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Chemical Vapour Deposition of AlN-Si₃N₄ Codeposits

F. Henry, B. Armas, C. Combescure, D. Thenegal and R. Flamand

Institut de Science et de Génie des Matériaux et Procédés, CNRS-IMP, BP. 5, Odeillo, 66125 Font Romeu cedex, France

Abstract. A hot wall CVD reactor has been especially adapted to the problem of producing codeposits of aluminium and silicon nitrides. The experimental set-up for preparing "in situ" aluminium trichloride or a mixture of AlCl₃ and SiCl₄ by the action of silicon tetrachloride on an aluminium supply, heated to temperatures (T_c) between 380 and 520 °C is presented. A study was also made of the deposition kinetics using a thermobalance with a continuous recording facility. The deposition kinetics of AlN and Si₃N₄ were measured and compared. The codeposits prepared at a temperature of 1200 °C and a total pressure of 1 Torr were found to be adherent when deposited on a graphite substrate covered by a layer of silicon carbide obtained by pyrolysis of tetramethylsilane at 1240 °C. The deposits were characterized by a variety of methods: X-ray diffraction, wavelength dispersive spectroscopy and scanning electron microscopy.

1. INTRODUCTION

Aluminium nitride has been used in numerous electronic applications and as a high temperature oxidation resistant coating [1]. Thin solid films [2] of aluminium nitride can easily be produced by chemical vapour deposition. We have recently studied the resistance to oxidation of this material [3] which appears to be especially interesting at temperatures above 1000°C.

Silicon nitride is also a material well known for its electrical properties and its highly refractory nature [4] [5]. In a previous study we have synthesized this compound by CVD using tetramethylsilane (TMS) and ammonia. The thermomechanical behaviour of the composite has been studied in a solar furnace with a high thermal flux [6].

More recently we have studied the Al-Si-N system in order to find new materials which exhibit a strong resistance to oxidation at high temperatures. A theoretical study has been made by other authors [7] to investigate the Al-Si-N system, considering it as a pseudo binary compound AlN - Si₃N₄. A more general study of the ternary system M-Si-N (M= Al, Cu, Zn,...) has been made by other authors [8]. The results of this work have suggested that there is no ternary phase or solid solution present in the Al-Si-N system. An experimental study [9] of the Al-Si-N system has been made on codeposited nitrides of silicon and aluminium on silicon and sapphire substrates, at temperatures from 600 to 1100°C by ammoniolytic action of aluminium trichloride and silane. The authors have shown that the deposition kinetics and thickness uniformity are influenced by the ratio NH₃/(AlCl₃, SiCl₄), but no thermodynamic study of the system was made.

In a previous study [10] we have successfully shown that it is possible to produce codeposits of aluminium and silicon nitrides using CVD. We have also made a thermodynamic study of the (Al, Si, N, Cl and H) system and shown the influence of the experimental parameters.

In this study we have accomplished the "in situ" preparation of aluminium trichloride through the chemical action of silicon tetrachloride on an aluminium supply heated to a suitable (T_c) temperature. Furthermore, by varying the temperature of the aluminium supply, this technique has allowed us to obtain a mixture of two chlorides. A thermogravimetric system has also been adapted which made it able to follow changes in the deposition kinetics.

2. EXPERIMENTAL PROCEDURE

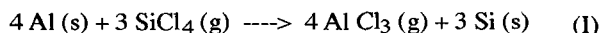
2.1 Experimental set-up

Figure 1 shows the deposition system which was constituted by a hot wall reactor, and a vertical axis coupled to an automatic thermobalance used to continuously follow the variation in the mass of the substrate. The substrate was suspended from the arm of the thermobalance by a molybdenum wire. The vacuum was produced using a mechanical primary pump with an achievable limit of 10^{-3} Torr. A liquid nitrogen trap protected the pump by condensing byproducts of the gas phase reactions. The precursors were SiCl_4 , AlCl_3 and NH_3 , with nitrogen as the carrier gas.

