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Low Pressure Chemical Vapour Deposition of AlN-Si_3N_4 Codeposits

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Abstract

Codeposits of AlN and Si_3N_4 nitrides are obtained by low pressure chemical vapour deposition (LPCVD) in a hot-wall reactor using $AlCl_3$, SiC_4 and NH_3 as precursors. The $AlCl_3$ is prepared by action of $SiCl_4$ on an aluminium supply, heated at 520°C. The nitrogen is used as a carrier gas. The deposits are made at the temperature of 1100°C and at a total pressure of 133 Pa, on graphite substrates covered with SiC. By modifying the gas phase composition in $AlCl_3$ and $SiCl_4$, a mixture of two phases AlN and Si_3N_4 in various proportions is obtained. The codeposits were characterized by: X-ray diffraction, WDS, XPS and Auger. © 1997 Elsevier Science Limited.

Résumé

Des codépôts des nitrures AlN et Si_3N_4 sont obtenus par dépôt chimique en phase vapeur sous pression reduite (LPCVD), dans un réacteur à paroi chaude, en utilisant $AlCl_3$, $SiCl_4$ et NH_3 comme précurseurs. Le ACl_3 est préparé par action de $SiCl_4$ sur une charge d'aluminium chauffée à 520°C. De l'azote est employé comme gaz d'entraînement. Les dépôts sont réalisés à la température de 1100°C et à une pression totale de 133 Pa sur des substrats en graphite recouverts de SiC. En modifiant la composition de la phase gazeuse en $AlCl_3$ et $SiCl_4$, un mélange des deux phases AlN et Si_3N_4 en proportions variables est obtenu. Les codépôts sont caractérisés par: diffraction de rayons X, WDS, XPS et Auger.

1 Introduction

The aluminium nitride (AlN) is a refractory compound stable at high temperature above 1000°C and an oxidation-resistant product.[1] In a previous work we have shown the influence of the experimental preparation conditions on the morphology of CVD AlN films.[2] AlN is also an insulator compound presenting a large forbidden band (gap ~6·2 eV) and may be used in electronic devices.[3,4]

The silicon nitride (Si_3N_4) is also widely known for its high refractarity and electrical applications.[5] The oxidation-resistance and its physico-chemical behaviour has been widely considered by many workers.[6-8]

Layers of aluminium and silicon nitrides may be employed for protection against oxidation at high temperature. Nevertheless if we consider each nitride taken separately:

- the AlN oxidation leads to the formation of a porous layer of alumina, consequently it is not protective against oxygen diffusion;
- the Si_3N_4 oxidation under oxygen low pressure leads to the formation of volatile SiO, consequently in this case the protection against oxidation is still not assured.

In a previous[9,10] thermodynamic and experimental study we have shown the simultaneous AlN-Si_3N_4 deposition possibility. The main difficulty in this study is the inlet gas phase and the deposit composition control.

In this paper we show the possibility of preparing AlN-Si_3N_4 deposits in a large range of compositions, using low-pressure chemical vapour deposition (LPCVD) as a preparation technique.

2 Experimental Procedure

2.1 Deposits preparation

In a previous study[10] we have described the experimental set-up (a vertical hot wall reactor). The source gases were $AlCl_3$, SiC_4, NH_3 and N_2 as a carrier gas. In this work the $AlCl_3$ is obtained by a chemical reaction between a gaseous $SiCl_4$ and a metallic aluminium supply heated at 520°C. At this temperature the $SiCl_4$ is entirely transformed in $AlCl_3$. The control of $SiCl_4$ gas flow allows us to

Table 1. Codeposit samples prepared at T = 1100°C, P = 133 Pa and with a variable gas phase composition. We give the deposition rate J(Å/s) corresponding to each gas phase composition

Codeposit samples	*T = 1100°C*		*P = 133 Pa*	
	Q($AlCl_3$) sccm	*Q($SiCl_4$) sccm*	*Q(NH_3) sccm*	*J (Å/s)*
1	3·0	1	10	13·0
2	2·5	1	10	7·8
3	1·5	1	10	5·2
4	1·0	1	10	3·6
5	1·0	4	10	2·3

control the $AlCl_3$ gas flow; the chlorides and ammonia were introduced separately to avoid reactions between them before the reactor inlet. This method of $AlCl_3$ preparation allows us to know exactly the gas composition introduced into the reactor. $SiCl_4$ is also used as the silicium source and introduced separately in the reactor. Besides, this method assures the reproductibility of the deposit composition.

A graphite base covered by an SiC layer produced by the pyrolysis of tetramethylsilane was used as a substrate for all deposits.[11] In this study all nitrides are deposited at 1100°C, according to the preceding kinetic studies.[10]

2.2 Experimental results

We have realized many experiments with different gas phase compositions with the aim of obtaining deposits from AlN to Si_3N_4 with intermediate compositions. We have chosen five samples corresponding to different values of the gas phase composition (Table 1).

We can observe (Table 1) that the deposition rate (J (Å/s)) is lowered when the $AlCl_3$ amount decreases in the gas phase.

