Low-frequency modulation of pulsed d.c. or r.f. discharges for controlling the reactive magnetron sputtering process

A. Billard, C. Frantz *

Laboratoire de Science et Génie des Surfaces (URA CNRS 1402), Ecole des Mines (INPL and Université Henri Poincaré, Nancy I), Parc de Saurupt, 54042 Nancy, Cedex, France

Abstract

Pulsed d.c. discharges (20–60 kHz) and r.f. discharges (13.56 Mhz) are known to prevent electric instabilities due to arcing when highly insulating compounds are deposited by reactive magnetron sputtering. This paper shows how a low-frequency modulation (1–10 Hz) of these discharges can overcome the difficulty due to the instability of the sputtering process itself with its associated hysteresis effect caused by the rapid transition between a clean target and a target poisoned by reaction products with the reactive gas. This new, simple and economical method does not need the use of a complex fast feedback control system of the reactive gas partial pressure. The application of this method will be particularly illustrated by the deposition of amorphous alumina films.

Keywords: Reactive magnetron sputtering; Pulsed discharges; Insulating compounds; Process-stabilizing method

1. Introduction

The deposition by reactive magnetron sputtering of numerous insulating ceramic compounds (oxides, nitrides, carbides) very often poses two kinds of problems caused by the strong interaction of the reactive gas (oxygen, nitrogen, methane) with the target surface (e.g., Al, Ti, Zr, Si). The rapid formation on the target surface of a thin layer of a nonconducting compound is responsible for electrical instabilities due to arcing and often leads to an uncontrollable shift in the working conditions of the reactor towards a compound sputtering mode for which a drastic drop of the deposition rate and a sudden increase of the reactive gas partial pressure are generally observed.

- If arcing – which is particularly violent for reactive direct current (d.c.) sputtering and can result in damage to the power supply and to the deposits – is generally avoided by the use of a radiofrequency (r.f.) power (13.56 Mhz), a technically and economically interesting alternative which is actually in development [1–5] consists in the use of a medium-frequency (20–50 kHz) periodic negative unipolar or bipolar voltage signal.
- Concerning the stability of the d.c. or r.f. reactive magnetron sputtering process, its control has been mainly performed until now by monitoring the partial pressure of the reactive gas [6–9] in the vacuum chamber using relatively complex closed loop feedback systems based on a highly sensitive pressure sensor (e.g., quadrupole mass spectrometer) or optical emission plasma analysis. We propose in this article a more efficient, simple and economical solution [10] which is not based on the usual monitoring systems but which consists of a low-frequency modulation in the 1–10 Hz range of the voltage signal applied to the target. Within one period of this low-frequency modulation, a controlled poisoning of the target by the reactive gas (oxidation, nitriding, carburizing) and its cleaning by sputtering are alternately realized. This leads to long time-stable conditions allowing the formation of a stoichiometric compound on the substrate with a growth rate only little lower than that of the pure material sputtered under non-reactive conditions.

* Corresponding author. Tel.: +33 83 584254; fax: +33 83 534764; e-mail: frantz@mnes.u-nancy.fr.

2. Experimental

The deposition of 1–6 μm thick stoichiometric ceramic films (Al_2O_3, SiO_2, TiO_2, ZrO_2, AlN, Si_3N_4, TiN) was performed using a 40 l cylindrical vacuum chamber pumped down to 2×10^{-4} Pa (1.5×10^{-6} Torr) by an oil diffusion pump before refilling with the appropriate reactive sputtering gas mixture (argon + oxygen or nitrogen). The magnetron sputter source is a 50 mm diameter target (Al, Si (resistivity lower than $0.5 \Omega \cdot cm$), Ti, Zr). Before each deposition, the target is pre-sputtered in pure argon for a period of approximately 15 min. It is powered from a SAIREM pulsed d.c. prototype generator in the unipolar mode (10–66 kHz) or in the bipolar mode (10–33 kHz). The voltage signal can also be modulated at low-frequency (1–100 Hz). The generator is equipped with a fast arc detector able to cut microarcs within 1–2 μs. For all depositions, the generator ran in the power-controlled mode constant (150–250 W) which results in discharge voltages between -300 and -430 V and in a deposition rate of 4–6 μm h^{-1} (1.1–1.7 nm s^{-1}) at a target-to-substrate distance of 80 mm. The flow rates of argon, oxygen or nitrogen were controlled with MKS mass flowmeters. The total working pressure was measured using an MKS Baratron capacitance manometer and the oxygen or nitrogen partial pressure was measured using both mass spectrometry and the capacitance manometer. Optical emission spectroscopy (OES) was also performed for plasma diagnostics. During deposition, the argon mass flow was kept between 30 and 45 standard cm^3 min^{-1} (sccm) and the argon partial pressure P_{Ar}, between 0.30 and 0.90 Pa (2.28 and 6.84 mTorr) while the oxygen or nitrogen mass flow was varied from 0 to 10 sccm (partial pressure in the 0–0.1 Pa range (0–0.76 mTorr)).

