Elaboration of nitride thin films by reactive sputtering

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Resumo

O objetivo desse artigo, em um primeiro momento, é uma melhor compreensão da vaporização em um ambiente magnetron reativo DC e as suas conseqüências, tais como o efeito da histeresis e o processo de instabilidade. A segunda parte desse trabalho está dedicada a um estudo de caso: o nitreto de alumínio.

Filmes finos de nitreto de alumínio foram depositados por vaporização triodo reativa. Estudamos o efeito dos teores de nitrogênio, na descarga, e da voltagem RF(bias), no crescimento dos filmes de AlN em Si(100) depositados por vaporização triodo. A estequiometria e a orientação cristalina dos filmes de AlN foram caracterizadas por espectroscopia infravermelha em transformada de Fourier, difração de raios X e microscopia de elétrons secundários. Camadas densas e transparentes de AlN foram obtidas em altas taxas de deposição. Independentemente do conteúdo em nitrogênio na descarga, os filmes têm uma orientação (002), mas, para um teor de 10%, obteve-se a melhor cristalização.Uma relação linear foi observada entre o parâmetro de rede c (perpendicular à superfície do substrato) do AlN e as tensões compressivas planas.A aplicação de um “bias” RF ao substrato leva a uma textura (100) e os filmes tornam-se amorfos. Além disso, a tensão compressiva aumenta atingindo valores de até 8Gpa antes de diminuírem lentamente na medida em que o “bias” aumenta.

Palavras-chave: vaporização em ambiente magnetron reativo DC, nitreto de alumínio, taxas de deposição.

Abstract

The aim of this paper is first a better understanding of DC reactive magnetron sputtering and its implications, such as the hysteresis effect and the process instability. In a second part, this article is devoted to an example of specific application : Aluminium Nitride.

AlN thin films have been deposited by reactive triode sputtering. We have studied the effect of the nitrogen contents in the discharge and the RF bias voltage on the growth of AlN films on Si(100) deposited by triode sputtering. Stoichiometry and crystal orientation of AlN films have been characterized by means of Fourier-transform infrared spectroscopy, X-ray diffraction and secondary electron microscopy. Dense and transparent AlN layers were obtained at high deposition rates. These films have a (002) orientation whatever the nitrogen content in the discharge, but the best crystallised ones are obtained at low value (10%). A linear relationship was observed between the AlN lattice parameter “c” (perpendicular to the substrate surface) and the in-plane compressive stress. Applying an RF bias to the substrate leads to a (100) texture, and films become amorphous. Moreover, the film’s compressive stress increases up to a value of 8GPa before decreasing slowly as the bias voltage increases.

***Keywords**: DC reactive magnetron sputtering, aluminium nitride, deposition rates.*

1. Introduction

Reactive sputtering is a method to deposit films which have a different composition from the target by adding a gas to the sputtering system to produce a material by reaction of the gas with the target material.

It has become a very popular technique in today's search for new material properties, for the deposition of a very wide range of compound and alloy thin films including oxides, nitrides, carbides, fluorides or arsenides. Besides the improved properties of non-reactively sputtered films, the popularity of DC reactive sputtering from elemental targets can be attributed to several factors, among them:

- It is capable of producing thin compound films of controllable stoichiometry [1] and composition [2] at high deposition rates and on an industrial scale [3-5] .
- Elemental targets are usually more easily purified, and hence, high-purity films can be produced [6].
- The complexity and expense of RF systems can be avoided since metallic targets are generally electrically conductive, and hence, DC power can be applied.
- Elemental targets are usually easy to machine and bond.
- Metallic targets are thermally conductive, which makes the cooling of these targets more efficient thus, the range of the applied power can be extended e.g. up to 50 $W.cm^{-2}$ and higher without the fear of being cracked.
- Films are deposited at temperatures less than 300°C [7].

Although reactive sputtering is conceptually simple, it is in fact a complex and non-linear process which involves many interdependent parameters [8]. The presence of the reactive gas at both the cathode surface and the substrate results in strong interactions of the reactive gas not only with the condensing material but also with the cathode surface, the so-called target poisoning. Reactions in the gas phase are ruled out for the same reasons that ions cannot be neutralised in the gas phase there is no mechanism which can dissipate the heat of neutralisation to conserve both momentum and energy in a two-body system, therefore it can only happen at a surface [9]. These cathode reactions are seen to increase suddenly at some rate of reactive gas flow. If flow control of reactive gas is used, such reactions are marked by a change in the impedance of the operating plasma, an abrupt increase in the system pressure or more precisely, in the reactive gas pressure, a drastic drop in the deposition rate and a change in the film from metal-rich to gas-rich i.e. a change in the stoichiometry .