The substrates used were graphite covered with a layer of silicon carbide, obtained by pyrolysis of a mixture of tetramethylsilane (TMS) and hydrogen. The SiC layer acts as a diffusion barrier between the graphite substrate and the deposited nitrides so that adherent nitride layers can be formed.

The chlorides and ammonia were introduced separately to avoid reactions between them before the reactor inlet. The different flow rates were controlled using mass-flow controllers. The silicon tetrachloride was of 99.95% purity. Because its vapour pressure at room temperature is very low thus it was necessary to preheat the SiCl_4 in a thermostat controlled bath at 40°C for vaporization.

The aluminium trichloride is a solid powder at room temperature and its vapour pressure is very low thus it is generally necessary to heat it and the flow control is very difficult. Therefore in this study the aluminium trichloride was prepared "in situ" by the action of SiCl_4 on the aluminium supply by following reaction :



In order to avoid condensation of SiCl_4 and AlCl_3 , all the gas lines and mass flow controllers were insulated maintaining an internal system temperature of 50°C . The high temperature valve is heated (see caption Figure 1) at 180°C .

2.2 Aluminium supply testing

The use of a solid aluminium supply allowed us to vary the composition of the gaseous mixture as a function of the supply temperature (T_c) from pure SiCl_4 to pure AlCl_3 , varying the ratio of the two chlorides.

The aluminium supply was composed of a mixture of aluminium powder of 99% purity (grain size $100\mu\text{m}$) mixed with spherulites of alumina (grain size $400\mu\text{m}$), all enclosed in a silica tube which is itself enclosed in a stainless steel tube. A resistance coil wrapped around the stainless steel casing allowed the aluminium supply to be heated up to the desired temperature. The exact temperature (T_c) was controlled using a thermocouple (see Figure 1). The aluminium supply has been tested in the following manner :

- It was studied in the temperature range from 300 to 530°C .
- An SiCl_4 gas flow of 1 SCCM was passed through the aluminium supply and the pressure maintained at 200 Torr by means of a nitrogen flow of 60 SCCM.

A high temperature valve controlled the connection between the aluminium supply and the reactor chamber.

The other experimental parameters were : ammonia flow rate $D_{\text{NH}_3} = 3$ SCCM, substrate temperature $T = 1000^\circ\text{C}$, total reactor pressure $P = 1$ Torr. A graphite substrate of dimensions 10 mm diameter and 2 mm thickness was introduced into the reactor and coated with SiC. The conditions of the SiC deposition were as follows : substrate temperature $T = 1240^\circ\text{C}$, total reactor pressure $P = 1$ Torr, hydrogen flow rate $D_{\text{H}_2} = 100$ SCCM and tetramethylsilane flow rate $D_{\text{TMS}} = 4$ SCCM, with a deposition time of 10 minutes. These experimental conditions allowed us to obtain well crystallized, compact, SiC coatings of approximately 1 mm thickness. The deposition of SiC and nitride layers was made successively in order to avoid opening the reactor and contaminating the deposited layers.

After the SiC layer was deposited the temperature was lowered to 1000°C and a series of experiments were made with the aluminium supply at different temperatures. Thus layers whose composition varied from pure Si_3N_4 to pure AlN by changing the proportion of the two nitrides were obtained.

The deposits made were then analysed using electron microwaves by "Wavelength Dispersive Spectroscopy (WDS)". Figure 2 shows a graphical representation of the composition variations (atomic percentage) as a function of aluminium supply temperature (T_c), between 300 and 530°C . It can be