3 Characterization of Codeposits

Composition of samples 1–5 (Table 1) were determined by an Electron Probe Micro-Analysis (EPMA) CAMECA using Wavelength Dispersive System (WDS). The results displayed in Table 2 show that the Al atomic composition (at %) decreases from sample 1 to sample 5 . This result can be related to the change in $AlCl_3$ concentration in the gas phase reported in Table 1.

Therefore, by contrast, we can observe that the amount of Si increases when the Al quantity decreases. The ratio R = Al/Si displayed in Table 2 accurately describes the composition variation of the samples with the change in gas phase composition.

The crystalline structure of the deposits has been characterized using the X-ray diffraction technique. 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. Inversely the aluminium nitride-rich codeposits were well crystallized.

The surface morphology observed for samples 2, 3 and 4 are very similar to that given Fig. 1(b), that shows a micrography obtained by SEM. This morphology is very different of a pure deposit AlN which shows a well crystallized surface (see Fig. 1(a)). We can conclude that a morphological change is observed with increasing the Si concentration in the codeposit. We have also observed (Fig. 1(c)) the surface morphology of the Si_3N_4 film, this surface being characteristic of an amorphous deposit. Finally the surface morphology of the codeposits are intermediate between that of the well crystallized AlN and the amorphous Si_3N_4.

Also, in a previous work,[12] by transmission electron microscopy 'nanocrystals' of AlN are shown to be present in an Si_3N_4 amorphous phase.

4 X.P.S. Measurements on AlN-Si_3N_4 Codeposits

AlN and Si_3N_4 are very insulating compounds, so the energy positions of the photoelectron peaks were shifted at lower energies: about −3 eV. Therefore, we used the calculations of Auger[9] parameters α' in an attempt to identify the presence of these compounds, the Auger parameters not being sensitive to surface changing effects.[13] We have reported in Table 3 the values of the Auger parameters measured for sample (a) (pure AlN), sample (e) (pure Si_3N_4), samples (b) and (d) corresponding respectively to samples 2 and 5 in Tables 1 and 2, and codeposit (c) which was prepared with the following experimental conditions: T = 1000°C, P = 133 Pa, $AlCl_3$ = 1·5 sccm, SiC_4 = 1 sccm, NH_3 = 8 sccm. The α' values of Si for sample (b) and Al for sample (d) were not measured, due to the poor accuracy resulting from the low intensities of the $KL_{2,3}L_{2,3}$ Auger transitions. The results reported in Table 3 indicate that these codeposits are constituted essentially by mixtures of Al and Si nitrides. However, the Si $KL_{2,3}L_{2,3}$ and Al $KL_{2,3}L_{2,3}$ transitions observed for codeposit (c) (Fig. 2) seem to indicate that the Si and Al chemical bonds present in this deposit are more numerous than Si(N_4) and Al(N_4) bonds which must be found in a mixture of Si and Al

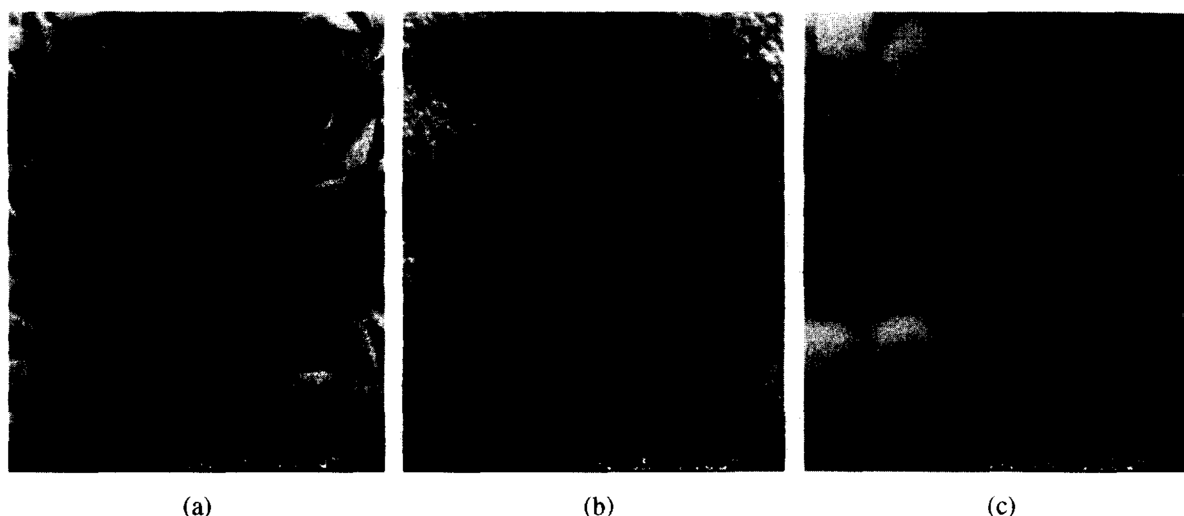

Fig. 1. SEM micrograph showing the morphology of different deposits obtained at T = 1100°C, P = 133 Pa: (a) pure AlN prepared with 1 sccm $AlCl_3$ and 10 sccm NH_3; (b) codeposit $AlN-Si_3N_4$ (sample (3); (c) pure Si_3N_4, prepared with 1 sccm $SiCl_4$ and 10 sccm NH_3.

