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Interest of Pulsed and Modulated dc Discharges for Depositing Insulating Compounds by Reactive Magnetron Sputtering

A. Billard and C. Frantz (*)

Laboratoire de Science et Génie des Surfaces (**), École des Mines, Parc de Saurupt,
54042 Nancy Cedex, France

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Abstract. — Reactive magnetron sputtering using dc discharges simultaneously pulsed at medium-frequency (a few tenths of kHz) and modulated at low-frequency (a few Hz) enables the deposition of insulating ceramic films with a high growth rate and an excellent physical quality. The medium-frequency pulses and the low-frequency modulation respectively favour the long time stability of the electric conditions (suppression of arcing) and of the sputtering process itself (dynamic control of the target poisoning by the reactive gas).

Résumé. — La pulvérisation magnétron réactive utilisant des décharges dc simultanément pulsées à moyenne fréquence (quelques dizaines de kHz) et modulées à basse fréquence (quelques Hz) permet d'élaborer des films céramiques non conducteurs avec une grande vitesse de croissance et une excellente qualité physique. Les pulsations de moyenne fréquence et la modulation à basse fréquence favorisent respectivement la stabilité, pendant de longues durées, des conditions électriques (suppression des arcs) et du processus même de pulvérisation (contrôle dynamique de l'empoisonnement de la cible par le gaz réactif).

Introduction

The production of numerous nonconducting ceramic compounds (oxides, nitrides, carbides ..) by reactive magnetron sputtering 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 an insulating compound is indeed responsible of electric instabilities due to arcing and often leading to an uncheckable 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.

- The micro-arcs are especially violent for reactive dc sputtering and must be detected and eliminated by means of a fast device because they can result in damage to the power

(*) Author for correspondence (e-mail: frantz@mines.u-nancy.fr)

(**) URA CNRS 1402 - INPL & Université de Nancy I

supply and to the deposits which present a great density of growth defects and droplet projections. Arcing can be suppressed by using Radio Frequency (rf) power (13.56 MHz) which, however, presents several drawbacks:

- a lower deposition rate than for dc;
- the necessity of good impedance matching for power transfer;
- high cost of rf generator.

In the agreement with the present tendency [1-5], the use of unipolar or bipolar pulsed dc power in the 20-50 kHz range is preferred for the reactive sputter deposition of ceramic compounds. Pulsed dc power is then a technically and economically interesting alternative to rf power.

- The instability of the pulsed dc or rf sputtering process itself is due to the undesirable hysteresis phenomenon which arises owing to two competing processes: sputtering of the target surface and poisoning by reaction products (oxides, nitrides, carbides ...). Experiment shows that the operating conditions of the sputtering reactor must often be maintained within the unstable transition region between a clean target and a poisoned target in order to synthesize, on the substrate, the wanted stoichiometric ceramic compound. Several factors are known to stabilize the sputtering process such as the increase of the pumping speed, the artificial decrease of the area of the reactor receiving surfaces and a judicious choice of site for the reactive gas inlet into the reactor. 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. Until recently, this difficulty was mainly overcome by monitoring the partial pressure of the reactive gas [6-9] in the vacuum chamber using closed loop feedback systems based on highly sensitive pressure sensor (*e.g.* quadrupole mass spectrometer) or optical emission plasma analysis.

In this article, a more efficient, simple and economical solution which is not based on the usual monitoring systems is proposed. This new method consists in a low-frequency modulation in the 1-10 Hz range of the voltage signal applied to the target [10] which enables an active on line control of the chemical reaction likely to occur at the target surface and leading to long time stable reactive sputtering conditions. Within one period of this low-frequency modulation, controlled poisoning of the target by the reactive gas (oxidation, nitriding, carburizing) and consecutive sputtering of the reaction product must be successively realized. The average operating conditions of the reactor can thus be kept in the normally unstable region (*e.g.* Figs. 1, 2) enabling 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.

