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The Chemical Vapor Deposition of Bulk Polycrystalline Silicon Carbide

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SUMMARY

The development of a process for chemical vapor deposition of polycrystalline α-phase silicon carbide onto carbon substrates is described. This process is based on the use of dichlorosilane and methane as reactants in nitrogen at atmospheric pressure. Deposits of fine-grained and hard material up to 12 mm thick have been obtained. The deposits are nonporous, relatively free of stress, free of cracks over large areas, and suitable for some structural applications.

1 INTRODUCTION

Silicon carbide exists in more than 130 polytypes, i.e. crystal structures, resulting from the fact that the various possible stacking sequences of close-packed layers have about the same energy.[1,2] The resulting structures range from the cubic 3C version (β-SiC) to a purely hexagonal 2H type with various hexagonal or rhombohedral intermediates collectively referred to as α-SiC. Polycrystalline SiC is a high-strength inert and oxidation-resistant ceramic. The fracture strength of SiC increases up to 1400°C making it suitable for high-temperature structural applications.[3]

Several methods are under development for the production of SiC shapes. The extremely high pressures and temperatures required to cause

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deformation of SiC powder grains makes hot-pressing difficult. It is usually necessary to add an impurity that forms a liquid at the pressing temperature or in some other way aids in densification. Sintering of very fine powder has been used to produce complex shapes; however, the sintered material is porous and of lower strength than the hot-pressed material. The only method capable of producing completely dense high-strength and pure silicon carbide is chemical vapor deposition (CVD). Unfortunately, this is the least advanced technique.

Chemical vapor deposition is carried out using one or more gaseous reactants to supply both silicon and carbon to a solid surface maintained at a high temperature. Under appropriate conditions a reaction proceeds and SiC is deposited on the hot surface. If process conditions, such as reactant concentrations and temperature gradient, are appropriate it should be possible to build up a dense fine-grained deposit. A variety of schemes for doing this have been explored but numerous problems have prevented their wide-scale application. The two most persistent problems have been the development of an irregular surface deposit, which with continued deposition leads to the formation of voids, and severe cracking of the deposit during cooling as a result of stresses built in during the deposition process.[4]

Most previous attempts to solve these problems have been based on the pyrolysis of vapor from a liquid organometallic compound containing both C and Si, such as CH_3SiCl_3. Deposits of pure β-SiC or of mixtures of α- and β-SiC have been obtained.[4] However, several complications remain with this process. To obtain reasonable deposition rates and morphology it has been found necessary to operate at a pressure of less than one atmosphere in the reactor. As a result, the large quantities of abrasive and reactive materials generated in the reactor must be handled by the pumping system. Secondly, the deposit tends to contain excess silicon if prepared at temperatures below 1400°C, and excess carbon at temperatures above this.[5] Thirdly, the material has a high level of grown-in stress, the magnitude of which is proportional to the growth rate.[4] At reasonable growth rates the stress is high enough to crack thick deposits extensively.

In view of the many properties that must be optimized simultaneously in the CVD of SiC it was decided at the beginning of the present work that it would be necessary to have control over as many parameters as possible. In particular, it was believed desirable to control the carbon-to-silicon ratio in the gas phase by utilizing separate sources of silicon and carbon. It was also decided that deposition should be carried out onto a heated substrate within an enclosure that could be either heated or cooled so as to control the temperature in the gas phase. Using this approach a process has been developed for the deposition of consistently fine-grained, dense, and crack-free α-SiC over areas of up to 64 cm^2, in thicknesses of up to 12 mm. The need

for hydrogen carrier gas has been eliminated and the system is operated at atmospheric pressure. By-product formation has also been reduced and procedures for safe clean-up of the system have been developed.

2 EQUIPMENT AND PROCEDURES

The gas supply system is shown in Fig. 1. The reactants, which are all gases at room temperature, were mixed with a carrier gas and filtered prior to introduction into the reaction chamber. Flow rates were controlled by needle valves and monitored by rotameter-type flow meters. The gas control system was constructed entirely of stainless steel. Figure 2 shows the reaction chamber, which consisted of a 94-mm-diameter quartz tube closed at each end by O-ring seals. Gas flow was in an upward direction so that the forced and thermal convective flows combined to minimize recirculation of reactants past the susceptor. Deposition took place onto an r.f. heated carbon substrate supported on an alumina tube containing a thermocouple. The substrate temperature was measured using an optical pyrometer and controlled automatically from the thermocouple emf. The lower part of the substrate consisted of a cylindrical stem drilled out to fit over the thermocouple tube. The upper part of the substrate had two large faces, 7 × 10 cm, and was tapered in thickness as shown. The small faces increased from 1·9 to 3·2 cm in width so as to increase the gas velocity v along the

