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EVIDENCE FOR FREE CARBON IN AMORPHOUS OMCVD SILICON-RICH $\text{Si}_x\text{C}_{1-x}$ COATINGS

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Résumé - Des films $\text{Si}_x\text{C}_{1-x}$ riches en silicium ont été déposés par OMCVD sous pression réduite entre 800 et 1000°C en utilisant SiEt_4 comme source de C et Si. Un enrichissement supplémentaire en Si a été obtenu par addition de SiH_4 dans la phase gazeuse. Malgré l'excès de Si, la présence de carbone libre a été mise en évidence par les différentes caractérisations (IR et XPS). La microstructure hétérogène de ces films amorphes dépend de la température et de la pression partielle de silane.

Abstract - Silicon-rich $\text{Si}_x\text{C}_{1-x}$ layers have been deposited by OMCVD at low pressure in the temperature range 800-1000°C using the organometallic compound SiEt_4 for both Si and C source. A Si enrichment of these amorphous $\text{Si}_x\text{C}_{1-x}$ coatings was obtained by addition of SiH_4 to the gas-phase. The influence of this silane partial pressure increase on the growth rate, the composition and optical properties of the films has been investigated. In spite of the silicon excess, evidence for free carbon was found both in the variation of the optical band gap and the IR spectra. The XPS (X-ray Photoelectron Spectroscopy) analysis argues also for a heterogeneous microstructure for these amorphous ceramic thin films.

1 - INTRODUCTION

Silicon carbide alloy is of great interest both in amorphous semiconductors and in high-temperature structural elements. They can be prepared by various deposition technics, however the Chemical Vapour Deposition is one of the most convenient processes according to the large variety of chemical precursors [1]. In order to prepare Si-rich $\text{Si}_x\text{C}_{1-x}$ films for the protection of ceramic matrix composites in a simple CVD process, we have proposed in an earlier work the use of SiEt_4 as a single organometallic precursor for both Si and C source. Amorphous $\text{Si}_x\text{C}_{1-x}$ films were obtained between 800 and 1000°C with a relative atomic percentage of silicon x in the range 0.3 - 0.7 [2]. To extend the adaptability of this process toward higher silicon concentration in the coatings, silane was added to the initial gas-phase. This paper deals with the influence of this addition on the growth rate, the composition and the optical properties of the layers. The layers were characterized by optical, IR and XPS (X-Ray Photoelectron Spectroscopy).

2 - EXPERIMENTAL

The classical low pressure cold wall horizontal CVD apparatus used in this study has been described previously /2/. To obtain the desired SiEt_4 partial pressure in the gas-phase, a mixture of SiH_4/H_2 was used as carrier gas and led through the SiEt_4 bubbler. This bubbler was thermostated between -5°C and $+10^\circ\text{C}$ and ascertained a SiEt_4 vapour pressure in the range 129-333 Pa. Any further dilution was realized at the entrance of the reactor. For safety reason, the initial SiH_4 concentration diluted in hydrogen was only 1% and 5%. A sketch of this growth apparatus has been given in ref. 2. The total flow rate and the total pressure in the reactor have been kept constant at 8.3 sccm and 1333 Pa (10 Torr), respectively. The initial gas-phase composition was then defined by the relative partial pressure ratio

$$R = p(\text{SiH}_4) / p(\text{SiH}_4) + p(\text{SiEt}_4)$$

The layer thickness has been measured on a fractured cross section using a SEM equipped with an EDX analyzer. FT-IR spectra were recorded on a Perkin Elmer 1710 spectrometer interfaced with a data station computer. IR spectra were obtained after subtraction of a reference Si wafer spectrum. The optical band gap were calculated from the measured transmittance in the wave-length range 200 - 3000 nm using the Tauc's relation /3/.

The photoelectron spectra were performed with a spectrometer V.G. 50 operating with the monochromatic $\text{AlK}\alpha$ X-ray source.

3 - RESULTS AND DISCUSSION

3-1 growth results

Amorphous $\text{Si}_x\text{C}_{1-x}$ films were deposited on various substrates at a constant temperature of 950°C under reduced pressure using the typical CVD conditions reported in table 1.

Deposition temperature	950°C
Total pressure	1333 Pa (10 Torr)
Total flow rate	8.3 sccm
$p(\text{SiEt}_4)$	$9.7 \cdot 10^{-1}$ - 2.5 Torr
$p(\text{SiH}_4)$	0 - 4.9 Torr
$p(\text{H}_2)$	8.1 - 8.9 Torr
Substrates	Si, Al_2O_3 , SiO_2

Table 1 :

Typical OMCVD growth conditions used for the deposition of $\text{Si}_x\text{C}_{1-x}$ layers.

