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Reactive magnetron sputtering: from fundamentals to high deposition rate processes

Tomas Kubart
Department of Solid State Electronics, The Ångstrom Laboratory, Uppsala University, Uppsala, Sweden
E-mail: Tomas.Kubart@angstrom.uu.se

Reactive magnetron sputtering is a widely used technique to deposit compound thin films such as oxides and nitrides. This contribution describes briefly basics of the reactive process and its modeling. Strategies for increasing deposition rate, especially for oxides, are discussed. Rather than detailed discussion, an overview of the basic principles and key results is provided together with selected references.

1. Introduction

Reactive magnetron sputtering is a very popular technique to deposit compound thin films such as oxides, nitrides, or carbides. Magnetron sputtering is very versatile and scalable with substrate dimensions up to several meters [1]. In reactive sputtering, a wide variety of compounds may be synthesized from low cost metallic targets by simple addition of a reactive gas to the working atmosphere of argon [2]. The composition of the compound can be readily varied by changing the amount and type of reactive gas.

Some examples of industrial applications of reactive sputtering are large area coatings on glass, transparent conductive coatings for photovoltaics, or decorative layers on various substrates [3].

Especially for industrial applications, high productivity is essential. Therefore, high deposition rates are required. Combining a high deposition rate and true compound stoichiometry of the deposited film turns out to be a contradicting desire. This is because of the complex interaction between the reactive gas and the sputtered metal which causes instability in the sputtering process. The relation between the deposition rate or composition of the coating and flow of reactive gas is very non-linear and usually exhibits hysteresis behavior when the reactive gas supply is changed [4].

The hysteresis behavior is illustrated in Figure 1, showing a typical processing curve for target erosion rate vs. flow of the reactive gas. Obviously, the film deposition rate is proportional to the erosion rate and shows the same dependency on the flow of reactive gas. Adding the reactive gas, such as O₂, to Ar atmosphere, results in a small initial decrease in the erosion rate until a critical point (A) is reached, where the rate drops in an avalanche manner to a very low value (B) corresponding to the so-called compound, or oxide, mode. In the compound mode, the target surface is covered with a compound layer which has typically sputtering yield much lower than the corresponding metal. Decreasing the flow from this point will leave the process in compound mode until another transition value (C) is reached. At this point, the deposition rate will come back to the metal mode (D). In metal mode, there is very little compound at the target surface and the deposition rates are comparable to rates for pure metals. Films deposited in metal mode are typically substochiometric, while operation in compound mode results in stoichiometric or over-stoichiometric coatings, depending on the material system.

![Figure 1: Typical experimental curve for sputter erosion rate in reactive sputtering process as measured by optical emission spectroscopy.](image)

For most materials, the sputtering yield and thus the deposition rate of oxides is much lower than that of the corresponding metals. Decrease of more than ten times has been reported for Ti or Al [5]. The deposition rate may be increased significantly by operation inside the transition area, between points A and D. Since the process is unstable when only the flow of reactive gas is controlled, a suitable feedback system may be necessary. Different feedback signals may be used and optical emission spectroscopy, mass spectroscopy or a lambda probes are commonly used [6].

2. Process modeling

Modeling of reactive sputtering is described in detail in a review article by Berg and Nyberg [4].
Therefore, only a brief description of the basic principles is provided together in this section.

The classical model of reactive sputtering is based on the assumption of steady state. Then it is possible to formulate balance equations for formation and removal of compound at the target surface, at the substrate, as well as balance of reactive gas introduced to the chamber and consumed or pumped away [7]. Despite its simplicity, the model well describes basic aspects of hysteresis in a reactive system and is therefore widely used.

Only chemisorption is assumed in the basic model. There are only few reports of the values of sticking coefficients in reactive sputtering [8]. The results suggest that values close to unity, often used in simulations, are overestimated. Depla et al. showed in a series of articles that implantation of reactive gas is very important and may present an alternative way for reactive gas incorporation [9, 10].

Implantation of reactive gas determines process dynamics because it leads to formation of relatively thick layers of compound on the target surface and thus increases the process response time [11].

