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Chemical vapour deposition of silicon carbide: an X-ray diffraction study

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Low-pressure chemical vapour deposition of siliconcarbide from tetramethyl silane pyrolysis was studied by X-ray diffractometry. *In situ* measurements at high temperature gave kinetic information. The crystallization state, grain size, microstrains and residual macrostresses were measured at room temperature.

1. Introduction

Silicon carbide coatings obtained by chemical vapour deposition (CVD) have been studied in many papers because of their high mechanical and chemical performances: wear resistance and chemical stability in oxidizing atmospheres at high temperatures [1].

The use of tetramethylsilane (TMS) as a gas precursor has the advantage of supplying silicon and carbon from one molecule, free from halogen [2]. The present work concerns the study of SiC deposition from low-pressure TMS decomposition on to a hot graphite substrate within the temperature and pressure ranges 1000 to 1400° C and 5 to 50 torr. Experiments were performed on an X-ray diffractometer at high temperature for kinetic approach, and at room temperature for CVD layer characterization.

2. Experimental details

2.1. CVD layer formation and kinetics

The deposition chemical reaction was performed within a cold-wall reactor where a graphite substrate was electrically heated. The reactive gas phase (TMS) was supplied in such a way that the inlet gas flow was perpendicular to the substrate surface. The flow rate was fixed at $10\,\mathrm{N\,cm^3\,min^{-1}}$ and controlled with a mass flowmeter. The low pressure was maintained by a primary pump and the temperature measured by optical pyrometry.

The CVD reactor was associated with an X-ray diffractometer including a position sensitive detector (PSD) which allows detection over a 12° (2θ) angular range [3] (Fig. 1).

X-ray diffractometry was used here for measurements of the deposited layer thickness changes as a function of temperature during the CVD reaction. This method consisted of the determination of the intensity of the (2 0 0) line of the graphite substrate. The X-ray beam intensity is lowered by absorption through the deposited material according to the classical exponential law [4]

$$I = I' \exp(-ks) \tag{1}$$

where I' is the X-ray beam intensity after absorption through a layer of thickness s, I is the intensity of non-absorbed X-ray beams, K is a coefficient including the mass absorption factor (μ/ϱ) and the specific mass (ϱ).

The CVD layer thickness (s) can be easily deduced from Equation 1 [5]

$$s(t) = -\frac{\varrho}{\mu}\left(\frac{\sin\theta}{2\varrho}\right)\ln\frac{I(t)}{I_0} \tag{2}$$

where $s(t)$ is the layer thickness at instant t, θ is the Bragg angle of the substrate, $I(t)$ the diffracted intensity at instant t, and I_0 the diffracted intensity before SiC deposition, $(\mu/\varrho)_{\mathrm{SiC}} = 43.8\,\mathrm{cm^2\,g^{-1}}$, and $\varrho_{\mathrm{SiC}} = 3.22\,\mathrm{g\,cm^{-3}}$.

2.2. Characterization of the CVD layer

The crystal structures of the deposited layers were determined from X-ray powder diffractometry (using a normal detector).

Information about crystallite size and microstrain related to the experimental conditions was obtained from diffraction line broadening. The "Waren–Averbach" method [6], which requires line profile analysis of two orders of one reflection, did not work here, so the simplified method of Keijser *et al.* [7] requiring analysis of only one line was used: after elimination of $K\alpha_2$ radiation by the Rachinger method [8] and of the instrumental contribution, the line profile is considered as a combination of "Cauchy" and "Gauss" profiles, the first being related to crystallite size (D) and the second to microstrain (e). D (nm) and e are given by

$$D = \frac{0.1\lambda}{\beta_c^F \cos\theta} \tag{3}$$

$$e = \frac{\beta_g^F}{4\tan\theta} \tag{4}$$

where λ is the X-ray radiation wavelength, θ the Bragg angle, β_c^F the internal breadth of the "Cauchy" profile after elimination of the instrumental contribution, and β_g^F the integral breadth of the "Gauss" profile after elimination of the instrumental contribution.

Residual macrostresses on the surface of the deposited layer modify reticular distances which change as a function of the angle Ψ formed by the reticular plane considered normal to the layer surface.

