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LPCVD of SiC layers in a hot-wall reactor using TMS precursor

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ABSTRACT

SiC polycrystalline layers were grown by LPCVD in a hot wall reactor using tetramethylsilane (TMS) diluted in hydrogen as precursor.

The morphology and the structure of the films were analyzed in terms of deposition temperature, total pressure in the reactor and TMS flow rate.

The layers have been characterized using various techniques: SEM, X-ray diffraction and TEM (HREM and EELS).

1. INTRODUCTION

Silicon carbide has attracted considerable interest in several fields of science and technology because of its outstanding thermochemical properties, in particular its high thermal and chemical stability [1].

SiC is also a semiconductor with remarkable physical properties such as a wide band-gap energy (ranging from 2.2 eV for β -SiC to 3.3 eV for 2H- α -SiC), high electron mobility (1000 cm²/V.s) and high drift velocity (about 10⁷ cm/s). These physical properties show that SiC is a potentially useful material for electronic devices operating under severe conditions such as high temperatures and oxidizing atmospheres.

Chemical Vapour Deposition (CVD) is one of the most attractive techniques for preparing SiC films, because the material is directly obtained by thermal decomposition of raw gases. Alkyl-silicon compounds are potentially useful as CVD source gases. They are effective because Si-C bonds are already preformed in the precursors [3].

This paper deals with the morphological and structural characterization of polycrystalline layers of SiC grown on graphite substrates in a hot-wall reactor, using the decomposition of tetramethylsilane (TMS) and hydrogen as carrier gas, by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The microstructure and chemical composition of the layers was studied by analytical transmission electron microscopy (TEM) including high resolution observations (HREM) and electron energy loss spectroscopy (EELS).

2. ELABORATION OF THE COATINGS

A vertical hot-wall CVD reactor was used consisting of a graphite reaction chamber of cylindrical geometry ($\Phi=44\text{mm}$, $h=80\text{mm}$). It was heated by RF induction with a power supply operating at 140 kHz. A polycrystalline graphite substrate was placed in the reaction chamber normal to the direction of the gas flow. The temperature of the reaction chamber ranged from 950 to 1400°C and was measured with an optical pyrometer. The total pressure in the reactor (P) was controlled by a "MKS Baratron" gauge and was regulated using a valve connected to the vacuum system. The gas flows were controlled by mass-flow controllers. For these experiments, the H_2 flow rate, Φ_{H_2} , was held constant at 100 sccm. The TMS flow rates, Φ_{TMS} , had two values, 4 and 10 sccm. The experiments were performed at two reduced pressures: 66 and 133 Pa.

3. CHARACTERIZATION OF THE COATINGS

3.1. SEM and X-ray results

The morphology of SiC films obtained by CVD strongly depends on process parameters such as deposition temperature, TMS flow, and total pressure in the reactor.

Figure 1 shows the evolution of the layer morphology as a function of TMS flow and total pressure in the reactor at $T=1230^\circ\text{C}$. At low Φ_{TMS} , the films are fine-grained and compact. At $P_{\text{TMS}}=2.54$ Pa, the layers exhibit well faceted crystals (3 μm in size) (fig.1a), while at $P_{\text{TMS}}=5.11$ Pa, the crystal morphology becomes less well defined (fig. 1c). An increase in TMS partial pressure, P_{TMS} , results in the formation of spherulites of different sizes. They are about 40 μm in size at $P_{\text{TMS}}=6$ Pa (fig. 1b) and about 8 μm at $P_{\text{TMS}}=12$ Pa (fig. 1d). As shown by SEM micrograph reproduced on figure 1b the spherulites are composed of faceted crystals. The films obtained at deposition temperature between 1300 and 1380°C present a changing morphology. The coatings are composed of individual pseudo-hexagonal pyramidal structures normal to the substrate surface (fig. 2). Above $T=1400^\circ\text{C}$, the individual pseudo-hexagonal structures disappear and a disordered porous layer with some well defined crystals is observed (fig. 3).

The structural characterization was performed by X-ray powder diffraction. This technique allows us to determine the crystalline planes parallel to the substrate surface (preferential orientation). The order in other directions should be studied by rocking curves [4] or texture diagrams.

The films deposited at $T=1230^\circ\text{C}$, $P=66$ Pa and $\Phi_{\text{TMS}}=4$ sccm exhibit X-ray diffraction diagrams corresponding to the cubic β -SiC structure with a strong preferential orientation along the [110] direction. This preferential orientation changed to [111] when Φ_{TMS} changed to 10 sccm. All films obtained at temperatures between 1300 and 1380°C show a strong preferential orientation along the [111] direction. At temperatures above $T=1400^\circ\text{C}$ the preferential orientation disappears leading to a powder diffractogram pattern.

