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Deposition of silicon carbide films by plasma enhanced chemical vapour deposition

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Abstract

Thin films of silicon carbide have been prepared by plasma enhanced chemical vapour deposition using $Si(Si(CH_3)_3)_4$ as a precursor. This compound is stable against moisture and air and has a high vapour pressure. Furthermore, the compositions of the films prepared from this precursor show very little dependence on the plasma parameters. Consequently, this precursor is especially suited for practical applications of hard coatings.

Keywords: Silicon carbide; Chemical vapour deposition; Silane; MOCVD

1. Introduction

Owing to its hardness (9.6 Mohs), high melting point (about 2700°C) and resistance to chemical attack, silicon carbide (SiC) is used as a refractory material, an abrasive, and a hard coating for tools [1]. Pure SiC has a resistivity of 100–200 Ω cm and a density of 3.22 g cm^{-3} [2].

There are numerous reports on the preparation of powders and thin films of SiC [2]. The pyrolysis of CH_3SiH_3 at 900–950°C, of $Si(CH_3)_4$ at 800–1400°C and of CH_3SiCl_3 yielded SiC powder. Below 1000°C the product was amorphous; in the range 1000–1800°C it was microcrystalline. Under most conditions the material contained hydrogen and had a carbon deficiency [2]. Crystalline SiC-films have been prepared by thermal chemical vapour deposition (CVD). Those deposited at more than 800°C normally consisted of mixtures of α- and β-SiC [3]. However, other authors working at 1150°C found only β-SiC, even when the films were deposited on crystals of α-SiC [4]. SiC was also formed when silicon was exposed to hydrocarbon vapours at 620–670°C [5] or by using C_{60} molecular source on Si(100) wafers at 900°C substrate temperature [6].

For bulk SiC, a hardness of 2250–2500 kp mm^{-2} has been reported [2], but for SiC-films values up to 7000 kp mm^{-2} have been found [7,8]. The highest values have always been obtained for films with the correct 1 : 1 stoichiometry.

Since films of amorphous SiC often vary in composition, they are described as $Si_{1-x}C_x$ or as $Si_{1-x}C_x:H$. Such films have been prepared by sputtering, by thermal or by plasma enhanced (PE) CVD techniques. Most CVD processes started with combinations of silane and hydrocarbons; occasionally silicon and carbon-containing compounds were also used as precursors. Films prepared by PECVD from silane–hydrocarbon mixtures had compositions varying from about Si_4C to SiC_4 depending on the ratio of precursors.

In combinations of SiH_4 with CH_4 and C_4H_{10}, the hardness was greatest at or close to the correct SiC stoichiometry. In general, butane led to softer films than methane [7]. More complex precursors are also reported: $(C_2H)_4Si$, $(C_3H_3)_4Si$, $(C_4H_8)_2Si$ or $(C_4H_6)_2Si$ were thermally decomposed at 400–700°C [9], but the composition of these films depended greatly on the nature of the precursor and on the deposition temperature and never led to the correct SiC stoichiometry.

The PECVD of $Si(CH_3)_4$ at 25 and 150°C yielded films with different C/Si atomic ratios, showing different reactivities when exposed to oxygen [10]. Dodecamethylcyclohexasilane $[(CH_3)_2Si]_6$; was also used

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successfully in hydrogen PECVD of SiC thin films [11]. The recent progress in the use of organometallics for PECVD processes [12,13] has also prompted the search for better precursors for the preparation of SiC films. Papers discussing the application of silacyclobutane [14], hexamethyldisilane [15] and ditertiary-butylsilane [16] as single-source precursors have been published.

Combined UPS-pyrolysis experiments revealed that $C(SiH_3)_4$ is a potential feedstock for the decomposition to amorphous hydrogenated SiC thin films [17].

In 1991, we reported the formation of SiC from $Si(Si(CH_3)_3)_4$ precursor [18]. Wrobel and coworkers used the same compound for producing SiC films in a series of remote plasma CVD experiments [15,19–22]. Here we report the formation of SiC films obtained from the same precursor in a parallel plate PECVD system.