3. Approaches for high deposition rate

There is a continuous interest in alternative high deposition rate approaches to avoid the complex control systems and increase process stability. Modeling has been very helpful in process development and optimization. Although existing models provide qualitative rather than quantitative results, they can reduce the need for trial-and-error development.

3.1. Increasing pumping speed

Kadlec et al. showed that for sufficiently high pumping speeds the hysteresis may be avoided [12]. This effect can be readily simulated by the basic model, as shown in Figure 2.

![Figure 2](image2.png)

**Figure 2:** Sputtering rate vs. the flow of reactive gas calculated for three values of pumping speed. With increasing pumping speed, the hysteresis is reduced.

S-shaped curve showed in the figure corresponds to response of a system with a feedback control. All points inside the transition region are then available and the transition region (inside hysteresis loop) is characterized by a reversed slope of the curve. With increasing pumping speed, the width of hysteresis is reduced and eventually a hysteresis free operation is achieved. In large deposition systems, however, the required pumping speeds are unrealistically high.

3.2. Substoichiometric targets

Hysteresis is caused by an abrupt change in the target erosion rate upon target oxidation, i.e. the difference in sputtering yields of metallic and oxidized target surface. This suggests that the hysteresis may be removed if the difference in sputtering yields is reduced. Such approach is widely used for sputtering of TiO$_2$ from substoichiometric TiO$_x$ targets [13]. Because the initial sputtering yield in Ar is lower than that of Ti, there is a smaller drop in the erosion rate and no hysteresis occurs.

Figure 3 shows the deposition rate as a function of oxygen flow for TiO$_x$ targets of different composition. The transition from metal to compound mode is more continuous with increasing x, i.e. more oxide in the target.

![Figure 3](image3.png)

**Figure 3:** Deposition rate from TiO$_x$ targets with different composition, x.

Substoichiometric targets may be used for other materials as well. In the case of TiO$_2$, however, in addition to the hysteresis free operation the deposition rate is also enhanced by high sputtering yield of Ti suboxides [14].

Similar idea led to the suggestion of introducing N into the sputtering atmosphere for TiO$_2$ deposition [15]. Part of the target surface is then covered by nitride with higher sputtering yield than the oxide and so the hysteresis is also reduced. There may be very little nitrogen left in the deposited coating due to a higher stability of oxide as compared to nitride.
3.3. Sputtering yield amplification

Strategies discussed in previous paragraphs aimed at tackling the hysteresis effect in order to avoid target poisoning. Sputtering yield amplification (SYA) is a technique to increase the deposition rate by increasing the sputtering yield of target material. SYA can be used in either metal or oxide mode. It can also be combined with process control to increase the rate even further.

In SYA, the sputtering target is doped by a heavy metal in order to change the penetration depth of the collision cascade. An increased fraction of the cascading light atoms will be reflected back towards the target surface due to the collisions with the added heavy atoms. This will increase the number of eroded atoms, i.e. the sputtering yield. It should be noted that the doping element is sputtered together with the target atoms and incorporated into the deposited film.

The effect is most pronounced for light elements with high surface binding energy, such as carbon. In this extreme case, about 6 times increase in the sputtering yield of C is predicted [16] as shown in Figure 4.

SYA was discovered by Berg et al. and demonstrated for C doped with Pt [17]. We have found recently that the effect is very suitable for reactive sputtering of oxides. Our initial simulations performed for Al using binary collision approximation code TRIDYN showed that while in metal mode about 30% increase in the deposition rate is expected, the rate may be more than doubled in oxide mode [18].

SYA requires that the doping element is mixed on atomic scale and so target production may present a serious limitation for the practical realization of SYA. An alternative to homogenous target is based on ion implantation of the heavy element. In this case, a thin layer of the dopant is deposited on the target surface and incorporated by recoil implantation. Such a process may be easily realized with rotating magnetrons, as illustrated in Figure 5 and described in more detail elsewhere [19].

In order to evaluate the range of operating conditions for SYA in the setup with rotating magnetron, we have extended our previous model to take into account the geometry of the setup [20]. The model describes mixing at the target surface and incorporation of reactive gas. It can be used to study an impact of process conditions, such as rotational speed or oxygen pressure and evaluate sputtering yields for any combination of materials.

