Thin film deposition by magnetron sputtering using energy flux diagnostics

A.L. Thomann[1], M. El Mokh[1], P.A. Cormier[2], S. Konstantinidis[2], A. Caillard[1]

[1]Groupe de Recherche sur l'Energétique des Milieux Ionisés, UMR7344, CNRS/ Université d'Orléans, 14 rue d'Issoudun, 45067 Orléans, France
[2]Laboratoire de Chimie des Interactions Plasma-Surface, Université de Mons, 23 Place du Parc, 7000 Mons, Belgium

Study of the energy transfer between plasmas and substrate surfaces is of major interest for many plasma processes of material modification, including magnetron sputter deposition. It is well known that the global energy deposited during the growth determines the features of the film, such as its crystalline phase, micro-structure, morphology etc. In this contribution we will focus on what energy transfer measurements could bring to the knowledge, first of the deposition conditions (control of the films properties), and second, to the understanding of the mechanisms involved both, in the sputtering process (at the target) and the film growth (at the substrate).

1. Introduction

It is well known that thin film growth widely depends on physical and chemical mechanisms which transfer energy to the growing film. The knowledge of energetic conditions at the substrate could give some insight into the involved mechanisms [1]. Their control is therefore a key aspect for tailoring the film properties to the envisaged application(s). Estimation of the energy deposited at the substrate during plasma magnetron sputtering is a quite old issue [2,3]. This can be done either by energy balances, carried out from data of the gas phase (specie density, flux and energy), or by measurements performed with specific probes [4,5,6]. In magnetron sputtering processes, calorimetric probes, based on the recording of the temperature evolution, have been widely used [7]. The main drawbacks of this type of probe are the quite long acquisition time (several minutes), preventing from the detection of low intensity or transient energetic contributions, and the impossibility to perform real time measurements [8].

Other kinds of heat flux sensors, exhibiting higher sensitivity and fast response time are now emerging to investigate magnetron sputtering deposition [4,9]. It will be shown in this contribution that, beyond the correlation between deposited energy and film characteristics, they will allow to evidence elementary mechanisms taking place at the target (sputtering process) and at the substrate (thin film growth).

2. Diagnostics to study the relationship between deposited energy and thin films properties

The energy flux diagnostic that has been the most often used to study magnetron sputter deposition is called the calorimetric probe. Based on an original idea of Thornton, several versions designed by Kersten and co-workers have been used in various low pressure plasmas and for the characterization of sputtering plasma [6,8]. A metal plane is connected to a thermocouple and the temperature is recorded during heating and cooling steps. Calibration is achieved by applying an electron beam. Energy flux is determined a posteriori after treatment of the thermograms that need several minutes to be recorded. Radiometers have also been designed by Ellmer et al, for example [9]. In this case the radial temperature gradient is studied between areas of the sensor that are submitted or not to the incoming flux. The thermocouple signal can be correlated to the power influx after a calibration performed using a laser beam as a heating source. The response time lies below 1s, which is better than that of the calorimetric probe.

In our laboratory an energy flux diagnostic has been designed composed of a thermopile, which is a heat flux sensor based on the Seebeck effect [10]. The thermopile is composed of 1600 thermocouple junctions/cm^2 ensuring a good sensitivity (less than 1mW/cm^2). Calibration is performed following a NIST protocol from the IR radiation emitted by a home-made black body. Time resolution being in the range of ms and delivered voltage being directly proportional to the energy influx, real time measurements can be carried out.

All these energy flux diagnostics exhibit advantages and drawbacks. They have been used in various magnetron sputter deposition systems in an attempt to correlate thin film properties to the energy brought to the substrate by the different particles impinging onto the surface during the deposition process. Many works have been done on this subject showing that a key parameter to predict thin film features (morphology, microstructure, crystallinity etc.) could be the global transferred energy per incoming atom. However recent studies have evidenced that, in some cases, this parameter alone may not be relevant [11]. The influence of the energetic vector, i.e. the particle that carried out the energy, will be discussed in this presentation. Moreover, with fast response sensors it is possible to decorelate energetic contributions of various kinetics. For instance it has been shown that IR radiation emitted by the sputtered-heated target has to be taken into account to predict the crystallinity of TiO_2 films for instance [12].

