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► To cite this version:

S. Berg, C. Nender. Modeling of Mass Transport and Gas Kinetics of the Reactive Sputtering Process. Journal de Physique IV Proceedings, 1995, 05 (C5), pp.C5-45-C5-54. 10.1051/jphyscol:1995502 . jpa-00253758

HAL Id: jpa-00253758

<https://hal.science/jpa-00253758>

Submitted on 1 Jan 1995

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Modeling of Mass Transport and Gas Kinetics of the Reactive Sputtering Process

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Abstract. Modeling of reactive sputter deposition processes is a very important tool for fast and inventive process development. A short review with some new results is given for a set of previously presented reactive sputtering models that has been successful in describing and predicting the processes. Examples are given for each case of reactive sputtering with one target and one reactive gas, reactive compound- and co-sputtering as well as reactive sputtering using two reactive gases. The importance of process control in order to control the inherent instabilities and composition, is emphasized.

1. INTRODUCTION

The use of reactive sputtering in modern materials processing, is becoming more common and important. Nitrides, oxides, carbides, borides and even sulfides of several metals can be produced by this technique. The versatility in varying the material properties and synthesis of materials that otherwise is difficult to produce, makes the reactive sputtering process favorable for many fields of applications. There are protective, wear resistant coatings that prolongs the lifetime of mechanical tools and machine parts, diffusion barriers used in microelectronics and thin films for optical purposes, just to mention a few. Many of these applications rely on precisely defined film properties such as e.g. stoichiometry, which increases the demands on the process development. For many industrial processes there is also a high demand on throughput, which emphasizes process development towards high deposition rates. In many reactive sputtering systems the process will be unstable for certain processing conditions, this also complicates the development of a well defined process. In order to understand the fundamentals, and to be able to predict and control new processing regimes, the reactive sputtering process has been extensively modeled [1-5,12-15]. In such modeling a need of better understanding of the physical processes involved is of high importance. Some newly experimentally observed phenomena for reactive co-sputtering would probably not have been thought of, if not preceded by computer simulations.

2. MODELING

The reactive sputtering model developed at the electronics department at Uppsala University has been described in detail in some previous publications [1-5]. For the sake of completion a short overview is given here as well, so the reader more easily can follow the discussions.

The reactive sputtering model is based on basic physical relations and some simplifying assumptions. In the model the reactive gas molecule or atom is assumed to stick to all surfaces with a certain sticking coefficient where a nonreacted metal atom is present, thereby forming the desired compound. The calculations are done at steady state with no spatial distribution of the partial pressure and all sputtering is caused by mono-energetic Ar-ions neglecting the ion current distribution from the partial pressure of the reactive gas. Two areas are introduced. First the target area from which sputtering occurs and where also some of the reactive gas is consumed and second the substrate area or rather the chamber wall area where the deposition of the thin film takes place and where also reactive gas is consumed. The deposited material is assumed to be evenly distributed on the chamber wall area. The two areas are then divided into two schematic parts, one part consisting of the reaction product and the other consisting of pure nonreacted metal. This defines the surface coverage ϑ , of the compound formed on the target and chamber wall areas.

Figure 1: Schematic of the target and substrate areas describing the different defined parameters in the model. The symbols are assigned in the text.

To model the reactive sputtering process one has to establish two balance equations. First the mass balance has to be described so that the surface coverages on both target and substrate areas can be calculated. The second step is to balance the gas transport in the system using the surface coverages to calculate the consumption of reactive gas and to find the corresponding total mass flow of reactive gas, q , into the processing chamber.

