preparation of Silicon Carbide Coatings from Liquid Carbosilanes by Chemical Vapor Deposition

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Liquid carbosilanes which were synthesized from polydimethylsilane (PDMS) were analyzed by infrared spectra (IR) and H-nuclear magnetic resonance (NMR). Silicon carbide coatings were prepared by chemical vapor deposition from liquid carbosilanes onto several different substrates. The coatings were characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD), and IR. The results show that liquid carbosilanes are mixtures of several oligomers which have Si-C backbone. The coatings prepared at 850 °C contain some organic segments, and those prepared at 900 °C are comparatively pure SiC which is partly crystallized. The coatings are glazed and very hard.

Keywords carbosilane, chemical vapor deposition, silicon carbide, precursor

synthesized, from which CVD SiC coatings were prepared and characterized.

1. Introduction

Silicon carbide (SiC) has attracted more and more interest in recent years for its use in electronic and optoelectronic devices, and circuits designed to operate at high temperatures, high powers, high frequencies, and high-radiation environments due to its good electrical and mechanical characteristics (Ref 1-3). Chemical vapor deposition (CVD) is one of the most widely used processes to prepare SiC. CVD SiC has many outstanding properties such as high density, good thermal conductivity, extreme hardness, as well as excellent resistance to chemical attack and thermal shock, which make it very appropriate for a high-temperature structural material (Ref 4, 5). In addition, its wide energy band gap and high-saturated drift velocity should make it a good candidate for high-temperature semiconductor applications (Ref 6).

The technical requirements of preparing CVD SiC and the properties of products mostly depend on the properties of precursor materials (Ref 7). Up to now, it has been common to prepare CVD SiC coatings from methyltrichlorosilane (CH_3SiCl_3 , MTS for short). MTS has some advantages such as that the ratio of Si and C atoms is 1. However, when it pyrolyzes, it gives out large quantities of HCl gas which has serious toxicity and corrosiveness harmful to people and equipment (Ref 8-11). In order to protect environment and to reduce the cost, we should search for a new non-corrosive precursor (Ref 12). In this work, a new precursor was

2. Experimental Procedure

Liquid carbosilanes which were synthesized from polydimethylsilane in advance were used as precursor. The deposition experiments were carried out in a hot-wall horizontal quartz tube reactor. Hydrogen was used as carrier gas (Ref 13), which delivered the precursor through the bubbler to the reactor; isotropy graphite and silicon films were chosen as deposition substrates. The flow rate of hydrogen was controlled by flowmeter. The deposition experiments were performed at 800-900 °C under a total pressure of 1.0 kPa. Figure 1 depicts a schematic diagram for the process of deposition.

The structure of carbosilanes synthesized was analyzed by infrared spectra (IR) and H-nuclear magnetic resonance (NMR). The structures of deposited coatings were analyzed by IR, and the crystalline phase and its preferred orientation were characterized by X-ray diffractometry (XRD) at a wavelength of 1.5418 Å (Cu K α radiation). The microstructures of the CVD SiC coatings were observed by scanning electron microscopy (SEM).

3. Results and Discussion

3.1 Structure Analysis of Liquid Carbosilanes

Liquid carbosilanes were transparent, colorless, and scentless at room temperature. An infrared spectrum of them is shown in Fig. 2. The absorption peaks located at 2900 and 2950 cm^{-1} are attributed to C-H stretching vibration, the strong absorption peak located at 2100 cm^{-1} is attributed to Si-H stretching vibration, the peak located at 1400 cm^{-1} is attributed to C-H vibration (Si- CH_3), that located at 1250 cm^{-1} is attributed to Si- CH_3 , and those located at 1030 cm^{-1} and 830 cm^{-1} are

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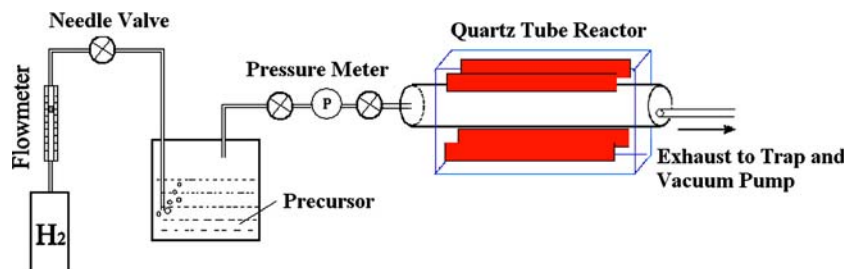