Table 2. Codeposit composition (at%) determined by WDS analysis of several points along a polished cross-section of the sample

Codeposit samples	*T = 1100°C*		*P = 133 Pa*	
	Al(at%)	*Si(at%)*	*N(at%)*	*R = Al/Si*
1	4·15	5·4	53·1	7·69
2	40·7	6·7	52·6	6·7
3	36·8	8·8	54·3	4·18
4	35·4	10·5	54·1	3·37
5	7·0	38·0	55·0	0·18

Table 3. X.P.S. compositions and Auger parameters values α' measured for AlN, SiN_X and $AlN-SiN_X$ codeposit

Codeposit samples	*XPS Compositions: at%*					*α' values: ±0·2 eV*	
	Al	*Si*	*N*	*O*	*C*	*α' Al*	*α' Si*
(a)	44 ± 4	0	47 ± 5	7 ± 1	2 ± 1	1463·1	
(b)	41 ± 4	4 ± 1	46 ± 5	5 ± 1	3 ± 1	1462·9	
(c)	21 ± 2	26 ± 3	42 ± 4	5 ± 1	5 ± 1	1463·1	1714·6
(d)	5 ± 1	35 ± 4	50 ± 5	6 ± 1	3 ± 1		1714·6
(e)	0	39 ± 4	55 ± 5	2 ± 1	3 ± 1		1714·4

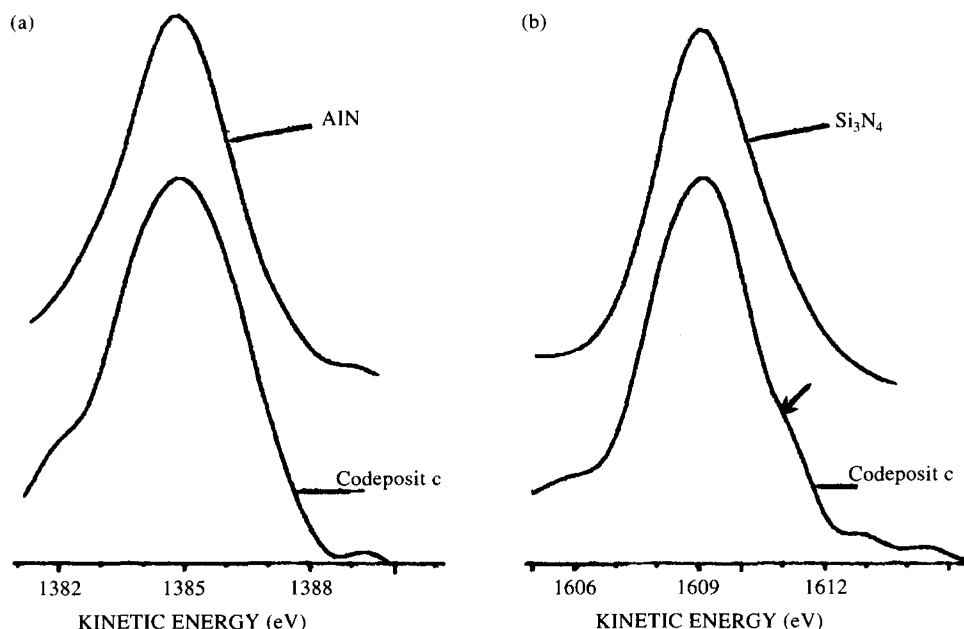

Fig. 2. X.A.E.S. Al $KL_{2,3}L_{2,3}$ (Fig. 2(a)) and Si $KL_{2,3}L_{2,3}$ (Fig. 2(b)) spectra collected on deposit (c) compared with reference spectra obtained for a crystallized AlN deposit (Fig. 2(a)) and an amorphous SiN_X deposit (Fig. 2(b)).

nitrides. Figure 2 shows that the Al KLL and Si KLL, X.A.E.S. transitions of codeposit (c) are broadened when compared with the Auger transitions collected for AlN and Si_3N_4 deposits. The broadening of the KLL peaks can be attributed to a large contribution of the interface domains between nanometric AlN crystals and amorphous Si nitride. In these interfaces domains the possibility of $Si(N_{xAly})$ tetrahedra, with $x+y=4$ can be expected. This possibility is especially suggested by the shoulder indicated by an arrow and located at the high energy side of the KLL transition collected for codeposit (c).

5 Conclusion

This study has demonstrated the possibility of preparing codeposits of AlN-Si_3N_4 in all ratios. A good control of $AlCl_3$ and $SiCl_4$ gas flows is obtained. Two independent gas inlets are then used in this experiment, one for $SiCl_4$ and one for pure $AlCl_3$ obtained by the complete conversion of $SiCl_4$ on an aluminium supply heated at 520°C.

The next stage will be the study of thermo-chemical properties of AlN-Si_3N_4 codeposits and particularly the oxidation resistance of carbon composites coated from AlN-Si_3N_4 mixtures.

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