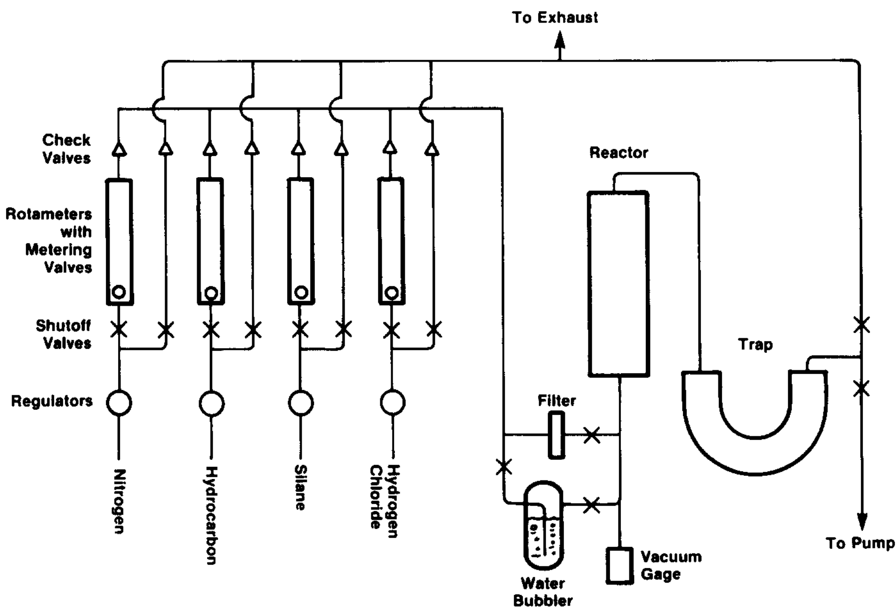


Fig. 1. Gas control system.

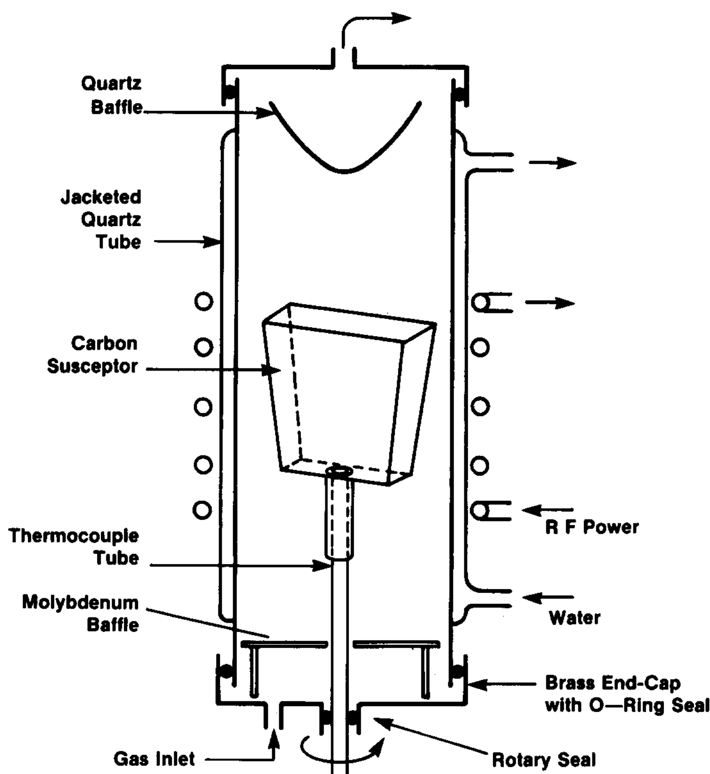


Fig. 2. Reactor and susceptor.

direction of gas flow. This shape was chosen to improve thickness uniformity in the direction of gas flow. Depletion of reactants tends to reduce the growth rate with distance along the hot surface. On the other hand, since the growth rate in CVD tends to increase as $v^{1/2}$, the increase in v resulting from taper of the substrate tends to increase the deposition rate and counteract the depletion effect. The substrate was also rotated at 10 rpm in order to improve thickness uniformity.

