A model of DC reactive magnetron sputtering for graded solar thermal absorbers

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Abstract. In this work we present process modelling of reactive in-line sputtering. Although modelling of reactive sputtering is often used, most models are based on assumptions which make them insufficient for use in this case. The presented model takes into account a realistic deposition rate profile and distribution of reactive gas pressure. The model has been applied to reactive sputter deposition of graded solar thermal absorbers. It has been shown that the presented model represents a simple alternative to complex Monte Carlo simulations while still representing all important features of the process.

1. Introduction
A thin film solar thermal absorber consists of two layers deposited onto a material with high thermal conductivity such as copper or aluminium. The base layer of the coating is metallic with high absorption while the top surface oxide layer serves as an antireflection film. A reactive magnetron sputtering of Ni₈₀Cr₂₀ target in argon/oxygen atmosphere was developed for industrial high-rate deposition. Optimum properties and composition of the coating were studied previously [1]. Graded coatings with desired optical properties are deposited during one passage through the sputtering zone at optimum conditions. The main advantage of such setup is the deposition of both layers from one target during one passage through.

In this work we report process modelling of the reactive in-line sputtering of such graded coatings. Although modelling of reactive sputtering is often used, most of the models are based on simplifications which prevent them from use in this case. In the classical model [2], homogeneous distribution of deposition rate and uniform pressure in the system is assumed. Since both quantities are highly non-uniform in the studied in-line coater, an extension has been made, taking into account a realistic deposition rate profile and the distribution of reactive gas pressure. Although a model for real 3D in-line processing has been developed previously [3], the use of Direct Simulation Monte Carlo for gas flow simulation and particles transport increases its complexity and demands on the computational power.

2. Experimental
The sputtering unit used in the study is a miniature copy of a full scale industrial roll coater. It has been described in detail elsewhere [4]. A schematic cross-section of the sputtering zone is shown in figure 1. The sputtering zone is separated by enclosures from the rest of the vacuum chamber with a vacuum pump. The system is equipped with a planar circular magnetron with a Ni₈₀Cr₂₀ target with the diameter of 158 mm, powered by a DC sputtering power supply. The main feature of the sputtering setup is the asymmetric position of the oxygen inlet. This facilitates a gradient of the partial pressure...
of reactive gas across the sputtering zone. The nozzles are oriented downwards, facing the substrate. The length of the sputtering zone is 320 mm, target-substrate distance is 120 mm and width of the substrate 145 mm. The standard substrate is an aluminium foil moving from left towards the right end, as indicated by arrow in the figure.

3. Model

The composition of target and substrate is solved from a reactive sputtering model. Results are then used to determine the corresponding pressure distribution. Steady state solution is obtained in an iterative manner.

3.1. Reactive sputtering model

A reactive sputtering model based on the original Berg’s approach [2] is used. In the model, the formation of compound is attributed only to the chemisorption on surfaces covered with metal. The composition of the target and substrate surface is described by the fraction of the surface covered by compound, \( t_q \) and \( s_q \), respectively. In order to account for non-uniform deposition rate, target and substrate are divided into cells. At the target, each cell can have different ion current density and the sputtered material is assumed to have cosine distribution. From the position of a substrate cell with respect to each target cell, the deposition flux at the substrate can be calculated as a sum of contributions from each part of the target.

If the condition of steady state is assumed, the rate of formation of the oxide must be equal to the rate of removal. Introducing \( F_{RG} \) as the flux of reactive gas atoms and assuming atomic sputtering of the compound [5], the balance equation for \( i \)-th target surface segment has a form

\[ j^i / q Y_{ic} \theta^i = \alpha F_{RG}^i \theta^i, \]

(3.1)

where \( j \) is the current density, \( q \) the elementary charge, \( Y \) the sputtering yield of oxygen from the oxide, and \( \alpha \) is the sticking coefficient. The balance for \( j \)-th substrate segment is

\[ \alpha F_{RG}^j \theta^j = F_m^j \theta^j, \]

(3.2)

where the term \( F_m^j \) denotes the total flux of metal atoms to the \( j \)-th segment. The flux of metal is calculated as \( F_m^j = \sum_i T_{ij} (j_i/q Y_m \theta^i + j_j/q Y_m (1-\theta^i)) \), where \( T_{ij} \) is a transformation matrix for a cosine source, \( Y_m \) is the sputtering yield of metal from oxide, and \( Y_m \) is the sputtering yield of metal from metallic part of the target.

3.2. Pressure distribution

The two balance equation for substrate and target surface (3.1) and (3.2) has to be completed with a balance for reactive gas. The distribution of the reactive gas is calculated using equation of diffusion. The argon pressure is assumed to be uniform and substantially higher than that of reactive gas. Then the flow of RG can be modelled as diffusion with the coefficient of diffusion \( D \) given [6] by

\[ D = \frac{4(v_{s1}^2 + v_{s2}^2)^{1/2}}{3\pi (n_s + n_a)(\delta_s + \delta_a)^2}, \]

(3.3)

where \( v_s \) is the average molecular speed, \( n \) the density of molecules and \( \delta \) the molecular diameter.