2. The hysteresis effect and process instability

Figure 1 shows the well-known and important feature of reactive sputtering at a constant partial pressure of non-reactive gas, when flow control of reactive gas is employed; an hysteresis curve of the totale gas pressure, P , as a function of the reactive gas flow rate, f , at a constant sputtering power.

At low values of f all the available reactive gas is gettered at the condensation sites. As a result, no essential change in P is observed from the background level and the deposited film is metal-rich. This situation prevails until f reaches a critical value where the flow rate of the reactive gas into the chamber becomes higher than the gettering rate of the sputtered metal. The reactive gas reacts, then, with the target surface to form a layer of the gas-metal compound. Sputtering rates from compound targets are less than that of pure metallic targets, for mainly two reasons: first the sputtering yield of metal atoms from a compound on the target surface is less than that from a pure metallic target; and secondary compounds have higher secondary electron emission coefficients than metals and hence most of the energy of the incident ions is utilised to breaking bonds with the resultant creation and acceleration of secondary electrons. Consequently, less metal atoms are sputtered and less reactive gas is consumed in the reaction, and a sudden and sharp rise in the reactive gas partial

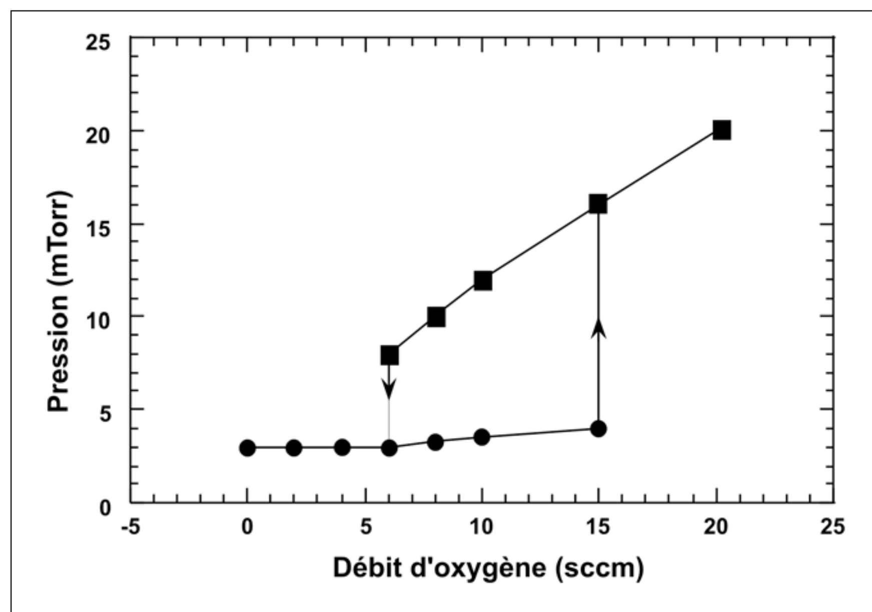

Figure 1 - Reactive sputtering at a constant partial pressure of non-reactive gas, when flow control of reactive gas is employed.

pressure occurs. The deposited film is then gas-rich. If *f* is reduced following an increase in *P* to a high level, *P* will not decrease following the same trajectory as it increased. The pressure *P* will stay constant until some value *f* where it abruptly increases and the reactive gas pressure decreases to the background level. This is because the reactive gas pressure remains high until the compound layer on the surface of the target is removed and metal is exposed to be sputtered once more. As a result, the consumption of the reactive gas increases and the deposited film is metal-rich again. The dependence of deposition rate on reactive gas flow rate is seen in Figure 2.

The hysteresis effect is very undesirable and is strongly dependent on the pumping speed, for example for a reactive gas flow of 10 sccm (0.12 Torr.l / s), the partial pressure of nitrogen would be 1.2 mTorr with a 100 l /s pump and 0.12 mTorr with a 1000 l /s pump.