After passing over the substrate the gases flowed around a tapered baffle as shown in Fig. 2. This baffle greatly reduced turbulence immediately above the substrate. The exhaust gases were then passed through a 4-in-bore Pyrex glass U-tube filled with glass beads, which trapped much of the by-product. Finally, the gases were mixed with an excess of nitrogen and vented directly into a fume hood. The gas-handling system and reactor were contained in cabinets vented to the outside as a safety precaution. The reaction chamber was evacuated prior to each deposition run to ensure that no leaks were present.

Deposits were removed from the substrate by breaking them or cutting them with a wire saw using a diamond-coated wire blade. Any carbon

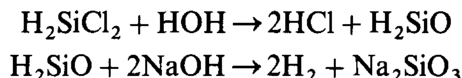
adhering was removed by oxidation in air at 650°C. Deposit grain structure was examined by polishing sections with diamond abrasives and then etching them in a molten mixture of 50 wt% KOH and 50 wt% KNO_3 at 500°C. Any cracking or porosity in the deposit could be seen after the polishing process.

3 RESULTS

Experiments were begun with a substrate temperature of 1400°C, using 1% silane (SiH_4) and 1% propane (C_3H_8) as reactants with hydrogen carrier gas at a total flow rate of 2 liters min^{-1}. An air-cooled reaction chamber was used. A large amount of gas-phase nucleation was seen, i.e. a smoke was formed adjacent to and above the susceptor. The smoke consisted of a red-brown powder, which was deposited on the chamber walls and trapped in the exhaust system. This deposition on the chamber walls made it impossible to measure the substrate temperature with an optical pyrometer after a few minutes of deposition time. X-ray diffraction patterns from the dust showed it to consist primarily of silicon with a small amount of SiC. Similar amounts of powder were obtained at temperatures of 1300 and 1500°C. In order to prevent the gas-phase reaction the chamber walls were water-cooled and the total gas flow was increased to 6 liters min^{-1} so as to reduce the gas temperature in the region of the substrate. In addition the reactant concentrations were reduced to $<0{\cdot}5\%$. These measures greatly reduced the amount of gas-phase reaction; however, the deposition rate was only 10 μm h^{-1} at 1500°C so that several weeks of continuous operation would be needed to deposit a layer a few millimeters thick. The deposit itself consisted of a mixture of α- and β-SiC. Experiments with methane in place of propane as the source of carbon gave essentially the same growth rate and amount of gas-phase reaction. Varying the C/Si ratio in the gas phase also had little effect.

Since the pyrolysis temperature of the silanes increases with degree of chlorine substitution, the use of dichlorosilane, H_2SiCl_2, at a concentration of 0·7%, as the silicon source along with 0·7% C_3H_8 as the carbon source was then tried. This resulted in a very much smaller amount of gas-phase reaction. A smooth deposit, 180 μm thick was obtained in 3·5 h at a substrate temperature of 1400°C. No dust was formed but some carbon was deposited on the chamber walls. The only other by-product evident was a white fog forming below the substrate, which condensed to a colorless viscous liquid on the water-cooled quartz walls above the substrate. This liquid hydrolyzed in air to give a white solid, which dissolved with evolution of hydrogen in dilute aqueous sodium hydroxide. Presumably the liquid was a mixture of

silanes, which were hydrolyzed to siloxanes in moist air and further decomposed in NaOH solution to yield Na_2SiO_3 and hydrogen. The reactions in the case of dichlorosilane itself, for example, are



$$H_2SiCl_2 + HOH \rightarrow 2HCl + H_2SiO$$
$$H_2SiO + 2NaOH \rightarrow 2H_2 + Na_2SiO_3$$

In subsequent runs it was found that carbon deposition on the chamber walls could be prevented by substituting methane for propane as a source of carbon. It was also found that the ambient hydrogen could be replaced by nitrogen without affecting either the structure or the morphology of the deposit, or the nature or quantity of the by-products. X-ray diffraction studies gave the surprising result that in all cases the deposit consisted of pure α-phase SiC with no Si_3N_4. This is in contrast with previous reports and theories, which lead one to expect the β-phase under the conditions of our experiments, i.e. below 1500°C.[2] The deposit consisted of a mixture of the 2H and 15R polytypes. This material should be comparable with hot-pressed or sintered SiC since these are also of the α-phase.