2. Experiments

For the depositions, two different previously described [23], parallel plate reactors were used. Type A had electrodes of equal diameter (16 cm); the substrates were placed at the lower, grounded electrode. In type B the upper electrode (diameter, 16 cm) was at ground potential while the lower, smaller electrode (diameter, 12 cm) was connected to the r.f. generator via a capacitor. The upper electrodes were made of aluminium; the lower was of stainless steel and could be heated to 500°C. The spacing was always 3 cm. As substrates, glass, quartz, Si(100), stainless steel and aluminium were used. Prior to the depositions the substrates were subjected to an Ar cleaning plasma (30 min, 0.5 W cm^{-2}).

Hydrogen was used as a carrier gas. It was passed through an evaporator containing the $Si(Si(CH_3)_3)_4$ and entered the plasma reactor through the upper electrode. The deposition rates were determined by weight gain and thickness measurements with an Alpha-step-200. Films were analysed by combustion analysis in a carbon analyser (Leco CS-224) and by electron microprobe analysis (EPMA) for carbon, silicon and oxygen. The hardness was measured by the Leitz Miniload 2.

$Si(Si(CH_3)_3)_4$ was synthesized based on a standard literature procedure [24]. The crude semi-solid product was further purified. It was washed with small portions of ethanol which largely removed the yellow-coloured impurities. Then the product was dissolved in chloroform and filtered. In this step a considerable amount of a white polymer was separated. Evaporation of the $CHCl_3$ in vacuo and washing the product with ethanol gave a pure white product (checked by GC-MS). Further purification of the compound was achieved through vacuum sublimation.

3. Results

With the substrates placed at the grounded electrode and no self bias being applied, the influence of the gas flow and of the substrate temperature were tested. At constant pumping speed, an increasing hydrogen flow from 25 to 300 sccm (standard cubic centimetres per minute) caused a pressure increase in the system from 0.1 to 0.55 mbar. Simultaneously, the deposition rate dropped from 0.89 to 0.33 $\mu g\ cm^{-2}\ min^{-1}$ (power, 0.5 W cm^{-2}; $T_{subst.}$, 400°C; time 60 min). The resulting colourless films, which contained 31 ± 3 wt.% carbon, were too thin for hardness measurements.

Raising the temperature from 150°C to 450°C caused a drop in deposition rate by a factor of two. At low temperatures the films were colourless and transparent; at higher temperatures they were slightly yellow. After 60 min deposition time (power, 0.5 W cm^{-2}; flow, 50 sccm H_2) the films were still too thin for hardness measurements. However, they were more scratch resistant when deposited at higher temperatures. Film analyses showed 33 ± 5 wt.% carbon and no electrical conductivity.

By changing to the reactor with self bias (type B) the deposition rates could be significantly increased. A variation of power from 0.13 to 1.24 W cm^{-2} caused a sixfold increase of the deposition rate (Table 1). Since there is a linear dependence between the power density and the self bias, this effect might have been caused by either parameter. However, a comparison with data obtained at similar power in reactor type A shows that the self bias caused a threefold increase in deposition rate and led to denser products. Fig. 1 shows the almost linear dependence of the deposition rate on the power density.

The resulting films were yellow, amorphous, scratch resistant, and had an average density of 2.8 ± 0.2 g cm^{-3} but no measurable conductivity. The two thickest films could be measured in the hardness tester and had values of 1300 and 1800 HK (Knoop hardness). The carbon content in this series, as determined by combustion, was 33 ± 1%. The EPMA analyses found 35 ± 2% C, 55.3 ± 0.8% Si and 4.6 ± 0.3% O. According to depth profiles by AES, there is a high oxygen concentration at the surface but very little inside the films.

Increasing the hydrogen flow from 75 to 300 sccm (power, 0.53 W cm^{-2}; T_{evap}, 80°C; $T_{subst.}$, 400°C) only caused a 10% drop in deposition rates, possibly due to a slight pressure increase, but otherwise had no influence. Variation of the vaporizer temperature in the range of 50–140°C caused the deposition rates to change by a factor of two, with the highest values at a medium setting (Fig. 2). All films of this series were yellow, non-conducting and contained 33 ± 2 wt.% carbon.