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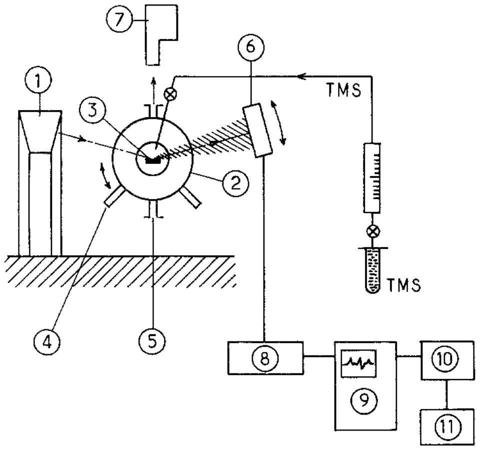

Figure 1 Schematic illustration of the high-temperature X-ray diffraction chamber. 1, X-ray generator; 2, diffraction chamber; 3, sample; 4, water cooling; 5, vacuum; 6, position sensitive detector; 7, optical pyrometer; 8, detector electronic system; 9, multichannel analyser; 10, calculator; 11, writer.

The stress, σ, can then be calculated by varying Ψ, using a θ–2θ goniometer at a given Bragg angle. σ can be calculated from the $\sin^2\Psi$ law [9]

$$\frac{d - d_0}{d_0} = \frac{1 + v}{E} \sigma \sin^2\Psi \qquad (5)$$

where σ is the residual stress ($\mathrm{N\,m^{-2}}$), v the Poisson coefficient, E Young's modulus ($\mathrm{N\,m^{-2}}$), d the reticular distance at a given angle Ψ, and d_0 the reticular distance at $\Psi = 0$. Because variations of d are very small, only large θ angle $(h\,k\,l)$ lines can be considered ($2\theta > 130°$). In the present case the $(3\,3\,3)_{\mathrm{SiC}}$ plane was chosen, $2\theta = 133.04°$.

3. Results

3.1. Kinetic approach

The thickness of the deposited layers was determined *in situ* as a function of time for several experimental conditions. The results obtained are presented in Figs 2 and 3 for total pressures of 5 and 20 torr, respectively, between 1000 and 1400° C. They show a linear layer growth after an initial non-linear period of several minutes.

TABLE I

P (torr)	E_a ($\mathrm{kJ\,mol^{-1}}$)	
	1000–1075° C	1075–1200° C
5	365	126
10	358	120
20	245	
50	344	

The deposition rate was calculated from the linear part of the curve. Fig. 4 shows the rate variations plotted against temperature for several pressures. A maximum appears on the curves, which is displaced towards high temperatures with decreasing pressure (50 to 5 torr).

Average values of an apparent activation energy (E_a) were calculated from the increasing part of the rate curves. For lower pressures (5 and 10 torr) E_a was different above and below 1075° C (Table I).

3.2. Deposited layer characterization

For a pressure of 5 torr, the deposited layers did not show any diffraction line below 1100° C. For higher temperatures, SiC was crystallized with the β fcc structure as shown in the X-ray diffractograms of Fig. 5. This is the structure commonly observed for CVD SiC layers [1, 10, 11]. Around 1100° diffraction lines are just distinct from the base line. In the 1100 to 1200° C range only the (1 1 1) line is really apparent, showing a preferential orientation of (1 1 1) planes along the support. Above 1200° C the diffraction lines become sharper and their full width at half maximum (FWHM) decreases with increasing temperature; this is related to crystallite size (D) and microstrain (e) changes. (D) and (e) have been calculated from Equations 3 and 4 for several temperatures (Fig. 6). In the 1250 to 1400° C temperature range, D was found to increase from 20.4 to 71.3 nm when e decreased from 1.5×10^{-3} to 0.63×10^{-3}.

The resulting changes of the aspect of the deposited surface are shown in scanning the electron micrographs of Fig. 7: when amorphous X-ray diffractograms were obtained, the surface exhibited a bubble

