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RADIOFREQUENCY REACTIVE SPUTTERING FOR DEPOSITION OF ALUMINIUM NITRIDE THIN FILMS

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RÉSUMÉ

Une cible d'aluminium est pulvérisée dans un mélange gazeux constitué d'argon et d'azote. Des résultats expérimentaux sont donnés concernant l'influence de l'azote sur les caractéristiques électriques de la décharge et sur le processus de dépôt. L'ionisation est plus intense et la vitesse de dépôt décroit en présence d'un tel gaz réactif.

Ces résultats, ainsi que l'étude du site de nitruration font l'objet d'une interprétation. La réaction se produit au niveau du substrat et une vitesse critique de dépôt de nitrure est obtenue. Pour des vitesses inférieures au seuil, les films ont été caractérisés comme étant constitués de nitrure AlN, les couches devenant semi-métalliques (Al–AlN) à vitesse de dépôt plus élevée. Les couches isolantes de nitrure d'aluminium ont fait l'objet de mesures électriques, optiques et cristallographiques. La constante diélectrique, la tangente de l'angle de pertes, le champ de claquage, les propriétés optiques et le spectre infrarouge dépendent de la vitesse de dépôt et de l'épaisseur des films d'AlN.

SUMMARY

An aluminium target was reactively sputtered in an argon–nitrogen mixture and the influence of nitrogen on the electrical characteristics of the discharge was studied.

In nitrogen, ionization is intensified and the deposition rate is increased. A tentative interpretation is given. For a set of deposition conditions, a critical rate of deposition was found. Below this rate films are AlN. This critical rate varies linearly as a function of the nitrogen quantity in the bell jar. A study of the nitridation shows that a synthesis reaction occurs on the substrate.

Electrical, optical and crystallographic measurements were made on the films, and dielectric constant, losses, dielectric breakdown field, optical index and infrared transmittance spectrum were investigated *versus* deposition rate and film thickness.

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1. INTRODUCTION

The investigation of AlN films is of interest in the field of insulating refractory materials. The piezoelectric properties of aluminium nitride suggest a possible application as a thin film transducer material[1,2]. We are only concerned in this paper with the preparation and the characterization of AlN films[3,4].

The reactive sputtering processes are then investigated and the multiple effects of nitrogen in the RF discharge are evaluated by comparison with argon.

2. EXPERIMENTAL

A complete description of the apparatus used has been given elsewhere[5]. The sputtering experiments were carried out in a modified "RF Sputtering" module. The vacuum in the bell jar is about 1×10^{-6} torr. Argon and nitrogen are admitted separately through needle valves. First, the nitrogen partial pressure is set at some few millitorrs, argon is then admitted until the desired total pressure is reached.

A generator and a coupling unit provide the target with RF power. This unit transforms the load impedance of the sputtering discharge to a value suitable for the output of the generator (50 Ω). The maximum power available in the plasma is 1 kW at a frequency of 13.56 MHz. The anode and the aluminium target are water cooled. The target diameter is about 10 cm. Substrates are mounted on the anode plate and clamped to achieve a good thermal contact. The relative temperature rise on the substrate is measured by a thermocouple enclosed in a copper sheet. This sheet is clamped to a 1 mm glass slide.

The following electrical parameters are measured:

RF forward power and reflected power;

RF peak voltage and d.c. bias voltage on the target.

Substrates are monocrystalline silicon slices (1 in. diameter) which have a good thermal conductivity.

3. DEPOSITION PROCESS

3.1. Influence of nitrogen on the deposition rate and on the RF plasma characteristics

The first important parameter in the preparation of thin films is the deposition rate. This rate decreases in Ar–N_2 sputtering gas when the nitrogen percentage