3.2. TEM results

This study has been focused on two representative samples in order to understand more precisely the effect of the deposition

temperature on the structure of the layers. The samples, obtained at 1320°C and 1400°C respectively, have been studied from the structural and chemical point of view. Transmission electron microscopy studies have been performed with a Philips CM30 ST equipped with a GATAN 666 spectrometer operating at 300 kV. The samples were thinned by mechanical polishing followed by Ar⁺ ion milling. The conventional dark-field images reproduced on figures 4a and 4b clearly show the change in the structure of the material when the deposition temperature increases.

At the lower temperature value, 1320°C, the continuous streaking of reflections observed on the electron diffraction pattern reproduced on figure 4a indicates that this material is constituted by a disordered stacking along the growing direction of the Si-C elementary layers. The dark field image obtained by selecting the arrowed diffraction spot allows the disordered arrangement of the layers to be clearly observed.

The conventional TEM observations of the layers obtained at 1400°C shows that β -SiC is heavily twinned. Extra spots due to the twins can easily be observed on the electron diffraction pattern reproduced on figure 4b and corresponding to a [110] incident beam direction. The dark-field image associated with the arrowed reflection reveals the distribution of twins in the crystal. It has been found that many crystals have the perfect zincblende structure of the β -SiC. This result is illustrated by the high resolution image reproduced on figure 5.

Chemical analysis performed by EELS has confirmed that the SiC crystals in the deposits are stoichiometric. An atomic ratio Si/C close to 1 has been measured for all the analyzed areas. These values result from the classical quantitative treatment of the EELS spectra as proposed by EGERTON [5]. Figure 6a shows an example of the Si L-edge and C K-edge distributions which are considered for this evaluation. The position of the plasmon peak in the EELS spectrum is measured at 22.6 eV which confirms the stoichiometric SiC composition [6]. In the case of the sample obtained at 1400°C, Fig.7, crystallized areas (b) have also been observed quasi-systematically around the SiC crystals (a). An EELS analysis of these areas revealed that they are essentially constituted by carbon (figure 6b). This is confirmed by the broad peak centered at 26.6 eV corresponding to the volume plasmon and the K inner-shell excitation edge observed at 285 eV [6].

4. DISCUSSION AND CONCLUSION

The evolution of the film morphology with the increase of TMS flow rate can be explained in terms of the increase of supersaturation in the system (related to the partial pressure of the precursors), and the different kinetics of growth of the three morphologically more important forms {100}, {111} and {111} of β -SiC.

4.1. TMS FLOW EFFECTS

At $\Phi_{TMS}=4$ sccm, heterogeneous nucleation of small crystallites leads to homogeneous coatings showing a preferential orientation along [110]. This orientation results from a crystal growth rate of the form {100} higher than the two other forms {111} and {111}. This fact could be explained by the high concentration of hydrogen

($P_{H_2}/P_{TMS}=24$) and low concentration of pyrolysis products (impurities: C_2H_4 , C_2H_2 , ...) [7] that allow the highly reactive cube polar faces (100), (010), (001) (included in the {100} morphological form) to grow faster than the non polar faces of the tetrahedra {111} and $\bar{1}\bar{1}\bar{1}$. Under these assumptions, [111] should be the faster growth direction (corner), because it corresponds to the composition of the normal to three fast growth faces. Nevertheless, this "corner direction" is blocked by the presence of {111} and $\bar{1}\bar{1}\bar{1}$ faces. Consequently, the higher rate of growth of the form {100} results in a preferential orientation along [110] because it is the edge between two faces of this form. At $P=133$ Pa, the orientation is less accentuated because the film surface is rougher and the crystals tend to form "rosettes".

The deposition rate strongly increases with Φ_{TMS} . Consequently, the tiny nucleated crystallites tend to agglomerate to form spherulites. The spherulites obtained at $\Phi_{TMS}=10$ sccm have different sizes as a function of the total pressure in the reactor. Furthermore, the augmentation of TMS flow leads to a relative diminution of hydrogen partial pressure ($P_{H_2}/P_{TMS}=10$) and an increase in the concentration of impurities [7] which contaminate and probably block the more reactive faces corresponding to the {100} morphological form. Thus, a higher rate of growth of both {111} and $\bar{1}\bar{1}\bar{1}$ forms results in a preferential orientation along the [111] direction. At $P=133$ Pa, homogeneous nucleation starts and consequently, the diffraction pattern looks like a powder diffraction pattern.