Substrate materials were polished steel samples and glass slides. Prior to sputter cleaning, the samples were ultrasonically rinsed in acetone and alcohol. Their temperature starts at room temperature and is lower than 400 K during sputtering. No negative bias was applied to the substrate during deposition.

The chemical and structural study of the deposits was performed by means of electron probe microanalysis (EPMA) using as reference samples pure Al, Si, Ti, Zr and metallized samples of oxides or nitrides of known composition, Auger electron spectrometry (AES), X-ray diffraction (XRD), optical microscopy (OM), transmission and scanning electron microscopy (TEM-SEM) and atomic force microscopy (AFM).

3. Results and discussion

3.1. Electric instabilities (suppression of arcing)

To prevent arcing, d.c. pulsed power was preferred to r.f. power which presents several drawbacks: (1) a lower deposition rate than for d.c.; (2) the necessity of good impedance matching for power transfer to the plasma; (3) high cost of r.f. power supplies.

The conditions of reactive d.c. pulsed magnetron sputtering with an argon partial pressure of 0.90 Pa (6.84 mTorr) will be first considered because they lead for all the systems to a time-stable sputtering regime with a target practically non-poisoned by the reactive gas [3,4]. At this operating pressure, the stability of the sputtering process is due to a pumping speed of the reactive gas (about 130 l s^{-1}) by the vacuum system greater than the critical pumping speed (about 100 l s^{-1} for Al_2O_3 deposition) leading to instability.

We will see later that with decreasing the argon partial pressure the critical pumping speed will increase and the hysteresis effect will no longer be avoided.

● For d.c. sputtered deposits, OM and SEM [3,4] showed a rough surface with a great density of growth defects and droplet projection due to arcing, as confirmed here by AFM (Figs. 1(a) and (b)). One hundred to 1000 arcs s^{-1} can be detected and suppressed by the fast arc detector for the most reactive systems (e.g., Al_2O_3, AlN, SiO_2). These arcs are in reality microarcs responsible for more than 10^4 defects cm^{-2} in the deposits. The dimensions of these defects in the plane of 1–2 μm thick deposits are generally submicron while their maximum height is about 200 nm. For amorphous stoichiometric Al_2O_3 films, the index of refraction measured in the 800–2000 nm range has an average value of 1.65.

● The use of rectangular unipolar pulsed d.c. discharge can reduce by several orders of magnitude the growth defect and projection density thanks to a quasi-suppression of arcing. The "pulse-on" time must be short enough (10–40 μs) to prevent the breakdown of the insulating layer formed on the target surface and which charges positively under Ar$^+$ ion bombardment. The "pulse-off" time must be long enough (e.g., 10 μs) to discharge that poisoned layer under bombardment with electrons which are still present in the plasma before its total extinction. Experiment shows that 50 or 20 kHz unipolar negative rectangular pulses with a "pulse-off time" of 10 μs are really suited to prevent arcing, respectively for Al_2O_3, AlN or SiO_2, Si_3N_4, TiO_2, ZrO_2. The film surface is in fact very smooth and the maximum height of the residual defects is about 10 nm (Fig. 1(c)). The refractive index of Al_2O_3 is 1.67. However, very fine microporosity (about 20 nm in diameter) was detected by TEM [3,4] in the alumina films deposited at this argon partial pressure of 0.90 Pa (6.84 mTorr). This pressure is therefore not optimised for a good compactness of alumina deposits.

