A5.3 Modeling of the Reactive Sputtering Process

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A5.3.0 INTRODUCTION

Manually operated coating processes are becoming quite rare in modern material fabrication. Small tolerances and demands to operate at optimal processing conditions call for very precise control of the various parameters. To be able to operate a process at optimal conditions, an in-depth understanding of the process is necessary. Only a full understanding of the behavior of the process will make it possible to judge if the selected set of parameters will result in the desired optimal processing condition.

Process modeling, often referred to as Technology-CAD, has become a powerful technique available to the processing industry for process control and optimization. Having access to a reliable theoretical model for a particular process will make it possible to carry out process simulation and ultimately to predict the outcome from a specific set of parameters. Experimentally it is normally not possible to independently vary all the parameters involved. In theoretical process modeling, however, this can be easily done. By carrying out systematic process modeling studies it is often possible to obtain a detailed understanding of the process behavior in quite a short time. On the other hand, to obtain the corresponding results by experimental studies may take weeks or months. Introducing process modeling may therefore save time (and money) in production as well as giving valuable help in finding appropriate processing conditions.

Sputtering is an example of a widely used industrial thin film coating process. By extracting positive ions from a glow discharge (normally inert argon gas) it is possible to sputter atoms from the negatively biased target (cathode) and form a thin film of this material on the surrounding surfaces. Basically this process is quite simple and straightforward. The inert gas does not react with the sputtered material. Furthermore the film composition will mostly be identical to the composition of the cathode. This 'insensitivity' to processing conditions has made sputter deposition a widely popular and used technique in the coating industry.

Sputtering is also a very flexible coating process. By adding e.g. a small amount of oxygen to the argon it is possible to induce reactions between the sputtered material and the oxygen molecules. In this way it is possible to form oxides by sputtering elemental metal atoms from the cathode in an argon/oxygen mixture. This process is called *reactive sputtering* [1]. Despite the similarities, the reactive sputtering process behaves dramatically different from the basic inert sputtering process. The primary cause of this big difference in behavior is that the reactive sputter deposition process is extremely sensitive to the partial pressure of the reactive gas. This partial pressure is influenced by both the electric power supplied to the cathode and of course to variations in the supply of the reactive gas. At first sight this may not seem to be a big problem. However, the way these parameters interact causes the reactive sputter deposition process to behave very non-linearly and in most cases also to exhibit hysteresis effects.

It should be noted that in reactive sputtering it is not enough to know the values of the desired processing parameters. The sequence in which these parameters are set may also be of vital importance. That is, one may not necessarily reach the same processing conditions, by first adjusting the supply of the reactive gas and then the electric power fed to the target as opposed to the reversed sequence. It may well happen that, in the first case, one deposits a compound material while, in the second case, the metal will be insufficiently reacted and a metal rich coating will be deposited. This effect makes it a somewhat delicate matter to apply process control to reactive sputtering processes.

We hope that the description of the reactive sputtering process given below sufficiently clarifies its behavior and serves to guide the reader to successfully design several reactive sputter deposition processes.

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A5.3.1 MODELING OF THE REACTIVE SPUTTERING PROCESS

Here we will outline a simple, but for most applications quite satisfactory, model for the basic reactive sputtering process referred to as 'Berg's model', first suggested 1987 by Berg and his co-workers at Uppsala University [2]. It has been proven to fit most experimental findings concerning the reactive sputtering process found in the literature [3]. From this model it is possible to predict the drastic variations in the deposition rate, the composition of the deposited film, the partial pressure of the reactive gas, the 'poisoning' of the target surface by the reactive gas and the position as well as the width of the hysteresis region. The model can easily be modified to include several targets (reactive co-sputtering) or reactive sputtering from an alloy (composite) target [4]. It can also be extended to include more than one reactive gas (e.g. oxy-nitrides) [5].

To be able to obtain a simple and instructive model, however, it is necessary to make a few simplyfying assumptions. It is up to the reader to improve the model at a later stage by modifying some of these basic assumptions and develop a somewhat more sophisticated model. However, referring to figure A5.3.1 below, we use the following assumptions.

- The target is an elemental metal material (Al, Cu, Ti etc).
- Only ions from the inert gas contribute to sputter erosion of the target. The sputter contribution by ions from the reactive gas is neglected.
- Compound molecules sputtered from the target surface are deposited as molecules.
- The target current is totally carried by the ions from the inert gas. The contribution from emitted secondary electrons from the target is neglected.
- The ion current at the target is uniformly distributed over the target surface (A_t).
- All the sputter eroded material from the target surface is uniformly collected at the 'collecting' substrate surface A_s. This collecting surface represents both the substrate surface and all other receiving surfaces in the vacuum chamber.
- During processing a fraction of the target metal surface will react with the reactive gas and form the corresponding metal compound. The fraction of the target covered by this compound is denoted Θ_t. In figure A5.3.1 this is illustrated by dividing the target area A_t into two parts: the surface fraction Θ_t consisting of the metal-compound and the surface fraction $(1 - \Theta_t)$ consisting of the 'fresh' unreacted metal.
- The same reaction takes place at the collecting area A_s. However, the fraction Θ_s covered by the compound material (= reacted target metal) at this surface may differ from the fraction Θ_t at the target surface.
- The reactive gas supplied to the processing chamber gives raise to a partial pressure, P_r, that is evenly distributed in the chamber. This pressure causes a flux, Γ_r, of reactive gas molecules to all surfaces in the chamber. The relation between P_r and Γ_r is

$$\Gamma_r = \frac{P_r}{\sqrt{2\pi mkT}} \tag{A5.3.1}$$

  where m is the mass of the reactive gas molecule, k is the Boltzmann constant and T the absolute temperature.
- The sticking coefficient is defined as the probability of a reactive gas molecule to stay on a surface when impinging on it. This probability is set to zero for the compound covered parts of the chamber and target surfaces.

