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INFLUENCE OF EXCITATION FREQUENCY ON ORIENTED ($10\bar{1}0$) GROWTH OF ALUMINIUM NITRIDE THIN FILMS BY PECVD

N. AZEMA*, J. DURAND*, R. BERJOAN**, J.L. BALLADORE*** and L. COT*

*Laboratoire de Physicochimie des Matériaux, URA 1312 du CNRS, 8 rue de l'École Normale, F-34053 Montpellier cedex 1, France
**Institut de Science et de Génie des Matériaux et Procédés, BP 5, Odeillo, F-66120 Font Romeu, France
***CEMES-LOE CNRS, 29 rue Jeanne-Marvig, F-31055 Toulouse, France

- ABSTRACT :

The Metal-Organic Chemical Vapor Deposition process assisted by reactive plasma, leads to AlN coatings with oriented ($10\bar{1}0$) structure. The Aluminium nitride was synthesized on a wide range of substrates (Silicon (100) or (111) wafers, graphite, polycrystalline Silicon Carbide and glass plates) from trimethylaluminium and ammonia at 330°C. The a-axis orientation of AlN coatings, which does not depend on the substrate, changes with the excitation frequency. Material crystallinity and elementary composition were examined mainly by X-ray diffraction and Auger Electron Spectroscopy respectively. Crystalline AlN was obtained for low frequency fields (35-110-440 kHz) with mean crystallite sizes of 200-600 Å, whereas amorphous films were obtained using a 13.56 MHz frequency. The AES analysis has revealed compositions similar to AlN with a small percentage of Carbon (2-4 %) and no Oxygen (for all experimental conditions). To corroborate these results, Scanning Transmission Electron Microscopy and Infra-Red absorption spectroscopy are used.

I - INTRODUCTION :

In recent years, a wide range of applications has been found for AlN in microelectronic/1/, optic/2/, Surface Acoustic Wave (SAW) techniques/3/... This paper deals with growth of Aluminium nitride as well as coating material.

AlN thin coatings have been studied as single crystal epitaxial films/4/ or polycrystalline structures/5/. A c-axis orientation is observed depending on the experimental process. There are several growth methods of this crystalline ceramic such as Chemical Vapor Deposition (CVD) process, reactive Molecular Beam Epitaxy, reactive RF sputtering. In all these cases the growing temperatures are upper 800-1200°C.

Hasegawa and al./6/ have shown that amorphous AlN thin layers can be deposited at 300°C by Metal-Organic Plasma Enhanced Chemical Vapor Deposition (MOPECVD).

Recently, the growth of polycrystalline AlN with a (0001) preferred orientation has been accomplished at a substrate temperature of 550°C by a coaxial-line-type Microwave Plasma Chemical Vapor Deposition process/7/.

In the present work, MOCVD assisted by reactive plasma allows the preparation at 330°C of AlN coatings, with a ($10\bar{1}0$) orientation, on a wide range of substrates. The influences of excitation frequency and of substrates kind were studied. The material crystallinity and elementary composition were examined respectively by X-ray diffraction and Auger Electron Spectroscopy, with complementary studies by Infra-Red absorption spectroscopy. On the other hand, Transmission Electron Microscopy (TEM) observations revealed the film-substrate interface and showed the AlN crystallites.

2 - EXPERIMENT :

2.1 - Deposition system :

The schematic arrangement, synthesis conditions (P=7 Pa, W=0.26 W cm^{-2}) and precursor utilization (TMA, NH_3, N_2) have been described in a previous work/8/.

Four different generators capacitively coupled to the system were used to supply RF power of 50 W. Thereby three different low-frequency fields (35 kHz, 110 kHz and 440 kHz, respectively Addax, Plasmatek and Celes) and a

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high frequency one (13,56 MHz, Plasma-Therm Inc.) could be used to synthesize crystallized or amorphous AlN films. The substrate temperature was always kept at 330°C.

From this reactive system, AlN films were successfully obtained in all these plasma atmospheres.