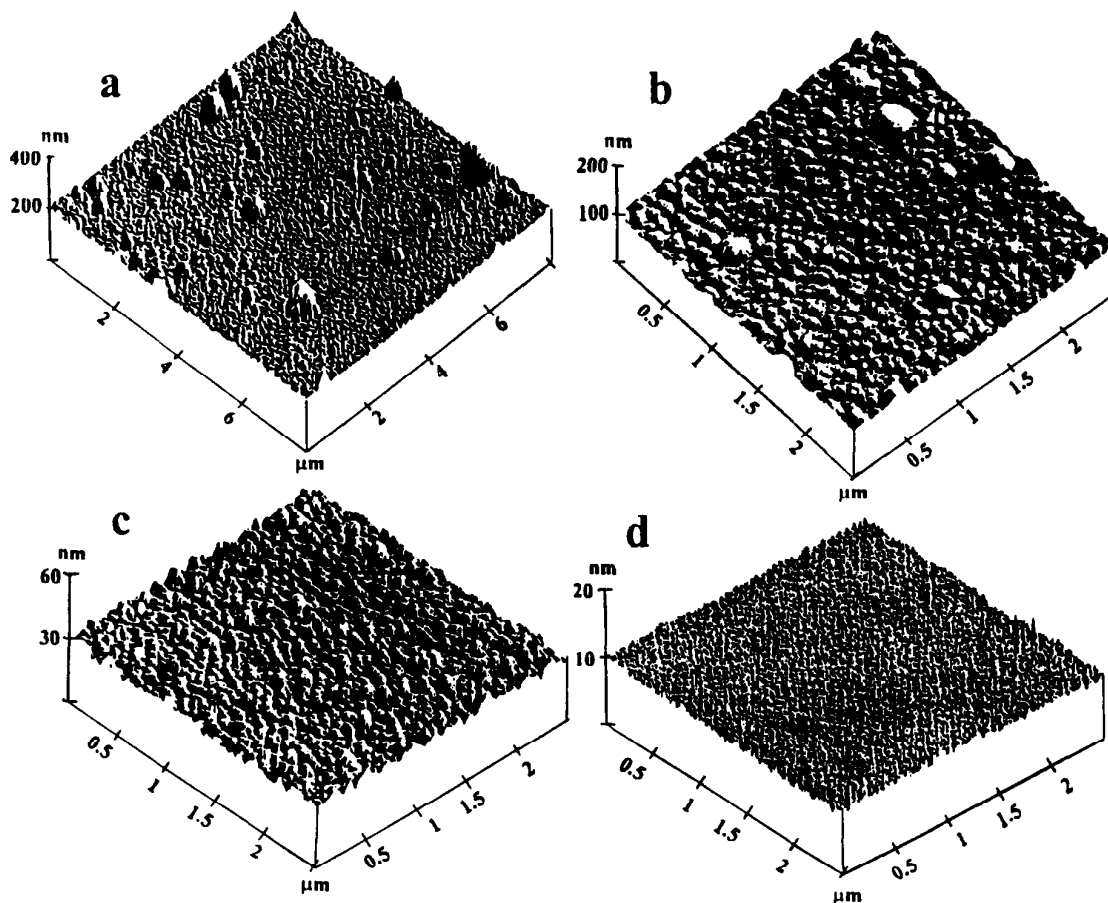● The use of bipolar pulsed d.c. discharge has been

Fig. 1. AFM images of the topography of a 1.5 μm thick amorphous alumina film deposited on glass slide: (a,b) d.c. discharge; (c) pulsed d.c. discharge (50 kHz); (d) pulsed d.c. discharge (50 kHz) modulated at low-frequency (about 1 Hz). For a, b, c deposits, argon partial pressure is 0.90 Pa. It is 0.30 Pa for d deposit.

revealed to be still more efficient in suppressing arcing but care must be taken to avoid sputtering of the reactor walls and accessories during the positive pulses if their magnitude is not kept to about 10–20% of the magnitude of the negative pulses.