A series of experiments were made in which the H_2SiCl_2 and CH_4 concentrations were increased while keeping their ratio constant, and the resulting growth rates were measured. Figure 3 shows these results. The growth rate increased linearly with reactant concentration and values in excess of 0·5 mm h^{-1} were obtained. At H_2SiCl_2 concentrations in excess of

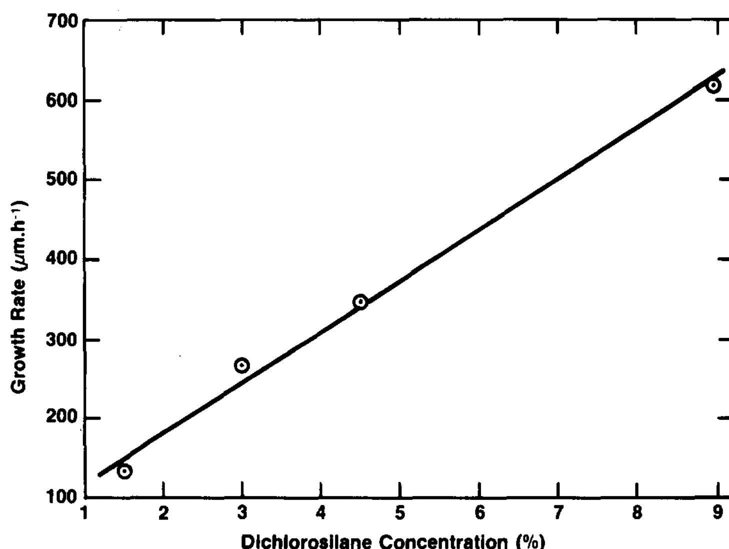


Fig. 3. The growth rate as a function of dichlorosilane concentration for growth at 1450°C. The methane concentration was kept a factor of 1·5 greater than the dichlorosilane concentration.

5% a rapid build-up of liquid along with a red film was noted on the reactor walls. The effect of substrate temperature on the growth rate was determined for an H_2SiCl_2 concentration of 1·5% and CH_4 concentration of 2·5% in helium. These results are shown in Fig. 4. A steep increase of growth rate with increasing temperature occurred up to 1600°C, above which it was much less temperature dependent. This behavior is typical for CVD processes. The steeply increasing region results from a situation in which the

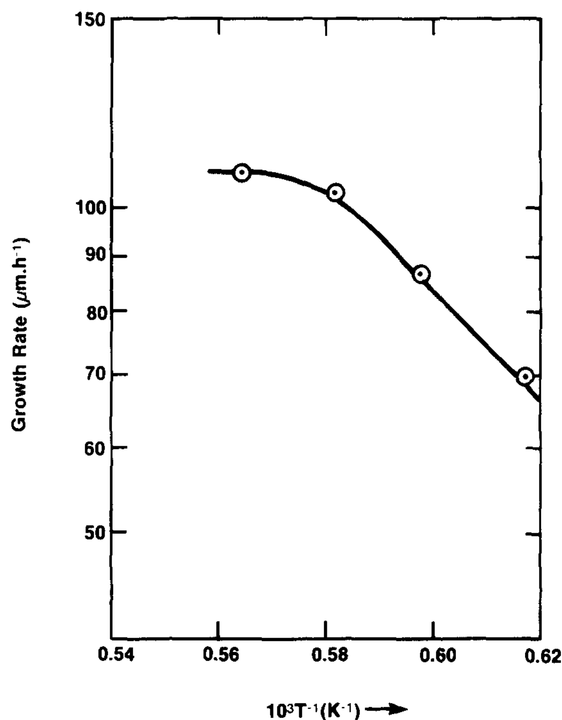
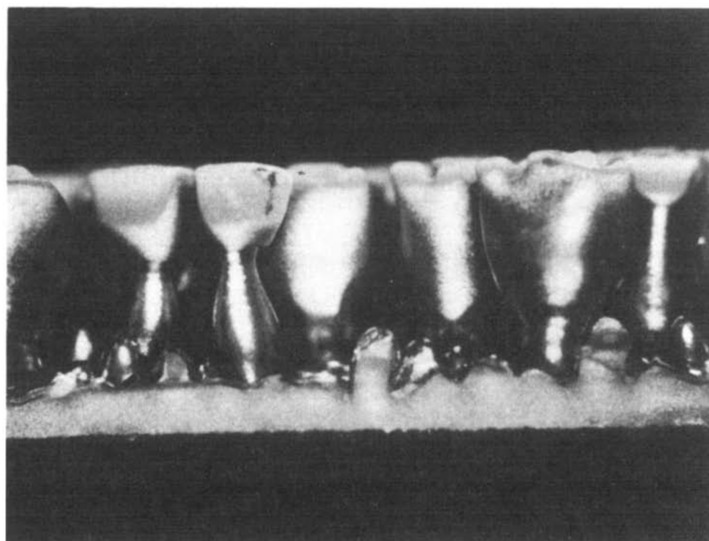