Based on the assumptions above it is possible to define three basic balance equations describing this 'simplified' reactive sputter deposition process.

Conditions at the target area A_t

Compound formation at the target surface will only take place due to reactions between the reactive gas and the fraction $(1 - \Theta_t)$ of the target consisting of the unreacted target metal. The rate of compound

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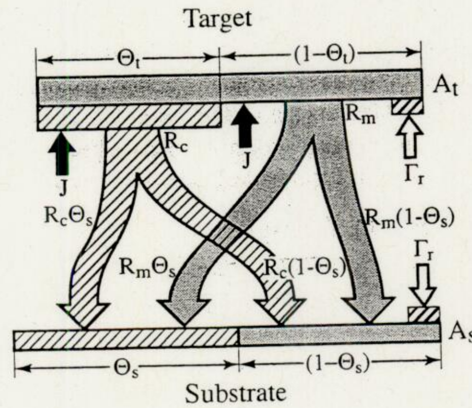

Figure A5.3.1. A schematic of the transport of the sputtered material from the target to the substrate, reactive gas fluxes and ion fluxes in a reactive sputtering process. The notations are defined in the text.

formation (number of molecules per unit time) at the target may be written as:

$$\Gamma_r \alpha_t (1 - \Theta_t) A_t b$$

where α_t is the sticking coefficient of the reactive gas molecules at the metal surface and b is a factor that defines the number of compound molecules formed by one reactive gas molecule.

The rate at which compound molecules are sputtered from the target surface can be written as

$$\left(\frac{J}{q}\right) \Theta_t A_t \gamma_c$$

where J is the ion current density (normally argon ions) at the target surface, q is the elementary charge, $(\Theta_t A_t)$ is the area of the target surface covered by the metal compound and γ_c is the sputtering yield of the compound for an incident energetic ion. Note that γ_c depends on the energy of the ion [6, 7].

At steady state the compound formation rate (due to reactions between the metal target and the reactive gas) must be identical to the sputter erosion rate of compound material from the target. This means that Θ_t has reached its steady state value. This gives us the first basic balance equation

$$\Gamma_r \alpha_t (1 - \Theta_t) A_t b = \left(\frac{J}{q}\right) \Theta_t A_t \gamma_c \tag{A5.3.2}$$

From equation (A5.3.2) in conjunction with equation (A5.3.1) it is possible to calculate Θ_t for any given value of P_r since all other parameters in the equation can be defined by the user.

The total sputter erosion rate R from the target can be expressed by

$$R = \left(\frac{J}{q}\right) \left[\gamma_c \Theta_t + \gamma_m (1 - \Theta_t)\right] A_t \tag{A5.3.3}$$

where γ_m is the sputtering yield of metal atoms due to sputtering by the energetic ions. The erosion rate here is expressed in units particles (metal atoms and compound molecules) per second. This could easily be converted into other units if desired.

Conditions at the collecting area A_s

A similar argument to that for the conditions at the target can be used for defining the conditions at the collecting area A_s. At steady state the rate of compound formation must be identical to the rate of

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'compound elimination' from this surface. No sputter erosion of compound material, however, takes place from this surface. Instead 'compound elimination' is carried out by the elemental metal atoms sputtered from the target which are deposited onto the compound fraction Θ_s of the collecting surface A_s. Due to this some 'fresh unreacted metal' is added on top of the compound covered fraction Θ_s of the collecting surface thereby converting it to a 'fresh metal' surface. This effect causes a decrease in the collecting surface coverage value Θ_s. An expression for this decrease in Θ_s can be obtained as follows.

The total sputter erosion rate of 'fresh target metal atoms', R_m, can be written as

$$R_m = \left(\frac{J}{q}\right) \gamma_m (1 - \Theta_t) A_t$$

This sputter eroded metal gives rise to a uniform deposition rate R_m/A_s on the collecting surface. The amount of R_m that is deposited onto the compound fraction Θ_s of the collecting surface is

$$R_m \Theta_s$$

This term describes the rate of decrease in Θ_s due to deposition of unreacted metal atoms. For simplicity the terms R_m, $R_m\Theta_s$ and $R_m(1 - \Theta_s)$ are illustrated as arrows in figure A5.3.1.

Note that the complementary fraction $R_m(1 - \Theta_s)$ of sputtered metal deposited onto the metal fraction $(1-\Theta_s)$ of the collecting area will not change the metal fraction at the collecting surface A_s since depositing metal onto metal does not change the composition at this position. The same holds for depositing sputtered compound material onto the fraction Θ_s at the collecting surface. Depositing compound material onto compound material does not change the composition of the area $A_s\Theta_s$.

Compound material can be formed by two different processes at the collecting surface. First the fresh metal fraction $(1-\Theta_s)$ of the collecting surface may react with the reactive gas thereby forming compound material on this surface. The total rate of compound formation for this process is

$$\Gamma_r \alpha_s (1 - \Theta_s) A_s b$$

where α_s is the sticking coefficient for the reactive gas to the metal surface at the collecting surface and $(1 - \Theta_s)A_s$ is the metal part of the collecting surface.

The second process that may lead to compound formation is the deposition of sputtered compound material onto the metal fraction $(1 - \Theta_s)$ of the collecting area. The total sputter erosion rate R_c of compound material from the target is

$$R_c = \left(\frac{J}{q}\right) \gamma_c \Theta_t A_t$$

This sputtered compound material is uniformly distributed over the collecting area A_s. The part that is deposited onto the metal fraction $(1 - \Theta_s)$ of the collecting surface is

$$R_c(1 - \Theta_s)$$

This term defines the rate of increase in Θ_s due to deposition of sputtered compound material onto the fresh metal part of the collecting surface. For illustration also the terms R_c, $R_c\Theta_s$ and $R_c(1 - \Theta_s)$ are shown as arrows in figure A5.3.1.