4. Instability of the reactive sputtering process: new stabilizing-method

4.1. Recall of the general processes of reactive sputtering

The hysteresis effect that often occurs in reactive d.c. or r.f. sputtering of ceramic compounds is a well known phenomenon resulting from the sudden covering of the target surface by reaction products (oxides, nitrides, carbides) which generally exhibit a lower sputtering rate [11–13]. The getter pumping effect due to the reaction between the sputtered atoms and the reactive gas is thus reduced, causing the partial pressure of the reactive gas and the metalloid concentration (O, N, C) in the deposits

to increase sharply, whereas the deposition rate rapidly decreases. The reactive sputtering is thus characterized by two stable states (with fast transition from one to the other) which can be conveniently discriminated by reference to the different generic hysteresis curves representing, as a function of the mass flow Φ_R of the reactive gas: the partial pressure P_R of the reactive gas; the metalloid concentration C_{Me} or the deposition rate R_D of the deposits; the optical emission intensity of sputtered metal atoms; the electric characteristics of the target (voltage and intensity).

As an example, the schematic P_R-Φ_R curve is presented in Fig. 2. It is typical of a strongly reactive metal (or semiconductor)/gas system such as Al/O_2 for forming Al_2O_3. The straight line in Fig. 2 shows the linear increase in P_R that would result from increasing Φ_R if no sputtering took place. In the metal sputtering mode (nonpoisoned target) where $\Phi_R < \Phi_{RA}$, there is negligible change in partial pressure P_R as Φ_R is varied. In the compound sputtering mode (poisoned target) where $\Phi_R > \Phi_{RB}$, the partial pressure varies linearly with Φ_R
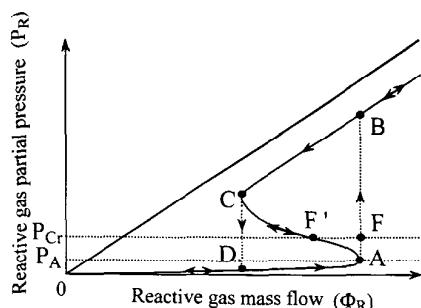
Fig. 2. Schematic curve of the reactive gas partial pressure with the mass flow for a strong reactive system (e.g., aluminium–oxygen system). Without discharge, linear relation between P_R and Φ_R; with discharge, hysteresis curve OABCD under reactive gas mass flow control; reversible S, shape curve OACB under reactive gas partial pressure control.

but is typically lower than that measured in the absence of sputtering: the greater the ratio of the sputtering yields of the metal atoms from the metal and the compound, the smaller will be the value of the reduction in pressure. Due to the kinetics of the sputtering and reaction processes, a runaway situation appears between these two states that shifts the operating point from A to B or from C to D depending on whether the reactive gas flow Φ_R is increased or decreased. Thus the AB and CD parts of the curves define a hysteresis region, all the wider and steeper, as the difference between the respective sputtering yields of the target in its metal and poisoned states increases. Experiment shows that the operating point of the sputtering reactor must often be kept in that unstable region between a clean target and a poisoned target in order to synthesize on the substrate the desired ceramic compound. It is noteworthy that changes in shape of hysteresis curves can be observed as a function of the pumping speed, the location of the reactive gas inlet and the effective area of the reactor walls. Indeed, the width of the hysteresis curve decreases as the reactive gas inlet is moved closer to the pump entrance [13] and tends to disappear as the pumping speed is increased [13–15] or as the wall area is artificially decreased by using adequate shields [16]: however, these factors are not always sufficient, especially when the reactive gas strongly reacts with the vapour emitted by the target (getter effect) or when the working pressure is lowered.