Fig. 4. The growth rate as a function of reciprocal temperature using 1·5% dichlorosilane and 2·5% methane.

overall rate is controlled by the surface reaction kinetics, which have an exponential dependence on inverse temperature. An activation energy of $1{\cdot}0 \pm 0{\cdot}1$ eV is obtained from the linear region of Fig. 4. At higher temperatures the process is diffusion limited, i.e. the rate of diffusion of reactants through the boundary layer adjacent to the hot surface is the limiting process, so that the rate should be less temperature dependent.

Smooth deposit surfaces are expected from the CVD process when the growth rate is limited by surface reaction rate, whereas an irregular surface morphology is expected when the growth rate is limited by the transport of reactants to the growing surface.[6] Under most conditions it was found that



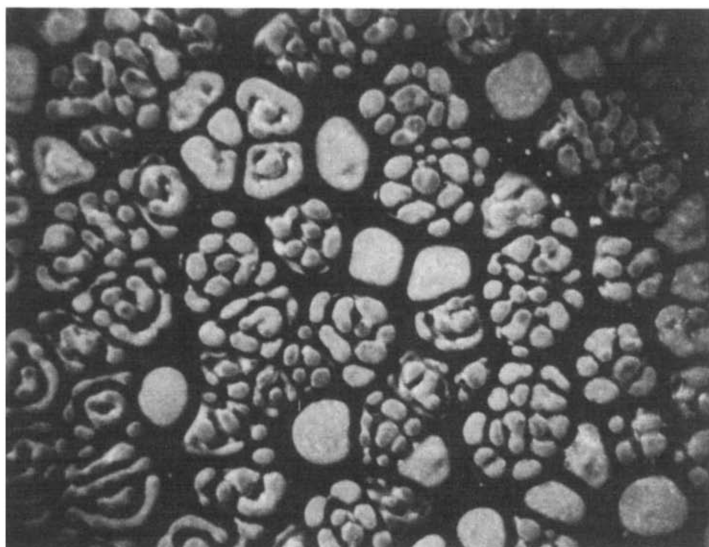


Fig. 5. A cleaved cross-section (top) and surface appearance (bottom) of a deposit prepared at 1400°C from 2·5% dichlorosilane and 3·7% methane.

thick deposits developed an irregular surface. For example, deposits more than 2 mm thick, made using 2·5% H_2SiCl_2 and 3·7% CH_4 at temperatures of 1350–1450°C, all showed a surface of the type shown in the two parts of Fig. 5. This consisted of an array of blunt nodules connected at their bases.

X-ray powder diffraction spectra obtained from these deposits showed them to contain an excess of elemental carbon in addition to the silicon carbide. A series of runs were therefore made at 1450°C, keeping the H_2SiCl_2 concentration fixed at 1·5% while varying the CH_4 concentration so as to change the C/Si ratio in the gas phase. X-ray powder patterns were obtained from these deposits and the relative height of the 3·4 Å carbon peak was measured as a function of this ratio. The results are shown in Fig. 6. As can be seen, at C/Si ratios of below 1·5 no excess carbon appeared in the deposits. No excess silicon was seen for ratios down to 0·7. The formation of a second phase of free carbon has been observed in films grown from SiH_4 and C_3H_8 by Harris *et al.*[7] and also by Wessels *et al.*[8] under carbon-rich conditions. Free silicon was also observed in deposits made under silicon-rich conditions by Harris *et al.*[7] On the other hand, Kim and Davis[9] have recently reported the presence of free silicon in films grown from the SiH_4-plus-C_2H_4 system at a C/Si ratio of 1·0 or below, while no free carbon was seen under any conditions. The authors believe that the absence of free