A more pronounced effect on deposition rates and

Table 1
Influence of power density and self-bias (constant parameters: T_{evap}, 80°C; flow, 75 sccm H_2; $T_{subst.}$, 400°C)

Power ($W\ cm^{-2}$)	Deposition rate ($\mu g\ cm^{-2}\ min^{-1}$)	C (wt.%) [a]	C (wt.%) [b]	Si (wt.%) [b]	O (wt.%) [b]	Thickness (μm)	Knoop hardness (HK)	Density ($g\ cm^{-3}$)	Self-bias (V)
0.13	0.53	34.86	n.d.	n.d.	n.d.	0.120	n.d.	2.67	−140
0.27	0.93	32.53	n.d.	n.d.	n.d.	0.166	n.d.	3.36	−219
0.53	1.55	19.91	n.d.	n.d.	n.d.	0.345	n.d.	2.69	−315
0.71	2.04	35.31	32.9	55.0	4.7	0.456	n.d.	2.69	−392
			32.6 [c]	56.7 [c]	4.4 [c]				
			33.8 [d]	55.8 [d]	4.5 [d]				
0.88	2.42	31.74	36.7	55.8	3.9	0.555	1299	2.62	−450
1.24	3.18	33.93	36.9	54.0	4.9	0.741	1784	2.58	−540
			36.2 [d]	54.4 [d]	5.2 [d]				
0.5 [e]	0.65	34.05	n.d.	n.d.	n.d.	0.24	n.d.	1.63	—

[a] Combustion analysis. [b] EPMA. [c] Deposition on Al substrates. [d] Deposition on Si(100) substrates. [e] Reactor with electrodes of equal diameter.

film properties was caused by variation of the substrate temperature (Table 2). Raising the temperature from 150°C to 450°C reduced the rate of 35% (Fig. 3). Combustion analyses showed a constant carbon content throughout the series (32.9 ± 0.9). The EPMA data were 54.1 ± 0.8% Si, 35.7 ± 1.4% C and 5.4 ± 1.2% O. The three elements only added up to 95 ± 1%. This result is a qualitative indication, that the films also contain some hydrogen. Owing to the different sampling technique the carbon values from EPMA are higher than those from combustion. While in combustion all the film material is analysed, with EPMA (6 keV electrons) only the upper 0.3–0.5 μm is analysed; this emphasized the surface contamination by carbon and oxygen.

There is a fairly regular increase of hardness and density with increasing substrate temperature (Figs. 4 and 5). The hardness reached 2200 HK, thus coming close to the value reported for bulk SiC (2480 HK). The peak observed at 350°C is probably accidental.

For further characterization, FTIR-spectra of the films were taken. All films showed strong absorptions at 800 and 1000 cm^{-1}. In addition, most spectra had a sharp absorption at 1250 cm^{-1} and small, but broad, bands at 2100 cm^{-1}. In some samples there were small peaks at 2990, 2900, 2360 and 2330 cm^{-1}.

The main peak was always at 800 cm^{-1}, but the relative intensity of the signals at 1000 cm^{-1} changed. With increasing flow this became more pronounced; with increasing power it became smaller. The small peaks of the spectra got smaller and broader with increasing power or substrate temperature, indicating a more complete reaction and less incorporation of impurities into the films. The application of a self-bias slightly augmented the small peaks.

In previous IR-studies on amorphous $Si_{1-x}C_x$ films all authors report a strong band at 800 cm^{-1}, which is attributed to the Si–C stretching vibration [2]. Impurities of SiO_2 are evidently responsible for the band at 1000 cm^{-1} [25]. The sharp absorption at 1250 cm^{-1} was attributed to CH_3 groups in $Si–CH_3$, and that at 2100 cm^{-1} to $Si–H_n$ streching vibrations [26].

Thus the FTIR spectra of the films show the strongest peak for the Si–C streching vibration. However, there are also Si–O signals which might indicate a surface layer of SiO_2. This seems to be especially pronounced at high flow rates. The films show only minute or no signals for $Si–CH_3$ (1259 cm^{-1}) or $Si–H_n$ (2100 cm^{-1}) which would indicate incomplete reaction.

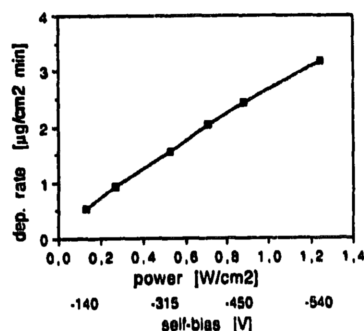

Fig. 1. Influence of power density and self-bias on deposition rate (constant parameters: T_{evap}, 80°C; flow, 75 sccm H_2; $T_{subst.}$, 400°C).