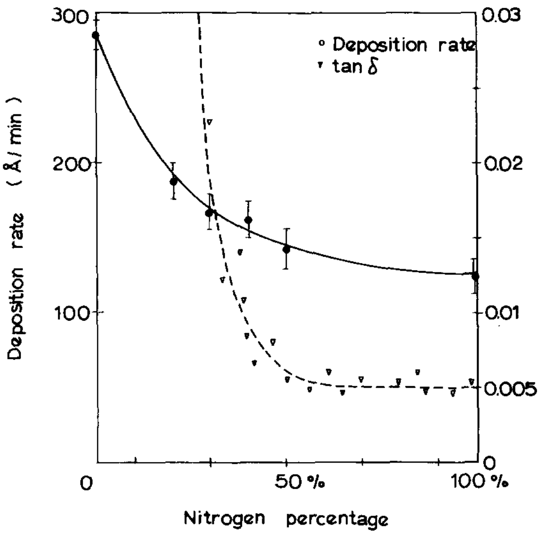


Fig. 1. Deposition rate and dissipation factor (tan δ) *vs.* nitrogen percentage (power and total pressure are constant) $p_{\text{total}} = 3 \times 10^{-3}$ torr.

increases as shown in Fig. 1. The electrical properties of the films, particularly dielectric losses are seen on the same figure. AlN dielectric films are synthesized when the nitrogen proportion is large enough. The slope of the deposition rate curve is unexpected. Indeed, the rate should be linearly decreasing with the replacement of argon by nitrogen. (The N_2^+ yield is about half the Ar^+ value).

To delimit the effect of the reactive gas only, we have added a variable amount of nitrogen to a given constant pressure of argon. Curves are plotted in Fig. 2 and

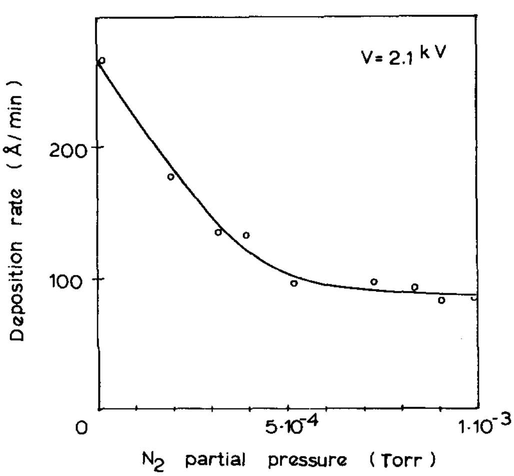


Fig. 2. Deposition rate *vs.* N_2 partial pressure at constant voltage, the argon pressure being maintained at 1×10^{-3} torr.

show the deposition rate to decrease when a small amount of nitrogen is added to the discharge, the Ar^+ sputtering rate being theoretically constant when the nitrogen pressure is increased. Moreover the substrate equilibrium temperature is measured during the deposition process and is found to increase sharply with the nitrogen percentage. There is a temperature difference of about 300 °C between discharges of nitrogen and argon at the same pressure (Fig. 3). This last result seems to indicate that the plasma properties are changed. That is confirmed by the increase in discharge current with the nitrogen percentage; the RF power increases when the d.c. bias voltage (or RF peak voltage which is equivalent) is maintained constant (Fig. 4). The composition of the films is evidently dependent on the reactive gas composition, but we shall see that the other deposition parameters (power and interelectrode spacing) can change the deposition rate and consequently the composition of the films.

3.2. Influence of the deposition rate on the composition of films–Critical rate for AlN deposition

We shall examine now what happens when the nitrogen partial pressure is kept constant, the deposition rate being varied by adjustment of the power, the total pressure or the target to substrate spacing. There is a transition from AlN (when the rate is low) to a metallic Al–AlN compound near a critical point (critical deposition rate of stoichiometric AlN film). Losses increase and the breakdown field decreases as shown in Fig. 5. The critical rate is linearly dependent on the N_2 proportion (Fig. 6). It may be noted that the target to substrate distance