3. Application to deposition of AlN thin film

3.1 Introduction

Aluminium Nitride could be used in many applications such as corrosion protection [10-13], passivation layers, dielectric films, insulating layers [14], solar cell coatings [15], short wave-length emitters, and is probably one of the most promising piezoelectric material for high frequency surface acoustic waves (SAW) devices [16] and thin films acoustic bulk resonator (FBAR) [17] because of its low acoustic loss and high ultrasonic velocity [18-20].

The use of AlN films for such applications, depends very much on the stoechiometry, transparency and texture of the films. AlN is prepared by various techniques, such as microwave plasma chemical vapour deposition [21], metallo-organic chemical vapor deposition [22], plasma-assisted molecular beam epitaxy [23] and reactively radio-frequency magnetron sputtering [24]. In this study, AlN films were deposited by triode reactive sputtering of an Al metal target on silicon and fused quartz substrates. The influence of nitrogen content in the discharge and the r.f. bias voltage applied to the substrate on the deposition rate, stoechiometry, the structural properties of the films and the stress have been studied.

3.2 Experimental

Triode Sputtering (TS)system (Figure 3) consists of a water cooled iron chamber (47cm x 18.5cm x 4cm) pumped down to 10^{-4}Pa by a diffusion pump.

The electrical discharge is created by an electron emitting hot tungsten filament (Ø=500µm) and a plate anode. Two removable magnetic coils assure a high rate of ionisation which enables to work at pressures as low as 0.05Pa. The target is made on 99.99% pure aluminium, nitrogen and argon were used as the discharge gases. AlN layers were deposited on silicon (100), fused glass substrates by varying nitrogen ratio $R_N=P_{N2}/(P_{N2}+P_{Ar})$ (P_{N2} and P_{Ar} are the nitrogen and argon partial pressures) and the RF bias voltage applied to the substrate. The spontaneous heating by the DC plasma give a substrate temperature of approximately T~300°C without substrate biasing (measured with a K type thermocouple) whereas it increases as the substrate bias voltage is applied. The aluminium target is cleaned in argon discharge during 20 minutes and pre-sputtered during 20 minutes as well before each deposition. A shutter in front of the target prevents deposition on substrates during these periods. The deposition conditions are summarised on Table 1.

The crystal structure of films were analysed by XRD in θ-2θ scaning mode using K_α copper radiation, Raman spectroscopy and Fourier-transform infrared spectroscopy. The composition of the films were measured by energy dispersive X-ray analysis (EDS). The mechanical stress was calculated from substrate curvature using the Stoney formula [25]. The substrate curvature and film thickness were measured by Dektak 3030 profilometer. The film's mass was measured using a micro-balance (Δm=0.3µg). The morphology of the films were observed by scanning electron microscopy (SEM) and optical properties were investigated by UV-Visible transmission spectrometry.

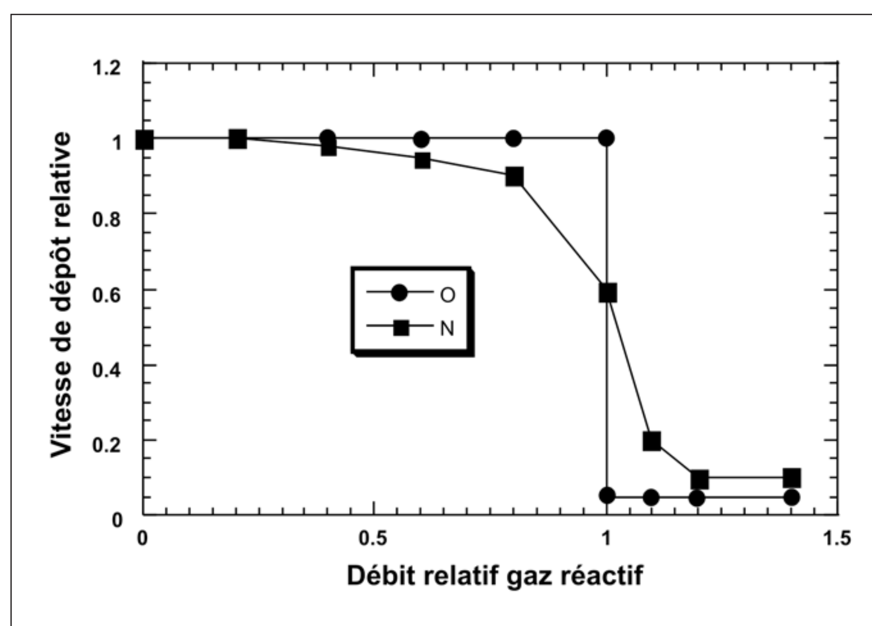

Figure 2 - Dependence of deposition rate on reactive gas flow rate.

