State of the art in reactive magnetron sputtering

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The reactive magnetron sputtering process is widely used for the production of oxide and nitride coatings. The primary drawbacks of this process are the hysteresis behaviour, which seriously limit the stability, and the poisoning of the sputtering target, which substantially reduces the sputter erosion rate. In the process of optimizing the process, we have recently developed processing conditions that may reduce and ultimately eliminate these drawbacks. These novel conditions will be described here.

i) Favourable conditions may be obtained in a mixed nitrogen/oxygen processing environment for deposition of oxide films. The hysteresis behaviour is reduced and higher deposition rates are obtained.

ii) We have found out that a reduction of the target sputter erosion area below a critical value, will completely eliminate the hysteresis of this process. Furthermore, processing with smaller target erosion zones also will give a significantly higher compound deposition rate than a larger target powered at the same level. It is believed that this effect together with a moderately high pumping speed and a compositional modification of the target will completely eliminate the hysteresis effect.

We will present experiments as well as computer simulation results to illustrate the process behaviour for both conditions i) and ii).

Introduction

Reactive sputtering is a widely used coating technique to deposit oxides, nitrides, carbides etc. However, the process has some generic drawbacks that seriously limit the stability of the process and unfortunately also decreases the compound deposition rate. Despite these drawbacks, the process is still one of the most frequently used PVD techniques.

Substantial process optimization and improvements have already been applied to the reactive sputtering process .[1-3]. One example is the pulsing of the target power for eliminating problems with arcing or increasing the ion density in the plasma in order to facilitate certain conditions for film growth. Further, special arrangements, such as dual magnetrons [4] or substoichiometric targets [3, 5], have been developed to facilitate reactive sputtering of dielectric materials. However, the major drawbacks in the reactive sputtering process are the hysteresis behaviour and the poisoning of the sputtering target which substantially reduces the sputter erosion rate. Several attempts have been made in the recent years to control the poisoning of the target's surface. Most of the effort has been focused on the control of the reactive gas partial pressure by an external feedback loop [6]. Moreover, Sophisticated systems have been developed for controlling and monitoring the process, where the plasma emission or the reactive gas pressure is monitored and used in feed-back system to control the reactive gas flow and the target power, making this approach costly and sometimes very cumbersome. The processing improvements given here are aimed at reducing or ultimately eliminating these effects in an easier way

During reactive sputter deposition, the composition of the surface of a metal target will depend on the partial pressure of the reactive gas, the target ion current and the sputtering yield of the target material. One part of the target surface will consist of the compound and the rest will consist of metal. The relation between these two parts is determined by the competition between the sputtering of compound material from the target and the formation of compound material due to gettering of reactive gas. Normally, the compound formed at the metal target surface has a significantly lower sputtering yield than the pure unreacted metal causing a drop in the deposition rate from targets covered with the compound. A typical deposition rate vs supply of reactive gas curve is shown in Fig. 1. Included in the figure is also the partial pressure vs supply of the reactive gas for the same process. The S-shaped curves in the Fig. 1 may only be obtained experimentally if the process is carried out with a feed back control system for the partial pressure of the reactive gas, or anything that is an unambiguous function of the pressure, e.g. the optical emission for the metal in the plasma.
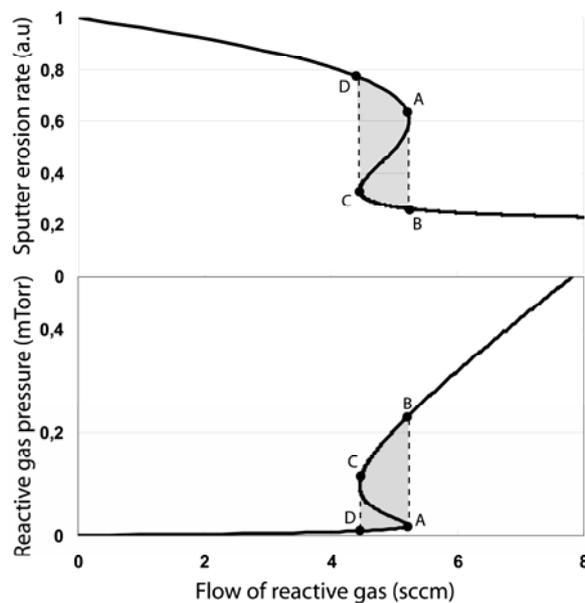

Fig. 1 Deposition rate (upper) and reactive gas pressure (lower) vs supply of reactive gas curve for a typical reactive sputtering process.

For a small partial pressure of the reactive gas a metal target will remain mainly metallic and the sputter erosion rate will not be affected. Unfortunately, this very low pressure of reactive gas is not sufficient to give the stoichiometric compound in the growing film at the substrate since a lot of the deposited metal atoms will stay unreacted. Therefore the supply of reactive gas has to be increased. However, if the gas supply q is used as the only control parameter, the system will avalanche from A to B for increasing values of q and will avalanche from C to D for decreasing values of q. The avalanche positions A-B and C-D defines the hysteresis width of the process. This is marked by the dashed line and shadowed area. It is common to refer to the A-C part of the curve as transition mode, while the (high rate) metallic mode is the part to the left of point A and the (low rate) compound mode the part to the right of point C. As long as the solid lines exhibit an S-shape with a negative slope in the hysteresis interval, the process will exhibit a hysteresis. It is common to refer to the A-C part of the curve as transition mode, while the (high rate) metallic mode is the part to the left of point A and the (low rate) compound mode the part to the right of point C.