2.2 - Film characteristics :

- SEM :

Scanning electron micrographs (figure 1) show uniform, dense AlN coatings with an excellent adherence to the substrate and a very good step coverage. These results are independent of the excitation frequency choice and of the substrates material (polished Silicon wafers, graphite substrate or polycrystalline sintered Silicon Carbide). The surface shows a low defect density.

- ELLIPSOMETRY :

The refractive index of the film deposited on (100) Silicon wafer was measured at 30° incidence angle/9/ by a Plasmos SD2300 ellipsometer on Silicon wafer substrates. The n values vary between 2.0 and 2.2 with a 6328 Å wavelength in good agreement with the literature/10/ (n = 2.17).

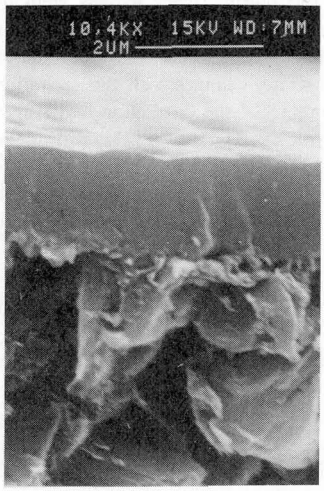


Fig. 1 : AlN coating on graphite substrate.

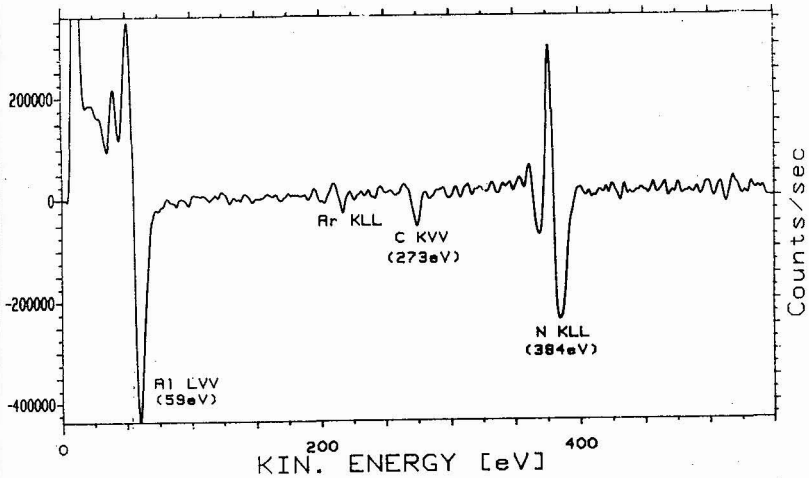


Fig. 2 : Auger electron energies spectra of AlN.

- IR ABSORPTION :

IR spectra of AlN deposited on (100) Silicon wafers were carried out with a Nicolet Fourier Transform Infra-Red (FTIR) spectrometer (model 5ZDX) in the 400-4000 cm^{-1} wave-numbers range. All the spectra show a broad single strong peak at 670 cm^{-1} associated to the stretching Al-N vibrating group. Two other absorption-band areas have also been identified in previous works/8/ : N-H (3205 cm^{-1}) and Al-H (2108 cm^{-1}). The Hydrogen source in the film was ammonia or TMA reactants.

- AES :

The samples Auger electrons were analysed by a Riber Mac-2 Auger spectrometer (analyser resolution is 1 eV). Parameters such as the primary beam electron energy and the gun electron emission current were kept constant. After a primary cleaning of the surface, the AES data are scanned while keeping ionic sputtering with a Riber CI 50 ion gun. The shift due to the charge effects for insulator materials and adsorbed surface contaminants (Oxygen and Carbon) were avoided by a surface cleaning.

In this way, the plasma deposits reveal few impurities : a small percentage of Carbon (2-4 %) and no Oxygen is detected (< <1 %), as shown in figure 2.