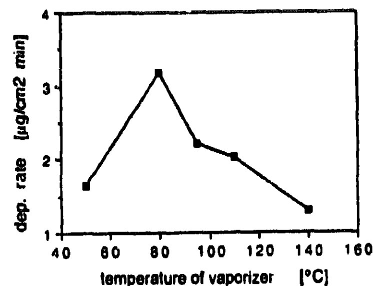

Fig. 2. Influence of vaporizer temperature on deposition rate (flow, 75 sccm H_2; power, 0.53 W cm^{-2}; $T_{subst.}$, 400°C).

Table 2
Influence of substrate temperature (constant parameters: T_{evap}, 80°C; flow, 75 sccm H_2; power, 1.24 W cm^{-2})

Substrate temperature (°C)	Deposition rate ($\mu g\ cm^{-2}\ min^{-1}$)	C (wt.%) [a]	C (wt.%) [b]	Si (wt.%) [b]	O (wt.%) [b]	Thickness (μm)	Knoop hardness (HK)	Density ($g\ cm^{-3}$)	Self-bias (V)
150	4.97	33.73	36.7	53.9	4.2	1.465	1134	2.03	−550
220	4.93	32.00	36.6	53.9	6.3	1.365	1341	2.17	−589
			39.8 [c]	53.3 [c]	5.6 [c]				
250	4.22	31.15	34.3	53.7	5.6	1.163	1272	2.18	−538
270	3.99	32.59	34.5	53.9	8.3	1.125	1336	2.13	−525
			35.3 [c]	51.3 [c]	8.2 [c]	1.125	1336	2.13	−540
			34.2 [d]	51.4 [d]	8.5 [d]				
290	3.94	31.82	37.2	54.0	4.1	1.088	1599	2.17	−540
			36.3 [c]	53.5 [c]	3.9 [c]				
350	3.88	32.72	37.3	54.4	3.8	1.004	2218	2.54	−538
375	3.56	33.53	35.3	53.6	6.3	0.914	1884	2.34	−535
			34.6 [c]	54.4 [c]	6.3 [c]				
			34.5 [d]	53.0 [d]	6.0 [d]				
400	3.18	33.93	36.9	54.0	4.9	0.741	1784	2.58	−550
			36.2 [d]	54.4 [d]	5.2 [d]				
450	3.27	34.65	37.4	54.3	4.1	0.778	1944	2.52	−540
			35.5 [c]	54.3 [c]	4.0 [c]				
			36.3 [d]	54.5 [d]	6.1 [d]				

[a] Combustion analysis. [b] EPMA. [c] Deposition on Al substrates. [d] Deposition on Si(100) substrates.

Two films were studied by AES and by XPS: (a) deposited at a flow of 300 sccm H_2; T_{subst}, 400°C; power, 0.5 W cm^{-2}, no bias; (b) flow, 75 sccm H_2; T_{subst}; 400°C; power, 1.24 W cm^{-2}; bias, −550 V.

As-deposited, in AES both show strong signals for silicon, carbon and oxygen at 90 eV, 272 eV and 516 eV respectively. The depth profiles show high oxygen concentrations at the surface. After about 1 min of sputtering, steady concentrations of the three elements are reached. Carbon and silicon are of about equal signal strength, while the oxygen signal has lost its intensity substantially. A comparison of both samples indicates there is less oxygen in film (b) at the surface and inside the film.

Similar results have been reported by other authors [10,27] who also found a highly oxidized surface for SiC films. This effect has been attributed to a post-discharge reaction of trapped radicals and dangling bonds [10] and it seems to be less important if the films are denser and highly crosslinked.

Film (b) was further studied by XPS for both as-deposited and after sputtering for 60 min. The spectra show signals of silicon, carbon and oxygen. The Si 2p at the surface is found at 103.0 eV. After sputtering there is a strong peak at 101.5 eV with a shoulder at 99.6 eV. The carbon signal of the as-deposited film is centred around 284.4 eV. After sputtering the main signal is at 282.8 eV with shoulders at 281.8 and 283.6 eV and a small peak at 284.6 eV.