At steady state the two terms that contribute to compound formation at the collecting surface must balance the term that describes the compound elimination at this surface. This defines the second basic balance equation

$$R_c(1 - \Theta_s) + \Gamma_r \alpha_s (1 - \Theta_s) A_s b = \left(\frac{R_m \Theta_s}{d}\right) \qquad \text{(A5.3.4)}$$

where d is a factor that defines the number of metal atoms in one compound molecule. The right-hand side of equation (A5.3.4) is divided by d to ensure that both sides are expressed in the same unit, i.e. compound molecules per time unit. When Θ_t has been calculated from equation (A5.3.2) it is possible to calculate Θ_s from equation (A5.3.4).

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Gas kinetics

Normally the experimental equipment is not outfitted to monitor the partial pressure of the reactive gas during processing. The reactive gas is normally fed into the vacuum chamber via a mass flow controller. This is the reason why the supply of the reactive gas normally is used as an input parameter when a reactive sputtering process is described. In the model we would therefore want to find an expression for the supply of the reactive gas. This can be done in the following way.

As has been described above, the reactive gas will react with 'fresh metal surfaces' both at the target and at the collecting surfaces. Due to this effect reactive gas molecules will be gettered (extracted from the gas phase by forming solid compound molecules) at these surfaces. The gettering rate Q_t (number of molecules per unit time) at the target surface at a specific partial pressure of the reactive gas can be written as

$$Q_t = \Gamma_r \alpha_t (1 - \Theta_t) A_t \tag{A5.3.5}$$

The corresponding gettering Q_s of reactive gas at the collecting surface will be

$$Q_s = \Gamma_r \alpha_s (1 - \Theta_s) A_s \tag{A5.3.6}$$

At a partial pressure P_r of the reactive gas the vacuum pump of the system will pump out Q_p (number of molecules per unit time)

$$Q_p = k_1 P_r S \tag{A5.3.7}$$

where S is the pumping speed of the vacuum pump and k_1 is a factor converting the expression to the desired unit. Equations (A5.3.5)–(A5.3.7) determine the total consumption rate Q of reactive gas in the processing chamber. At steady state the contribution from equations (A5.3.5)–(A5.3.7) must balance the total input flow Q of reactive gas. This defines the third basic balance equation

$$Q = Q_t + Q_s + Q_p \tag{A5.3.8}$$

Since Γ_r, Θ_t and Θ_s can be calculated from equations (A5.3.1)–(A5.3.4) it is possible to also calculate Q from equation (A5.3.8) for all values of P_r. Equation (A5.3.8) states that to maintain steady state (constant partial pressure of the reactive gas) it is necessary to supply the reactive gas at a rate Q to the chamber to compensate for the total loss Q of this gas due to the three gettering mechanisms described by equations (A5.3.5)–(A5.3.7).

Calculations

Equations (A5.3.1)–(A5.3.8) uniquely describe the reactive sputtering process under the assumptions made. Since the gas supply of the reactive gas (Q) normally is the parameter used to vary the conditions during reactive sputtering processes we have chosen to use this parameter as an independent parameter in the graphical representation of our results. The simplest way to obtain results from equation (A5.3.1)–(A5.3.8) is to perform the calculations in the following sequence.

First select suitable values for the system parameters J, A_t, A_s, γ_m, γ_c, α_t, α_s, T, m, b and d.

- Assume a certain value for P_r
- Use equation (A5.3.1) to calculate the corresponding flux value Γ_r
- Calculate Θ_t from equation (A5.3.2)
- Calculate Θ_s from equation (A5.3.4)
- Calculate Q_t, Q_c, Q_p and Q from equations (A5.3.5)–(A5.3.8)
- Calculate R from equation (A5.3.3)
- Select a new value for P_r and repeat the calçulation sequence, etc. In this way it is possible to generate a number of processing curves illustrating the relations between the different processing parameters. Any spread sheet program can be used to carry out these calculations. Below we show the results of such calculations.

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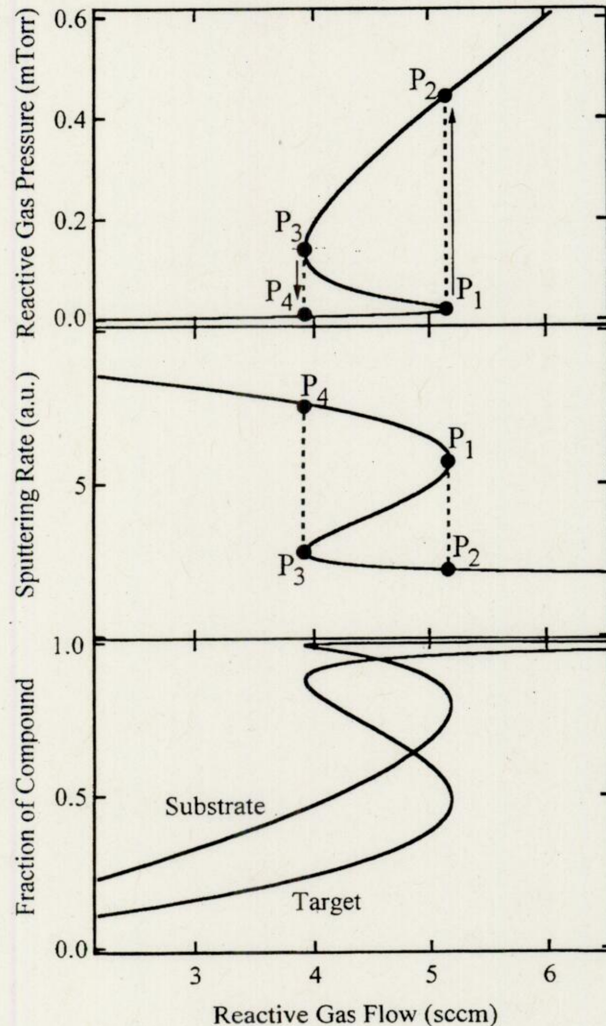

Figure A5.3.2. (Top) Simulation results of the reactive gas pressure versus flow in a standard reactive sputtering process. The points (P_1–P_4) are referred to in the text. (Middle) Simulation results of the sputtering rate versus reactive gas flow in a standard reactive sputtering process. The points (P_1–P_4) are referred to in the text. Same simulation parameters as in top part. (Bottom) Simulations results illustrating the different compositions of the target and the substrate surfaces as a function of the reactive gas flow. Same parameters as in top part.