4.2. DEPOSITION TEMPERATURE EFFECT

The increase in the deposition temperature has four effects :

- a) the mobility of the growth units on the surface is favoured
- b) the surface roughness increases
- c) the desorption of hydrogen and other impurities from the surface is promoted
- d) there is an increase in the impurity concentration due to the augmentation in the TMS pyrolysis rate.

The first two effects favour crystal growth and result in a crystal morphology bounded by well-defined facets. The third effect decreases the concentration of hydrogen and other impurities on the surface. In fact, the decrease in the impurity concentration is balanced by the fourth effect. Consequently, the more reactive faces such as {100} cannot grow faster than {111} and $\bar{1}\bar{1}\bar{1}$. A preferential crystallization along [111] develops. These mechanisms could explain the morphologies exhibited by the layers deposited at temperatures ranged between 1300 and 1380°C.

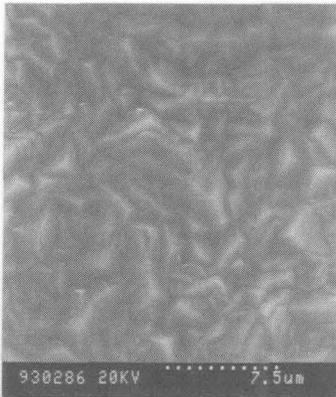
At a working temperature of 1400°C, we observe an increase in the free carbon concentration in the layers, which prevents the crystals growing, and the film consists of randomly orientated crystallites surrounded by carbon. Consequently, the X-ray diffraction pattern corresponds to a randomly oriented β -SiC powder diagram. This fact suggests that the formation of these crystallites is a gas phase homogeneous nucleation mechanism. Perhaps the high concentration of free carbon is due to reevaporation of Si.

ACKNOWLEDGEMENTS

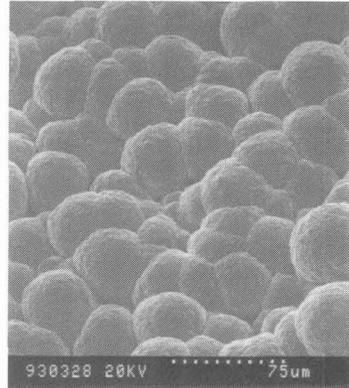
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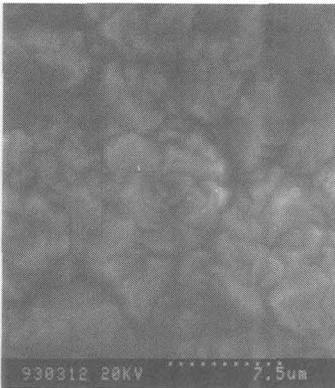
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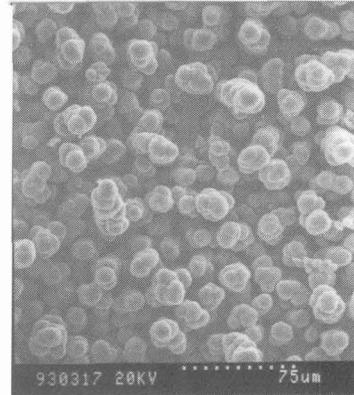
a: $\Phi_{TMS} = 4$ SCCM
P= 66 Pa



b: $\Phi_{TMS} = 10$ SCCM
P= 66 Pa



c: $\Phi_{TMS} = 4$ SCCM
P= 133 Pa



d: $\Phi_{TMS} = 10$ SCCM
P= 133 Pa

Fig.1 - SEM micrographs corresponding to as grown layers obtained at $T=1230^{\circ}\text{C}$

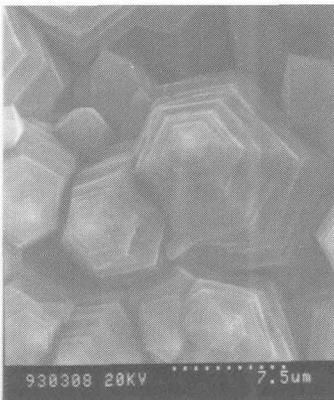


Fig.2
Surface morphology exhibited by the layers obtained at $T=1380^{\circ}\text{C}$, $P=66$ Pa, $\Phi_{TMS}=4$ SCCM