3 - INFLUENCE OF THE EXCITATION FREQUENCY :

3.1 - Deposition kinetics :

We have mentioned that in this work the situations in PECVD reactor differ only by the discharge frequency. First, the dependence on the deposition rate is studied in figure 3 for the three frequencies : 35-440 kHz and 13.56 MHz. The deposition rate decreases when the frequency value increases. Those differences mainly account for the ionic bombardment effects during the film growth (flux and energy of the positive incident ions) when the excitation frequency varies. This may cause changes in the growth kinetic, stucture, composition and stresses in the film. The higher ionic bombardment (with more energetic species at low frequency) favours an important number of adsorption sites/11/ and therefore increases the deposition rate.

Later on, we will study the structure variation and verify by AES, to know whether the composition is disturbed by frequency changes.

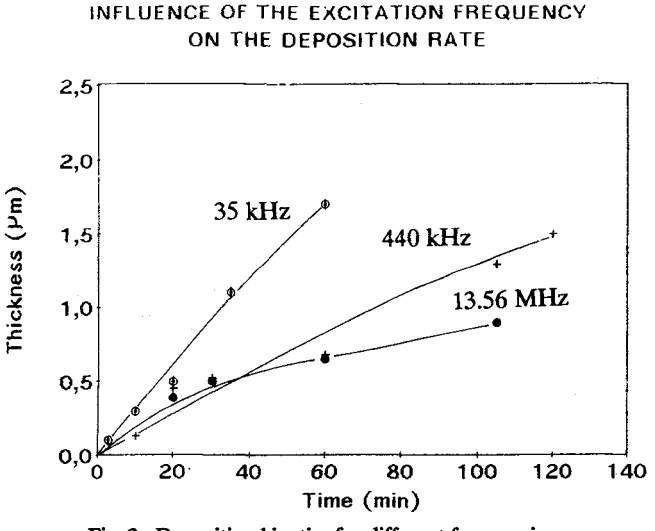


Fig. 3 : Deposition kinetics for different frequencies.

3.2 - X-Ray measurements :

3.2.1 - Frequency influence on the crystallite size.

We use a Curved Position Sensitive Detector for X-ray diffraction. In figure 4 significant differences in film crystallinity produced with high and low frequency RF excitations are observed when all the other parameters are the same. For the 35-110-440 kHz frequencies, the films diffraction patterns indicate a strong preferential orientation of the microcrystallites along the (1010) direction (ASTM data card n°25-1134). Only for the 13.56 MHz frequency no peak are present. AlN thin films are amorphous under these last synthesis conditions, which is in good agreement with the Hasegawa's works/6/.

Furthermore, the mean crystallite grain size is investigated, L (in Angstroms), from the measurement of the additional broadening due to small particles size (<2000 Å). The commonly accepted formula is the Scherrer formula/12/ :

$$L = (0.9\ \lambda) / (B \cos \theta_B)$$

where λ is the X-ray wavelength (Cu $K_{\alpha 1}$ radiation : λ = 1.54183 Å), θ_B the Bragg angle, and B the line broadening

obtained from the Warren formula/12/ :

$$B^2 = B_M^2 - B_S^2$$

where B_M and B_S are the full width half maximum (FWHM) for the film and the standard sample respectively. The (104) line (ASTM data card n°10-173) of α alumina powder (PECHINEY Gardanne) with a granulometry of 5.6 μm was choosed as a standard peak.

The crystallite size is similar for the 35 kHz and 110 kHz frequencies (with a 500-600 Å range) ; these values decrease until 260 Å at 440 kHz. In opposition to A. Matsuda/13/, an increase in the ions energy (low frequency) induces a decrease in crystallites size. The thin film becomes amorphous at 13.56 MHz (low ionic energy). For a given frequency, the crystallite dimensions are the same even though the coating thickness changes.