concluded that the compositions of deposits vary with of aluminium supply temperature (T_c). It may be seen that the quantity of silicon decreases with an increase in supply temperature while the quantity of aluminium increases gradually with increasing supply temperature (T_c). The characterizations (X-ray, WDS) that the deposits are composed of a mixture of aluminium and silicon nitrides (see § 4). The aluminium nitride AlN layer, has a corresponding atomic composition of 50% Al at 50% nitrogen. Silicon nitride Si_3N_4 has an atomic composition of 42.9% Si and 57.1% N. It can be seen that the quantity of nitrogen in the deposit decreases steadily when a transition is made from a Si_3N_4 -rich deposit to an AlN-rich deposit. However the stoichiometry of coatings tends to be preserved. As T_c is increased the deposit becomes richer in AlN, which is produced by the enrichment of the gaseous phase with $AlCl_3$. It may also be concluded that to obtain pure aluminium nitride it is necessary to work with a supply temperature greater than 500 °C.

These results indicate that the aluminium supply is effective for producing the desired codeposit. The changes observed in the composition of deposits were caused by variations in the temperature of the reactor and aluminium supply. However all compositions calculated were subject to a certain degree of error due to fluctuations in the reactor and supply temperature.

Before making a study of codeposits of AlN and Si_3N_4 the deposition kinetics of the two component nitrides were studied separately in order to make quantitative comparisons.

3. COMPARISON OF THE DEPOSITION KINETICS OF AlN AND Si_3N_4

A comparison is made of the deposition rates of the two nitrides AlN and Si_3N_4 measured at the same temperature. The deposition rates are plotted as a function of the partial pressure of chloride P_{Cl} at the same temperature. P_{Cl} represents the partial pressure of silicon chloride for the Si_3N_4 deposit and of aluminium chloride for the AlN deposit. This comparison was made for several temperatures in the same range of deposition rates (0-50 mg/h).

The results of this comparative study (Figures 3 to 6) show that for all cases the aluminium nitride deposition is more significantly affected by changes in the partial pressure of chloride than Si_3N_4 . As the reactor temperature increase to 1250 °C the rate of deposition of Si_3N_4 increases and that of AlN decreases, with the two deposition rates approaching on another.

At 1250 °C it may be observed that while the deposition temperature increases, for a given gaseous phase composition the deposition rates of the two nitrides vary inversely. It has also been established from a previous thermodynamic study [10] that increasing the deposition temperature causes the deposition rate of AlN to decrease. It may therefore be concluded that codeposits of different compositions may also be produced from the same gas phase composition when the deposition temperature is varied.

4. STUDY OF THE AlN AND Si_3N_4 CODEPOSIT

4.1 Codeposit experimental kinetics

The codeposits were deposited at a total pressure $P = 1$ Torr, a reactor temperature $T = 1200$ °C, a silicon chloride flow rate $D_{SiCl_4} = 1$ SCCM, an ammonia flow rate $D_{NH_3} = 3$ SCCM and a supply temperature T_c which was changed in order to produce codeposits of varying compositions.

A series of six samples has been made of various compositions in the range from pure AlN (a) to pure Si_3N_4 (f). The preparation conditions of this series are summarized in Table 1.

Table 1 : Experimental deposition rates (V_e , V_b) for different values of aluminium supply temperature (T_c).

V_e : deposition rate mg/h obtained from the sample weight measurement before and after deposition (see text).

V_b : deposition rate mg/h continuously recorded by the thermobalance.

Samples	a	b	c	d	e	f
T_c (°C)	494	450	416	394	366	40
V_e (mg/h)	15.1	9.5	9.1	6.9	3.1	1.5
V_b (mg/h)	19.0	14.9	14.4	11.4	6.2	5.0

It should be noted that an AlN deposit was obtained at a corresponding supply temperature of 494 °C. This temperature is much lower than expected, considering the results obtained at 1000 °C from the aluminium supply as shown in Figure 2. The deposition rate V_e of the sample was calculated from the mass variations subtracting the mass contribution from SiC (obtained from a previous experimental measurement of SiC deposition rate). The deposition rate V_b obtained using the thermobalance recordings, is calculated from the mass increase of both the sample and the sample holder.

