Hysteresis effect during reactive sputtering

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Abstract. In this work, we studied the effect of constant parameters of the sputtering system on the width of the hysteresis loop during reactive sputtering. The sticking coefficient of the reactive gas to the surface, the chamber pumping speed, the target area, etc. are taken as parameters. The comparative study was carried out by numerical solution of systems of algebraic equations describing the chemisorption and physicochemical models of metal target reactive sputtering in a single reactive gas. The calculations were performed for sputtering a tantalum target in an Ar + O₂ mixture. The studied dependences were non-linear in all cases.

In the processes of reactive sputtering, which are used to deposit films of simple compounds such as oxides, nitrides, oxynitrides, etc., a metal target is sputtered in an environment usually containing a mixture of argon and one or two reactive gases [1, 2]. It was found that the target in these processes can have two stationary modes [3]. In the reactive mode, the target surface is completely covered with a compound film; in the metal mode, the target surface is pure metal.

Discharge current and reactive gas flow rate are independent process variables. When you change one of them, the operating mode of the target can change. A characteristic feature of reactive sputtering is hysteresis [4]. This effect is detected by measuring the dependence of the partial pressure of the reactive gas or the sputtering rate on one of the specified variables. It results from the fact that the value of the independent variable, at which there is a change in the operating mode of the target, depends on the direction of its change. The width of the hysteresis loop is determined by the difference between these values.

These features are not widely recognized by the specialists using reactive sputtering for film deposition. Authors describing the experimental conditions very often indicate either the total pressure of the mixture or the ratio of the flow rates of argon and reactive gas, or their sum [5]. Different physical models are used to describe reactive sputtering, which demonstrate the effect of hysteresis in different gaseous environments and for different types of targets [3, 4, 6–9].

An experimental study of hysteresis is undertaken to establish a stable mode of deposition of the compound film. A theoretical study of this effect is useful for revealing the influence of constant parameters of the sputtering system. This is especially important if we take into account that the calculations based on the model use parameters such as the sputtering yields of materials and adsorption of gases on their surfaces, the pumping speed of vacuum chamber, etc. The values of some of these quantities are usually not known exactly, so it is important to find out how significantly they influence the discussed effect.

The purpose of this work was to study the influence of the parameters describing the sputtering system on the hysteresis. The calculations were performed for chemisorption [4] and physicochemical [3] models. As parameters, the materials' sputtering yields, the sticking coefficients of the reactive gas...
molecules to the surfaces, the vacuum chamber pumping speed and the target area are taken. The first two of them describe the physical properties of materials. Their values are obtained experimentally, and different authors most often publish different data. The second pair characterizes the sputtering system. The researcher can select their values, thereby to control the process.

Without going into details, we only note that the main difference between the two models results from the assumption about the mechanism of the formation of the compound film on the inner surfaces of the vacuum chamber. In the chemisorption model, the chemisorption of the reactive gas on the \(i\)-th surface is taken as such a mechanism, at which the growth rate of the film of the compound is equal to

\[
\left( \frac{d\theta_i}{dt} \right)_\alpha = 2aF \left( 1 - \theta_i \right),
\]

(1)

where \(a\) is the sticking coefficient of reactive gas molecules to the metal on the \(i\)-th target surface, \(\theta_i\) is the fraction of the \(i\)-th surface covered by the compound, \(F\) is the density of the flux of reactive gas molecules to the surface defined by the Hertz–Knudsen equation:

\[
F = \frac{p}{\sqrt{2\pi m_i k T}},
\]

(2)

where \(p\) is the partial pressure of the gas, \(m\) is the mass of the molecule, \(k = 1.38 \times 10^{-23} \text{ J/K}\) is the Boltzmann constant, \(T\) is the temperature. Three surfaces are usually distinguished inside a vacuum chamber: targets, walls and substrates, therefore the index \(i\) can take three values, which are denoted as \(t, w\) and \(s\).

In another model, the authors consider the chemical reaction between the metal \(M\) and the reactive gas \(X_2\) to be such a mechanism:

\[
M + \frac{n}{2m} X_2 \rightarrow \frac{1}{m} M_mX_n,
\]

(3)

which proceeds on all surfaces. The growth rate of the compound film on the \(i\)-th surface in this case is equal to:

\[
\left( \frac{d\theta_i}{dt} \right)_{ch} = \frac{k(T_i)}{N_{ch}} \frac{\theta_i^{0_i/2m}(1 - \theta_i)}{N_{ch}}.
\]

(4)

where \(k(T_i)\) is the constant of a chemical reaction rate (Arrhenius function), \(N_{ch}\) is the surface concentration of chemical reaction centers, \(\theta_{0_i}\) is the fraction of the \(i\)-th surface covered with adsorbed gas molecules, which is set by the Langmuir isotherm. A detailed description of these models can be found in the previously referenced publications.