3.3 Influence of the r.f. bias voltage

As AlN is a nonconductive material, an R.F. bias voltage has been used to study the influence of bias voltage applied to the substrate during deposition. The XRD patterns exhibit 2 kinds of preferential orientations for a self bias voltage varying from 0V to -200V. Firstly, the film deposited without bias presents an huge peak at 2θ=36° with a full width at half maximum (FWMH) of 0.179° which corresponds to a highly oriented (0002) w-AlN (JCPDS 25-1133). Secondly, by increasing the bias voltage, only a small peak located between 2θ=32° and 2θ=33° which could be attributed to (220) c-AlN (JCPDS34-679) or (100) h-Figure 2). At the same time, after a large rising until the substrate bias voltage value of -50V, the compressive stress slightly decreases for higher voltage (Figure 3). This behaviour is in good accordance with the model proposed by C.A. Davis [26]. However, these results indicate that the bias voltage, then the ion bombardment during the deposition process, leads to a change in the films texture and stress. The films switch from (002) orientation to (100) one and become amorphous for high bias voltages, whereas the stress largely increases and slowly decreases for higher bias voltage.

In general, the application of a bias voltage during film growth leads to thin films having better structural properties [27]. However, in such assisted discharge as triode sputtering one, the difference between the plasma potential and the floating potential is large (~30V) which corresponds to an ion energy bombardment strong enough to enhance the crystalline growth of the film without bias [28].

According to the literature, there are three concomitant phenomena to explain the (100) or (002) orientation growth :

- It is generally considered that the basal plane in the hexagonal structure has the lowest surface energy and the maximum atomic density [29].
- Al is very easy to sputter then for ions energy higher than 50eV there are

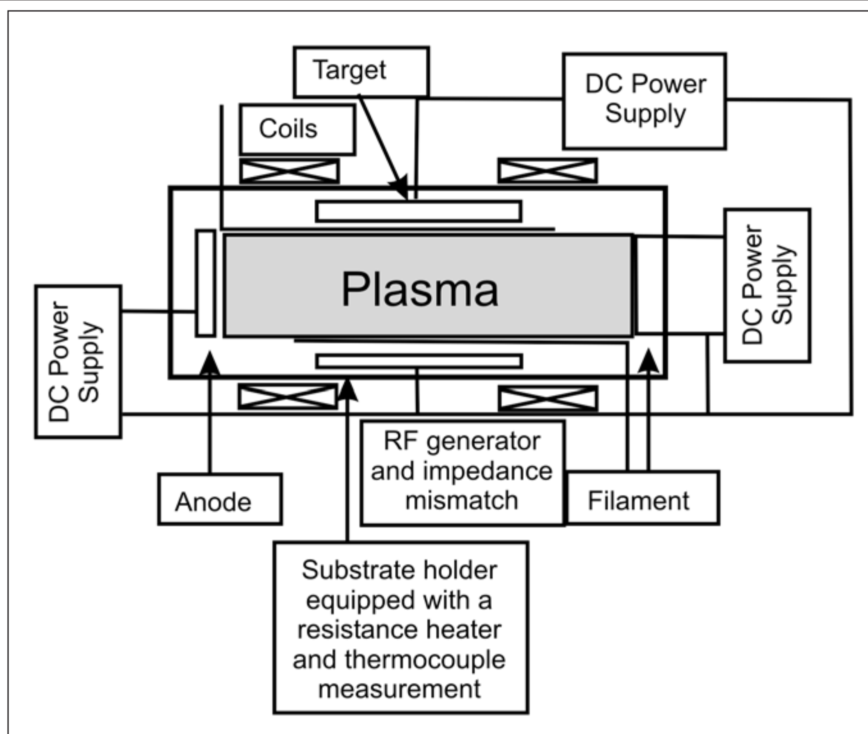

Figure 3 - Triode Sputtering System.

Table 1 - Sputtering conditions of aluminium nitride films.

