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The Effects of C_3H_8 on the Chemical Vapor Deposition of Silicon Carbide in the $CH_3SiCl_3 + H_2$ System

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Abstract

C_3H_8 was added in order to obtain stoichiometric β-SiC in the MTS + H_2 CVD system. The experiments were carried out by using a cold-wall reactor under atmospheric pressure in the temperature range 1100–1500°C. XRD, Vickers microhardness tester and SEM were used in characterizing the stoichiometry and morphology. In the absence of C_3H_8 the temperature required for the deposition of stoichiometric SiC was above 1500°C, otherwise excess Si was codeposited with SiC. With C_3H_8 addition, however, stoichiometric SiC could be obtained even at temperatures as low as 1200°C and the preferred orientation was changed from (220) to (111). The microstructure and hardness value were related to the preferred orientation and stoichiometry of the coating layers, respectively.

Es wurde die Zugabe von C_3H_8 im System MTS + H_2 CVD mit dem Ziel untersucht, stöchiometrisches β-SiC herzustellen. Die Experimente wurden mittels eines Kalt-Wand-Reaktors unter atmosphärischem Druck im Temperaturbereich von 1100°C bis 1500°C durchgeführt. Um die Morphologie und die Zusammensetzung zu untersuchen, wurden Röntgendiffraktometrie, die Messung der Mikrohärte und Rasterelektronenmikroskopie herangezogen. Wird kein C_3H_8 zugegeben, so liegt die Abscheidungstemperatur stöchiometrischen SiC oberhalb von 1500°C. Bei tieferen Temperaturen scheidet sich ein Überschuß an Si zusammen mit SiC ab. Mit der Zugabe von C_3H_8 kann stöchiometrisches SiC bereits bei Temperaturen unterhalb von 1200°C gebildet werden, wobei die Vorzugsorientierung von (220) zu (111) wechselt. Das Gefüge und die Härtewerte wurden mit der Vorzugsorientierung und der Zusammensetzung der Beschichtung in Verbindung gesetzt.

Par ajout de C_3H_8 au système MTS + H_2, on obtient une phase β-SiC stoechiométrique par dépôt chimique en phase vapeur. Les expériences ont été réalisées en utilisant un réacteur à parois froides, sous pression atmosphérique, dans la gamme de température 1100–1500°C. Pour les caractérisations stoechiométriques et morphologiques, on a utilisé les RX, la microdureté Vickers et la microscopie électronique à balayage. En l'absence de C_3H_8, le dépôt de SiC stoechiométrique requiert une température supérieure à 1500°C, sinon l'excès de Si se codépose avec SiC. Par contre, avec un ajout de C_3H_8, le dépôt de SiC stoechiométrique peut même être obtenu à des températures aussi basses que 1200°C et l'orientation préférentielle passe du plan (220) au plan (111). La microstructure et la dureté sont respectivement reliées à l'orientation préférentielle et à la stoechiométrie des couches déposées.

1 Introduction

Many gaseous precursors are available for chemical vapor deposition (CVD) of silicon carbide (SiC). Organosilicon compounds like methylsilanes, ethylsilanes and propylsilanes have been used by many investigators.[1–4] Among the precursors, especially methyltrichlorosilane (CH_3SiCl_3; MTS) has been most frequently used,[5–7] because it contains the same number of Si and C atoms in the molecule. Therefore it has been expected to give stoichiometric SiC. Recently, from thermodynamic studies on the CVD of SiC in the MTS + H_2 system,[8,9] it has been shown that SiC is the only stable solid phase present in the wide range of process parameters such as

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pressure, temperature and concentration of the reactants. In experimental work, contrary to the thermodynamic prediction, there have been a lot of reports in the literature[10–12] which have shown that excess Si has been codeposited with SiC at lower temperatures. Price[5] reported that the strength of SiC containing excess Si was seriously reduced, and furthermore, in the present authors' previous work conducted in the MTS + H_2 system,[13] it was shown that the hardness of the coating layer obtained below 1400°C was reduced, because of codeposited excess Si. Therefore it appears to be necessary to supply excess carbon sources in the MTS + H_2 system in order to obtain stoichiometric SiC at lower temperature.

It is the purpose of the present study to prepare stoichiometric SiC at lower temperature and to investigate the morphological change by supplying propane (C_3H_8) to the MTS + H_2 system.