The relation between the partial pressure and the supply of the reactive gas is shown in figure A5.3.2 (top). Note that each value of the partial pressure uniquely defines a corresponding value of the reactive gas supply Q. However, the same simple situation does not generally hold for each value of the reactive gas supply Q. In a certain region of the curve three different values of the partial pressure satisfy conditions resulting in identical values of the reactive gas supply. This region of the curve is called the hysteresis region. The reason for this can be explained in the following way.

Starting from zero flow, a small increase in the supply of the reactive gas will not significantly increase the partial pressure of the reactive gas. The reason for this is that most of the reactive gas supplied to the processing chamber is consumed by reactions with metal atoms at the surfaces A_t and A_s. Therefore only a small fraction of the reactive gas will be left over to build up a partial pressure of this gas. At a certain point P_1, however, the balance conditions for the partial pressure and the gettering at A_s and A_t will change drastically. As the partial pressure slowly increases, Θ_t will slowly increase causing less unreacted

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atoms to be sputtered and deposited onto the collecting surface. Since fewer unreacted atoms arrive at A_s, less reactive gas will be consumed in reactions with these atoms. Due to this effect an increasing fraction of the supplied reactive gas will contribute to building up an increase of the partial pressure of this gas. An increase of the partial pressure in turn will cause an even more effective compound formation at the target and subsequently even less pure metal sputtering. At P_1 this positive feedback effect will cause an avalanching increase of the partial pressure of the reactive gas. This avalanching effect will continue until the process reaches another stable point of operation. This new stable point of operation is denoted as P_2 in figure A5.3.2 (top). Increasing the supply of the reactive gas beyond this point will result in almost all the excess gas contributing to an increase of the partial pressure. No further reactive gas is needed to react with the sputtered metal since primarily almost only the metal compound is sputter eroded in this mode of operation.

At this point, decreasing the gas supply will initially result only in a decrease in the partial pressure. Passing the point P_2, however, will not result in a sharp decrease of the partial pressure. Since the latter is far too high to allow any substantial metal sputtering from the target, no significant increase in the consumption of reactive gas will take place at the collecting area A_s at the processing conditions corresponding to P_2. A further decrease of the supply of the reactive gas will ultimately result in reaching a point P_3 where 'insufficient' reactions with the gas at the target surface will result in an increase of unreacted metal atoms at this surface. At this point more unreacted target atoms will be sputtered and deposited onto the collecting area A_s. However, since A_s normally is much larger than A_t, the probability of reacting this metal at the surface A_s will be higher than at the target surface. Therefore gettering of the reactive gas will take place at A_s and subsequently less gas will remain to provide a partial pressure of the reactive gas. Therefore the partial pressure of the reactive gas will drop. This in turn will cause a further increase of sputtering of unreacted metal atoms that will cause an even larger gettering of the gas, etc. This is also an avalanching effect resulting in that the process avalanches from P_3 to the position P_4 on the processing curve.

From the above description it can be understood how the hysteresis effect appears during reactive sputtering. The hysteresis appears when increasing and decreasing the reactive gas flow without any further control of this gas. The process will thus follow the dotted lines in the figure. It is an unavoidable effect of the complex gettering mechanisms that occur during processing.

It should be noted, however, that if the processing chamber is equipped with some kind of a control unit capable of controlling the partial pressure in the chamber, it will be possible to follow the theoretical solid line in figure A5.3.2 (top). In fact this curve was calculated by first assuming a certain value of the partial pressure and thereafter calculating the necessary flow of the reactive gas. Experimentally this is done in the same manner. The control unit will automatically adjust the gas flow to obtain the desired partial pressure.

The corresponding curve for the sputtering rate R versus reactive gas flow, Q, is shown in figure A5.3.2 (middle). For the same reason as described above this curve also exhibits the hysteresis effect. The dotted line is the expected experimental curve when the partial pressure is not controlled. The solid curve corresponds to the same conditions as the solid curve in figure A5.3.2 (top).

In figure A5.3.2 (bottom) is shown the corresponding surface coverage curves Θ_t and Θ_s as a function of the reactive gas flow Q. It should be noted that Θ_s represents the composition of the deposited film and that Θ_t represents the so called 'target poisoning', i.e. the fraction of compound on the target surface. $\Theta_t = 0$ represents a clean metal target while $\Theta_t = 1$ represents target conditions where all metal atoms at the target surface have reacted with the reactive gas. In the case of reactive sputtering of Al in a mixture of oxygen and argon the sputter erosion rate from the target may differ by more than one order of magnitude between $\Theta_t = 0$ and $\Theta_t = 1$. It has been experimentally found, however, that it may be possible to operate the process at the high sputter rate mode as close as possible to the avalanche point (P_1) and still obtain a film coating having $\Theta_s = 1$ (Al_2O_3). This can easily be done in the partial pressure control mode if the feedback control has a fast enough response, but is much more delicate in the reactive gas supply mode since the risk of an avalanche runaway is obvious in this mode of operation close to this processing point.

The S-shape (solid lines) of the theoretical curves has been experimentally verified in systems having partial pressure control [3, 8]. In such controlled systems it is possible to make small increments of P_r

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and obtain uniquely defined values of R, Q, Θ_t and Θ_s.

If the system is only supplied with a mass flow controller and has no system for pressure control the situation is somewhat different. In such systems only small increments in Q can be generated. At point P_1 in figure A5.3.2 (top), the system will respond to any further increase in Q by avalanching to the corresponding upper value (P_2) on the curve (dotted line). From here on the process will follow the solid line for a further increase in Q.