For sample (f), a second mass flow controller and a separate gas line (Figure 1) allowed the introduction of silicon tetrachloride without contact with the aluminium supply. A nitrogen flow was maintained through the vessel containing the supply in order to insure convenient hydrodynamic conditions.

The rate recorded by the thermobalance allows easily calculation of the deposition rate V_e and is a very accurate method since it takes into account the weight gain by the molybdenum substrate support.

An increase in the supply temperature (T_c) produces an increase in the deposition rate V_e of AlN proportionally larger than expected, because 1 SCCM of SiCl_4 should lead to the formation of 1.33 SCCM of AlCl_3 (reaction I). The deposition rates of the two pure nitrides give some explanation for the two nitrides codeposition mechanism.

The deposition rate V_e of AlN is approximately ten times greater than the deposition rate V_e of Si_3N_4 (Table 1).

Therefore it can be suggested that the increase in AlN deposition rate caused by varying the supply temperature is the result of an increase in the rate of exchange (reaction I) and thus an enrichment of the gaseous phase in aluminium trichloride. The greater quantity of AlCl_3 thus leads to more AlN in the codeposit. It can be concluded that as T_c is increased the rate of deposition increases passing from that of Si_3N_4 to that of AlN.

4.2 Codeposit composition

The composition of samples was determined by W.D.S. analysis of several points along a polished cross section of the sample. The calculated compositions are summarized in table 2, with all values given in atomic per cent. The values quoted for samples (a) to (f) show that the deposited nitrides have close to stoichiometric atomic ratios. The two extreme cases were also studied, in sample (a) contained less than 0.5 at % silicon. Similary sample (f) did not reveal any traces of aluminium, indicating that these samples were of pure aluminium and silicon nitrides respectively, samples (b) to (e) being a mixture of these two nitrides.

Table 2 : Codeposit composition (at %) determined by W.D.S. analysis of several points along a polished cross section of the sample.

samples	$T_c(^{\circ}\text{C})$	Al (at%)	Si (at%)	N (at%)	C (at%)	O (at%)
b	450	40.9	3.6	46.1	4.8	4.6
c	416	37	9.4	47.7	2.9	3
d	394	30.3	14.5	48.6	1.8	4.8
e	366	22.1	22.3	52.3	2	1.3

The results displayed in Table 2 show that the quantity of Al decreases going from sample (b) to sample (e) ; this corresponds to the decrease in aluminium supply temperature (T_c).

The same result has already been established, as discussed in section 2.2, and also, as previously shown, the silicon content decreases with increasing aluminium supply temperature.

In conclusion the feasibility of this method for producing codeposits of AlN and Si_3N_4 has been shown. The aluminium supply has been tested and this work clearly demonstrates that it is possible to control the composition of codeposits by varying the aluminium supply temperature.

The deposition rates measured illustrate that the thermodynamic results from our previous work [10] are not always in agreement with the conclusions of this experimental kinetics study.

A possible explanation for these disagreements is that the thermodynamic calculations assume the equilibrium of the system, considered as closed. However, the real system is open and kinetic limitations probably lead to a significant deviation from the thermodynamical equilibrium which is then not practically reached in our experiments.

4.3 Characterization of codeposits

The crystalline structure of the deposits has been characterized using X-ray diffraction techniques.

It was observed that as the quantity of silicon nitride in a given codeposit sample increased, the corresponding X-ray diffraction peaks were broadened revealing an amorphous nature, by contrast, aluminium nitride-rich codeposits were well crystallized.

A previous high resolution transmission electron microscopy study [11] revealed that silicon nitride-rich samples contained dispersed nanocrystals of aluminium nitride. Codeposit samples which were aluminium nitride-rich exhibited large aluminium nitride crystals again surrounded by amorphous silicon

nitride. Electron diffraction studies confirmed the trends observed by X-ray diffraction. In the present work, the surfaces of AlN, Si₃N₄ and codeposits samples were examined using scanning electron microscopy (S.E.M.).