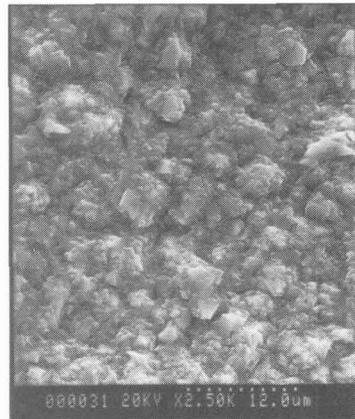


Fig.3
Surface morphology exhibited by the layers obtained at $T=1400^{\circ}\text{C}$, $P=66$ Pa, $\Phi_{TMS}=4$ SCCM

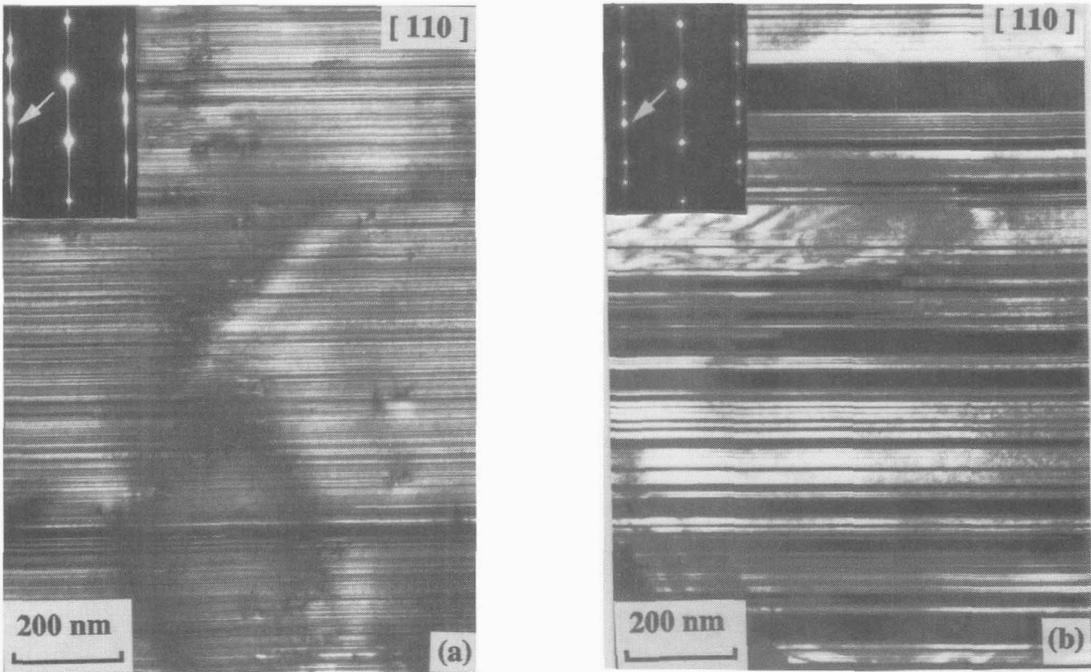


Fig.4- TEM dark-field images and corresponding diffraction patterns of SiC deposits obtained at $T=1320^{\circ}\text{C}$ (a) and $T=1400^{\circ}\text{C}$ (b).