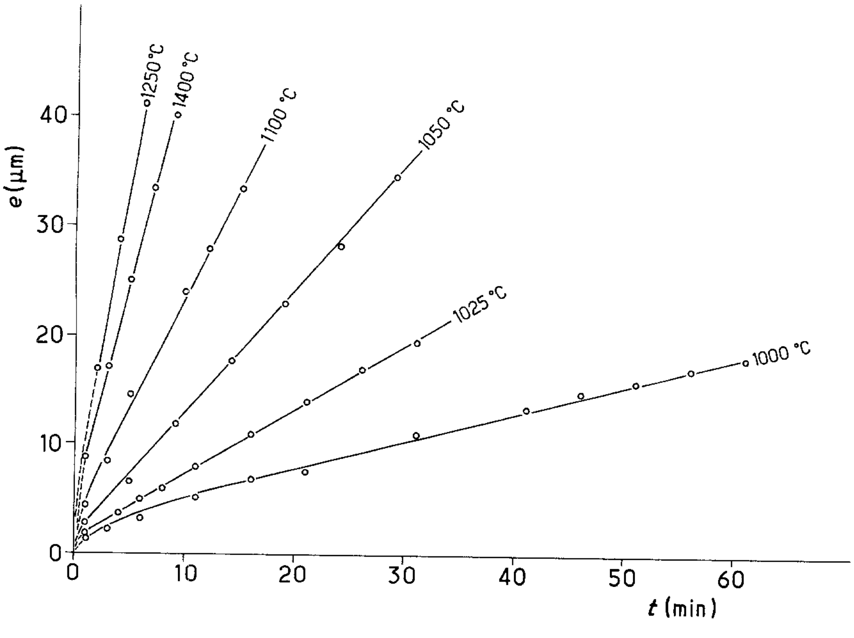

Figure 2 Thickness of the deposited SiC layer plotted against time of reaction for a total pressure of 5 torr at several temperatures.

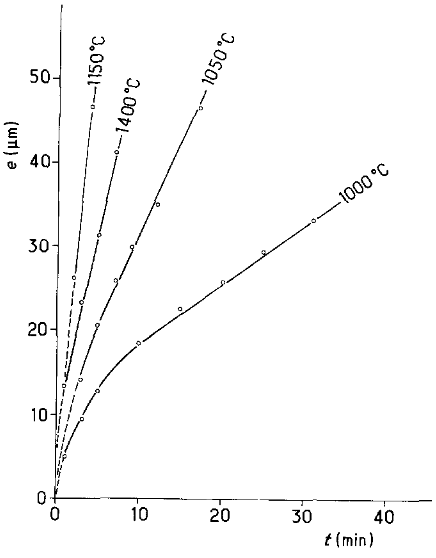

Figure 3 Thickness of the deposited SiC layer plotted against time of reaction for a total pressure of 20 torr at several temperatures.

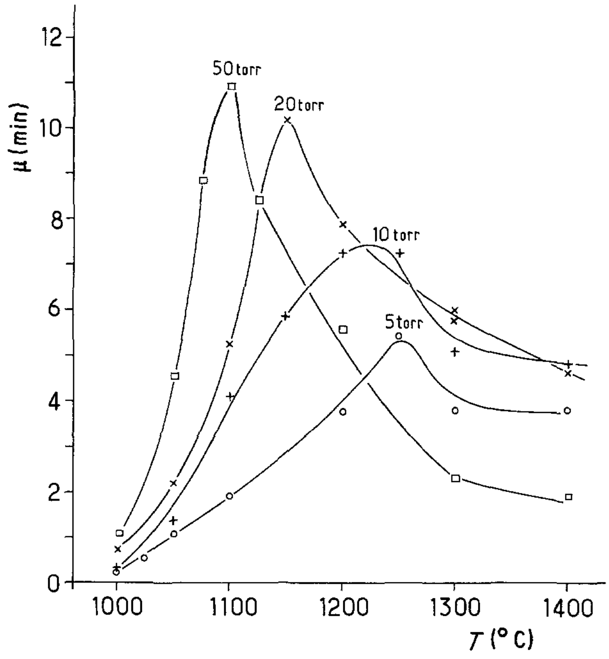

Figure 4 SiC deposition rate plotted against temperature for several pressures.

structure (Fig. 7a); when the deposited layers crystallized, the micrographs showed a crazed sublattice (Fig. 7b, c) which became more and more distinct as the temperature increased; this was the only surface structure seen at the higher temperature of 1400° C (Fig. 7d).

The effect of pressure on the deposit morphology is illustrated in Fig. 8 for CVD layers prepared at 1300° C in the 5 to 50 torr pressure range: with increasing pressure the lines become broader which means that the crystal size is increasing and microstrains decreasing.

The mechanical quality of a CVD layer is related in one part to the superficial residual stress intensity. This was measured here for CVD layers of different thickness prepared at 1400° C. The $\sin^2\Psi$ method applied to the (3 3 3) SiC line lead to the 2θ–$\sin^2\Psi$ curves presented in Fig. 9. The following information could be deduced: the slopes show compressive stresses; the slopes and consequently stress intensities increase as the thickness decreases; assuming $E_{\text{SiC}} = 400 \times 10^3\,\text{MN}\,\text{m}^{-2}$ [1] and $v = 0.2$, values of σ were determined as a function of thickness e (Fig. 10).