2 Experimental

The experiments were carried out with a cold-wall-type horizontal reactor heated by a r.f. induction generator. The temperature of the substrate was measured through a window using an optical pyrometer calibrated with the SiC emissivity.[14] Graphite plates (10 × 10 × 1 mm) and SiC-coated graphite were used as substrate and susceptor, respectively. The MTS vapor saturated with H_2 carrier gas was introduced into the reactor from a MTS container which was maintained at 0°C. C_3H_8, diluted with H_2 (1%), was added independently. Throughout the experiment the total system pressure was held at atmospheric pressure and the total flow rate of MTS + C_3H_8 + H_2 gas mixture was kept constant at 1600 standard cubic centimeter per minute (sccm) corresponding to a linear velocity of 5·0 cm/s in the reactor. The input mole fraction of MTS in H_2, MTS/(MTS + H_2), was held constant at 0·01, while the mole fraction of C_3H_8 was varied from C/Si = 1·0 to 2·5, where C/Si denotes the atomic ratio C to Si in the reactants. The concentration of reactants was controlled with float-type flow meters. Prior to deposition the reactor was pumped out and flushed with Ar before the substrate was brought up to a selected temperature. An experiment was ended by bypassing the reactants, and flowing H_2 while the substrate cooled.

The growth rate was estimated by measuring the weight increase during deposition periods. The crystal structure was analyzed by X-ray diffractometry (XRD) using Cu-K_α radiation at a scan rate of 2°(2θ)/min. The surface morphology of the coating layer was investigated with a scanning electron microscopy (SEM). The Vickers microhardness was measured with a 0·98 N load on a polished cross-section of the coating layer.

3 Results and Discussion

The effect of excess C reactant on the deposition rate and morphology of the deposits was examined. Figure 1 shows the effect of the C_3H_8 addition on the deposition rate, where C/Si = 1·0 represents that only MTS + H_2 was supplied. The deposition rate increases with increasing C/Si ratio and is almost constant at a ratio exceeding C/Si = 1·5. It has been reported in the SiH_4 + C_3H_8 + H_2 system that the deposition rate is independent of the SiH_4 concentration but depends linearly on the C_3H_8 concentration because the reactivity of C with the growing surface is lower than that of Si.[15] This explanation is in accord with the present investigation at lower C_3H_8 concentration; however, a saturation of the deposition rate at higher concentration is observed.

The effect of the C_3H_8 addition on the surface morphology is shown in Fig. 2. Without C_3H_8 addition the surface is composed of many small particles, and it appears that these particles are a mixture of SiC and codeposited excess Si from the XRD measurement. On the other hand, the morphology obtained in the presence of C_3H_8 is quite different, as shown in Fig. 2(b) to (d), where fine crystallites are developed on an apparent large grain. With increasing C/Si ratio the apparent grain size increases and inner fine crystallites grow needle-like structures at C/Si = 2·5.

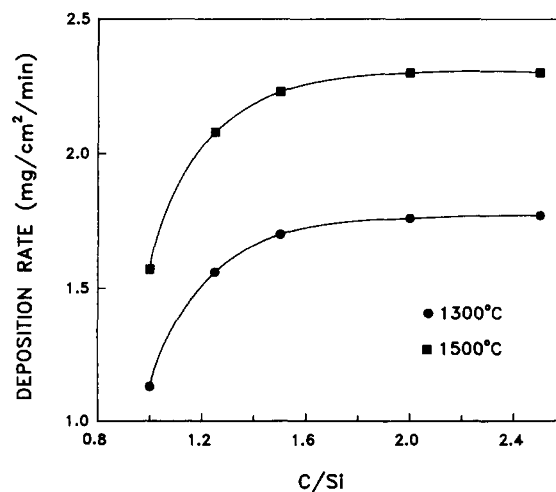

Fig. 1. Effects of C/Si ratio on the deposition rate. C/Si denotes the atomic ratio of C and Si in the reactant (total flow rate = 1600 sccm, MTS mole fraction = 0·01, deposition time = 20 min).