The surface morphology observed for the deposits made at 1200 °C are shown in Figure 7 and 8, representing coatings of aluminium and silicon nitride respectively. It was found that AlN layers were of a crystalline nature with well defined facets observed in the S.E.M. images. By contrast, the surface appearance of Si₃N₄ samples was amorphous, as previously shown by X-ray diffraction studies. Figure 9 shows the image recorded for a codeposit sample (c), (see § 4). The sample surface is composed of a type of "orange skin" with small crystals present. The corresponding chemical analysis of this sample indicated that it was composed mainly of aluminium nitride (ratio of Al/Si approximately 4:1). However it exhibits a surface morphology which is more Si₃N₄ like than AlN. It is thought that the presence of silicon nitride phase prevents the development of well defined AlN crystals. Figure 10 shows the surface of the codeposit whose composition corresponds about to 50% of aluminium nitride and 50% of silicon nitride. As with the previous sample, the surface morphology does not exhibit well defined crystals.

A cross section of codeposit (c) is presented in Figure 11, an image which shows the successive layers of the graphite substrate, the SiC layer and finally the codeposit of AlN and Si₃N₄. It can be observed that there seems to be good adhesion between the different layers and the graphite substrate. Figure 12 shows an X-ray image of the same sample cross section illustrating the distribution of the elements aluminium and silicon throughout the cross section. The broadest strip contains both Si and Al; this is the AlN and Si₃N₄ codeposit. At the left side of the codeposit strip, the silicon X-ray micrograph shows clearly a brightest strip due to the high Si concentration, and the aluminium X-ray micrograph shows that this high Si concentration zone does not contain Al. Therefore, we could conclude that the brightest strip observed on the silicon X-ray micrograph was caused by the presence of the silicon carbide film.

5. CONCLUSION

This study has clearly demonstrated that it is possible to prepare "in situ" AlCl₃ or a mixture of aluminium trichloride and silicon tetrachloride using an aluminium supply heated to the appropriate temperature.

An experimental set-up consisting of a hot wall reactor coupled with a thermobalance allowed us to study the deposition kinetics AlN, Si₃N₄ deposits and codeposits of these two nitrides. The crystalline structure of the codeposit samples has been characterized using X-ray diffraction techniques, and only deposits having a strong concentration of AlN exhibited spectra with well defined peaks corresponding to aluminium nitride, whereas silicon nitride was always found to be amorphous under our experimental preparation conditions. The scanning electron microscopy examination of the surface of codeposits prepared at 1200 °C allowed us to observe the morphological evolution of the surface as a function of composition, and showed that an increased presence of silicon nitride leads to a reduction in the size of the aluminium nitride crystals.

The results obtained in this study lead the way for the synthesis of other codeposits of aluminium and silicon nitride. It is thought that at very high temperatures (higher than 1300°C) it should be possible to coprecipitate well crystallised aluminium and silicon nitrides, and not only that of aluminium nitride as it was the case in the present study. It is hoped that the thermomechanical and oxidation resistive properties of these codeposits will be studied.

Finally, in order to have a very good control of the codeposit composition, the reactant flow rates of both SiCl₄ and AlCl₃ have to be known precisely. Two independent gas inlets will then be used in the future, one for the SiCl₄ and one for pure AlCl₃ obtained by the complete conversion of SiCl₄ on an aluminium supply heated up to 500 °C.