3. Sputtering process

As mentioned above, beyond the study of the film features, energy flux measurements allow to study mechanisms occurring at the target, i.e. driving the sputtering process. We have investigated the IR radiation emitted from the target surface in various sputtering discharges: dc, pulsed-dc, HiPIMS and with different magnetic field configurations [13]. It appeared that this contribution can exceed 50% of the total transferred energy and that it is the highest in the case of HiPIMS discharge and for a balanced magnetic field. This could be explained since in this configuration the sputtering plasma is confined close to the target and efficiently heats its surface. This has to be compared to the unbalanced case, where energetic particles are allowed to leave the target area and reach the substrate. This leads to a limited heating effect at the target and to a higher energy transfer by collisions at the substrate.

From the IR energetic contribution it is possible, using the Stefan law, to estimate the target surface temperature during the sputtering process. This could be of particular importance when working in a so called regime of “hot target”. That means when the cooling at the backside of the target is limited in order to increase its surface temperature up to the melting point [14]. The idea behind is to enhance the deposition rate of some elements by adding evaporation to the sputtering ejection process. Knowledge of the target surface temperature would allow a better controlled of this particular deposition process.

4. Thin film growth mechanisms

Several works have shown that real time study of the energy transferred to the substrate gives some interesting insight into the elementary mechanisms taking place at the substrate during the film growth. For instance, investigation of the well-known transition between metal and compound (or poisoned) modes in reactive sputtering have been carried out in the case of TiO_2 and Al_2O_3 oxide deposition. Kinetics of the energy transfer when turning from metal-to-compound or compound-to-metal modes were found completely different in the case of Al_2O_3. This was attributed to different involved mechanisms: progressive oxidation of the metal growing film (chemical reaction) in the first case, and kinetic energy transfer by negative ions born at the target surface that gain energy through the cathode sheath (physical transfer by collision) in the 2nd case. This last very fast phenomenon was not observed in TiO_2 reactive deposition. This was explained by the fact that TiO_2 is able to be progressively reduced under ion bombardment, which is not the case for the very stable Al_2O_3. Consequently, when turning from poisoned to metal mode, O^- could be progressively released from the TiOx surface, whereas Al_2O_3 stays stable until all oxygen is abruptly removed from the oxidized aluminium target, leading to a high and short peak in the energy transfer evolution.

[1] I. Petrov et al, *J. of Vac. Sci. Technol. A* **21**(5) (2003) S117.

[2] J. A. Thornton, *Thin Solid Films* **54**(1) (1978) 23.

[3] W. D. Westwood, Sputter deposition processes, *MRS bulletin* **13** (1988) 6.

[4] R. Gardon, *The Rev. of Sci. Instrum.* **24** (1953) 366.

[5] D. J. Ball, *J. Appl. Phys*. **43** (1972) 3047.

[6] H. Kersten et al, *Vacuum* **63** (2001) 385.

[7] T.P. Düsedau et al, *Surf. Coat. Technol.* **133–134** (2000) 126.

[8] P-A. Cormier et al, *J. Phys. D: Appl. Phys.* **43** (2010) 465201.

[9] K. Ellmer, R. Mientus, *Surf. Coat. Technol.* 116–119 (1999) 1102.

[10] A.-L. Thomann et al, *Rev. of Sci. Instrum.* **77**(3) (2006) 033501.

[11] G. Abadias et al, *J. Phys. D: Appl. Phys.* **46** (2013) 055301.

[12] P.A. Cormier et al, *Surf. Coat. Technol*. **254** (2014) 291.

[13] P.A. Cormier et al, *Thin Solid Films* **545** (2013) 44–49

[14] D. Mercs et al, *Surf. Coat. Technol.* **201** (2006) 2276.

[15] A.L. Thomann et al, *Thin Solid Films* **539** (2013) 88.