4. Discussion and conclusion

Kinetics showed firstly that the deposition rate followed a linear law after an initial non-linear period, and

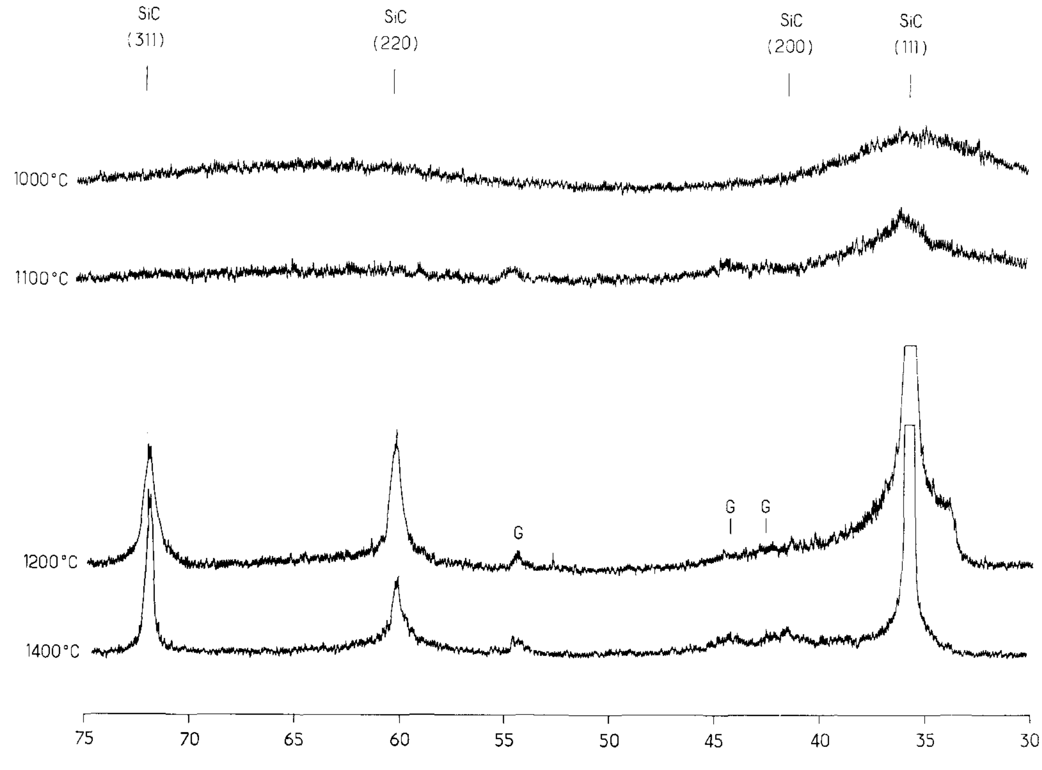

Figure 5 X-ray (2θ Cu$K\alpha$) diffractograms (using a normal proportional detector) of SiC deposited layers prepared at several temperatures under a pressure of 5 torr (G = graphite line).

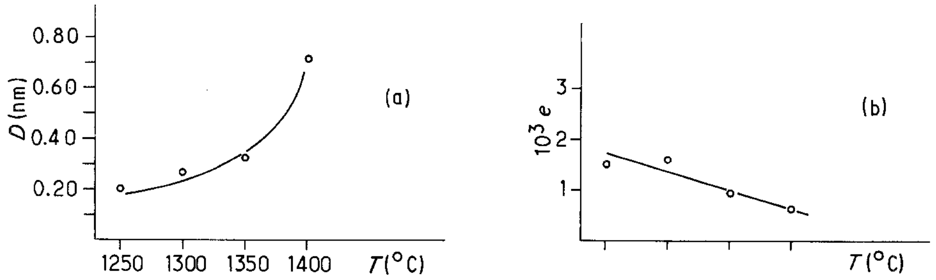

Figure 6 Variation of (a) crystallite size (D) and (b) microstrains (e) with temperature of SiC deposited layers (P = 5 torr) calculated from the SiC (3 1 1) line profile analysis using a position sensitive detector.