1. Experimental

The production of 1 to 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 dm³ cylindrical vacuum chamber pumped down to 2×10^{-4} Pa by an oil diffusion pump before refilling with 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 ohm cm), Ti, Zr). Before each deposition, the target is pre-sputtered in pure argon during approximately 15 min. It is powered from a SAIREM Company pulsed dc 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 working 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 V and -430 V and in a deposition rate of 4 – 6 $\mu\text{m h}^{-1}$ 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 a 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 diagnostic. During deposition, the argon flow rate was kept between 30 and 45 standard $\text{cm}^3 \text{min}^{-1}$ (sccm) and the argon partial pressure P_{Ar} between 0.3 and 0.9 Pa, while the oxygen or nitrogen flow rate was varied from 0 to 10 sccm (partial pressure in the 0 - 0.1 Pa range).

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 remains lower than 130 °C after 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 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).

2. Results and Discussion

2.1. ELECTRIC INSTABILITIES (SUPPRESSION OF ARCING). — We first consider the sputtering conditions with an argon partial pressure of 0.9 Pa which lead for all the systems to a stable sputtering regime with a target practically non-poisoned by the reactive gas [3,4]. At this pressure, the stability of the sputtering process is due to a pumping speed of the reactive gas by the vacuum system better than the critical pumping speed leading to instability.

For dc sputtered deposits, OM, SEM and AFM show a rough surface with a great density of growth defects and droplet projections due to arcing. One hundred to one thousand 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 micro-arcs responsible of more than 10^4 defects cm^{-2} in the deposits [3,4]. However, the dimensions of these defects in the plane of 1-2 μm thick deposits are submicronic while their maximum height is about 100 nm. The index of refraction of amorphous stoichiometric Al_2O_3 films measured in the range of 800-2000 nm has an average value of 1.65.

The use of rectangular unipolar pulsed dc discharge can reduce by several orders of magnitude the growth defect and projection density [3,4] thanks to a quasi-total suppression of arcing. The “pulse-on” time must be short enough (10 to 40 μs) to prevent the breakdown of the insulating layer formed on the target surface and which charges positively under Ar^+ ions bombardment. The “pulse-off” time must be long enough (*e.g.* 10 μs) to discharge that poisoned layer under electrons bombardment which are still present in the plasma before its total extinction. Experiment shows that 50 kHz or 20 kHz rectangular negative unipolar 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. The refractive index of Al_2O_3 is 1.67. Very fine microporosities (about 20 nm in diameter) are however visible by TEM [3,4] and AFM in the alumina films deposited at this argon partial pressure of 0.9 Pa. This pressure is then not optimized for a good compactness of the alumina deposits.

Fig. 1. — Sputtering instability observed at $P_{Ar} = 0.30$ Pa and average power = 240 W for aluminium-oxygen system: target voltage (Curve a), target current (Curve b) and oxygen partial pressure (Curve c) vs. total oxygen mass flow for a negative unipolar 50 kHz pulsed discharge.

The use of bipolar pulsed dc discharge has revealed to be still more efficient to suppress arcing but care must be taken to avoid sputtering of the reactor walls and accessories during the positive pulses. It seems important to use pulsing power supplies which can vary the magnitude of the positive pulses.

2.2. INSTABILITY OF THE REACTIVE SPUTTERING PROCESS: NEW STABILIZING-METHOD.

A further improvement of the film quality (morphology and compactness of the microstructure) often requires lower working pressure. However, for a critical argon partial pressure (e.g. 0.8 Pa for Al_2O_3 or 0.3 Pa for ZrO_2 and TiN), the sputtering instability with its associated hysteresis effect occurs because of the increase of critical pumping speed of the reactive gas as the working pressure decreases. For the aluminium-oxygen system and a 50 kHz unipolar pulsed discharge, Figure 1 shows the classical sputtering instability observed at an argon partial pressure of 0.3 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 rf reactive sputtering of aluminium in Ar/ O_2 plasma even if the working pressure is increased up to 0.9 Pa. Then, it becomes very difficult to synthesize a stoichiometric compound on the substrate otherwise 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 extend, 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.

For the aluminium-oxygen system where the rise in the reactive gas partial pressure is very rapid when 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 (Fig. 2).

For moderately reactive systems, a solution to this 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

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.

and exhibits a S-shape (Fig. 2). To obtain stoichiometric compound films with satisfactory deposition rates requires to be able to operate on the negative slope of the processing curve, for instance in F'.