Target	**Aluminium (99.999%, 7.5cm diameter)**
Target to substrate distance	5cm
Substrate	(100)Si , glass, (001)Al_2O_3
Base pressure	10^{-4}Pa
Sputtering pressure	0.5Pa
Nitrogen ratio: R_N	0-100%
Target current	100mA
Target voltage	1000VDC
Coils current	3A
Anode voltage	150V
Substrate bias voltage	0 to 200(-V)
Deposition temperature	300-600°C

- perturbations in the growing film due to resputtering.
- The plane h-AlN (100) is composed of lower energy bonds than the plane h-AlN (0002) [30].

Then, it needs medium energetic species (usually obtained in high power discharge) or substrate heating to obtain (0002) oriented h-AlN thin films. For discharges which have a plasma potential higher than 20V such as R.F. and triode discharge, a bias voltage onto the substrate is detrimental to good quality layers in contrary to low plasma potential discharge such as DC discharges (V_p~2-3V) where a low bias voltage could be beneficial to obtain high oriented (0002) h-AlN layers [28].

3.4 Influence of the sputtering gas composition

The mass (v_m) and thickness (v_t) deposition rates as function of the nitrogen ratio in the sputtering gas are shown in Figure 4.

The deposition rate drops at R_N=10% from v_t=5.1µm/hto v_t=1.3µm/h and then decreases slowly to v_t=0.5µm/h as the nitrogen ratio increases. The deposition rates are close in magnitude to those obtained with reactive magnetron sputtering [31,32]. These rate behaviours are attributed to the compound formation on the target surface. It is well known, that when we introduce a reactive gas such as N_2 or O_2 in the discharge, the deposition rate decreases rapidly at the transition between metallic mode to poisoning mode [9]. The best compromise is located between a high deposition rate (metallic mode) and steochiometric films (nitride mode). The film density was determined from the thickness and the mass measurement. It is found that the density is situated between 3.2 and 3.3 which is in good agreement with the bulk density (3.25).

The film stœchiometry were evaluate by EDS analysis measurements (Figure 5).

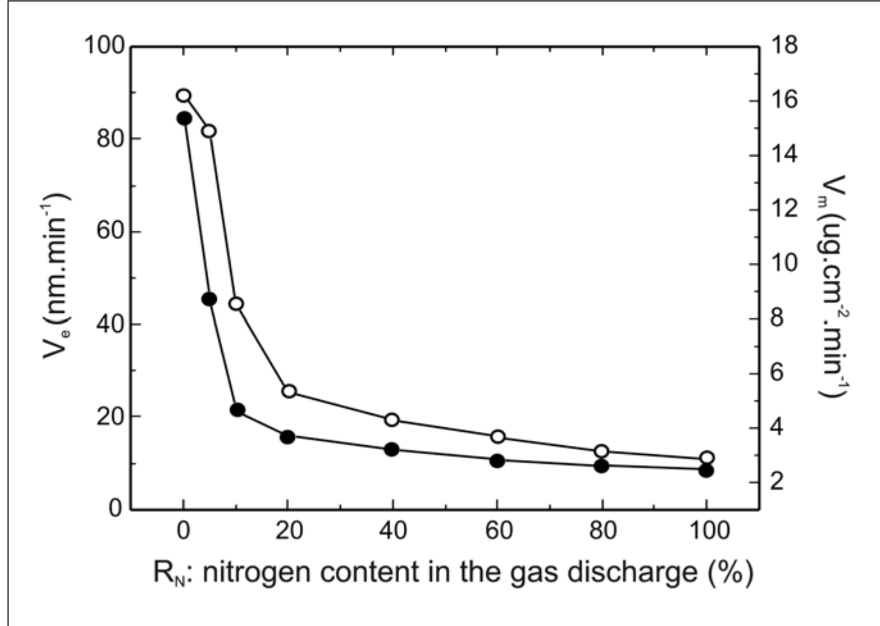

Figure 4 - Mass and thickness deposition rates as function of nitrogen ratio.