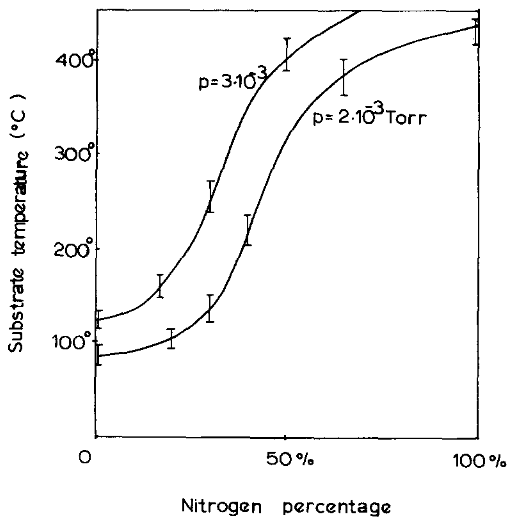


Fig. 3. Substrate equilibrium temperature *vs.* nitrogen percentage for two values of total pressure (2×10^{-3} and 3×10^{-3} torr).

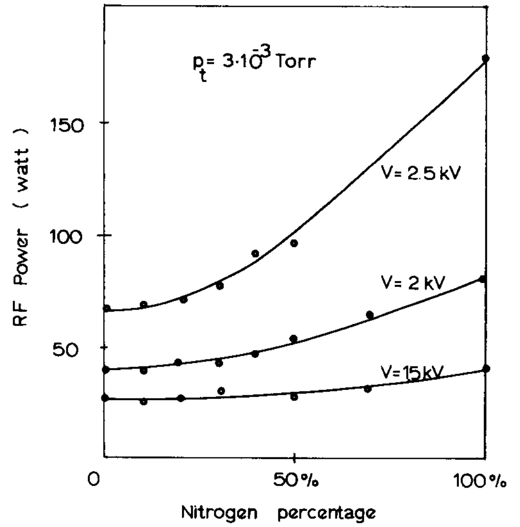


Fig. 4. RF power as a function of nitrogen percentage for three values of d.c. voltage. (Total pressure is 3×10^{-3} torr).

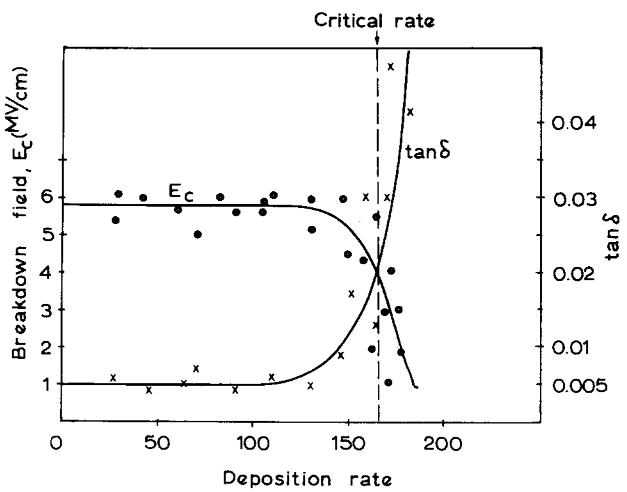


Fig. 5. Breakdown field and dissipation factor *vs.* deposition rate (total pressure 3×10^{-3} torr, nitrogen percentage 30%, spacing 5 cm).

has no effect on the critical rate; nevertheless this rate is increasing with the total gas pressure (Note that the deposition rate varies with the interelectrode spacing, but its critical value is unchanged).

These results are summarized in Fig. 7. The nitridation boundary is a linear function of the absolute quantity of nitrogen in the bell jar.

4. DISCUSSION

4.1. Nitrogen pressure effects

In nitrogen, ionization is experimentally more important; several possible explanations are listed below.

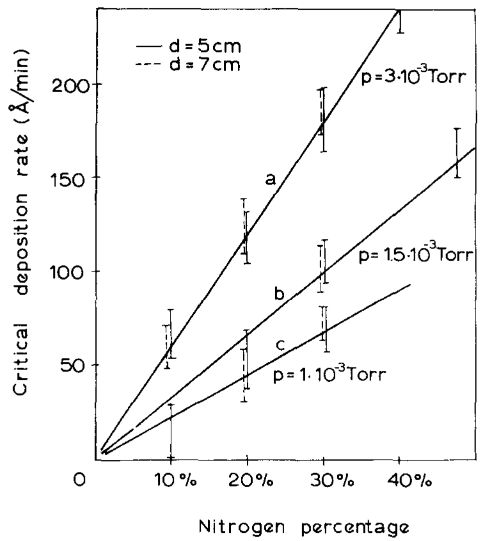


Fig. 6. Critical deposition rate *vs.* nitrogen percentage for three values of total pressure (a) $p = 3 \times 10^{-3}$ torr (b) $p = 1.5 \times 10^{-3}$ torr (c) $p = 1 \times 10^{-3}$ torr. The target to substrate spacing is 5 cm or 7 cm.