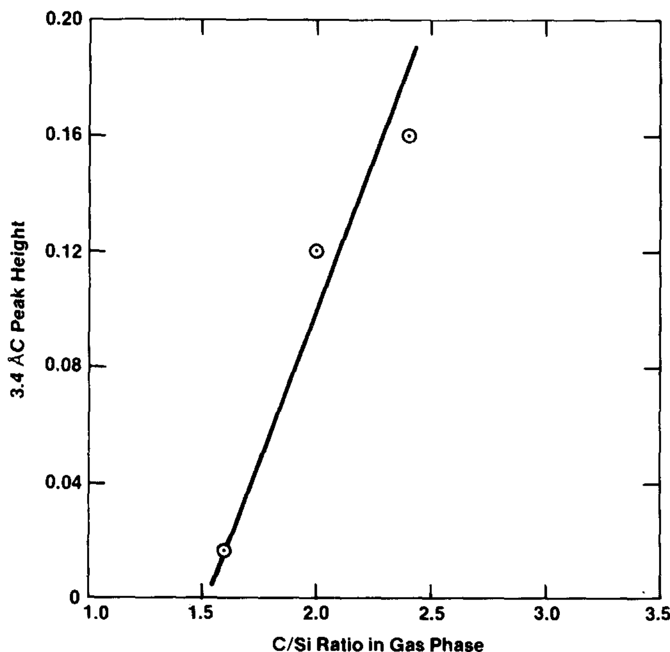


Fig. 6. The 3·4 Å X-ray diffraction peak due to free carbon as a function of the C/Si ratio in the gas phase for deposition at 1450°C.

silicon in their films can be attributed to the greater stability of Si—Cl bonds as compared with Si—H bonds so that any excess silicon is kept in the vapor phase as chlorides.

The appearance of the deposit surfaces also changed dramatically with C/Si ratio, smooth surfaces being obtained at ratios of $< 2{\cdot}0$. At 1450°C with a C/Si ratio of 1·6 (2·8% H_2SiCl_2; 4·4% CH_4), smooth 2- to 3-mm-thick deposits of pure α-SiC were obtained, which were free of excess C or Si. The deposition rate under these conditions was 227 μm h^{-1}. The deposits unfortunately cracked into pieces 1·0–4·0 cm in diameter on cooling. Increasing the deposition temperature above 1450°C resulted once again in the development of an irregular surface,. presumably as a result of a transition from a surface-kinetics- to a gas-transport-limited deposition process. Any temperature excursion above 1450°C resulted in the development of porosity in the deposit. On the other hand, the deposition rates became unacceptably low at temperatures below 1300°C. Neither these changes in deposition temperature nor changes in growth rate resulting from changes in the total reactant concentration at the same C/Si ratio had any effect on the degree of cracking.

Several difficulties were encountered in extending this process to obtain thicker deposits. Continued deposition of the red-orange by-product within the quartz reactor prevented temperature measurements using the optical pyrometer during long runs. This proved to be a problem because build-up of SiC on the substrate changed its thermal characteristics so that although the thermocouple temperature was kept constant, the temperature of the growing surface increased and a porous deposit formed. Clean-up of the system between runs also presented problems because of the large amount of liquid by-product obtained. Larger quantities of this material were no longer completely hydrolyzed in moist air. The resulting mixture of silanes and siloxanes was highly flammable and in some cases ignited spontaneously or detonated when mechanically disturbed or brought into contact with water. In addition a white powdery material was deposited at the point where the exhaust gases were vented to the atmosphere. This material was highly reactive.

Since the red-orange solid appeared to be elemental silicon, resulting from gas-phase decomposition of the H_2SiCl_2, some HCl gas was added to the reactants to suppress this reaction. It was found that an HCl concentration equal to the H_2SiCl_2 concentration was effective and that as a result the reaction chamber remained reasonably clear for 30–60 h of deposition time. This enabled temperature measurements to be made with an optical pyrometer throughout lengthy deposition runs. The addition of HCl also greatly reduced the volume of liquid by-product and reduced its reactivity. An unexpected result of the addition of HCl to the reactants was that the