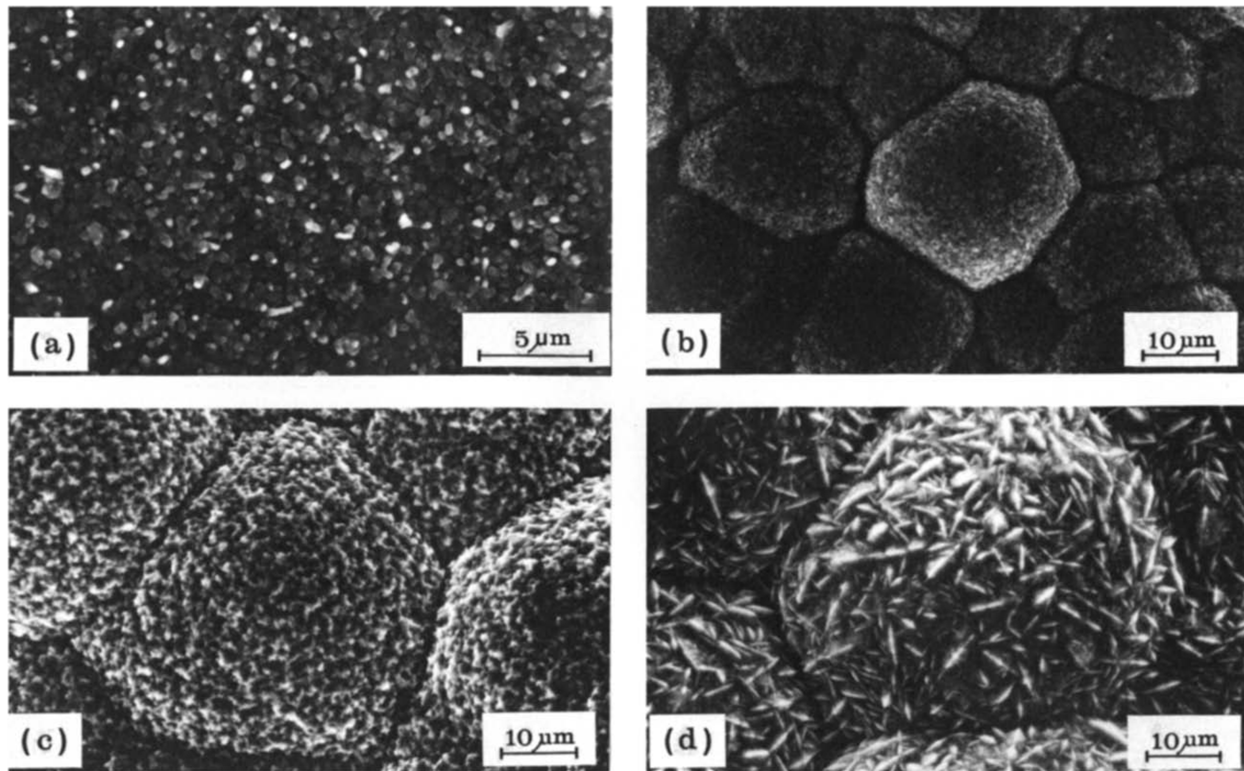

Fig. 2. Scanning electron micrographs of the coating surfaces obtained at C/Si ratio of (a) C/Si = 1·0, (b) C/Si = 1·25, (c) C/Si = 2·0 and (d) C/Si = 2·5 (total flow rate = 1600 sccm, MTS mole ratio = 0·01, deposition temperature = 1300°C).

The dependence of growth rate on the deposition temperature is shown in Fig. 3. As is the case with CVD, the temperature dependence can be divided into two linear regions, following the Arrhenius-type relationship, namely deposition rate controlled by surface reaction at lower temperature and diffusion limited at higher temperatures.[16] Several investigators have reported that the thermal etching effect in the higher temperature region decreases the deposition rate.[17,18] However, the present authors could not find the decrease of the deposition rate combined with the blank etching test at 1500°C.

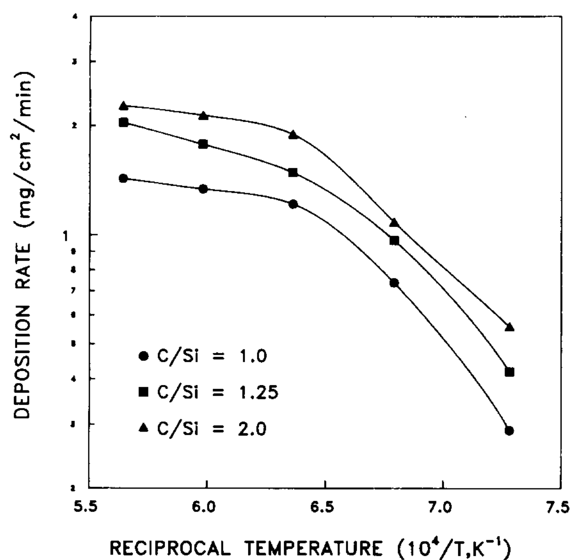

Fig. 3. Dependence of deposition rate on the temperature and C/Si ratio (total flow rate = 1600 sccm, MTS mole fraction = 0·01).