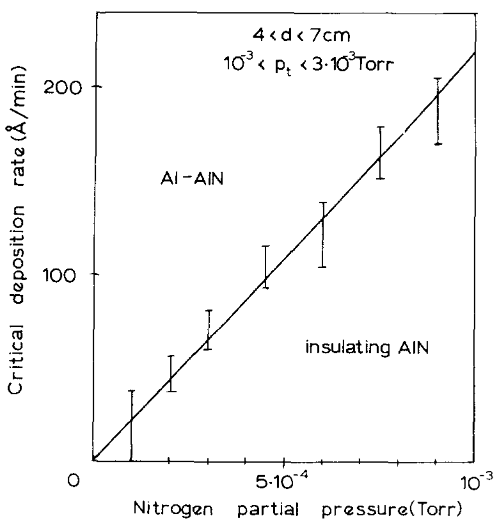


Fig. 7. Critical deposition rate as a function of the nitrogen pressure only, whatever the conditions are.

(i) The discharge current depends on the square root of the ion mass. The current will increase in nitrogen (lower mass than the argon one).

(ii) The probability of N^+ ions is certainly weak but not negligible (two electrons being liberated by each ionizing collision).

(iii) The secondary electron emission from the target can increase in the reactive gas.

The number of electrons and ions that strike the substrate plane would increase with the nitrogen percentage and then the substrate temperature. Although the ionic density is higher as mentioned above, the deposition rate decreases when nitrogen is admitted. Even with a small quantity of reactive gas, we think that there could be adsorption or chemisorption of nitrogen on the aluminium target surface, inhibiting sputtering and masking the increase of current density.

4.2. *Reactive sputtering process*[6, 7]

We suppose that, when the quantity of reacting nitrogen is not sufficient or the deposition rate too high to allow a complete nitridation, metallic particles are in significant concentration in the films (Al–AlN). A complete nitridation reaction is achieved only if the ratio between the aluminium flux to the substrate and the density of nitrogen molecules is lower than a critical value.

We can write the following equations

$[\phi \text{ Al}]$ critical $= K.\phi \text{N}_2$

that is to say $v_c = K' p\text{N}_2$

with $[\phi\text{Al}]$ is critical aluminium critical flux, ϕN_2 is nitrogen colliding rate on the substrate, v_c is critical deposition rate, $p\text{N}_2$ is partial pressure of nitrogen, and K and K' are constants.

So we assume that nitridation takes place on the substrate. The nitrogen molecules are adsorbed on the growing aluminium layers and combine with the metal atoms. The energy required for a chemical reaction is provided by the sputtered atoms and charged particles from the plasma.

5. NOTES

Nitridation could occur on the aluminium target (nitride molecules being sputtered) during the target to substrate transit of the Al atoms, or on the substrate as we assume. We exclude the possibility of a nitridation process in the vapour phase. The gas pressure is about 10^{-3} torr and the mean free path of aluminium in nitrogen is 7 cm, the target to substrate spacing 4 to 5 cm only. That could explain that this spacing has no influence on the critical deposition rate.

The possibility of nitridation on the target surface cannot be excluded but is a secondary effect. Indeed, the important critical parameter is the deposition rate and not the sputtering rate on the target surface which depends on the total gas pressure and on the electrode spacing.

Optimum conditions for AlN film deposition are summarized below:

Target to substrate spacing:	4 cm
Total pressure:	3×10^{-3} torr
Nitrogen partial pressure:	1.5×10^{-3} torr (50%)
d.c. bias voltage:	3.5 kV

The RF power level is about 250 W and the deposition rate as high as 250 Å/min.