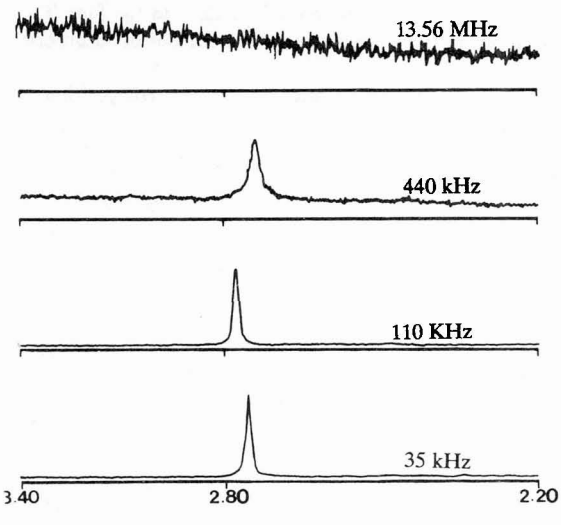


Fig. 4 : Influence of the excitation frequency on the film crystallinity.

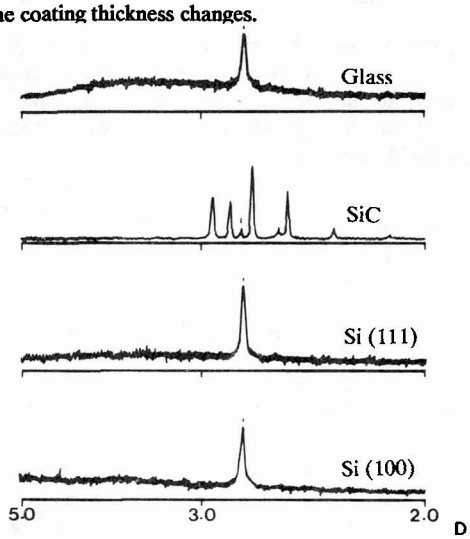


Fig. 5 : Influence of the substrate on AlN crystalline orientation.

Table 1 : Mean values of crystallite sizes (L).

Samples (thickness) (μm)	θ_B (°)	B_S or B_M (°)	B (Å)	L (Å) (+/- 50 Å)
Alumina (5.6)	17.45	B_S=0.14	-	granulometry= 5.6 μm
AlN-35kHz (0.5)	16.24	B_M=0.21	B=0.16	530
AlN-35kHz (1.2)	16.32	B_M=0.20	B=0.14	580
AlN-35kHz (1.73)	16.40	B_M=0.22	B=0.17	490
AlN-110kHz	16.13	B_M=0.21	B=0.16	500
AlN-440kHz	16.31	B_M=0.33	B=0.30	260

3.2.2 - Effect of the substrate :

A similar study investigated influences of both substrate crystalline orientation and surface roughness. In the figure 5, AlN is deposited on polished Silicon wafers with two different crystalline orientations (Si (100) and Si (111)) : no impact is observed. The same behaviours are shown on other crystallized substrates with more important roughness surface (sintered Silicon Carbide) and on amorphous glass plates. As it will be confirmed by crystallite size measurements (in table 2) and by TEM micrographs (figure 8), the type of substrates (crystallinity and roughness) has no consequential effects on the coating crystallinity.

Table 2 : AlN synthesized at 440 kHz for two experiments.

Substrates	θ_B (°)	B_M(°)	B(°)	L (Å) (+/- 50 Å)
Experiment 1 :				
glass plate	16.33	0.32	0.29	280
Silicon(100)	16.32	0.33	0.30	270
Experiment 2 :				
α Alumina	16.52	0.40	0.38	220
Silicon(100)	16.53	0.34	0.31	260

3.3 - IR and TEM :

3.3.1 - Infra-Red absorption measurements :

Figure 6 shows the broadening of Al-N band at a 13.56 MHz frequency which represents the amorphous AlN films with regard to the three others. This is in good agreement with the X-ray data.

An amount of Hydrogen can be trapped in the growing films. It is bonded to Aluminium or Nitrogen atoms. Figure 7 shows the height peak with respect to the coating thickness. A maximum quantity of hydrogen, bonded to Aluminium atoms, seems to exist for the amorphous samples. It may act an important part in the AlN amorphous state.