In order to find the material balance at steady state on the target, the rate of formation of the reaction product must equal the number of compound molecules that are sputter eroded at the same time interval.

$$\frac{xi}{y} \Gamma_r \alpha (1 - \vartheta_t) = \Gamma_i \gamma_c \vartheta_t \quad (1)$$

Where α is the sticking coefficient, ϑ_t the target surface coverage, Γ_i the flux of ions, and γ_c the sputtering yield of the reaction product. The factor xi/y corrects for the number of atoms in the various molecules present, i is the number of atoms per reactive gas molecule, x the number of metal atoms per compound molecule and y the number of reactive gas atoms per compound molecule. Γ_r is the corresponding flux of reactive gas molecules at the partial pressure p , defined by basic gas kinetics as :

$$\Gamma_r = \frac{p}{\sqrt{2\pi m k T}} \quad (2)$$

Where m is the mass of a reactive gas molecule, k Boltzmann's constant and T the absolute temperature. By similar considerations at the chamber wall area one finds the equation :

$$\frac{xi}{y} \Gamma_r \alpha (1 - \vartheta_c) + \Gamma_i \gamma_c \vartheta_t (1 - \vartheta_c) \frac{A_t}{A_c} = \Gamma_i \gamma_m (1 - \vartheta_t) \vartheta_c \frac{A_t}{A_c} \quad (3)$$

Where the index c corresponds to the chamber wall area, A_t is the target area, A_c the chamber wall area and γ_m the sputtering yield of the metal. The first term on the left hand side is the increase of ϑ_c due to reactions with the reactive gas at the substrate. The second term corresponds to deposited compound material also increasing ϑ_c . The term on the right hand side is the balancing deposition of metal from the $1 - \vartheta_t$ part of the target.

The equations can be simplified by introducing two new constants:

$$Y = \frac{\frac{xi}{y} \Gamma_r \alpha}{\Gamma_i \gamma_c} \quad \text{and} \quad a = \frac{\gamma_m}{\gamma_c}$$

Solving for ϑ_t , then gives :

$$\vartheta_t = \frac{Y}{1 + Y} \quad (1')$$

and for ϑ_c one obtains:

$$\vartheta_c = \frac{Y^2 + Y(1 + \frac{A_t}{A_c})}{Y^2 + Y(1 + \frac{A_t}{A_c}) + a \frac{A_t}{A_c}} \quad (3')$$

To establish the gas balance in the system the total flow q , must equal the consumption of reactive gas at the target and chamber wall areas plus the flow of the gas through the pumping system.

$$q = \Gamma_r \alpha (1 - \vartheta_t) A_t + \Gamma_r \alpha (1 - \vartheta_c) A_c + pS \quad (4)$$

Where S is the pumping speed.

An other important parameter, the sputtering rate R , from the target, can also be found through the expression:

$$R = \Gamma_i (\gamma_c \vartheta_t + \gamma_m (1 - \vartheta_t)) \quad (5)$$

3 Modeling results.

A model like this enables an easy way of making numerical experiments. The equations 1', 2, 3' and 4 then gives a possibility to calculate the relation between the different measurable quantities p and q . It is, however, not easy to find $p=p(q)$. This does not complicate any calculation at all, since one then assumes different values for p and then calculate q instead. A number of calculations can be performed to follow what trends a change in the processing parameters can cause.

In figure 2 a typical calculation of p versus q has been done for a typical reactive sputtering process for TiN. The features of the well known hysteresis region is easily seen. This type of process behaviour has been reported frequently by several other authors [6-10].

Figure 2 : Calculated curve for the partial pressure of the reactive gas versus mass flow. This specific case corresponds to reactive sputtering of Ti in N_2 . The parameters used in the model was : $T=20[^\circ C]$, $A_T=127[cm^2]$, $A_C=1270[cm^2]$, $S=80[l/s]$, $\gamma_{Ti}=1.5$, $\gamma_{TiN}=0.3$, $\Gamma_i=0.1[A]$ and $\alpha=1$.

If the mass flow of the reactive gas is increased from zero to point A, the target remains basically metallic maintaining a high deposition rate. If the flow is further increased beyond point A, the target surface will be almost completely reacted or what is usually referred to as poisoned. The gettering is then reduced and the consumption of the reactive gas lowered causing the partial pressure to increase in an avalanche to point B, indicated in figure 2 with the dotted line. Usually the sputtering yield of the compound is lower compared to that of the metal, leading to a rapid decrease in deposition rate. Reducing the flow to a lower value than point C, will cause a similar avalanche to point D, also indicated as a dotted line. The points A-D thus set the limits for the hysteresis region of the process. The part of the solid curve between A and C has a negative slope and can not be reached, without using an automated control system. In such a system the partial pressure of the reactive gas, obtained by means of mass spectrometry or other methods, is used to control to the gas flow controller to obtain the desired pressure. The partial pressure can then be stabilized to any point along the curve.