Pure nitrogen discharge is unattractive because of the temperature rise of the parts exposed to plasma.

6. CHARACTERIZATION AND PROPERTIES OF AlN

6.1. Measurements

The thickness of the deposit is checked with a Talysurf. An aluminium coating is deposited on the AlN film by evaporation. This metallic film is etched to form the upper electrodes. The silicon slice is biased to achieve a metallic contact for the lower electrode (n^+doped layer). A capacitance bridge allows measurements of the dielectric constant and losses.

6.2. Structural properties

Our first purpose was to determine the deposited film structure. The electron transmission diffraction experiments indicate a polycrystalline structure with an average crystallite size of a few hundred angströms. The lattice is of the hexagonal wurtzite type, the lattice parameters being the bulk material values (see Fig. 8). Examination of the films deposited above the critical conditions (composition Al–AlN) shows the aluminium characteristics. The structure and the granularity of the deposits are nearly constant in the field of stoichiometric AlN preparation.

The infrared transmittance spectrum shows that the films have a sharp absorption peak near 15 μ wave length (instead of the 14 μ given value)[1,2]. Two conclusions may be derived from this:

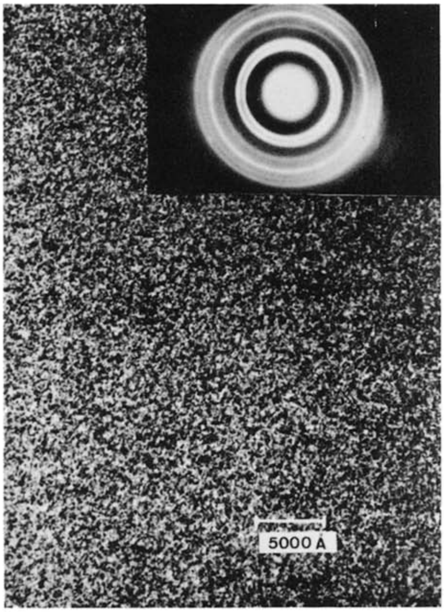
(i) the compound seems to be stoichiometric

(ii) the sharpness of the peak as shown in Fig. 9 is a confirmation of the crystallinity of the films.

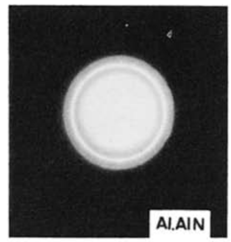
A value of $n = 2.10$ near the bulk value is found for the optical index. Etch rate measurements are not reproducible and do not allow consequent conclusions.

6.3. Electrical properties

As mentioned before, the dielectric constant ε and the losses increase, the breakdown field Ec decreases near the critical deposition rate, below which the dielectric properties are nearly independent of the preparation conditions.



(a)



(b)

Fig. 8. Electron diffraction pattern.

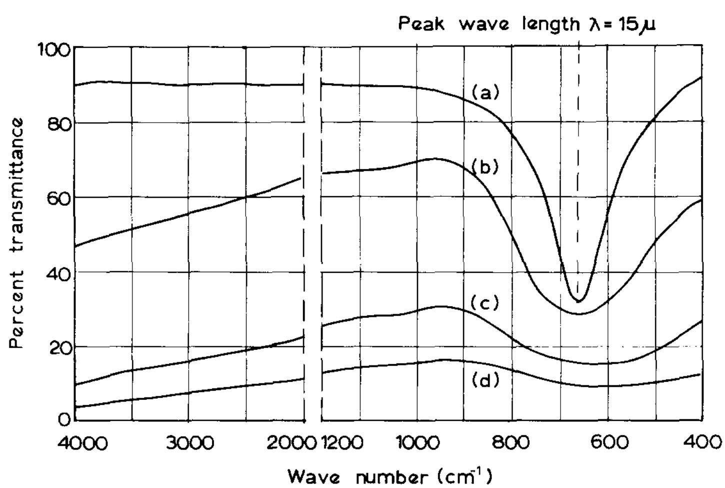


Fig. 9. Infrared spectrum of AlN films (2000 Å thickness deposited on silicon).
(a) transparent AlN film $V/Vc \simeq 0{,}8$
(b) semi-metallic Al–AlN films $V/Vc \simeq 1.1$
(c) semi-metallic Al–AlN films $V/Vc \simeq 1.3$
(d) semi-metallic Al–AlN films $V/Vc \simeq 1.4$

The average values of the electrical parameters are listed below:-

$\varepsilon \simeq 8.5$–10
$\tan \delta \geqq 0.005$
and $Ec \simeq 6$ mV/cm at best.