Fig. 1 Schematic diagram for the preparation of SiC coatings by CVD

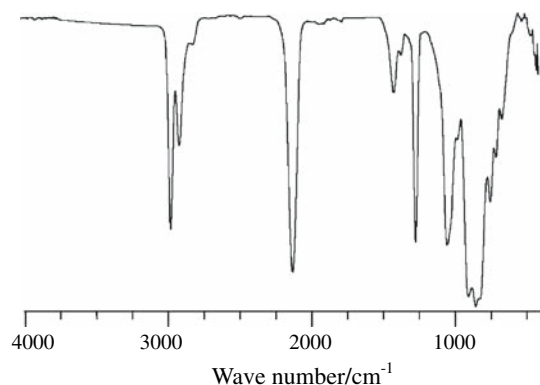


Fig. 2 Infrared spectrum of liquid carboranes

attributed to Si-CH₂-Si and Si-H, respectively (Ref 14). It can be inferred that bonds of Si-H, Si-CH₃, Si-CH₂-Si, C-H exist in the structures of carboranes. No absorption is detected at 1080 cm⁻¹, which suggests that little oxygen be introduced.

Figure 3 shows an H-NMR pattern of liquid carboranes. The sharp peak centered around zero is attributed to H atoms in CH₃- and -CH₂-, while the weak peak around 4.0 is attributed to H atoms in Si-H. The ratio of integral areas of two peaks referred above is about 5.4:1, which indicates that the ratio of C-H and Si-H is also 5.4:1. Considering the results of infrared spectrum analysis and molecular weights of carboranes, several possible structures of liquid carboranes are shown in Fig. 4. Liquid carboranes are likely mixtures of several molecules with structures shown in Fig. 4 or other similar structures.

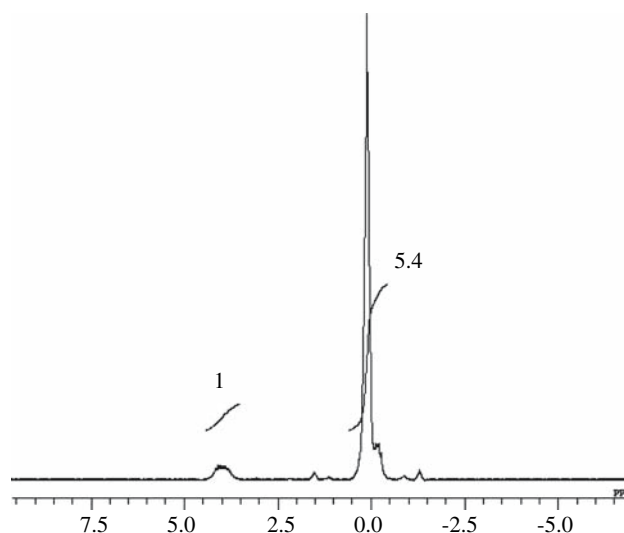


Fig. 3 H-NMR pattern of liquid carboranes

3.2 Effect of Temperatures on Products

Thin coatings were deposited on silicon flakes at 850 and 900 °C using liquid carboranes as precursor. The infrared spectra of them are shown in Fig. 5.

As shown in Fig. 5, besides the absorption peak of Si-C stretching vibration (830 cm⁻¹), the coatings prepared at 850 °C still contains a strong peak of Si-CH₂-Si(1030 cm⁻¹). In 900 °C products, there is only a strong peak of Si-C (830 cm⁻¹). The peak of Si-CH₂-Si(1030 cm⁻¹) exhibits a weak shoulder. No other peak is visible. It indicates that the precursor pyrolyzes incompletely at 850 °C, the products still have some organic segments. When heated to 900 °C, the content of organic segments reduce obviously.

3.3 Characterization of Coatings Prepared at 900 °C

Coatings were prepared on graphite and silicon substrates at 900 °C. The surfaces of coatings were shiny and glazed, and

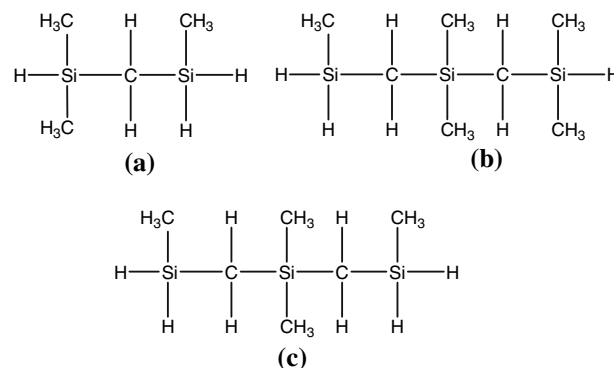


Fig. 4 Several possible structures of liquid carboranes

presented colorful stripes caused by diffraction. The microstructure of a deposited coating is shown in Fig. 6. The surface of the coating is very smooth, and it has very tiny structure units, about 10 nm, which are quite compact.

The hardness of the coatings was about 2800-3200 kgf/mm² (Hardness Vickers), which nearly reach the theoretic value of β-SiC. The thickness of coatings could be calculated according to the increased weight and the theoretic density of SiC (3.21 g/cm³), by which the depositing rate could be estimated. In practical experiments, depositing rate could reach 40 nm/min (2.4 μm/h) and above.