Acknowledgements

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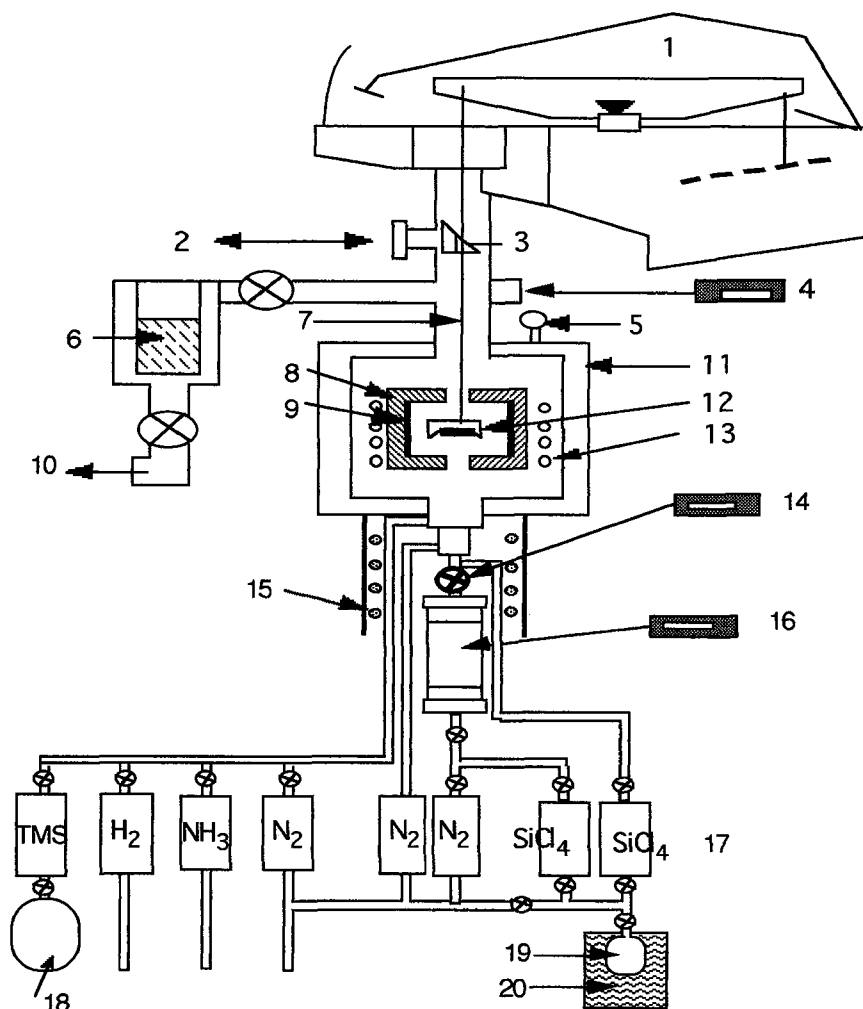


Figure 1: Experimental set up: (1) thermobalance, (2) to micropyrometer, (3) optical prism, (4) vacuum gauge, (5) Bourdon manometer, (6) liquid nitrogen trap, (7) Molybdenum wire, (8) graphite insulator, (9) graphite susceptor, (10) to vacuum pump, (11) reactor chamber, (12) substrate, (13) high frequency inductor, (14) high temperature valve controller, (15) high temperature valve heater, (16) Aluminium supply temperature controller, (17) mass flow controllers, (18) TMS evaporator, (19) SiCl₄ evaporator, (20) thermostat controlled bath.

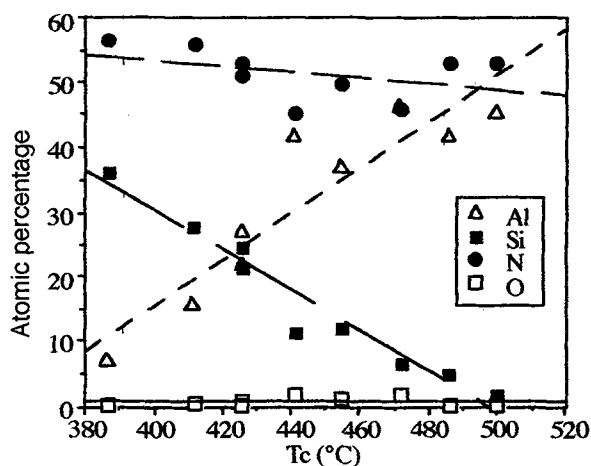


Figure 2: Codeposit composition vs Tc at 1000 °C.