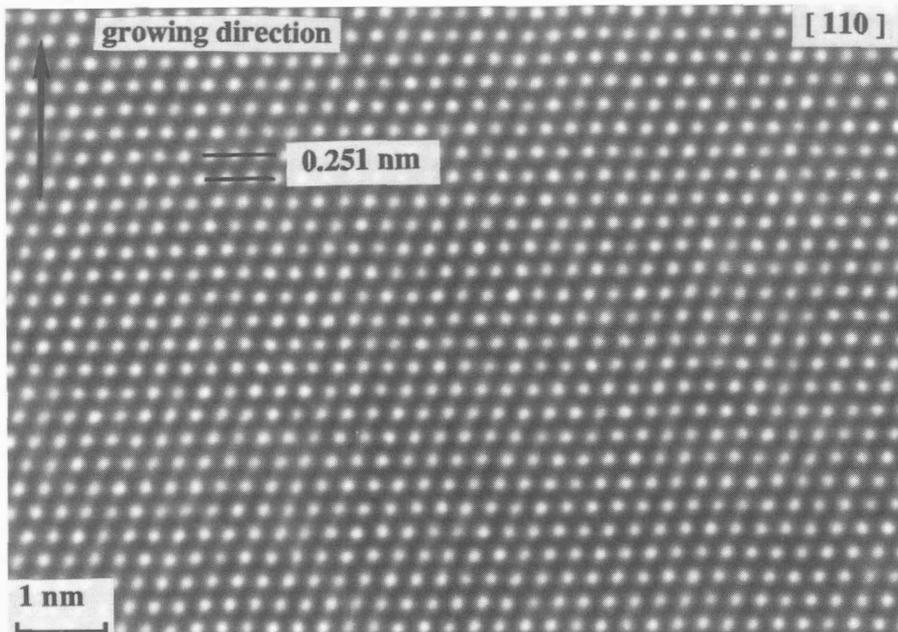


Fig.5- High resolution image of a SiC crystal observed in the $[110]$ orientation. It shows the stacking of the 0.251 nm distant elementary Si-C layers in agreement with the perfect zincblende structure (deposit elaborated at 1400°C)

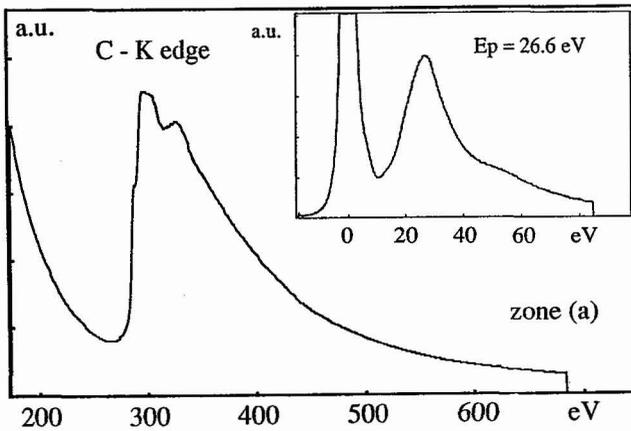


Fig.6a - Electron energy loss spectrum showing the L and K inner-shell distributions related to silicon and carbon respectively and corresponding to zones (a) on figure 7. Insert shows the low energy loss a distribution with plasmon peak at 22.6 eV.

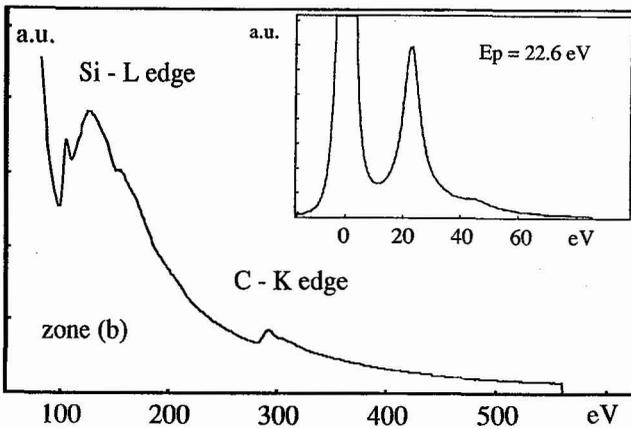


Fig. 6b - Electron energy loss spectrum associated to zones (b) on figure 7. It shows the K inner-shell distribution and the plasmon peak corresponding to carbon

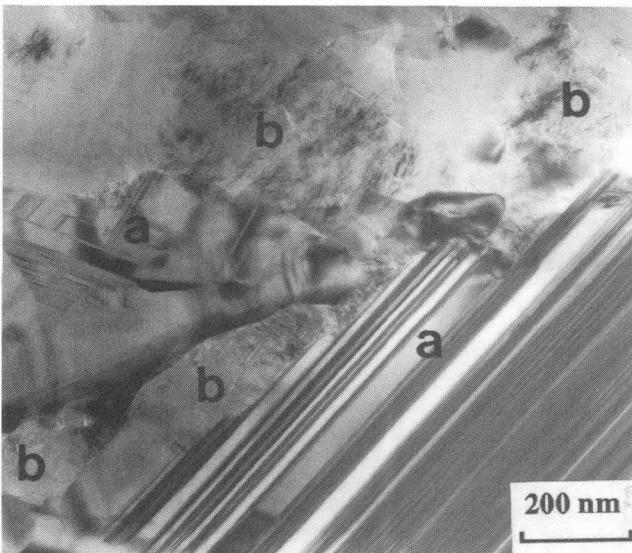


Fig. 7 - TEM bright-field image of a deposit obtained at 1400°C showing that SiC crystals (a) are surrounded by crystallized domains (b) identified as carbon by chemical analysis.