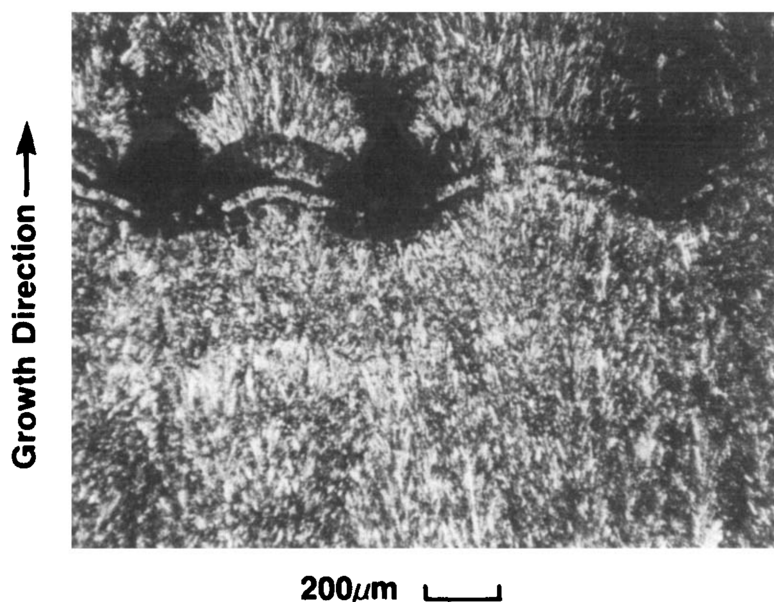


Fig. 7. Pores in a deposit caused by a temporary increase of temperature from 1340 to 1360°C during growth.

temperature above which a porous deposit formed was lowered from 1450 to 1350°C. Figure 7 shows an occurrence of pores in an otherwise solid deposit as a result of an increase in operating temperature from 1340 to 1360°C for a period of about 9 h during a 60-h deposition run.

Solids deposited at the exhaust continued to be highly reactive and flammable. The exhaust system was therefore modified so that the gases from the reactor were mixed with excess air in a furnace maintained at 800°C. Under these conditions all silicon compounds were oxidized to SiO_2 powder and a mixture of N_2, H_2O, and HCl was vented to a water-filled scrubber. To further improve the safety of the system, nitrogen saturated with water vapor was passed through the reaction chamber and trap after the completion of each run. This hydrolyzed the small amount of liquid by-product still formed to a relatively nonreactive white solid. The apparatus could then safely be disassembled and this solid dissolved in dilute NaOH with evolution of hydrogen.

To minimize cracking of the deposit several modifications to the carbon substrate were tried. First, a carbon layer was deposited onto the substrate by pyrolysis of 2·5% CH_4 in N_2 at 1500°C for 2 h. This did not reduce cracking but reduced adhesion between the deposit and substrate sufficiently for the deposit to be easily pulled away from the substrate after each run. It was observed that even 0·5-mm-thick sheets of SiC when removed from the

substrate in this way remained planar, indicating a low level of internal stress. Substantial stress gradients in the deposit would have caused distortion of these relatively thin sheets of material when released from the substrate. This is in contrast with the behavior of deposits prepared from CH_3SiCl_3, which have been reported to become appreciably distorted when removed from the substrate.[4] It was therefore concluded that cracking is probably due to the mismatch of thermal expansion coefficient between substrate and deposit and not to the presence of internal stresses resulting from the deposition process. All experiments up to this point had been made using carbon with a thermal expansion coefficient of $3{\cdot}3 \times 10^{-6}/°C$. Cracks formed perpendicular to the deposit surface, indicating that the deposits failed under tension. Carbons having a higher expansion coefficient were therefore evaluated as substrates by depositing 5–8 mm of material on them. Substrates with an expansion coefficient of $6{\cdot}0 \times 10^{-6}/°C$ resulted in a large number of cracks, which were parallel to the surface. Pieces of material spalled away from the surface in a way indicative of compressive stress in the deposit. Substrates with a coefficient of $5{\cdot}1 \times 10^{-6}/°C$ showed very few cracks. Those cracks that did form were predominantly along the corners of the substrate and did not penetrate the deposit completely. These results are consistent with the reported thermal expansion coefficient of α-SiC, which is $4{\cdot}7 \times 10^{-6}/°C$.[10] Deposits up to 12 mm thick of void-free material free of cracks over the large face of the susceptor were made by this process.