The equation of diffusion is solved on a rectangular area with three different boundary condition. First, the target and substrate getters an impinging reactive gas atom with probability \( \alpha (1-\theta) \).
Pumping orifices fulfil the condition \( \frac{1}{2} D \nabla p = S p \), where \( S \) is the pumping speed and \( p \) is the pressure of reactive gas. The rest of the boundaries act as a passive wall with no pressure gradient in the direction perpendicular to the surface. Finite element method is employed for solving of the problem.

4. Results and discussion

There is no pressure gauge inside the sputtering zone. Due to the presence of enclosures, the pumping speed is expected to be substantially reduced. A value of 100 l/s has been used for pumping speed, obtained by fitting. This results in a reasonable argon pressure of 2.5 Pa for given Ar flow. Other parameters used in this work are: sticking coefficient \( \alpha = 1 \); sputtering yields \( Y_a = 0.6 \), \( Y_{nc} = 0.06 \); \( Y_{cc} = 0.12 \); target-substrate distance 120 mm; substrate width 290 mm; and target width 145 mm.

In this study, films deposited at static substrates of glass were used in order to determine sputtering conditions at different positions of the sputtering zone. The deposition conditions were: sputtering power of 10 kW, Ar flow of 150 sccm, and \( \text{O}_2 \) flow of 24 sccm, unless stated otherwise. Based on the optical measurements, the best properties are obtained for films prepared at oxygen flow of 24 sccm. The composition of the films has been evaluated by two different methods, XPS and by fitting of the reflectance spectra. Each method, however, has certain drawbacks when used for composition analysis.

XPS itself is surface sensitive method which does not affect the sample, but it requires a sputter cleaning of the surface prior to the measurement. The ion cleaning, in case of oxides, alters substantially the composition due to the preferential sputtering of oxygen. This effect is very strong for NiO [7]. Moreover, surface enrichment as a result of Cr diffusion has been reported for Ni/Cr alloy. The results are therefore normalized to the composition of the sample at \( x=320 \text{ mm} \), which is very close to stoichiometric oxide. The optical evaluation is only indicative as the dependence of reflectance on the composition is not exactly known [8]. However, the agreement of results obtained by both methods is very good.

The compositional results are shown in Figure 2, together with the simulated composition. The simulated profile is less steep than measured, the general behaviour is resembled well. In order to resolve the origin of the deviations, more accurate quantitative analytical methods have to be used.

![Figure 2: Composition of samples (q_{O2}=24 sccm) as measured by XPS and fitted from reflectance spectra, and simulated profile.](image)

An important modelling parameter is the diffusion coefficient \( D \). Its higher value indicates higher diffusion rate and hence smaller pressure gradients. The influence of pressure gradients is shown in Figure 3 displaying the composition of films for three different values of \( D \) corresponding to the pressure of 0.5 (\( D=3.54 \text{ m}^2/\text{s} \)), 1 (1.86), and 2.5 Pa (0.75). Although the effect on the hysteresis curve is negligible (not shown), the impact on the composition distribution is obvious. Lower \( D \), i.e. lower sputtering pressure, causes a shift in composition toward the left end of the sputtering zone. No analysis of composition for other conditions has been carried out, but the simulated compositional curves represents well the measured DC conductivity distribution [1].
There is an obvious difference between films sputtered in metal ($q_{RG}=18$ and 29.4 sccm) and compound ($q=34$ sccm) mode. (figure 3). In the compound mode, due to the excess of oxygen, the pressure is very high and all growing surfaces receive enough oxygen to form stoichiometric compound. The situation is different in metal mode. Since the gettering rate of metal surfaces is substantially higher than the pumping speed of the pump, a pressure gradient is established across the sputtering zone resulting in a composition gradient.

There are two main effects contributing to the compositional gradient. As mentioned above, there exists a gradient of oxygen pressure and hence the flux of oxygen to the growing surfaces differs across the sputtering zone. Due to the differences in deposition rate, also the arrival rate of metal atoms varies. The main quantity governing the composition of resulting film is the ratio between the oxygen flux $F_{RG}$ and the flux of metal $F_m$. For $D=3.54$ m$^2$/s, the flux of reactive gas is about two times higher near to the oxygen inlet compared to the other end. The flux of metal, however, differs four times. We can therefore conclude that the main effect responsible for the gradient in composition is the distribution of deposition rate. This leads to a more symmetric distribution of the composition. When $D=0.75$ m$^2$/s, the dominating effect is the pressure gradient, as there is a five times difference in $F_{RG}$ between the ends at the flow of 29.4 sccm. As a results, the minimum of the oxide content shifts towards the left.

5. Conclusions
A simple model describing the compositional behaviour as a function of the position over the substrate in the reactive sputtering process in an in-line coater with asymmetric reactive gas inlet has been presented. The model assumes a realistic deposition rate profile and the distribution of reactive gas pressure. The main advantage of the suggested approach is its simplicity compared to complex models based on Monte-Carlo simulation. The model can be used to tune the deposition process and geometry of the system to optimize properties of thermal absorbers, or graded coatings in general. More sputtering sources and/or different shape of the sputtering zone can be readily included.

The two most important parameters of the sputtering process are the operating pressure and the target-substrate distance. The former influences the gradient of reactive gas across the deposition zone. The later affects the distribution of deposition rate. Influence of other process parameters has also been studied but their effect has been found negligible, in agreement with experimental findings.

6. References
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