A Si 2p value of 103.2 eV has been found at the surface of $Si_{1-x}C_xH$ films prepared in glow discharges and has been attributed to SiO_2 [27]. Inside the films there were signals at 102.8 and at 99.5 eV which were interpreted as SiC (99.5 eV) and SiO_2 (102.8 eV). Other authors attributed the signal at 99.6 eV to Si–Si bonds [25]. Amorphous $Si_{1-x}C_xH$ films prepared by r.f. sput-

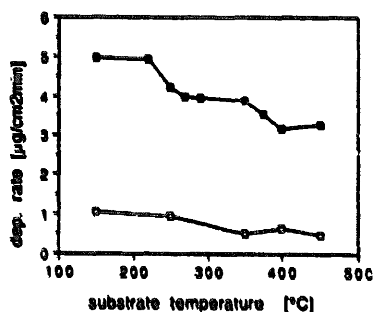

Fig. 3. Influence of substrate temperature on deposition rate. Full symbols: with self-bias of about −540 V. Open symbols: similar experiments in the reactor without self-bias. (Power, 1.24 W cm^{-2}; flow, 75 sccm; T_{evap}, 80°C).

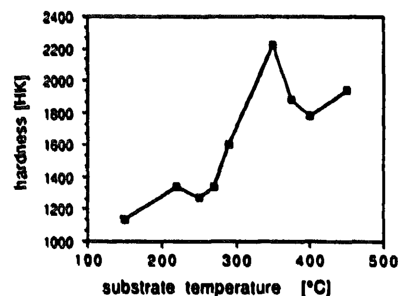

Fig. 4. Influence of substrate temperature on Knoop hardness (constant parameters: power, 1.24 W cm^2; flow, 75 sccm; T_{evap}, 80°C).

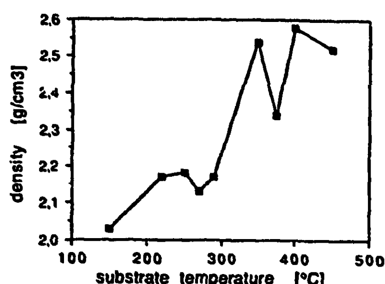

Fig. 5. Influence of substrate temperature on density (constant parameters: power, 1.24 W cm^2; flow, 75 sccm; T_{evap}, 80°C).

tering showed a shift of the Si 2p signal from 98.0 to 101 eV with increasing carbon content [28].

A C 1s value of 284.4 eV points to graphite or hydrocarbons and has been observed by many authors at the surface of SiC. A signal at 282.2 eV has been attributed to carbidic carbon. The shoulders around this signal (281.8 and 283.6 eV) have also been observed by other authors [27].

4. Discussion and conclusion

The precursor $Si(Si(CH_3)_3)_4$ has been used to deposit transparent amorphous films on a variety of substrates. The most important experimental parameters are the substrate temperature and the self-bias. The hardness of the deposits increases in the range 150 to 450°C from 1100 to 1940 HK. Simultaneously, film densities change from 2.0 to 2.6 g cm^{-3} A self-bias seems to be essential for the deposition of hard and dense materials. The bias greatly enhances the deposition rates.

Spectroscopical analyses of the films show the presence of SiC but also point to contamination at the surface by carbon and oxygen. While in AES, carbon and silicon signals are of about equal strength, combustion and EPMA analyses find carbon/silicon ratios of about 1.4 and 1.6 respectively (calculated by the use of data from Table 2). The discrepancy between the values from spectroscopy, combustion and EPMA can in part be explained by surface contamination.

As far as physico-chemical properties are concerned, $Si(Si(CH_3)_3)_4$ has several advantages over other precursors. It is stable in contact with air or moisture and thus does not require special handling. This is in strong contrast to the pyrophoric SiH_4 which has been used in several investigations. At temperatures of 80°C and above the vapour pressure of $Si(Si(CH_3)_3)_4$ is sufficient for CVD work. The carbon/silicon ratio is 2.4; more advantageous than in most of the precursors used so far.

$Si(Si(CH_3)_3)_4$ differs in another aspect from starting materials used in previous studies. The mixtures of SiH_4 with hydrocarbons or other organosilicon compounds yielded films of compositions which varied over a wide range, and which depended strongly on the deposition parameters. In contrast, the films prepared from $Si(Si(CH_3)_3)_4$ show only a slight variation in composition under all experimental conditions used. This is in close agreement with the results of remote plasma CVD investigations [21].

The experiments reported here thus further demonstrate that $Si(Si(CH_3)_3)_4$ is a precursor which is especially suited for practical applications in the field of hard coatings.

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