Typical XRD patterns of the deposited layers are shown in Fig. 4. These patterns indicate that the crystals are cubic β-SiC phases; hexagonal α-SiC phases were not observed. Without C_3H_8 addition in the MTS + H_2 system, as illustrated in Fig. 4(a), the peaks of Si as well as SiC are detected in the layers prepared below 1400°C and the intensities of excess Si decrease with increasing deposition temperature, while as the temperature is raised to 1500°C only SiC peaks are observed. With C_3H_8 addition, however, it can be seen in Fig. 4(b) that peaks of Si are not detected at all temperatures investigated.

It has been well established in the CVD of SiC that the following reactions should proceed in sequence to obtain the stoichiometric SiC:[19,20]

(1) Decomposition of MTS into chlorosilanes and hydrocarbons.
(2) Decomposition of chlorosilanes and hydrocarbons to elemental Si and C.
(3) Combination between elemental Si and C at the growing surface.

Since the weak Si–C bonds in MTS molecules are easily broken in the gas phase above the heated

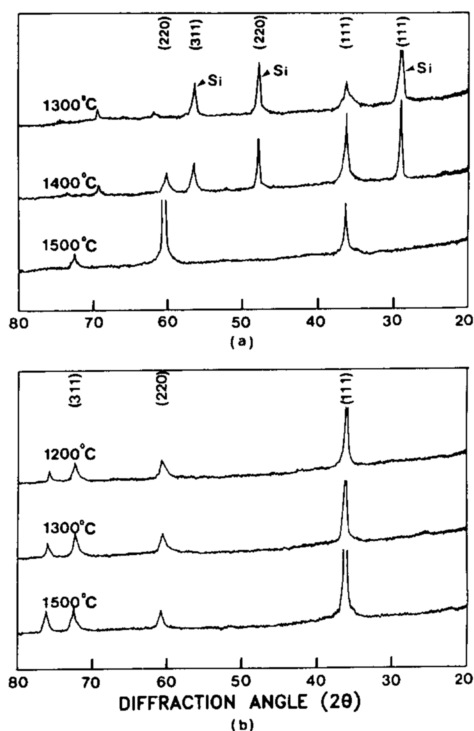

Fig. 4. Typical XRD patterns of the coating layers prepared at (a) C/Si = 1·0 and (b) C/Si = 2·0 (total flow rate = 1600 sccm, MTS mole fraction = 0·01).

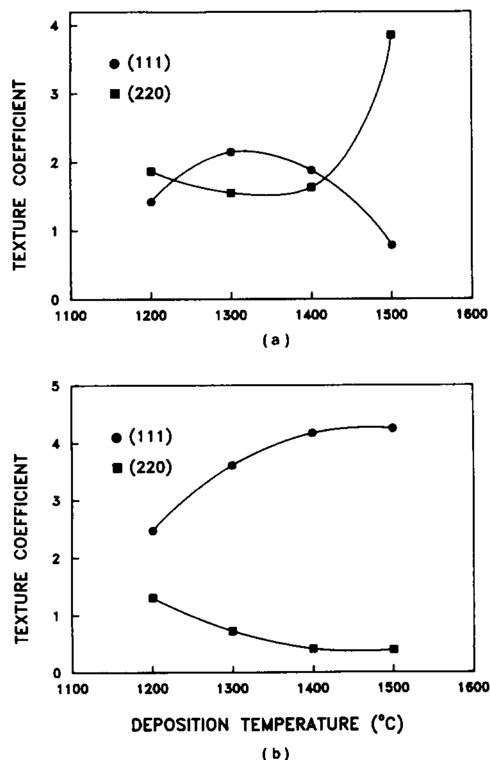

Fig. 5. Effects of temperature on the texture coefficient of coating layers at (a) C/Si = 1·0 and (b) C/Si = 2·0 (total flow rate = 1600 sccm, MTS mole fraction = 0·01).