Without addition of SiH_4 or for low values of SiH_4 partial pressure, the morphology of $\text{Si}_x\text{C}_{1-x}$ coatings deposited at 950°C exhibit the typical nodular structure of amorphous CVD films (fig. 1a) whereas for higher values of $p(\text{SiH}_4)$ ($R \sim 21\%$) the films are homogeneous and compact, with a relatively smooth surface (fig. 1b). They present many microcracks

whose proportion is not until now clearly related to the heterogeneous structure as suggested in the literature /4/.

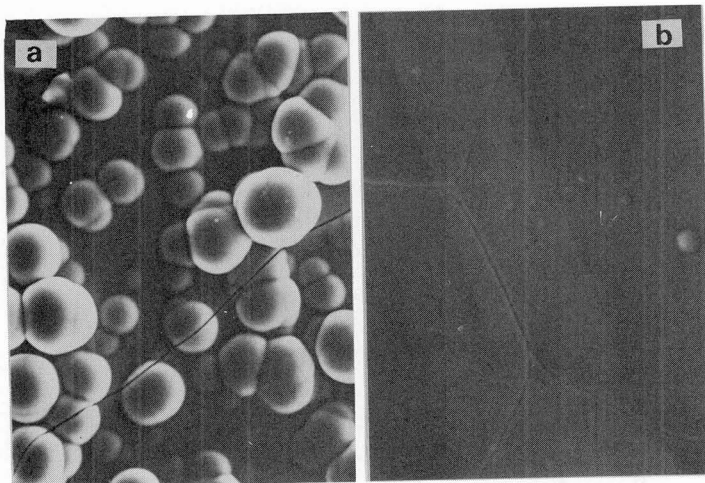


Fig. 1 :
Typical micrographs of
Si-rich $\text{Si}_x\text{C}_{1-x}$ films as
a function of the gas-phase
composition : a) $R = 8\%$ and
b) $R = 21\%$ (950°C ;
Si substrate ; $\times 1000$).

The influence of the silane addition on the growth rate is shown in the fig. 2. It appears clearly that the growth rate increases with the tetraethylsilane partial pressure whatever be the relative SiH_4 concentration. Furthermore, in spite of the low silane partial pressure, the growth rate of the layer increases significantly for each SiEt_4 partial pressure with the relative SiH_4 concentration. This indicates that the SiH_4 decomposition supplies supplementary elemental Si for the growth of the layer. This deduction must then involve a silicon enrichment of the layers. The silicon content of these $\text{Si}_x\text{C}_{1-x}$ coatings has been estimated by EDX analysis following a method previously described /2/ and the results shown in fig. 3 are on the whole in good agreement with this assumption since the

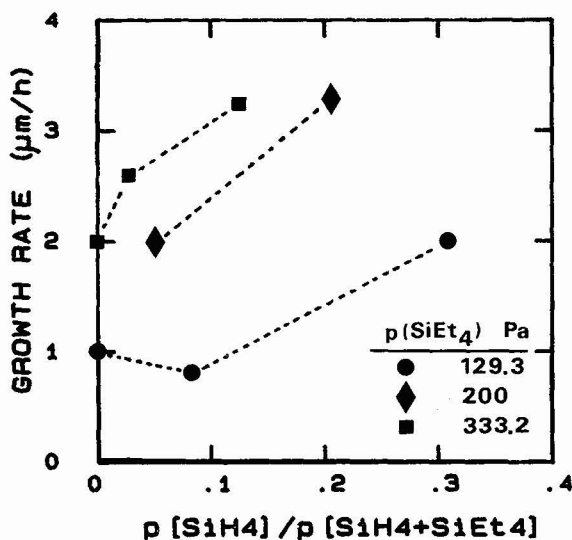


Fig. 2 :
Growth rate of $\text{Si}_x\text{C}_{1-x}$ films versus
the relative concentration of silane
and the SiEt_4 partial pressure.

the film tends to increase with the relative SiH_4 concentration. All $\text{Si}_x\text{C}_{1-x}$ coatings obtained are X-ray amorphous and no evidence for graphite or Si crystallites has been found by X-ray diffraction.