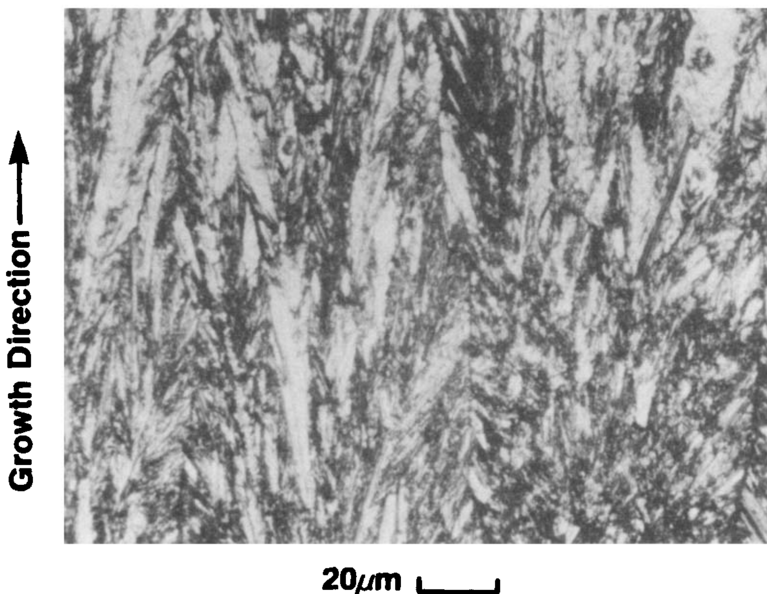


Fig. 8. The microstructure of a dense deposit showing the dendritic structure.

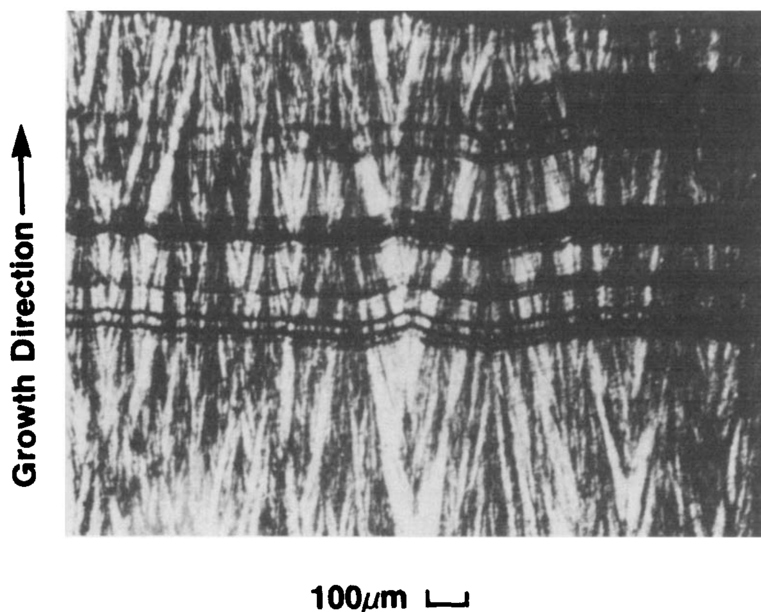


Fig. 9. Lamellar features in the microstructure due to disturbances in reactant flow rates during growth.

The grain structure of the deposits was revealed by polishing cross-sections using diamond pastes and then etching in the molten KOH–KNO_3 mixture. A micrograph of the structure is shown in Fig. 8. Grains are elongated in the growth direction as is typical for CVD deposits of this type. Typical grains are 1–2 μm in diameter and 20 μm long. This grain structure did not change through the thickness of the deposit unless a change in growth conditions, such as a temperature change, occurred. Even minor changes in growth conditions caused an interruption of the columnar structure, which could be seen in cross-sections of the deposit as shown in Fig. 9. These laminar striations reduced the fracture strength of the deposit. Any fractures tended to follow the plane of the striation.

The Knoop indentation hardness of material from two different deposition runs was measured using a 100-g load. An average hardness of 2750 ± 50 HK 0·1 was obtained on polished cross-sections and 2950 ± 50 HK 0·1 on surfaces parallel to the substrate.

4 CONCLUSIONS

A process has been developed for the deposition of thick overgrowths of polycrystalline silicon carbide onto a carbon substrate using dichlorosilane

and methane as reactants in nitrogen. Cracking of the deposit can be minimized by appropriate choice of the expansion coefficient of the carbon used. This process offers advantages over others based on the use of organosilanes. It can be operated at atmospheric pressure and does not require the use of hydrogen as a carrier gas. Because reduced pressures are not necessary, the part to be coated can be inductively heated. As a result deposition onto the reaction chamber itself is avoided. The morphology and carbon-to-silicon ratio of the deposit can be controlled independently of the deposition temperature.

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