4.2. New stabilizing method of the reactive sputtering process

The improvement of the ceramic films quality (morphology and compactness of the microstructure) often requires a lowering of the working pressure. However, for a critical argon partial pressure (e.g., 0.80 Pa for Al_2O_3 or 0.30 Pa for TiO_2, ZrO_2 and TiN), the sputtering instability with its associated hysteresis effect occurs

because of the increase of the critical pumping speed of the reactive gas as the working pressure decreases. For the aluminium–oxygen system and a 50 kHz unipolar pulsed discharge which prevents arcing, Fig. 3 shows the classical sputtering instability observed at an argon partial pressure of 0.30 Pa on the curves which relate the oxygen partial pressure and the electric characteristics of the discharge (target voltage and current) to the total oxygen mass flow entering the reactor. A similar phenomenon is observed for r.f. reactive sputtering of aluminium in Ar/O_2 plasma even if the working pressure is kept at 0.90 Pa (6.84 mTorr). Then, it becomes very difficult to synthesize a stoichiometric compound on the substrate, other than sputtering a totally poisoned target which often leads to a drastic drop in the deposition rate, especially for Al_2O_3, TiO_2 and, to a lesser extent, for ZrO_2, TiN and AlN. For SiO_2 and Si_3N_4, poisoning of the target may be tolerable because the sputtering yield of the oxide or nitride is only little lower than that of pure silicon.

In the case of the aluminium–oxygen system where the rise in the reactive gas partial pressure is very rapid when mass flow control is used, the high rate deposition of stoichiometric amorphous optically transparent alumina is impossible because it requires a critical value P_{Cr} of the oxygen partial pressure just slightly above P_A in the unstable region, for instance in F on the hysteresis curve OABCD (Fig. 2).

In the case of moderately reactive systems, a solution to the instability problem can sometimes be found by controlling the partial pressure of the reactive gas instead of the mass flow with the help of a more or less sophisticated closed-loop feedback control system [6–9]. With such a control, the curve of the reactive gas partial pressure with the mass flow is reversible when equilibrium is reached and exhibits an S-shape (Fig. 2). To obtain stoichiometric compound films with satisfac-
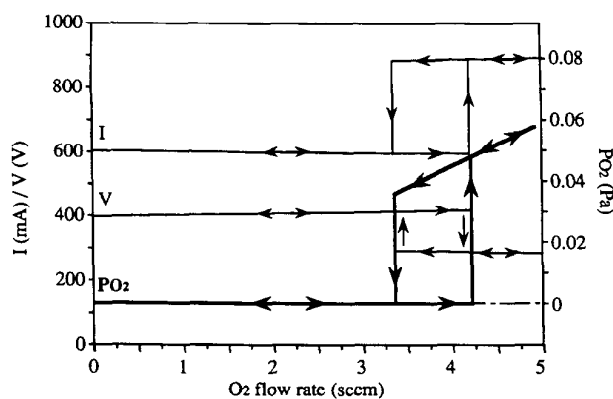

Fig. 3. Sputtering instability observed at $P_{Ar} = 0.30$ Pa and average power = 240 W for aluminium–oxygen system: target current (I), target voltage (V) and oxygen partial pressure (P_{O_2}) as a function of the total oxygen mass flow for a negative unipolar 50 kHz pulsed discharge.

tory deposition rates requires to be able to operate on the negative slope of the processing curve OACB, for instance in F'.

In the case of very reactive systems where the ceramic compounds have a low sputtering yield, a new method which allows the control in real-time of the target poisoning [10] is proposed. The principle of this method consists of a low-frequency (1–10 Hz) modulation of the voltage signal applied to the target, in order to cyclically reduce and increase the instantaneous power in such a manner as to alternate controlled chemical reaction (e.g., oxidation, nitriding, carburizing) between the target surface and the reactive gas and sputtering of the reaction products. Within a period of this modulation, the instantaneous operating point oscillates between two steady limits corresponding, respectively, to conditions close to the metal and compound sputtering modes. Several characteristics (period, shape and magnitude) of this modulation were tested. It seems that a simple voltage ramp, with a period of about 1 s and a magnitude of about 100 V, works well in keeping the average operating point of the reactor in the normally unstable region and in avoiding any risk of chemical modulation of the film.