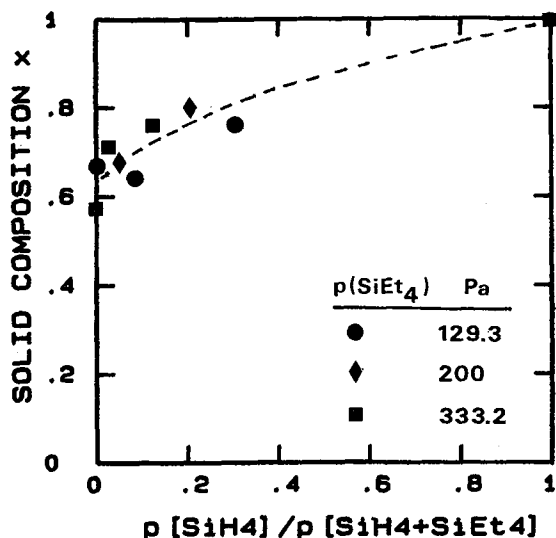


Fig. 3 :

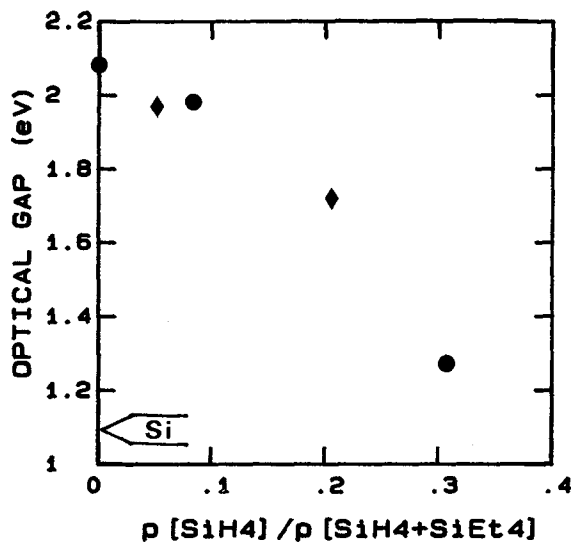
Influence of the relative gas-phase composition on the silicon content of the films (the dotted line is just a guide for the eyes).

3-2 Optical properties

The optical band gap, E_o , of these $\text{Si}_x\text{C}_{1-x}$ films decreases with an increase of SiH_4 partial pressure (fig. 4). This is consistent with an increase of Si content in the layer /5/ since it can be speculated that the optical gap decreases with the density of bonds stronger than Si-Si such as Si-C and C-C ; this assumption will be true as long as four fold coordination is dominant in the amorphous network. Then the optical gap tends to decrease toward the Si value. However a poor correlation is found between E_o and x indicating that a more complex

Fig. 4 :

Variation of the optical gap with the relative concentration of silane ($p(\text{SiEt}_4) = 0.97$ Torr (●) and 1.5 Torr (◆).



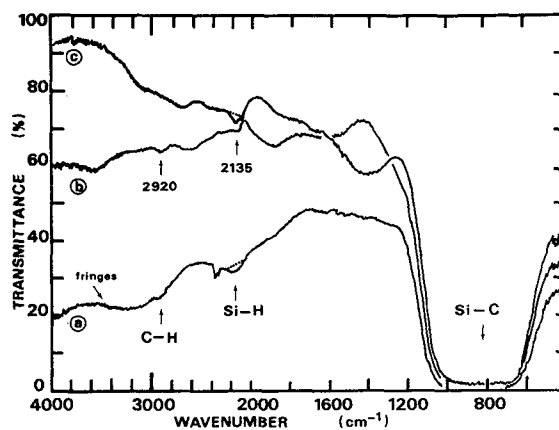
phenomenon occurs. We suppose that this can be due to a heterogeneous structure containing threefold coordination carbon, i.e. graphitic zones. This assumption explains generally the decrease of E_0 in carbon-rich $\text{Si}_x\text{C}_{1-x}$ films /5,6/ and such a carbon segregation has even been already found in Si-rich glow discharge films /7/. For Si-rich $\text{Si}_x\text{C}_{1-x}$ CVD films deposited above 900°C using SiEt_4 as single precursor, some evidence for free carbon were found /2/. For instance, the increase of the background absorption of their IR spectra with the deposition temperature has been ascribed to an increase of free carbon amount according to literature results /8/.