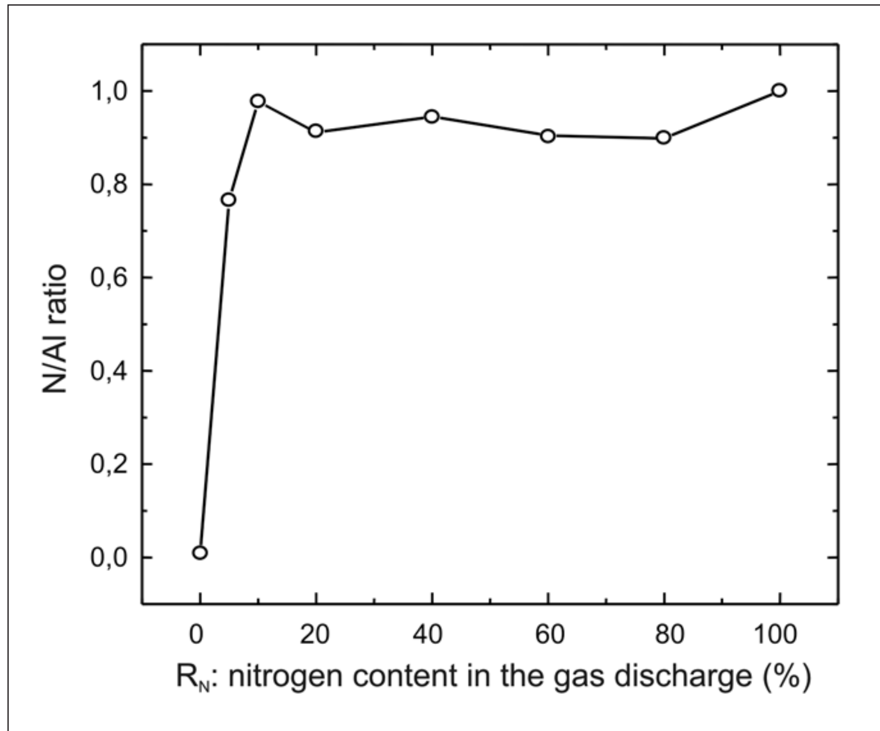

Figure 5 - Influence of the sputtering gas composition on film stoechiometry.

One can see that the main constituents of the films are aluminium and nitrogen. We can see a small contamination with oxygen, probably due to the air exposure . The calculated ratio Al/N is a little bit lower than 1 which is attributed to a charge effect during analysis [20,32]. Stœchiometric films are obtained for ratio R_N≥10%. The films obtained with R_N=5% are substoechiometrics and look green-yellow whereas for higher percentages of nitrogen, the films are stoechiometric and transparent. These results indicate

that the target surface become fully nitrided as the nitrogen ratio in the sputtering gas exceeds 10%, at this point the surface target is probably constituted of AlN.

Formation of aluminium nitride was also supported by FTIR spectrometry. The films were characterised in normal and oblique incidence methods using unpolarized light in the range 400-4000cm^{-1}. The spectra were obtained by computer subtraction of the Si (100) substrate absorption (background).

These spectra (Figure 6) exhibit a unique absorption peak for n=675cm^{-1} which is characteristic of Al-N bond: the E_1 transverse optical (To) mode [33]. For 5% N_2, the spectrum presents a large FWMH ($\Delta\nu$=274cm^{-1}) which is attributed to the non stoechiometry of the film. For the higher percentages, the FWMH is lower than 116 cm^{-1} and minimum for 20% N_2 ($\Delta\nu$=88cm^{-1}). These values are comparable to the ones obtained by H. Windischmann at the same temperature [34]. Nevertheless, they are higher than those obtained with substrate heating up to 700°C ($\Delta\nu$=56cm^{-1}) and 5 times higher than a c-axis monocrystal ($\Delta\nu$=20cm^{-1}) [34].

The texture of AlN film deposited on Si (100) have been analysed by XRD (Figure 7).

AlN films show a (002) preferential growth with a peak at 2θ=36°. One can note that the (002) peak position decreases as the nitrogen ratio increases, indicating that AlN films have residual tensile strain along the c axis, perpendicular to the substrate [20,32] as the R_N is increasing. This strain is correlated to the compressive stress determined from curvature measurement as it can be observed on Figure 8.

Such tensile strain perpendiculars to the in-plane compressive stress with a linear relationship have been only reported by S. Six et al. [35] until now. For stoichiometric films, the FWHM increases from 0.179° to 1.761° as the N_2 percentage in the discharge increases. These results indicate that the most crystallised films are obtained at low nitrogen ratio. In addition, the SEM cross-section (Figure 9) of a thick AlN film deposited on the optimal condition shows a dense structure and a smooth surface that is confirm by AFM in contact mode. The determined root mean squared rougghness is R_{RMS}~2nm. These results shows that stœchiometric AlN films with c orientation were obtained by triode sputtering without external substrate heating at low nitrogen content.