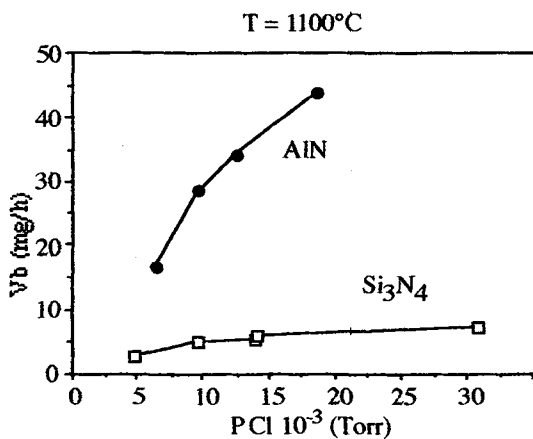


Figure 3: Deposition rate of AlN and Si₃N₄ as a function of Al and Si chlorides partial pressures at 1100 °C.

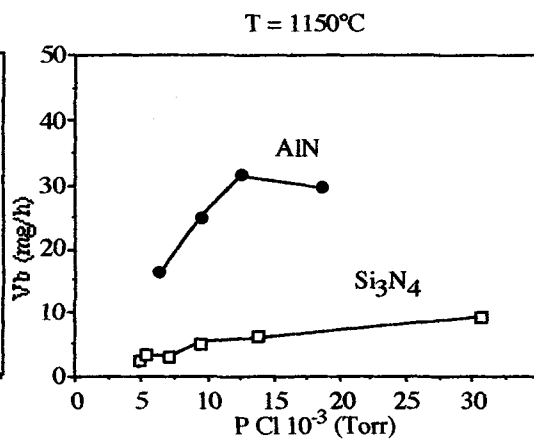


Figure 4: Deposition rate of AlN and Si₃N₄ as a function of Al and Si chlorides partial pressures at 1150 °C.

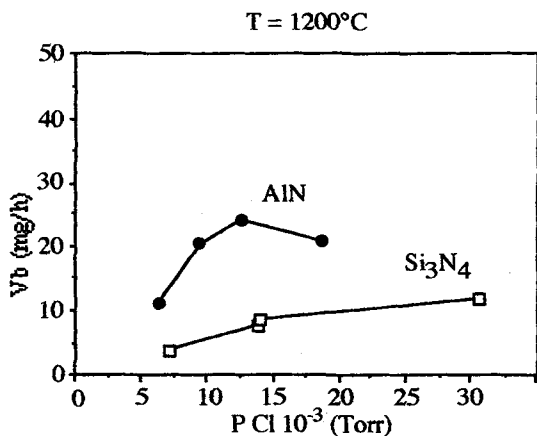


Figure 5: Deposition rate of AlN and Si₃N₄ as a function of Al and Si chlorides partial pressures at 1200 °C.

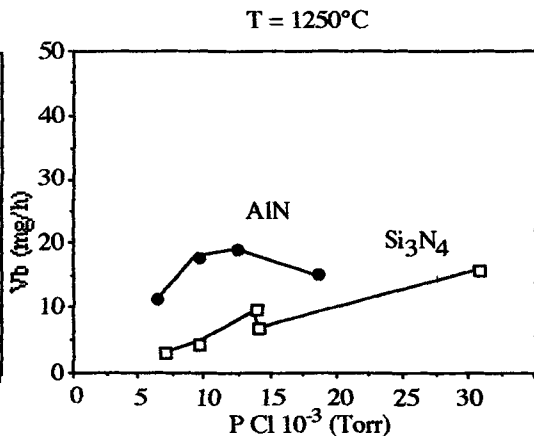


Figure 6: Deposition rate of AlN and Si₃N₄ as a function of Al and Si chlorides partial pressures at 1250 °C.