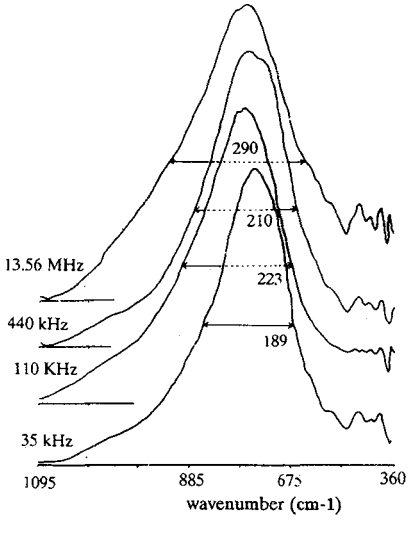


Fig. 6 : Broadening of Al-N vibrating bond.

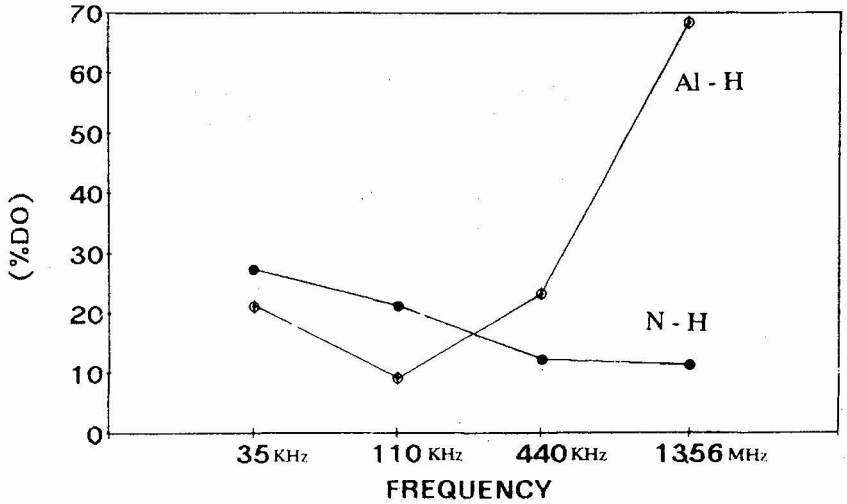


Fig. 7 : Intensities of Al-H and N-H bond observed in IR.

3.3.2 - TEM observations :

Sample preparations have been made by the cross section method/14/ and observed on a Jeol 200 CX-T. The micrographs (figure 8) reveals AlN crystallites with a perpendicular orientation to the (100) Silicon direction.

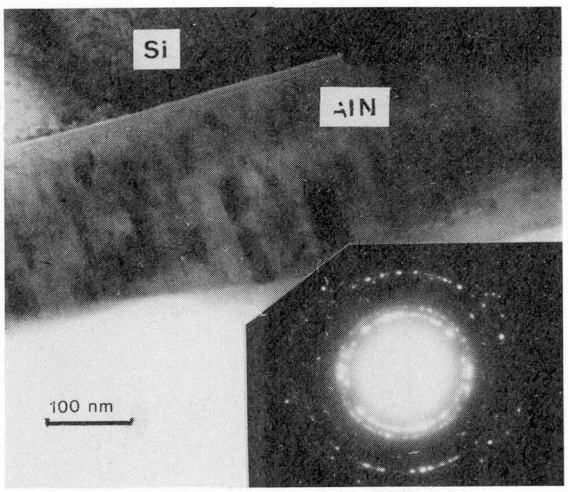


Fig. 8 : Bright field image of cross section with diffraction pattern of the AlN domain.

3.4 - AES analysis :

We were interested in the evaluation of molecular concentrations in the Al_xN_y films. They have been obtained from the E.N(E) Auger spectra scanned in the 50-520 eV range for the N KLL peak at 375 eV, and 1350-1450 eV for Al $KL_{23}L_{23}$ peak at 1390 eV. The intensity of the both peaks has been determined by measuring peak heights with respect to the background level/15/. The peak to background ratios (P/B) of the N KLL Auger transition measured on

the synthesized Al_xN_y and on the standard Si_3N_4 film (Philipps Eindoven) were compared. Identical comparaison is made with (P/B) of AL $KL_{23}L_{23}$ transition in Al_xN_y films and in pure Aluminium.