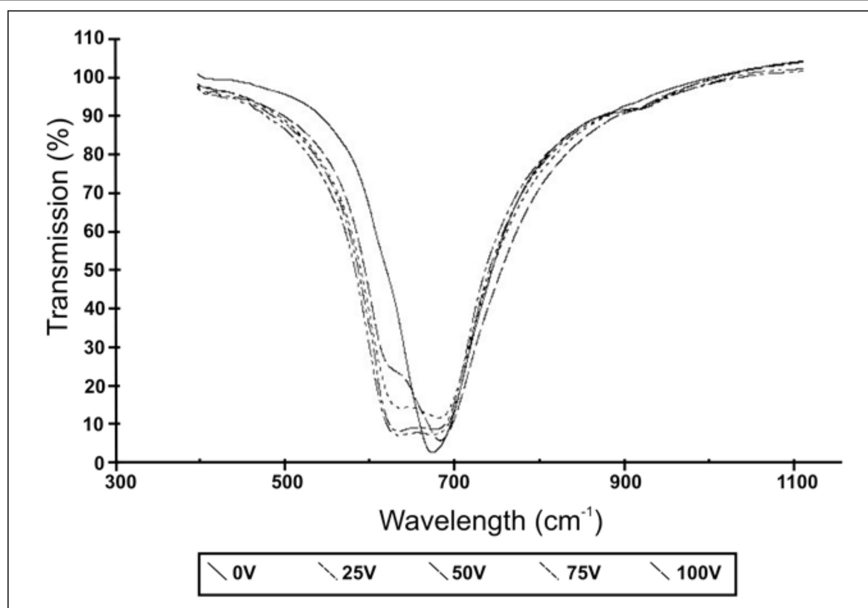

Figure 6 - FTIR spectrometry of films.

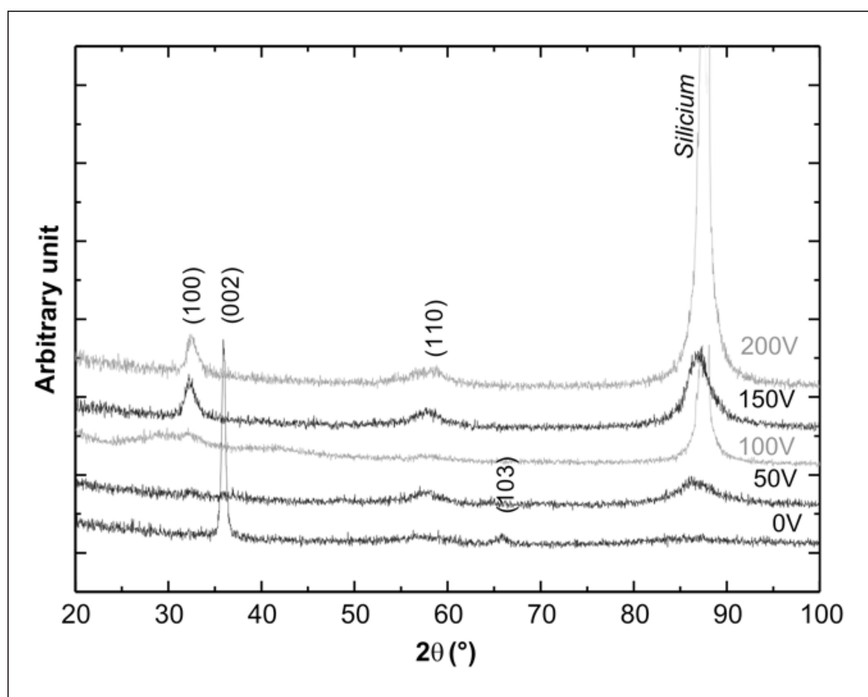

Figure 7 - X rays diffraction patterns of AlN.

4. Conclusion

Effect of nitrogen content in the discharge and the RF bias voltage on the growth of AlN films on Si(100) deposited by triode sputtering have been studied. Stoechiometric, dense (ρ~3.2 - 3.3), transparent AlN films are deposited as long as the target surface is fully nitrided (i.e. $R_N \geq 10\%$). The AlN grow was confirmed by the presence of the E_1(To) absorption mode in normal incidence FTIR. These films have an (002) orientation whatever the nitrogen content in the discharge but the best crystallised one are obtained at low value (i.e. R_N=10%). A linear relationship were observed between the AlN lattice parameter c (perpendicular to the substrate surface) and the in plane compressive stress.