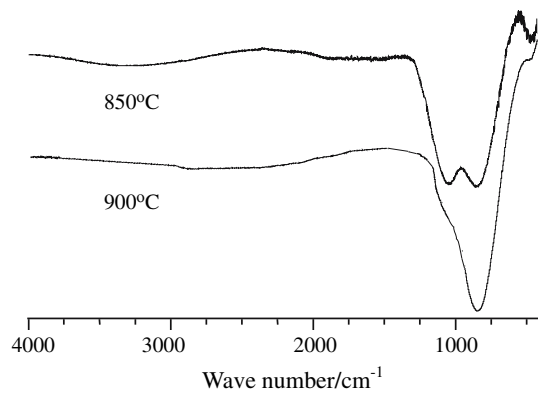


Fig. 5 Infrared spectra of coatings on Si flakes prepared at 850 and 900 °C

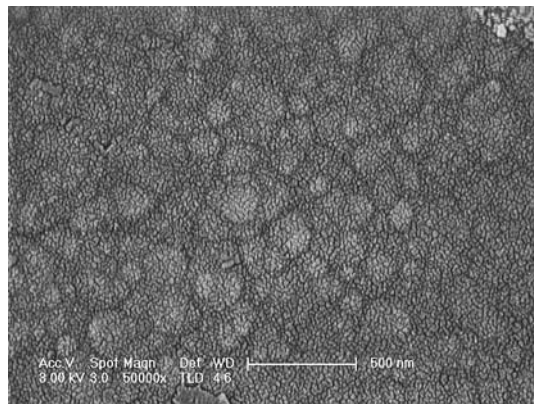


Fig. 6 SEM photograph of a coating deposited on Si film

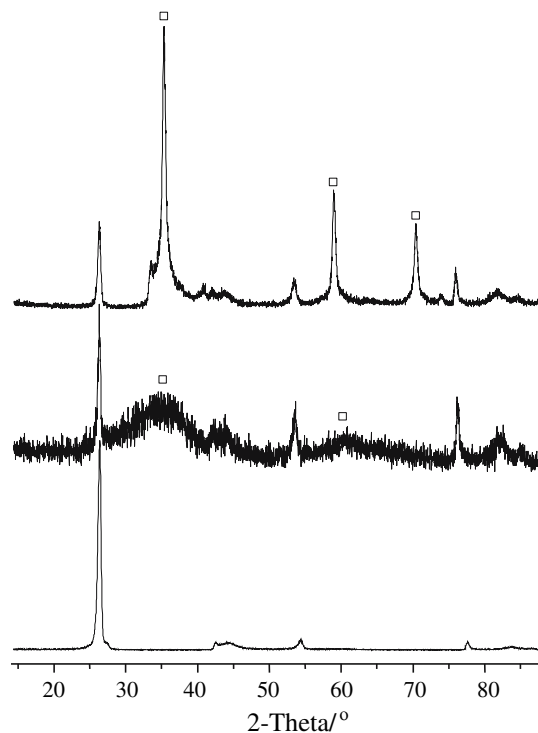


Fig. 7 XRD patterns of coatings on graphite substrates

Figure 7 shows XRD patterns of coatings prepared on graphite films. The middle pattern is from a coating prepared at 900 °C, and the top one is from a coating after heat treatment at 1600 °C for 2 h, compared with the bottom one which is from graphite only. It can be found that there are two obvious diffraction peaks located at 35.7°(111) and 60°(220) which are attributed to β -SiC. After the coating was treated to 1600 °C, all of the characteristic diffraction peaks of β -SiC are present explicitly, which locate at 35.7°(111), 41.4°(200), 60°(220), 71.8°(311). No other diffraction peak is found.

When preparing SiC coatings from MTS, 1000 °C and above are needed for quality products, but it releases corrosive gas HCl. Compared to using MTS, the temperature when using liquid carbosilanes is reduced obviously, and the byproducts mainly are small molecule gases such as H₂, CH₄. No corrosive gas is released. Moreover, the liquid carbosilanes process can reach a much higher-depositing rate. Therefore, using liquid carbosilanes as precursor can reduce the requirements of temperature and equipment, and it makes good sense for the environment.

4. Conclusions

- (1) Liquid carbosilanes were synthesized from polydimethylsilane. Bonds of Si-H, Si-CH₃, Si-CH₂-Si, C-H existed in the structures of carbosilanes. Little oxygen was introduced, and there was no corrosive element such as Cl.
- (2) CVD SiC coatings could be prepared from liquid carbosilanes at low temperature (900 °C) under a low pressure of 1.0 kPa. There was no corrosive byproduct.
- (3) The surface of the coatings was smooth, and they had very tiny structure units. The hardness of coatings was high enough.
- (4) The product deposited at 900 °C was comparatively pure SiC which was partly crystallized.

Acknowledgment

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