In a previous publication [3] it has been shown theoretically that there exists a "critical" pumping speed where the "hysteresis effect" disappears. This has also been reported experimentally by others [11]. As an illustration of this phenomenon a series of curves for the sputtering rate at different pumping speed values are plotted in figure 3. The width of the hysteresis region changes with the pumping speed and disappears if the pumping speed exceeds a certain value. This indicates one way of avoiding the problems with hysteresis. But for practical situations when large sputtering systems are used the pump sizes needed for a hysteresis-free operation may be unrealistically big. The only possibility that remains, if one wants to operate in the hysteresis region, is then to use an automatic feedback system for the mass flow controllers.

Figure 3 : Normalized sputtering rate versus reactive gas flow for the same parameters as in figure 1 except for the pumping speed. For curve a) $S=30$ [l/s] b) $S=150$ [l/s] and c) $S= 450$ [l/s].

4 Reactive sputtering from an alloy target and reactive co-sputtering

Many of today's advanced thin film processing involves reactive sputtering of two or several materials in combinations to form complex thin film compositions. There are examples in the fields of superconductivity (YBaCuO) and in multilayer formation of different metal nitrides for hard coatings to mention a few. In some of these processes a single multi element alloy target is used, in others the films are formed by sputtering from two or more targets simultaneously (co-sputtering). The processes allow a lot of flexibility, especially reactive co-sputtering where the targets can be operated independently from each other.

Figure 4: Schematic of conditions during reactive sputtering of an alloy target. Note that the surface composition y , is not equal to the bulk composition x , due to the difference in sputtering yields for the two metals. The indices 1 and 2 corresponds to the two different metals.

To model both the reactive alloy- and co-sputtering cases it is possible to use basically the same arguments as shortly presented before for the one target reactive process, [12]. The two cases of reactive alloy- and reactive co-sputtering seems similar, but have a fundamental difference for the composition of the deposited film. The treatment of the substrate or chamber wall area is however the same, there will be fluxes of two metals and their reaction products for both cases.

On the surface of a two metal alloy target the composition will differ from the bulk of the target due to differences in the sputtering yields of the two elements. At steady state, however, the sputtering yields in combination with the compositions will adjust the sputtering rate of the two metals so that the deposited film will have the same metal composition ratio as the bulk of the target. The metal composition, z , of the growing film will thus be independent of the mass flow of the reactive gas.

Figure 5: Schematic of conditions during reactive co-sputtering. The substrate area A_c can be treated similarly as for alloy sputtering. A_{t1} and A_{t2} are the two target areas

For the case of reactive co-sputtering from two metal targets, the situation is quite different. Each target will have its own surface coverage depending on the partial pressure of the reactive gas. Since the sputtering yields are different for the reaction products from the two targets the deposition rates for the different materials will depend on the partial pressure of the reactive gas. This results in a complex dependence of the deposited film composition on the reactive mass flow.

In figure 6 and 7 the normalized deposition rates for the two different metals are plotted versus the mass flow of the reactive gas. The sputtering rates are normalized so the rate is 1 when the reactive gas flow is zero. Because of the sputtering yields values both for the two metals and their nitrides are different, the extreme values of the curves are not the same. If one takes the ratio of the atomic contents of one metal to the sum of the two in the deposited film, this will result in a complex curve plotted in figure 8. For certain values of the mass flow there exists a region with three values for the composition. If one in an experiment would just set the mass flow of the reactive gas to a fixed value in this region it would be impossible to control the resulting film composition. For other values than the ones used in figure 8, one can obtain different curve shapes, also having three values for some mass flow regions. Consequently it is of highest importance to control the partial pressure, not only for stability reasons but also for composition control.