As a nonrestrictive example, an application of this method is shown in Fig. 4 for alumina prepared at the argon partial pressure of 0.30 Pa (2.28 mTorr) with a
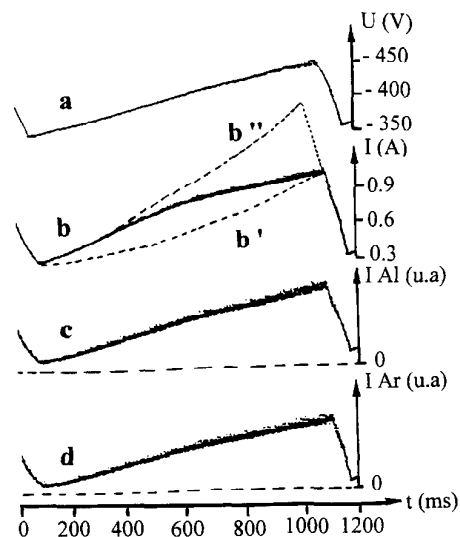
50 kHz pulsed discharge. All the microporosities have disappeared as confirmed by TEM [3,4] and by the increase of the refractive index ($n = 1.69$). The alumina film is perfectly transparent and chemically homogeneous as confirmed by AES analysis as a function of depth. AFM shows (Fig. 1(d)) that the alumina film surface is very smooth with a maximum relief of 3 nm. With an average power of 240 W, the deposition rate is about 1.3 nm s^{-1} and is only 20% lower than for pure aluminium sputtered under non-reactive conditions.

With such a method where the reactive gas mass flow is fixed at its critical value in the absence of the low-frequency modulation of the voltage signal, long time-stable sputtering conditions can be achieved with a correct positioning of the low-frequency voltage ramp. For this purpose, because of the difference in the secondary electron emission yield between a metallic (Fig. 4(b)') and a poisoned (Fig. 4(b)") target surface, it is often possible as shown by the characteristic shape of the target current intensity curve in Fig. 4(b) to know if the necessary condition of alternate controlled poisoning and sputter-cleaning of the target surface is satisfied within a period of the low-frequency modulation of the voltage signal. If the sensitivity of the target current to the target surface poisoning is not high enough, OES can generally be used. It is based on the intensity of a suitable emission line, preferably, belonging to sputtered metal atoms and initially calibrated at two stable sputtering conditions corresponding to metallic mode and compound mode. The prerequisite for this control is the steady and monotonous correlation between target poisoning and intensity of the plasma emission line chosen. For most combinations of target material and reactive gas, this requirement is satisfied (e.g., the emission line of aluminium atoms at 396.1 nm is suitable for an Al target sputtered by Ar/O$_2$ (Fig. 4(c))). If both target current and OES are not available, it is then necessary to perform several tests to find the correct positioning of the voltage ramp or, for a given voltage ramp, the right mass flow of the reactive gas that leads to the desired stoichiometric compound deposited on the substrate at a high rate. When the right operating conditions are found, OES with its short response time can be very useful for a possible automatic working of the reactor for a long time in enabling to move, if necessary, the voltage ramp up or down according to the intensity level of a characteristic optical emission line belonging to sputtered target metal atoms.

It is noteworthy that, as for d.c. pulsed discharge, this method could also be successfully applied to r.f. discharge when an instability of the reactive sputtering process exists.

Fig. 4. Example of a low-frequency modulation (about 1 Hz) of the 50 kHz pulsed voltage applied to an aluminium target under Ar/O$_2$ plasma leading to stoichiometric amorphous alumina at the argon partial pressure of 0.30 Pa. Oxygen mass flow is fixed at 4.2 sccm. (curve a) target voltage within a period of the low-frequency modulation; (curve b) target current. The dotted lines b' and b" correspond to an oxygen flow of 3 and 6 sccm for which the target is respectively metallic and oxidized; (curve c) optical emission intensity of aluminium atoms at 396.1 nm; (curve d) optical emission intensity of argon atoms at 811.5 nm. All these quantities are averaged values with respect to the 50 kHz negative unipolar pulses.

5. Conclusion

As recently reported [1–5], it has been shown that it is possible to deposit by reactive magnetron sputtering

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