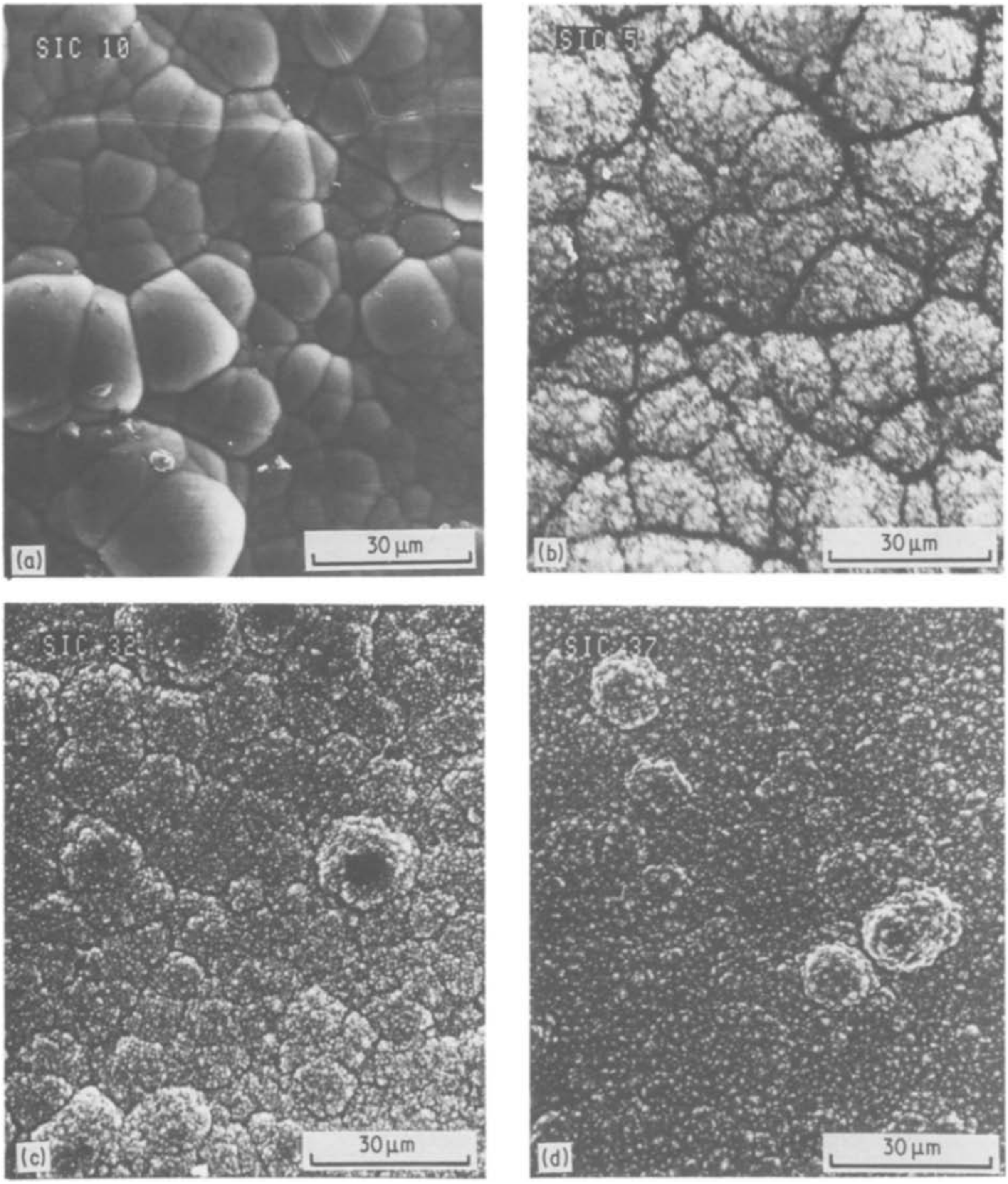

Figure 7 Scanning electron micrographs of several SiC deposited layers prepared at a total pressure of 5 torr and several temperatures: (a) 1000° C, (b) 1200° C, (c) 1300° C, (d) 1400° C.