The IR spectra of $\text{Si}_x\text{C}_{1-x}$ films obtained after addition of extra SiH_4 are reported in fig. 5. They exhibit the broad absorption band at 800 cm^{-1} expected for Si-C bond stretching mode /9/. Moreover, the background absorption in the high wavenumber range decreases clearly by increasing the SiH_4 partial pressure that will be in good agreement with a reduction of the amount of free carbon. Another feature of these IR spectra is the C-H stretching mode (sp^3 bonding) near 2900 cm^{-1} observed only with some samples having a film thickness higher than $5\text{ }\mu\text{m}$ and a carbon content near or higher than 30 at. %, according to an early work /10/. Furthermore, silicon hydride stretching modes are found for all the samples between $2135 - 2160\text{ cm}^{-1}$ and their frequency seems to increase with the carbon amount (fig. 6). The more probable local surrounding of the Si-H bond vibrations are $\text{H}_2\text{Si}(\text{C}_2)$ and/or $\text{H}_3\text{Si}(\text{Si})$ expected at 2149 cm^{-1} /11/ and 2145 cm^{-1} /12/, respectively. In amorphous or microcrystalline Si or $\text{Si}_x\text{C}_{1-x}$ films these modes may be considered as surface or interface modes and they are found in heterogeneous structures with, for exemple, microvoids /13/.

Fig. 5 :

Typical IR absorption spectra of $\text{Si}_x\text{C}_{1-x}$ films deposited at 950°C with $p(\text{SiH}_4) = 0$ (a) ; $8.9 \cdot 10^{-2}$ Torr (b) ; $4.1 \cdot 10^{-1}$ Torr (c).

The layer thickness is about $6\text{ }\mu\text{m}$.



3-3 XPS characterization

In addition of the C and Si peaks, the O 1s core - electron level appears on the spectra of the outer surface of the films ($\sim 532\text{ eV}$). However, after Ar^+ sputtering its intensity decreases clearly whereas those of Si and C increase, that is consistent with a partial oxydation near the surface. The insulating feature of the samples involving a slight energy shift (charge effect), all the binding energies were referred to the O 1s transition from the oxygen contamination at 531.4 eV .

Fig. 6 : Variation of the Si-H stretching frequency ν with the carbon amount in the $\text{Si}_x\text{C}_{1-x}$ layers.

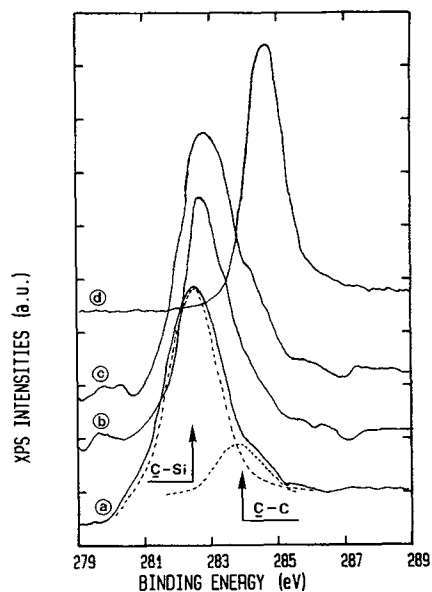
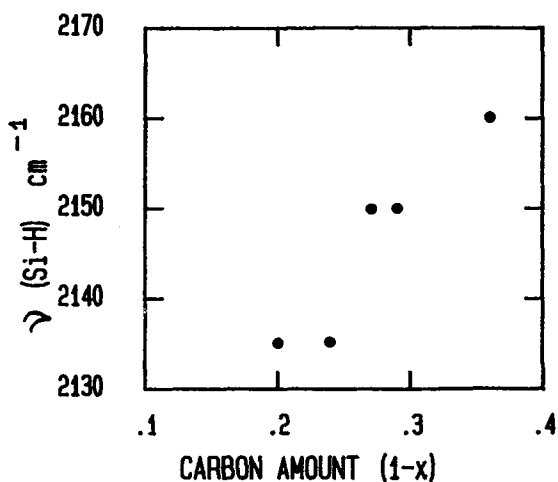


Fig. 7 : Variation of XPS C 1s energy region with SiH_4 partial pressure :
 a) $p(\text{SiH}_4) = 4.1 \cdot 10^{-1}$ Torr ($x = 0.76$);
 b) $p(\text{SiH}_4) = 8.9 \cdot 10^{-2}$ Torr ($x = 0.68$);
 c) $p(\text{SiH}_4) = 0$ ($x = 0.73$);
 d) graphite given for reference.