The mathematical description of each model is a system of linear algebraic equations. Its numerical solution gives a set of dependences for a number of variables on independent factors (discharge current and reactive gas flow rate). The main dependent variable is the partial pressure of the reactive gas. It can be measured experimentally. Other physically correct variables are not experimentally measurable. These include, for example, the flux of reactive gas to each inner surface of the vacuum chamber.

The selection of the target material and the type of reactive gas for solving the problem is not limited. In this work, the influence of the calculation system parameters on the hysteresis is illustrated by using the example of the reactive sputtering process of a tantalum target in an oxygen-containing environment \((\text{Ar} + \text{O}_2)\). This choice was made only because the adequacy of the physicochemical model in the first publication [3] was shown using the experimental results from [10]. The following parameters were set in it: pumping speed of the chamber \(S = 8.6 \text{ l/s}\); target area \(A_t = 100 \text{ cm}^2\); wall area \(A_w = 300 \text{ cm}^2\); sticking coefficient \(a = 1\); sputtering yield of oxide \(S_c = 0.024\) and tantalum \(S_m = 0.6\); the temperature of the gas and all surfaces is the same \(T = 300 \text{ K}\). In the physicochemical model, the substrate was isolated as a separate surface with an area of \(A_s = 10 \text{ cm}^2\) and a temperature of \(T_s = 600 \text{ K}\). The
values of other parameters were taken equal: \( A_w = 290 \text{ cm}^2 \); \( T_i = T_w = 300 \text{ K} \). In addition, the experimental data were used to select the parameters that set the constant of the chemical reaction rate \( k(T) \): the activation energy \( E_a = 3.09 \times 10^{-20} \text{ J} \) (or 4.46 kcal/mol) and the constant \( k_0 = 2.4 \times 10^{33} \text{ m}^{-2} \text{s}^{-1} \). In all calculations, the current density was assumed to be 100 A/m².

Next, we present the most significant results of studying the influence of the parameters of the sputtering system on the width of the hysteresis loop. First of all, let's pay attention to the influence of the sputtering yields. Figure 1 shows the results of calculations for the sputtering yields of tantalum oxide \( S_c \). Through \( Q_1 \), \( Q_2 \) and \( \Delta Q \) in figure 1 (as below) denotes the transition point of the tantalum target from the metallic mode to the oxide mode, reverse, the point of the reverse transition, and the width of the hysteresis loop, respectively.

The quantities \( Q_1 \) and \( Q_2 \) in figure 1 increase nonlinearly with increasing \( S_c \). If the loop width \( \Delta Q \) for both models changes insignificantly, then the values of \( Q_1 \) and \( Q_2 \) in the range \( 0.02 < S_c < 0.08 \) increase almost three times.

The value of the tantalum sputtering yield \( S_m \) has a similar effect on the process. The only difference is that the width of the hysteresis increases with increasing \( S_m \).

The found influence can lead to a significant error in the prediction using the model of the deposition mode of the oxide film. This error for the chemisorption model is illustrated in figure 2, which shows that a decrease or increase in the value of \( S_c \) or \( S_m \) leads to a shift in the point of transition of the target from the metallic to oxide mode \( Q_1 \). This can lead to an error in predicting the conditions for film synthesis. It is especially dangerous if a film is synthesized when the oxygen consumption is within the hysteresis region.

Further, the influence of the parameters describing the sputtering system on the hysteresis was studied. Figure 3 illustrates the results of calculations for the chamber pumping speed.
the obvious nonlinearity of all curves in figure 3, both models show that in the region of small values of $S$, the position and width of the hysteresis change insignificantly.

It also follows from figure 3 that the width of the hysteresis can be reduced to zero by increasing the pumping speed. A similar conclusion was made by the authors of [11].

Further in the work, attention was paid to other parameters. Thus, it was found that at a qualitative level both models show the same influence of the target area on hysteresis. An increase in the target area, firstly, leads to a shift of both points of change in the target operating mode to the region of higher values. Second, in all cases, the dependences are essentially nonlinear.

Summing up, we note that, on a qualitative level, both models lead to identical dependences of the width of the hysteresis loop on the parameters of the sputtering system. At the same time, it was established that the greatest influence in both cases is exerted by the areas of the target and the walls of the vacuum chamber.

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