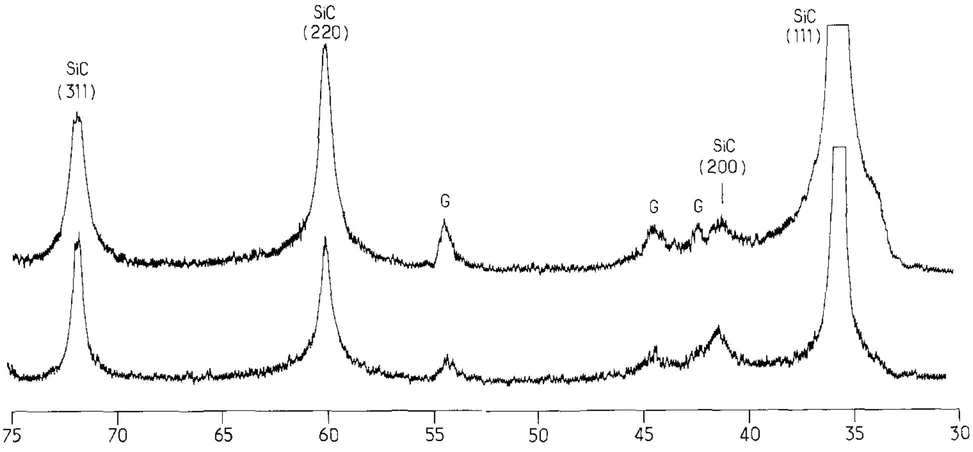

Figure 8 X-ray diffractograms (2θ Cu$K\alpha$, normal proportional detector) of SiC deposited layers at 1300° C. (a) $P = 50$ torr, (b) $P = 5$ torr. (G = graphite line.)

secondly the existence of a maximum rate value with temperature.

The first point can be interpreted by assuming that before reaching a steady state the deposition rate was transitorily controlled by the gas phase diffusion into the reactor.

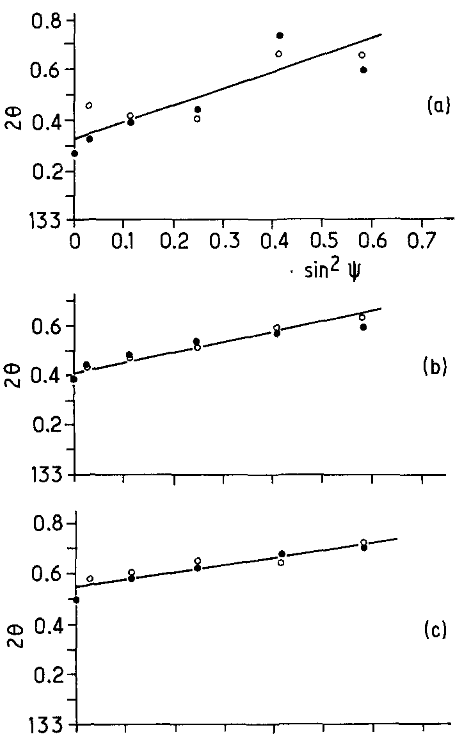

Figure 9 Variations of Bragg angle (2θ deg) with $\sin^2\Psi$ for SiC deposited layers of several thicknesses (a) $e = 13\,\mu$m, (b) $e = 34\,\mu$m, (c) $e = 41\,\mu$m.

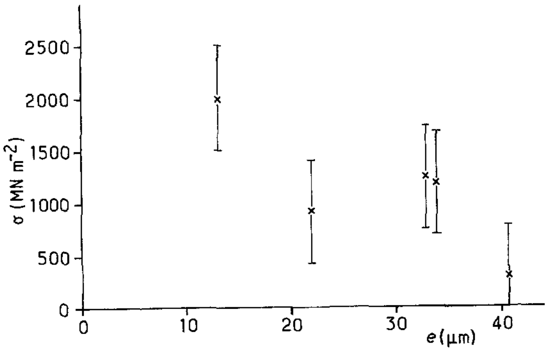

Figure 10 Variation of residual macrostresses of SiC deposited layers with thickness, e (μm), calculated from the $\sin^2\Psi$ law, assuming for SiC, $E = 400 \times 10^3$ MN m^{-3} and $\nu = 0.2$.

The second point is related to the TMS decomposition itself: such a maximum was previously observed for similar deposition reactions [1, 10] and was explained by the occurrence of a gas phase nucleation process in competition with the deposition.

Above 1200° C the deposited layers were crystallized and the crystallite size increased with temperature. Furthermore they showed compression residual stresses which could be due to the thermal expansion difference between the layer and the graphite substrate.

Thus, using SiC as an example, the interest of the X-ray diffraction technique for CVD studies was demonstrated: useful characterizations may be performed such as structure morphology residual stresses, and, using the same apparatus, deposition kinetics can be studied. Furthermore, *in situ* X-ray diffraction can give an interesting alternative to the more classic thermogravimetric method in cases where side reactions (corrosion, by-product formation, etc.) may occur.

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