When an RF bias substrate is applied to the substrate holder, the texture shifts to (100) one and films become amorphous. Moreover, the film's compressive stress increase to a value up to 8GPa before decreasing slowly as the bias voltage increase.

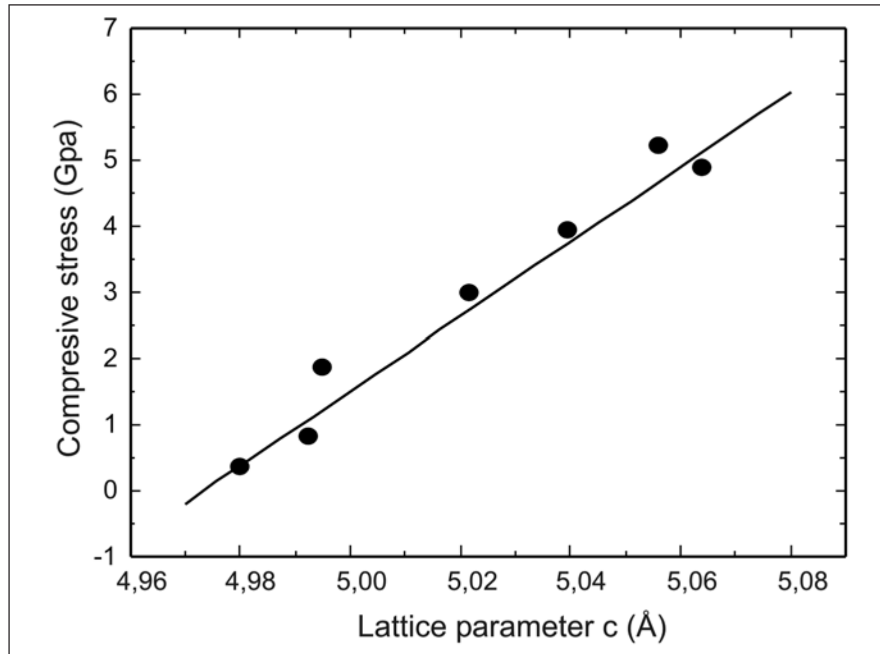

Figure 8 - Lattice parameter and Compressive Stress relationship.

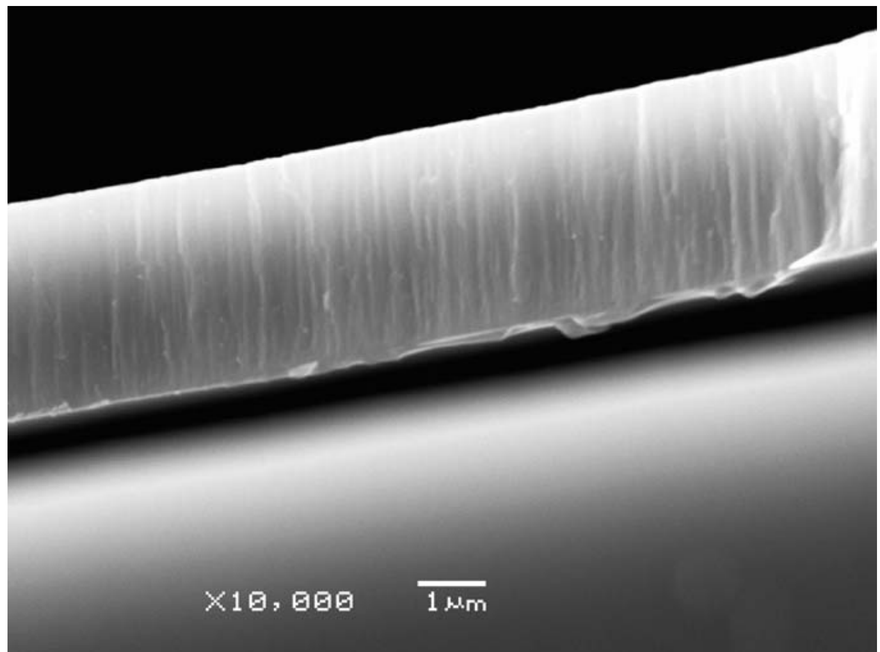

Figure 9 - SEM cross-section of a thick AlN film deposited on the optimal condition.

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Artigo recebido em 25/07/2005 e aprovado em 10/02/2006.

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