Figure 6 : Calculated normalized deposition rate of metal 1 versus the mass flow of the reactive gas.

Figure 7 : Calculated normalized deposition rate of metal 2 versus the mass flow of the reactive gas.

It is thus obvious that partial pressure control is necessary to be able to operate within the "loop". Preliminary experimental results from reactive co-sputtering of Ti and V confirms the existence of the "loop". This example illustrates that the reactive co-sputtering process can be quite complex. The addition of more targets will of course make the process even more intricate. We believe that the use of computer modeling in such cases will be a necessity.

Figure 8: Calculated fractional composition of metal 1 versus mass flow of the reactive gas for reactive co-sputtering. The parameters used are $\gamma_{1m}=1.5$, $\gamma_{1n}=0.3$, $\gamma_{2m}=2.8$, $\gamma_{2n}=0.6$, $\Lambda_{11}=127[\text{cm}^2]$, $\Lambda_{12}=40[\text{cm}^2]$, $A_c=4000[\text{cm}^2]$, $\Gamma_1=0.1[\text{A}]$.

5. Reactive sputtering using two reactive gases

There are situations where one would like to involve two reactive gases e.g. to deposit oxy-nitrides. Correspondingly it is possible to use the same arguments as before to make the same type of model for this case [13,15]. In such a process the two gases are simultaneously fed to the reaction chamber using independent mass flow controllers. The composition of the growing film will be totally dependent on the partial pressures of the gases. The process using two reactive gases is, however, much more complex than a one-reactive-gas process.

A thorough investigation of the behaviour of the partial pressures needs a 3D representation where the partial pressures forms a surface that is dependent on both mass flows. It is though possible to get a lot of information by cutting the surface with planes for a constant flow of one gas. The partial pressures will interact in a complex way.

It is e.g. possible to show that an increase of the mass flow of one gas not only influences the partial pressure of that gas but also the other gas. This can be explained in the following way. Assume that we have a constant flow of oxygen and that the target used is Ti. At steady state a certain part of the target will then be TiO_2 leaving the other part unreacted as metallic Ti. By increasing the flow of nitrogen into the chamber the unreacted Ti will then form TiN and consequently reduce the Ti part on both the target and chamber wall areas. This reduction will cause the gettering of oxygen to decrease, leading to a higher oxygen partial pressure. The reduction of gettering will of course also increase the nitrogen partial pressure.

Figure 9: Schematic of target and substrate areas for the model of reactive sputtering using two gases. The indices 1 and 2 corresponds to the different gases.

Another intriguing effect is that the process may be trapped under some conditions. The trapping means that it is impossible to run the process around a hysteresis loop by just varying the mass flow of one reactive gas. This may happen if we are very close to an avalanche point using gas 1. By adding some of gas 2 we may avalanche to a new processing point. A reduction of the mass flow of gas 2 may not be sufficient to go around the hysteresis loop.

Figure 10: Schematic of the sputtering rate versus the mass flow of one reactive gas (number 2 in text) for three different settings of the mass flow of the other reactive gas (number 1 in text). The constant mass flow is increasing from a) to c). For the case c) it is impossible to get back to the original state of the process just by decreasing the mass flow of one gas.

Conclusion

Modeling of reactive sputtering processes enables an easy way of studying new processing behaviour. In spite of the assumptions and limitations of such a model it is possible to draw many conclusions about the processes. It is, however, obvious that computer simulation must be accompanied by experimental observations. For multi-gas and multi-target processes, nevertheless, the experimental situation can be quite complex. Simulations using computer models can in such cases be a very versatile tool for the investigation procedure. Recently a software package for the models of reactive sputtering from one target, a compound target and reactive co-sputtering from several targets has been developed for use on a Macintosh. Free copies of this software may be obtained by sending an e-mail to Claes.Nender@Teknikum.uu.se or by contacting the authors by other means.

Acknowledgements

Most of this work has been done within the Ångström Consortium, supported by the Swedish Natural Science Research Council (NFR) and the Swedish National Board for Industrial and Technical Development (NUTEK).

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