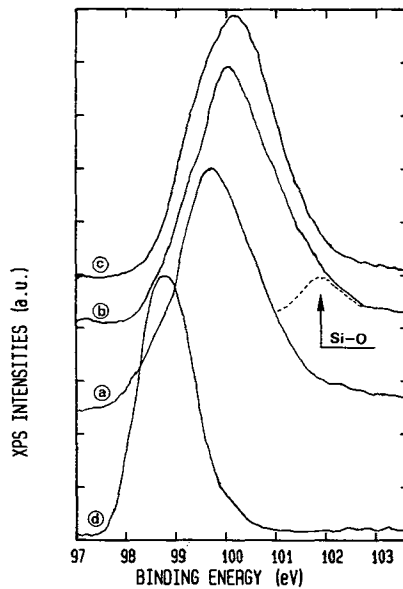


Fig. 8 : Variation of XPS Si 2p energy region with SiH_4 partial pressure :
 a) $p(\text{SiH}_4) = 4.1 \cdot 10^{-1}$ Torr ($x = 0.76$) ;
 b) $p(\text{SiH}_4) = 8.9 \cdot 10^{-2}$ Torr ($x = 0.68$) ;
 c) $p(\text{SiH}_4) = 0$ ($x = 0.73$);
 d) Si wafer given for reference.

Table 2 : XPS data of $\text{Si}_x\text{C}_{1-x}$ films deposited by OMCVD. Graphite and silicon are given for reference. The binding energies are referred to the O 1s transition at 531.4 eV and the uncertainty is estimated to ± 0.2 eV.

T(°C)	p(SiH ₄) (Torr)	K _C (%)	(1-x)	Si _{2p} (eV)	C _{1s} (eV)
800	0	13.3	0.61	99.8	282.5
850	0	23.4	0.51	99.6	282.6
900	0	29.1	0.29	100.0	282.8
950	0	31.7	0.27	100.2	282.7
950	$8.9 \cdot 10^{-2}$	20.0	0.32	100.1	282.8
950	$4.1 \cdot 10^{-1}$	14.7	0.24	99.7	282.5
C	graphite and silicon	-	1	-	284.6
Si	references	-	0	98.8	-

The C 1s binding energy is found at 282.5 eV and that of a pyrolytic graphite standard at 284.6 eV (table 2). This low energy shift is due to the lower electronegativity of Si and confirms that the C atoms are mainly bonded to Si, according to the high intensity of the Si-C stretching band in IR spectra. However, the shoulder near 284 eV is assigned to carbon bonded to carbon atoms /14/ (fig. 7). After deconvolution of this C 1s level, using an automatic procedure of a peak fitting programme, we can obtain the intensity, I_{CSi} and I_{CC} , of the peaks due to C-Si and C-C bonds, at about 282.5 and 284.5 eV, respectively, and a free carbon amount may be calculated with the ratio

$$k_c = I_{\text{CC}} / (I_{\text{CSi}} + I_{\text{CC}})$$

The result in table 2 shows that, without SiH₄ addition, the free carbon ratio in the film increases with the deposition temperature although the total amount of carbon decreases. On the contrary, for Si-rich $\text{Si}_x\text{C}_{1-x}$ films deposited at 950°C, the free carbon ratio decreases from about 31 to 14% when p(SiH₄) increases. Thus, as for IR results, an opposite influence of the deposition temperature and the silane partial pressure on the free carbon amount is found.

In homogeneous $\text{Si}_x\text{C}_{1-x}$ films, the Si 2p binding energy decreases monotonically as x increases while the Si 2p line - width remains constant /15/. In fig. 8, spectra a), b), and d) are in good agreement with this correlation since the Si 2p level decreases when x

increases from 0.68 to 1. However, if the free carbon ratio, k_c , is higher, that is the case when $p(\text{SiH}_4) = 0$ (fig. 8c), the chemical shift of Si 2p level is very low and is not in agreement with the previous correlation. Moreover, the Si 2p binding energy increases slightly with the free carbon amount (table 2), i.e. with the heterogeneity of the material. The non-significant chemical shift of C 1s and the behavior of Si 2p level are probably the result of an heterogeneous structure.

IV - CONCLUSION

Si-rich $\text{Si}_x\text{C}_{1-x}$ layers were grown by LPCVD using SiEt_4 as single source of Si and C. In spite of the Si excess, evidence for free carbon was found from optical, IR and XPS layer characterizations. A slight extra addition of SiH_4 in this process tends to increase the growth rate, the silicon content and decreases the free carbon content in the films leading to a less heterogeneous structure. The carbon segregation is important at high temperature or low silane partial pressure. A multizone microstructural model may be proposed, that would be constituted by free carbon clusters embedded in a Si-rich $\text{Si}_x\text{C}_{1-x}$ region with a boundary zone containing the hydride modes $\text{H}_2\text{Si}(\text{C}_2)$ and $\text{H}_3\text{Si}(\text{Si})$.

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