Table 3 : Molecular concentrations in the Al_xN_y films.

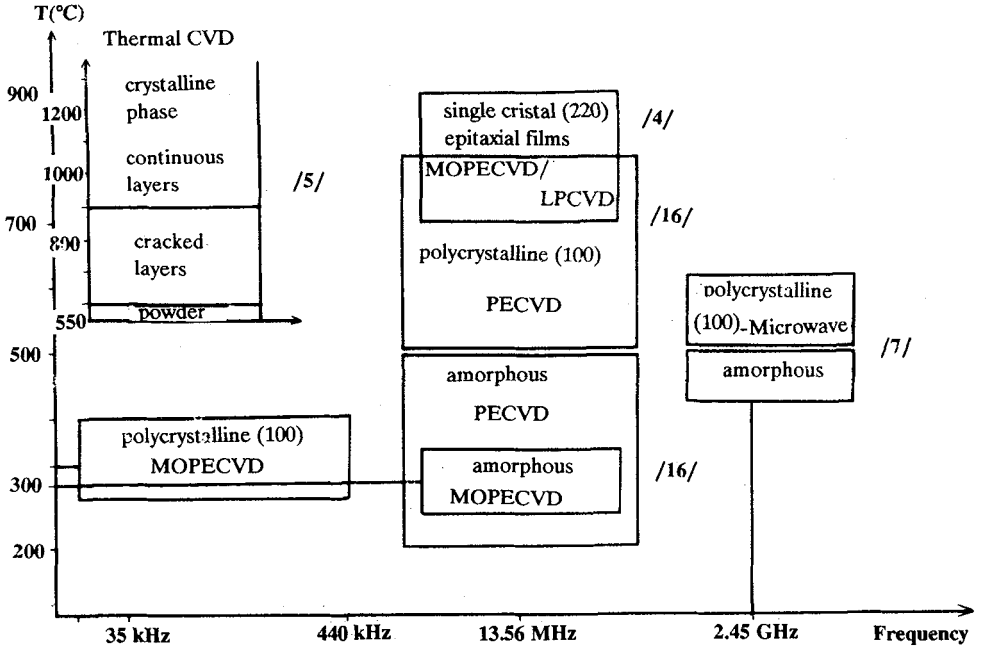
Samples	$(P/B)_{NKLL}$	$(P/B)_{AlKLL}$	d	C_N	C_{Al}	C_N/C_{Al}
	(+/- 0.02)			(mol / cm^3)		
references :						
Si_3N_4	0.5	-	3.12	0.089	-	-
Al pur	-	0.32	2.698	-	0.1	
experiments :						
35kHz	0.43	0.24		0.077	0.075	1.03
110kHz	0.45	0.21		0.080	0.067	1.19
440kHz	0.45	0.25	3.26	0.080	0.078	1.03
13.56MHz	0.47	0.26		0.084	0.081	1.04

In the following calculations, theoretical compound densities were considered without taking into account the small percentage of Carbon.

We can conclude that the values of Al and N molecular concentrations calculated using peak to background ratios for Al_xN_y have presumably a composition which is similar to AlN.

4 - CONCLUSION :

Table 4 : Influence of growing temperatures and frequency on AlN coating crystallinity.



We summarize in table 4, the AlN structure of thin layers obtained in various CVD methods. At high frequencies and low temperature, AlN is always amorphous whereas low frequencies lead to crystalline AlN. The crystalline orientation is strongly dependent on the temperature deposition.

In our conditions, we observed that the particules size of AlN $(10\bar{1}0)$ coatings (the deposition rate too) decrease when the frequency values increase. Furthermore, it has been shown that the substrate has no effect on the crystalline orientation. Above a frequency value of about 13.56 MHz, AlN thin films are amorphous. AES studies show that all the samples have a composition which is similar to AlN.

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