For 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 in modulating at a low-frequency (1-10 Hz) 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. Several characteristics (shape and magnitude) of this modulation were tested. It seems that a simple voltage ramp between two values V_1 and V_2 such as the difference $|V_1 - V_2|$ is about 100 V works well as shown in Figure 3 for alumina prepared at the argon partial pressure of 0.3 Pa with a 50 kHz pulsed discharge. All the microporosities have disappeared [4, 5] as confirmed by AFM and by the refractive index value of 1.69. The alumina films surface is very smooth with a maximum relief of 2 nm. The deposition rate is only slightly lower (about 20%) 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. 3b') and a poisoned (Fig. 3b'') target surface, it is often possible as shown by the characteristic shape of the target current intensity curve in Figure 3b, to know if the necessary condition of 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

Fig. 3. — Example of a low-frequency modulation (about 1 Hz) of the 50 kHz pulsed voltage applied to an aluminium target under Ar/O₂ 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. All these quantities are averaged values with respect to the 50 kHz negative unipolar pulses.

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/O₂ plasma, Fig. 3c). 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 the right oxygen mass flow for a given voltage ramp that lead to the wanted 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.

This method can also be applied to reactive magnetron rf sputtering.

Conclusion

It has been shown as recently reported [1–5] that it is possible to deposit by reactive magnetron sputtering highly insulating ceramic compound films (*e.g.* oxides, nitrides, carbides ...) with low defects density when a fast arc detector is used in conjunction with a medium-frequency dc pulsed discharge in the 20–50 kHz range which quasi totally suppresses micro-arcing. With a low-frequency modulation in the 1–10 Hz range of the power supply, all compounds compositions can be made, in particular, at a low working pressure, without use of relatively complex automatic feedback control system of the reactive gas partial pressure. Indeed, this new simple economical and efficient method stabilizes the reactive sputtering process by on line control of the target poisoning by the reactive gas. High rate deposition of ceramic compounds having an excellent physical quality can be achieved including compounds which belong to the most reactive systems such as the aluminium-oxygen system.

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References

- [1] Schiller S., Goedicke K., Reschke J., Kirchhoff V., Schneider S. and Milde F., Pulsed magnetron sputter technology, *Surface and Coatings Technology* **61** (1993) 331-337.
- [2] Stauder B., Synthèse et caractérisation de films Al-O, Al-N et Zr-O préparés par pulvérisation cathodique magnétron en condition réactive, Thèse INPL, Nancy (5 Juillet 1994).
- [3] Stauder B., Perry F. and Frantz C., Chemical and structural analysis of aluminium-oxygen coatings obtained by dc magnetron reactive sputtering: some features of the process, *Surface and Coatings Technology* **74-75** (1995) 320-325.
- [4] Stauder B., Perry F., Sanchette F., Tran Huu Loi, Billard A., Pigeat Ph. and Frantz C., Use of medium and low-frequency pulsed dc plasma for depositing reactively sputtered ceramic compounds, *Le Vide : Science et Applications* **275** (1995) 406-409.
- [5] Sproul W.D., Graham M.E., Wong M.S., Lopez S., Li D. and Scholl R.A., Reactive direct current magnetron sputtering of aluminium oxide coatings, *J. Vac. Sci. Technol. A* **13** (1995) 1188-1191.
- [6] Hmiel A.F., Partial pressure control of reactively sputtered titanium nitride, *J. Vac. Sci. Technol. A* **3** (1985) 592-595.
- [7] Schiller S., Heisig U., Steinfelder K., Strümpfel J., Friedrich A. and Fricke R., The use of a Plasma-Emission-Monitor for the control of the reactive sputter process and its application in the production of indium-tin oxides layers, Proc. 6th Int. Conf. IPAT, Brighton, UK (1987) pp. 23-30.
- [8] Sproul W.D., Rudnik P.J., Gogol C.A. and Mueller R.A., Advances in partial pressure control applied to reactive sputtering, *Surf. Coat. Technol.* **39/40** (1989) 499-505.
- [9] Spencer A.G. and Howson R.P., Dynamic control of reactive magnetron sputtering, *Thin Solid Films* **186** (1990) 189-195.
- [10] Stauder B., Perry F., Billard A., Pigeat Ph., Henrion G. and Frantz C., Method for self-stabilizing deposition of a stoichiometric compound by reactive sputtering, French Patent N° 92-15924 (30 Dec 1992), European Patent N° 93 403153.5 (23 Dec 1993), US Patent N° 08/172.549 (23 Dec 1993).