By decreasing the value of Q from a high level to smaller values the process will follow the solid line down to point P_3. A further decrease in the value of Q will result in that the process avalanches down to the corresponding lower value (P_4). From here on the process will follow the solid line for any further decrease in the value of Q.

The positions of the upward-avalanche and the downward-avalanche are clearly separated from each other. This separation defines the hysteresis width of the reactive sputtering process. This is a characteristic feature of most reactive sputtering processes.

It is possible to eliminate the hysteresis effect by increasing the pumping speed of the vacuum pump [9]. To illustrate this, a set of R versus Q curves are plotted in figure A5.3.3 for different pumping speeds of the vacuum system. The calculations clearly predict that the hysteresis is eliminated as the pumping speed is increased.

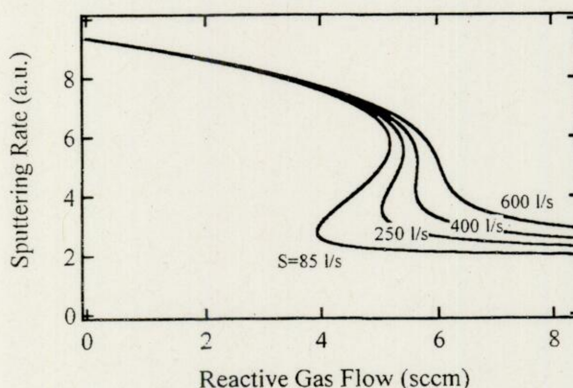

Figure A5.3.3. Simulation results illustrating the influence of the external pumping speed on the hysteresis width.

Another interesting processing behavior is illustrated in figure A5.3.4. In this figure, curves for R versus Q for different ion current densities J are plotted. It can be shown from the model outlined above that the dotted straight lines from the origin in this figure represent constant compositions (Θ_t and Θ_s) of the target and collecting surfaces [10]. This figure thus to some extent gives information on deposition rate as well as illustrating the effect of the composition of the deposited thin films. This figure also illustrates the aforementioned importance of applying the different parameters in a proper sequence. Applying 5.5 sccm of reactive gas flow and then a target current of 1.2 A will cause the process to move in the directions indicated by the arrows towards point P_A. If the target current is applied first, however, the process will follow the arrows to point P_B. Subsequently, it is possible to operate the process in both metallic and compound mode for the same reactive gas flow and target current depending on the sequence they are applied.

A5.3.2 REACTIVE CO-SPUTTERING

Sometimes it may be desirable to deposit a multi-element oxide, nitride or carbide, etc, by reactive sputtering. This can be realized by sputtering from several elemental metal targets (co-sputtering). At first sight this might seem like a simple solution for multi-elemental reactive sputter deposition. However, it is not possible to vary the conditions at the different targets independently. A power increase at one target in order to increase the deposition rate of this element will cause an increase in the gettering rate of reactive

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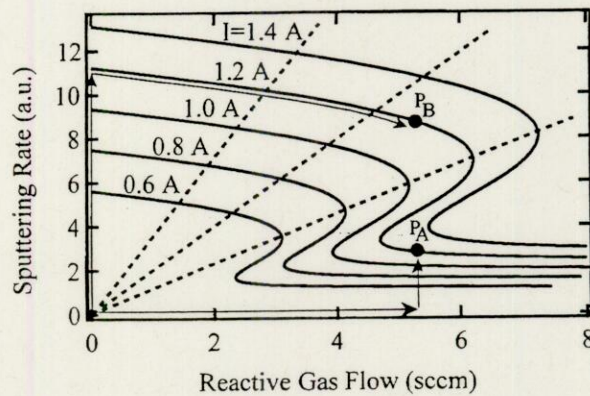

Figure A5.3.4. Simulation results of the sputtering rate versus reactive gas flow for different constant target currents. The dotted straight lines represent constant Θ_t and Θ_s.

gas molecules. This in turn will cause a decrease in the partial pressure of the reactive gas. This decrease will also affect the composition of the material sputtered from the other target, since both targets are in the same vacuum system and hence are exposed to identical partial pressure of the reactive gas.

It is quite straightforward, however, to apply the reactive sputtering model presented above to this case as well. Below we will outline the treatment of reactive sputtering from two separate elemental metal targets T_1 and T_2 (see figure A5.3.5(a).

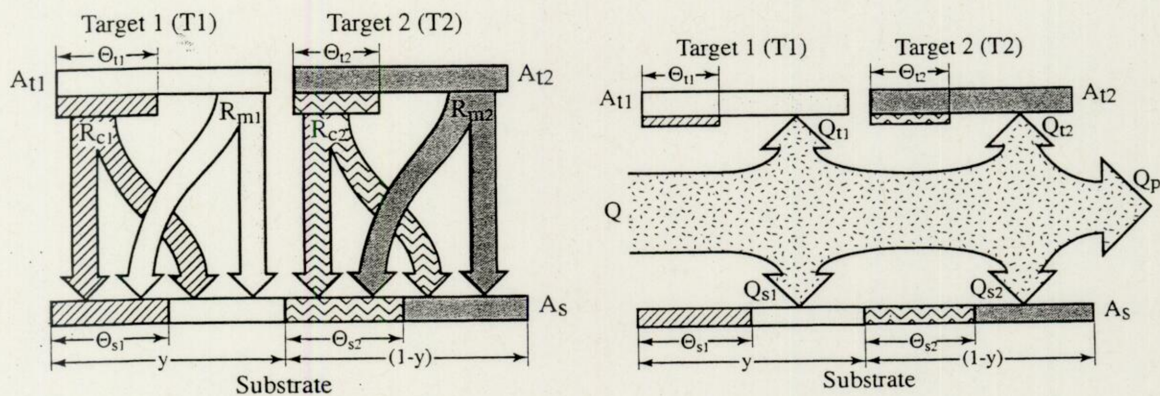

Figure A5.3.5. (a) Schematic of a two-target reactive sputtering system illustrating the flows of sputtered material. The expressions are referred to in the text. (b) An illustration of the reactive gas flux during reactive sputtering of two targets. The gas is either gettered at one of the targets ($Q_t = Q_{t1} + Q_{t2}$) or substrate ($Q_s = Q_{s1} + Q_{s2}$) metal surfaces or pumped out (Q_p).