substrate, reaction (1) completes at an early stage. Reaction (2) is the slowest among these reactions because the reactivity of hydrocarbons with the SiC surface is lower than that of chlorosilane.[21,22] Thus the growth rate is limited by the decomposition of hydrocarbons into elemental C at the surface, which results in codeposition of excess Si. In the case of C_3H_8 addition, the hydrocarbon species such as C_2H_4 and more reactive C_2H_2 produced by pyrolysis of C_3H_8 react rapidly with the excess Si to form SiC, which results in an increase of the deposition rate. In addition, from Fig. 4 it is readily seen that the preferred orientation is changed from (220) to (111) in the presence of C_3H_8.

Figure 5 demonstrates the effect of temperature on the texture coefficient (TC) of the coating layer. The texture coefficient was calculated by the following equation:[23]

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{(1/n)\sum[I_{(hkl)}/I_{0(hkl)}]}$$

where $I_{(hkl)}$ and $I_{0(hkl)}$ are the integrated intensities of (hkl) reflections measured for an experimental specimen and an isotropic standard powder sample, respectively, and n is the total number of reflection planes. Through the XRD measurement the strong peaks are always (111) and (220), whereas (200) is not detected and (311) is very weak compared to (111) and (220), thus they were not shown. When C_3H_8 is not added, as shown in Fig. 5(a), the preferred orientation is not noted below 1400°C, while (220) orientation dominates at 1500°C. With the C_3H_8 addition, however, the (111) orientation dominates and grows vigorously with increasing deposition temperature, as shown in Fig. 5(b). Recently Kuo *et al.*,[24] who studied the preferred orientation of CVD SiC in the $MTS + CH_4 + H_2$ system, reported that the preferred orientation was altered from (220) to (111) or from (111) to (220) with CH_4 addition according to temperature and growth rate, and they suggested that in determining the preferred orientation the growth rate played a major role at lower temperature and the effect of stereo hindrance at higher temperature, respectively. The present observations are in good agreement with them in the absence of C_3H_8 (C/Si = 1); however, the (111) orientation always dominated regardless of the temperature and C_3H_8 concentration in the presence of C_3H_8. The exact role that is played by C_3H_8 is complex and merits further study.

Figures 6 and 7 demonstrate the influence of the temperature on the surface morphology of SiC obtained without and with C_3H_8 addition, respectively. In the case of C/Si = 1 the surfaces deposited below 1400°C are fine, as shown in Fig. 6(a) to (c). However, Fig. 6(d) shows the remarkable change of microstructure at 1500°C, when the SiC crystals