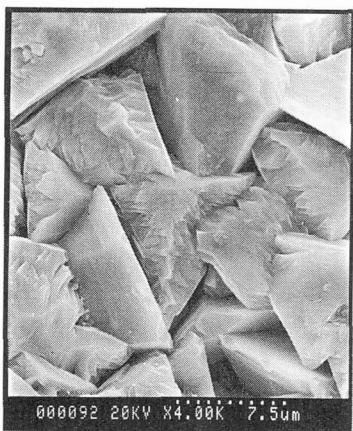


Figure 7 : AlN prepared at $T = 1200\text{ }^{\circ}\text{C}$,
total pressure $P = 1\text{ Torr}$.

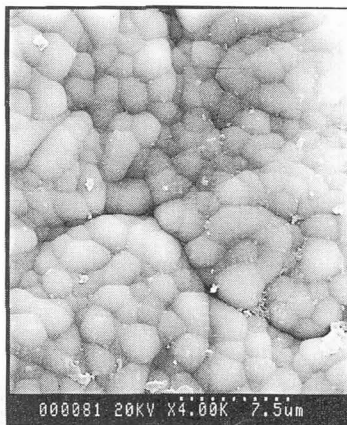
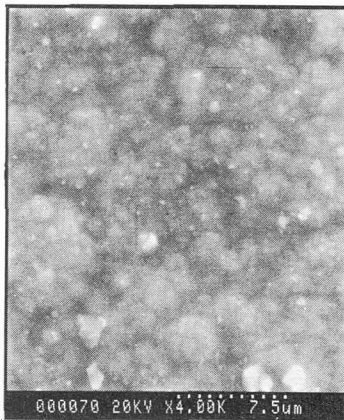


Figure 8 : Si_3N_4 prepared at $T = 1200\text{ }^{\circ}\text{C}$,
total pressure $P = 1\text{ Torr}$.



$\text{Al/Si} \approx 4$

Figure 9 : AlN and Si_3N_4 codeposit . Deposition
conditions: $T = 1200\text{ }^{\circ}\text{C}$, $P = 1\text{ Torr}$, $T_c = 416\text{ }^{\circ}\text{C}$.



$\text{Al/Si} \approx 1$

Figure 10 : AlN and Si_3N_4 codeposit . Deposition
conditions : $T = 1200\text{ }^{\circ}\text{C}$, $P = 1\text{ Torr}$, $T_c = 366\text{ }^{\circ}\text{C}$.

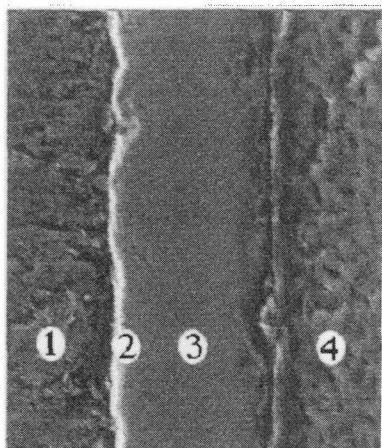


Figure 11 : Cross section (electronic image) of the
codeposit shown in Fig. 9: (1) graphite substrate,
(2) SiC layer, (3) AlN and Si_3N_4 codeposit , (4) resin.

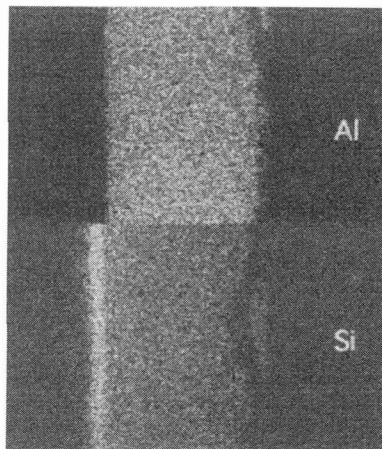


Figure 12 : X image of the sample in Fig. 11
illustrating the distribution of Al and Si.