Two balance equations for the individual targets (identical to the single target case derived above) can be derived by assuming that the partial pressure of the reactive gas is identical at the two targets.

The sputtered metal and metal-compound rates from T_1 are denoted R_{m1} and R_{c1} respectively. The corresponding outsputtered materials from T_2 are denoted R_{m2} and R_{c2} respectively. All the outsputtered material is assumed to be evenly collected at the collecting surface A_s. We then define a fractional 'composition' y of the deposited material at the collecting surface A_s as

$$y = \frac{R_{m1} + d_1 R_{c1}}{(R_{m1} + d_1 R_{c1}) + (R_{m2} + d_2 R_{c2})}$$

where d_1 and d_2 define the number of metal atoms in the corresponding compound molecules. For simplicity and similarly to the arguments above we assume that the sputtered material from target T_1 will be collected at the fraction y of the collecting surface A_s and that the sputtered material from target T_2 is collected at the complementary fraction $(1 - y)$ of the collecting surface A_s. Mathematically we treat

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this situation as two separate collecting surfaces for materials coming from targets T_1 and T_2 respectively. The problem of describing a dual target reactive sputtering process has thus been simplified to consist of two single element reactive sputter deposition processes linked together via the condition that they both must have the same partial pressure of the reactive gas. Note that the fractional 'composition' y will change its value according to the processing conditions. In figure A5.3.5(a) we show a schematic outline representing the flux of sputtered material for a reactive co-sputtering system with two separate targets. In figure A5.3.5(b) the corresponding flow of the reactive gas is also shown. Note that there are four different areas where the gas may react with 'fresh' metal surfaces. One at each target and one at the metal M_1 fraction yA_s and one at the metal M_2 fraction $(1 - y)A_s$ of the collecting surface. The mathematical treatment of the target surfaces and the collecting surfaces yA_s and $(1 - y)A_s$ can easily be dealt with analogous to the treatment of two single target reactive sputtering processes joined together by sharing identical partial pressure of the reactive gas [4].

The behavior of a reactive co-sputtering process having two different targets can be predicted by applying the mathematical treatment outlined above. Results from such calculations are shown below.

In figure A5.3.6 are shown the R versus Q curves for three different processing conditions. Included in this figure are first the R versus Q curves for each target calculated under the assumption that no sputtering takes place from the other target. Due to the different reactivity of the two target materials the hysteresis width and the position of the hysteresis may be quite separated. However, when both targets are in operation simultaneously, the reactive co-sputtering process will only generate one hysteresis region.

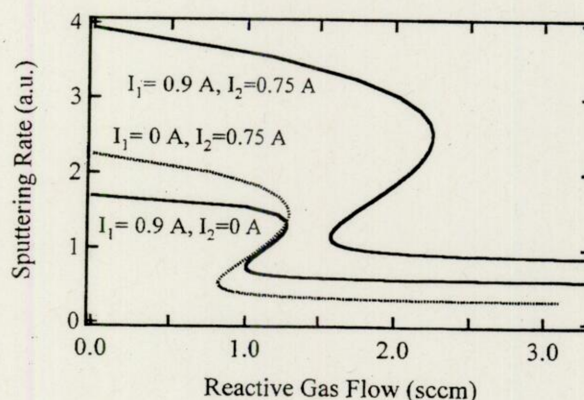

Figure A5.3.6. Simulation of a dual target reactive sputtering system for different combinations of the target currents.

The fractional 'composition' y in the deposited film may change dramatically. This is shown in figure A5.3.7. In this case y exhibits a loop in the hysteresis region. This illustrates an extreme processing behavior that may occur during reactive co-sputtering. This variation in composition is due to the fact that the sputtering rates from the individual targets may change quite differently depending on the reactivity of the target atoms to the reactive gas as the flow is varied. This behavior has been experimentally observed for reactive co-sputtering of Ti and V in nitrogen gas [11].

A5.3.3 REACTIVE SPUTTERING FROM AN ALLOY TARGET

To avoid the problem of controlling the composition of the deposited film in reactive co-sputtering it may be advantageous to carry out reactive sputtering from an alloy target. The mathematical description of this deposition process will almost be identical to the treatment of the reactive co-sputtering. However, we have to calculate the alloy target surface composition since this composition, owing to the so called preferential sputtering effects [6] will differ from the bulk composition of the target. This deviation from the bulk composition results in a pressure dependent surface composition. This is illustrated in figure A5.3.8 together with all material flows. For a two element alloy target with a bulk composition of $M1_xM2_{(1-x)}$ this can be treated in the following way.

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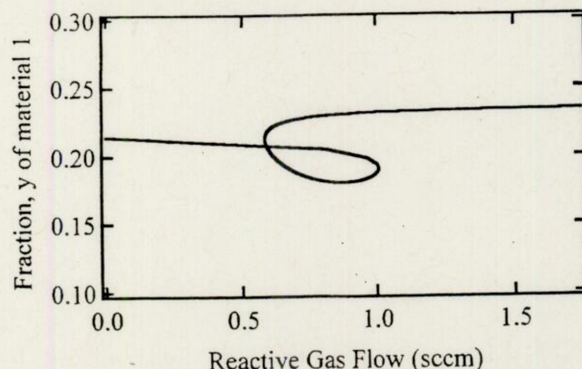

Figure A5.3.7. The relative amount of material from target 1 in the deposited film versus reactive gas flow according to simulations of a two target system.