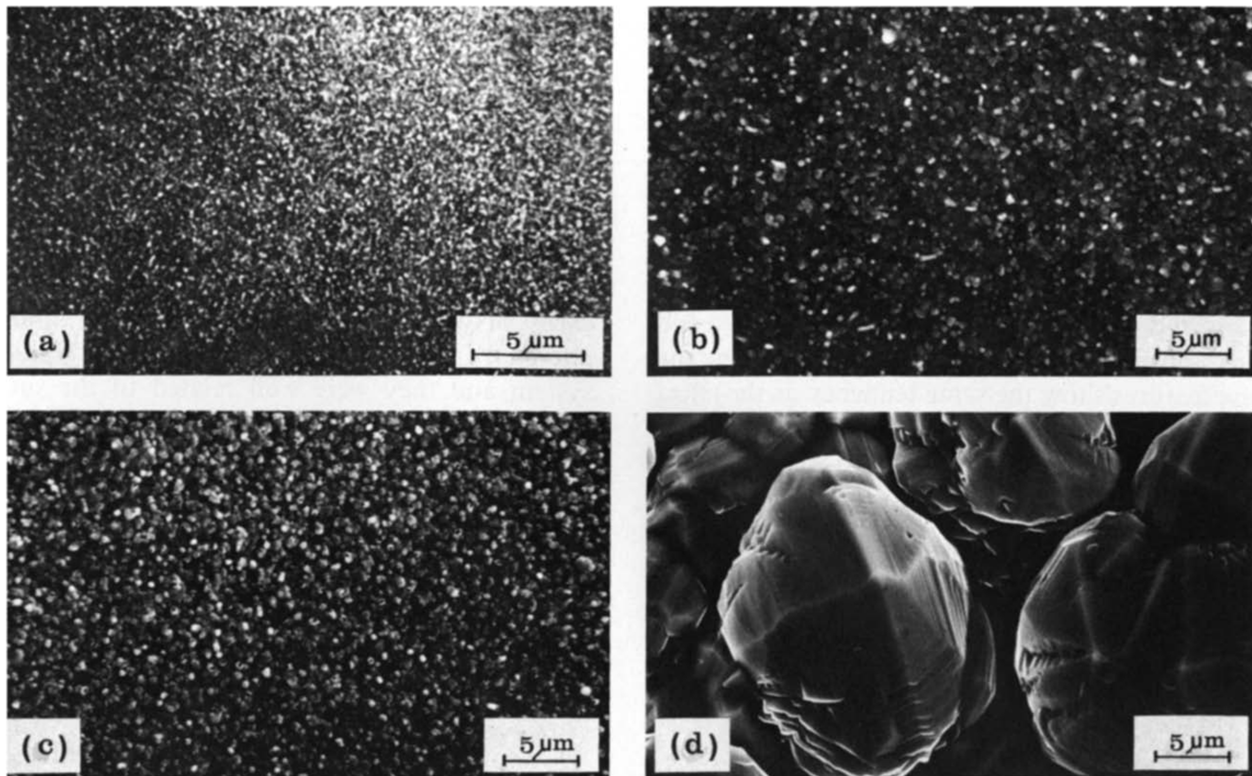

Fig. 6. Scanning electron micrographs of coating surfaces prepared at (a) 1200°C, (b) 1300°C, (c) 1400°C and (d) 1500°C (C/Si = 1·0, total flow rate = 1600 sccm, MTS mole fraction = 0·01).