An example of results predicted by the model is shown in Figure 6. With increasing amount of W, expressed as the deposition rate on the back side of the primary target, the Al yield increases. After initial fast increase, Al yield saturates for W rates above 0.1 nm/turn while the fraction of W is proportional to the W deposition rate. W deposition rates of 0.04 to 0.08 nm/turn lead to a 65 to 80% increase in the deposition rate with only 0.6 to 1.2 at.% of W in the resulting film. Simulated results were confirmed experimentally [19] and the results are shown in Figure 7.

\[ \text{Figure 4: Calculated partial sputtering yield values for C and W from C target doped with W bombarded with 300 eV Ar ions. Dashed line marks sputtering yield from undoped C target.} \]

\[ \text{Figure 5: Serial co-sputtering system consisting of a primary cylindrical rotating magnetron and a secondary planar magnetron. Doping element is deposited on the back side of the primary target, during rotation brought into the primary erosion zone and recoil implanted into the primary target surface.} \]

\[ \text{Figure 6: Simulated Al sputtering yield} \]
normalized to the Al value (solid), and the fraction of W in the sputtered metal flux (dashed line) versus W rate in oxide mode.

Figure 7: Experimental values of Al sputtering yield as a function of W doping as determined from [19].

In addition to the atomic mass of the doping element, its surface binding energy is also important. This can be demonstrated in the case of Bi and W. Bi is heavier than W but does not lead a significant increase in the deposition rate. Our simulations showed that this is because of the low value of Bi surface binding energy. Bi is quickly removed from the target surface and cannot affect collision cascades. W, on the other hand, stays in the target for very long time as a result of repeated recoil implantation deeper into the target [20]. This “recycling” mechanism increases the concentration of W in the target surface and reduces its concentration in coatings.

3.4. Hysteresis in reactive HiPIMS
High Power Impulse Magnetron Sputtering (HiPIMS) is a technique which provides highly ionized flux of sputtered material [21]. In HiPIMS, the discharge power is applied in short pulses with low duty cycle. High ionization is achieved thanks to the high instantaneous plasma density in the HiPIMS pulses, about two orders of magnitude higher than in standard magnetron sputtering. Among other interesting aspects of HiPIMS, the effect of the process on hysteresis has attracted attention. Wallin and Helmersson reported hysteresis free operation with HiPIMS of Al₂O₃ while the same DC process exhibited hysteresis [22]. Because stoichiometric oxide could be deposited in the metal mode by HiPIMS, the deposition rate in HiPIMS was substantially higher than in DC sputtering.

The exact origin of the effect is not clear yet and some authors did not observe the effect [23]. An example of experiments carried out in the same system as used by Walling is shown in Figure 8 for Ce sputtered in Ar+O₂ [24]. In DC sputtering, there is a clear hysteresis loop (black line). In HiPIMS, the width hysteresis of hysteresis is decreasing with increasing frequency of pulsing. Because the average power and pulse on time was kept constant, the duty cycle was increasing with frequency while the peak power was decreasing. There exist an optimum frequency of pulsing which leads to minimum hysteresis. For lower and higher frequencies, the hysteresis is more pronounced. Although several different explanations of the effect have been put forward, most cannot explain the effect of frequency.

Figure 8: Discharge voltage in DC magnetron sputtering and HiPIMS with Ce target. The average power was kept constant at 70 W.

We have observed a correlation between the size of sputtering target and the optimum frequency, the optimum frequency was lower for larger targets. [25]. This may indicate that the effect is caused by gas rarefaction which occurs during a HiPIMS pulse. The depleted volume is bigger for larger targets and so the time required for refill of gas is longer. At this moment, however, more data is needed. Also, it seems that for larger systems, the effect is less pronounced as compared to small lab-scale setups.

HiPIMS is certainly an area where more work is necessary to get a reliable model of the process. Because of the higher plasma density, there is much stronger coupling between surface and plasma processes. In the basic reactive model, only surface processes are considered and an extension which incorporates also the plasma is not straightforward.

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5. References