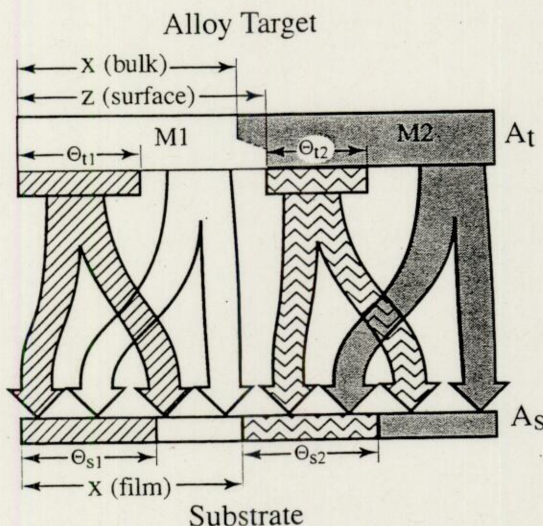

Figure A5.3.8. A schematic of an alloy target reactive sputtering system illustrating the flows of sputtered material. The expressions are referred to in the text. Note that the surface concentration z of the target differs from the target bulk concentration x.

As in the previous treatments we separate the target materials at the surface in two separate regions assuming that the 'composition' of the surface during processing will be $M1_zM2_{(1-z)}$ where M1 represents the first metal and M2 represents the second one irrespective of whether they are in pure metal or compound state. The total number of metal atoms of type M1 that are sputter eroded from the target surface region zA_t will be

$$R_1 = \left(\frac{J}{q}\right) zA_t(\gamma_{m1}(1-\Theta_{t1}) + d_1\gamma_{c1}\Theta_{t1}) \tag{A5.3.9}$$

and the corresponding expression for the metal 2 surface region $(1-z)A_t$ will be

$$R_2 = \left(\frac{J}{q}\right)(1-z)A_t(\gamma_{m2}(1-\Theta_{t2}) + d_2\gamma_{c2}\Theta_{t2}) \tag{A5.3.10}$$

The ratio between the sputter erosion rates R_1 and R_2 must correspond to the bulk composition of the target. The following relation must therefore hold

$$\frac{R_1}{R_2} = \frac{x}{1-x} \tag{A5.3.11}$$

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The alloy target can thus be treated like the reactive co-sputtering having two separate targets one having a surface area zA_t (metal 1) and the other a surface area $(1 - z)A_t$ (metal 2). z will vary and has to be calculated for each value of the partial pressure of the reactive gas. Θ_{t1} and Θ_{t2} can be calculated by applying the same balance description for the separate target surfaces as for the single target case. By inserting the values of Θ_{t1} and Θ_{t2} in equation (A5.3.11), z can also be calculated.

Equation (A5.3.11) ensures that the model correctly incorporates the obvious steady-state conservation requirement that the relative concentrations of M1 and M2 type of atoms are identical to their relative bulk concentrations. It should be noted, however, that this condition does not imply that both metals react at the same rate with the reactive gas. Calculations based on the arguments described above are shown in figure A5.3.9 where the film composition is plotted versus reactive gas flow. The reactive gas has arbitrarily been assumed to have a sticking coefficient to M2 of 0.05 and the value 0.3 for M1. It is clearly seen that one may expect that metal 1 forms a compound much easier than metal 2. Consequently, operating close to the avalanche point P_1 may not necessarily yield films in which both metal species are fully reacted, as is often the case of the single element reactive sputtering process. To ensure fully compound formation one may have to increase the supply of the reactive gas far beyond the avalanche point and thus carry out the deposition process in the low sputtering rate mode.

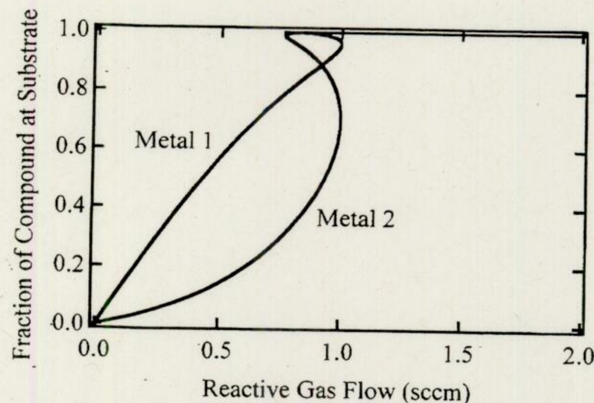

Figure A5.3.9. Fractions of the different metals that have formed a compound versus reactive gas flow according to simulations of reactive sputtering from an alloy target.

A5.3.4 REACTIVE SPUTTERING INCLUDING TWO REACTIVE GASES.

By adding two reactive gases to a sputter deposition process it is possible to form e.g. oxy-nitrides and carbon-nitrides, etc. At first sight this might look as not too complicated a process. However, as has already been pointed out, the reactive sputtering process is extremely sensitive to the partial pressure of the reactive gas. Using two reactive gases will add an extra very sensitive parameter to the process. For an elemental target that forms separate compounds with the two reactive gases the conditions at the target are illustrated in figure A5.3.10.

We may define two surface coverage coefficients Θ_{t1} and Θ_{t2} representing the fractions of the surfaces that are covered by the compound formed by reactions with gas 1 and gas 2 respectively. The arguments to obtain balance equations will be very similar to the previous cases.

At the target, the compound formation rate by gas 1 has to be equal to the sputter removal rate of compound 1 from the fractional area Θ_{t1} of A_t. This yields the following balance equation for the compound 1 part of the target:

$$\Gamma_{r1}\alpha_{t1}\,[1 - (\Theta_{t1} + \Theta_{t2})]\,A_t b_1 = \left(\frac{J}{q}\right)\gamma_{c1}\Theta_{t1}A_t \qquad \text{(A5.3.12)}$$

where the indices and the symbols are defined analogous to previous definitions. A similar balance equation can be defined for the compound 2 part of the target.