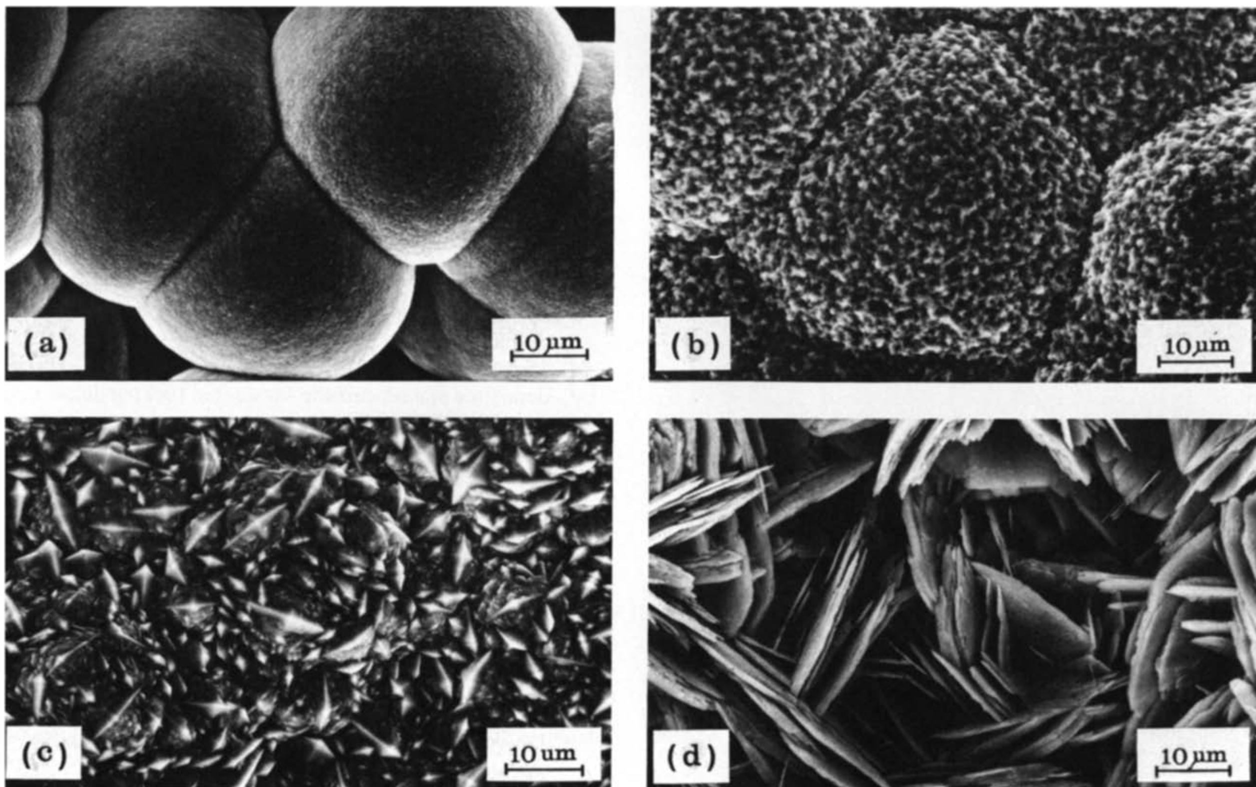

Fig. 7. Scanning electron micrographs of coating surfaces prepared at (a) 1200°C, (b) 1300°C, (c) 1400°C and (d) 1500°C (C/Si = 2·0, total flow rate = 1600 sccm, MTS mole fraction = 0·01).

grow large and have well-developed facets. The causes of the fine microstructure at the temperature below 1400°C can be explained as follows: firstly, codeposited excess Si hinders the growth of SiC crystals. Secondly, atoms adsorbed on the growing surface have insufficient migration energy at the lower temperature. By the addition of C_3H_8, on the other hand, the microstructures are remarkably changed. The surface is composed of the apparent grains and their size increases with increasing deposition temperature, as shown in Fig. 7(a) and (b). These features show the same tendency as the effect of C_3H_8 concentration, as shown in Fig. 2. As the deposition temperature is raised to 1500°C the SiC crystals grow plate-like. It is worth comparing the microstructures of Fig. 6(d) with Fig. 7(d). These two inverse microstructures are well related to the preferred orientation; that is to say, (220) planes parallel to the substrate in the MTS + H_2 system and perpendicular to the substrate in the MTS + C_3H_8 + H_2 system.

Figure 8 shows the change of hardness as a function of deposition temperature. The Vickers microhardness H_V of the coating layer obtained in the MTS + H_2 system is quite low and increases slightly with increasing temperature, whereas at 1500°C it increases drastically up to $H_V = 3000$, the inherent value of the SiC crystal. The poor hardness value at the lower temperature is due to codeposited excess Si. With C_3H_8 addition, however, although the error bars are somewhat large, their values are almost above $H_V = 3000$, which shows further evidence for stoichiometric SiC. The slight decrease in hardness above 1400°C is thought to be caused by the plate-like microstructure, as shown in Fig. 7(d).

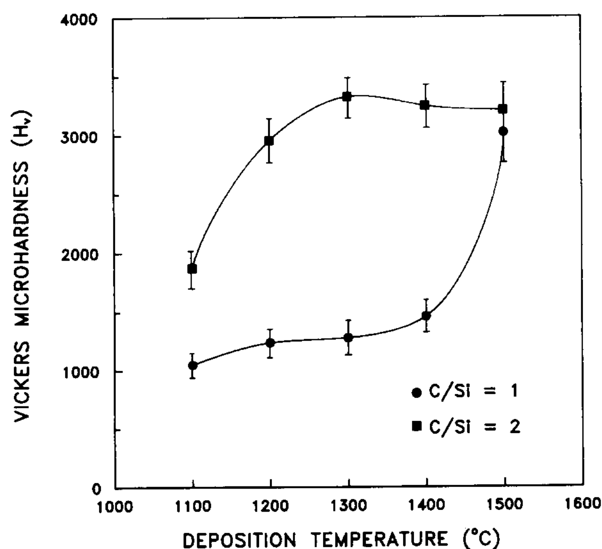

Fig. 8. Effects of temperature and C/Si ratio on the microhardness of coating layer (total flow rate = 1600 sccm, MTS mole fraction = 0·01).

4 Conclusions

In the absence of C_3H_8 excess Si is always codeposited with SiC below 1400°C. With the addition of C_3H_8, however, stoichiometric β-SiC could be obtained at all temperatures investigated. In addition, the deposition rate was increased with the addition of C_3H_8, because highly reactive C species, formed by pyrolysis of C_3H_8, react with excess Si to form SiC. The preferred orientation was altered from (220) to (111) in the MTS + C_3H_8 + H_2 system and they were well related to the surface morphology. In the MTS + H_2 system the Vickers microhardness value of the coating layer was very poor because of the codeposited excess Si, whereas with C_3H_8 addition it increased up to the inherent value of SiC even at temperatures as low as 1200°C.

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