The d.c. resistivity of AlN films is about 10^4 Ω cm, leakage currents being more important than in Al_2O_3 films.

It is interesting to note that the dielectric properties of the films depend on thickness. The dielectric constant increases until the thickness is about 4000–5000 Å. It attains a value of 10 at most (see Fig. 10). The loss tangent is high, even in the best films, when thicknesses are less than 2000 Å. The dielectric breakdown field increases with thickness; its value can be as low as 3 mV/cm for 1000–1500 Å films (Fig. 11).

A possible explanation for the increase of the dielectric constant with thickness is in the crystallinity of the film. The measured values of ε are to be corrected if we take into account this granularity effect. Indeed, thickness measurements are made with a profilometer which gives a peak value, the true thickness being that of an average flat surface. This average thickness is nevertheless unimportant when considering the breakdown field and losses (dissipation factor). Indeed, the field effects of the upper metal electrode boundary defects overlook the breakdown phenomenon. It is realistic to assume that the number and the relative size of such sharp defects are predominant for small thicknesses. When the thickness is large, the upper film surface can be considered as a flat one and the breakdown field is independent of the thickness.

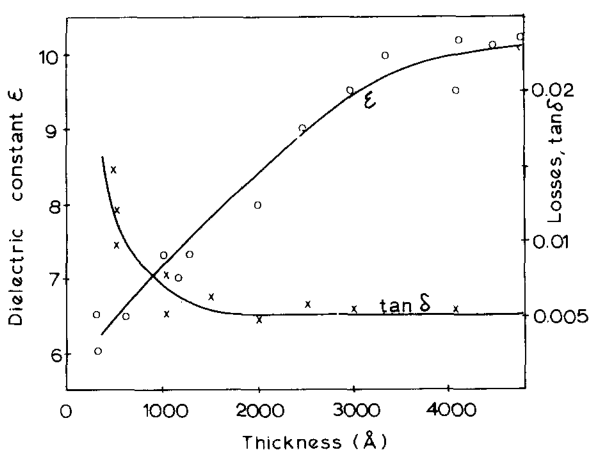


Fig. 10. Dielectric constant and dissipation factor (tan δ) *vs.* thickness (for the best films).

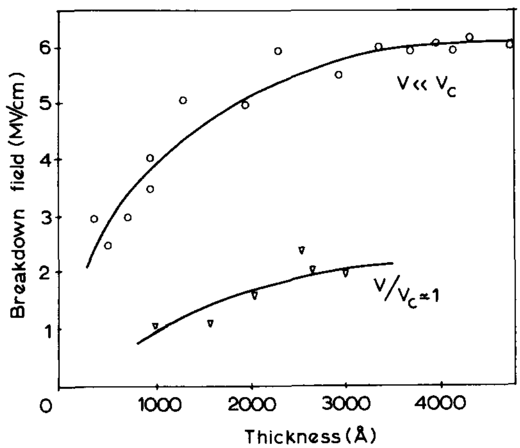


Fig. 11. Breakdown field as a function of film thickness for two different values of the ratio *V/Vc* (between deposition rate and critical value).

7. CONCLUSION

Among the different thin film preparation processes, RF sputtering offers advantageous possibilities. We have seen that the reactive process could enlarge the film deposition field. Reactive sputtering phenomena are now partially understood in the case of low pressure and nitrogen gas, but experiments must be done in order to correlate them with the reaction mechanism. Moreover, utilization of AlN films as a dielectric in microelectronics in place of silica or alumina seems potentially possible.

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