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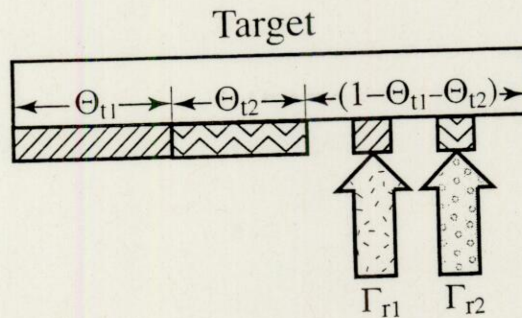

Figure A5.3.10. A schematic illustrating how the target is assumed to be divided into three parts for reactive sputtering using two gases. One pure metal part and one part for each compound.

At the collecting surface one may also define three separate regions, the unreacted metal region, the compound 1 region and the compound 2 region. By similar arguments as described above it is also possible to define balance equations for this area. Due to the similarities with the previous treatments, however, we do not include the mathematical details in this presentation. The interested reader is referred to [5] for further details. We will, however, make some remarks concerning this process.

It is recalled that an increase in the partial pressure of a reactive gas causes an increase in the fraction of the target that is covered by the compound. This in turn causes a decrease in the sputter erosion rate of unreacted metal atoms causing a decrease in the gas gettering which in return reduces gas consumption that further increases the partial pressure and so on.

In the two gas reactive sputtering process, any of the two gases may start this avalanche. In fact, it may happen that one of the gases may poison the target to such an extent that adding a small amount of the second gas will trigger an avalanche. This effect is illustrated in figure A5.3.11. This figure shows the results of the simulations during the conditions that a constant supply of one reactive gas (1) is supplied to the processing chamber. This supply level is not large enough to force the process to pass the avalanche point from high sputter rate mode to low sputter rate mode. However, by adding a supply of the second gas (2) the process is forced to pass the avalanche point. From the figure it can be seen that this may well result in that an increase in the supply of gas 2 causes a larger increase in compound 1 formation than compound 2 opposite to what one might expect. An increase in the supply of gas 2 causes a larger increase in the partial pressure of gas 1 than of gas 2. Due to this effect formation of compound 1 will be favored.

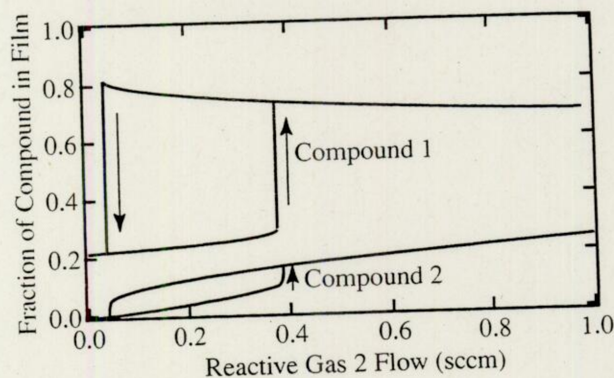

Figure A5.3.11. Diagram illustrating simulation results of the substrate composition versus flow of reactive gas 2 in a two-reactive-gas sputtering system. The flow of gas 1 is assumed to be constant.

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The above effect serves to illustrate that it may be quite a delicate matter to control the partial pressure of the two gases during reactive sputtering with two reactive gases. Since the supply of one gas significantly may influence the partial pressure of the other there exists no simple straightforward way of applying process control in this case.

A5.3.5 CONCLUSIONS

The above presentation serves to illustrate that by quite simple physical arguments it is possible to set up mathematical models for different reactive sputtering processes. Despite all simplifications made to obtain simple and manageable models the results predicted by these models fit remarkably well to most experimental results published in the literature. Hopefully this may encourage the reader to add his/her own improvements to the model by modifying some of the equations to obtain better accuracy.

Computer power has reached such a level that the reason for making crude approximations to obtain simple mathematical expressions may no longer be necessary. Therefore more detailed information of the reactive sputtering process may now be included to form more advanced models of the reactive sputtering process. We will point out a few new ways of expanding the computer simulations of the reactive sputter deposition process.

It is well known that the sputtering yield for an ion impinging on a surface is strongly dependent on e.g. the matrix and composition of the surface layer. However, there exist computer simulation codes that with reasonable accuracy predict these variations [7]. Since the composition of the target surface varies for different processing conditions it should be valuable to include the variation in the sputtering yield due to this effect in a reactive sputtering model.

The transport of sputtered material from the target to the substrate (and chamber walls) is quite more complicated than assumed in the models above. There exist, however, Monte Carlo based simulation programs [12] that calculate scattering due to gas collisions and also the flux distribution of the sputtered material in the vacuum chamber. Furthermore, the race-track (the limited area on the target surface from which material is sputter eroded) of a magnetron target indicates that the ion current density does vary significantly on the target surface resulting in non-uniform sputter deposition fluxes at various receiving surfaces. Due to this effect material is sputter eroded inhomogenously from the target surface. Such effects may also be included in the model. By considering a sufficient number of collecting surfaces much higher precision in the calculations of the gettering of the reactive gas may be obtained.

The current through the target consists of the ion current and the electron current originating from secondary electrons created by the energetic ions impacting onto the target surface. This electron current may contribute to a substantial part of the total current. Moreover, the secondary electron yield depends strongly on the surface composition. Due to this effect a constant current in the external electric circuit does not necessary imply a constant ion current during the reactive sputtering process. To increase the precision in the reactive sputtering modeling work the effect of the variation in the secondary electron yield should also be included.

The list of 'second-order effects' can of course be very long. One has to justify the amount of work put into the model against the expected value of the improvements of the calculations. In most practical applications it is quite satisfactory, if possible, to obtain a good solid basic understanding of the processing behavior. The 'fine tuning' of the process will be done on-site in any case. However, accurate processing models are necessary in the work of obtaining adequate process control.

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