It is common to try to operate reactive sputtering processes as close to point A in Fig. 1 as possible. Properly designed systems may give close to stoichiometric compound

films at high rates for this processing condition. Unfortunately, often fully compounded films are required. Notice furthermore, that a small increase in the supply of reactive gas may "push" the process down to position B, the low rate target poisoned mode. This illustrates the critical conditions at the position A and the need for extremely stable process control.

Herein we present processing conditions that offer significant advantages with respect to the hysteresis problem, and to the related problem of the reduction in deposition rate of compound.

First, we describe a method for reducing and ultimately eliminating hysteresis effects for reactive sputtering of metal oxides and oxynitrides. This is achieved by the addition of nitrogen to the oxygen process, which stabilises the processing behaviour and leads to higher deposition rates, since sputtering rates of nitrides are typically higher than those of the corresponding oxides. This can be qualitatively explained and theoretically predicted using an extention of Berg's model to two different reactive gases under the assumption that the formation of oxide is energetically favourable to that of nitride. Although the nitrogen addition leads to pronounced changes of the processing characteristics, incorporation of nitrogen into the growing film is very small.

Secondly, a recently developed reactive sputtering design that enables total elimination of the hysteresis effect will be shown. It will also be shown how the sputtering chamber can be modified to make it possible to operate the reactive sputtering process inside the hysteresis region, far away from the avalanching point, and have an almost metallic target and still have fully compounded films at the substrate.

Process stabilization and increase of the deposition rate in reactive sputtering of metal oxides

The reactive sputtering of metal oxides is very often highly unstable in the transition zone between the metallic mode and the compound mode and a pronounced hysteresis behaviour is observed. Typically, oxides exhibit larger hysteresis as well as a more significant drop in the deposition rate as compared to nitrides. It is therefore desirable to avoid sputtering from a completely oxidized target.

Fig. 2(a) shows the oxygen partial pressures and (b) the normalized mass deposition rates simulated with the Berg's model [7, 8] which has been extended to include two reactive gases. Details and parameters for the simulations can also be found in ref. [9]. It can be clearly seen that with increasing nitrogen addition the hysteresis gradually disappears. The origin of the vanishing hysteresis is the higher effective sputter yield due to a lower binding energy of the nitride compared to that of the corresponding oxide. In general, a higher sputter yield of the compound leads to a reduced hysteresis effect. The nitrogen addition into the oxygen process yields a coexistence of a nitride and an oxide compound system at the target surface. The higher the nitrogen addition the higher the effective sputtering yield and therefore the smaller is the hysteresis effect. Simulations indicate further (not shown) that the nitrogen incorporation into the growing film can be small at sufficient oxygen flow. In fact, simulations suggest that it is possible to obtain films with the nominal stoichiometry at a higher deposition rate when 1.5 sccm of N2 is added than the maximal achievable deposition rate in oxide mode for a process with only oxygen.The very low nitrogen incorporation into the film is a result of the replacement reaction as also experimentally found by others [10]. Simultaneously, the nitrogen coverage at the target is always higher compared to that of the film since an already formed metal nitrogen bond is more likely sputtered away before it can be displaced by a metal oxygen bond.
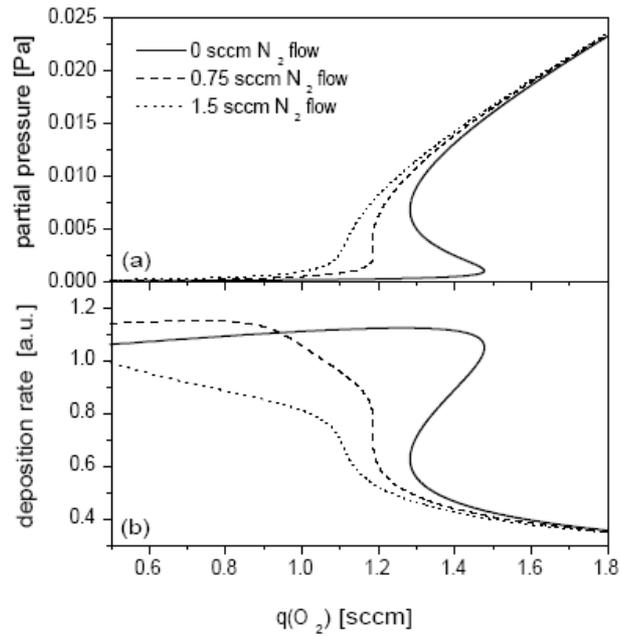
Fig.2: Simulated oxygen partial pressure (a) and normalized mass deposition rate (b) at three different fixed flows of nitrogen addition.

In order to confirm our calculations we sputtered ZrO_2 reactively from a metallic Zr target. The sputter deposition took place at a constant current of 400 mA from a circular target with a diameter of 75 mm, a total pressure of 0.8 Pa as measured by a Baratron gauge and a target to substrate distance of 55 mm. Fig. 3 (a-c) shows the target voltage versus oxygen flow for three different fixed amounts of nitrogen flow (0, 0.75 and 1.5 sccm). It can is clearly seen that the typical hysteresis behavior is vanishing for increasing nitrogen addition, which is in good agreement with the theoretical prediction. Moreover, not only the deposition rate, as measured by a profilometer (Fig. 3d), has a very smooth transition, but also deposition rates for stoichiometric oxide films are higher when nitrogen is added to the process. Again this is in good agreement with the theoretical findings. Furthermore, the nitrogen incorporation into the oxide film, as measured by electron probe microanalysis (EPMA), for sufficient oxygen flow and 0.75 sccm nitrogen addition is very small (Fig. 3e). At 1.2 sccm oxygen flow the nitrogen incorporation is less than 0.5% but the deposition rate is increased by a factor of almost three compared to the film deposited with 1.8 sccm oxygen flow and without nitrogen addition.
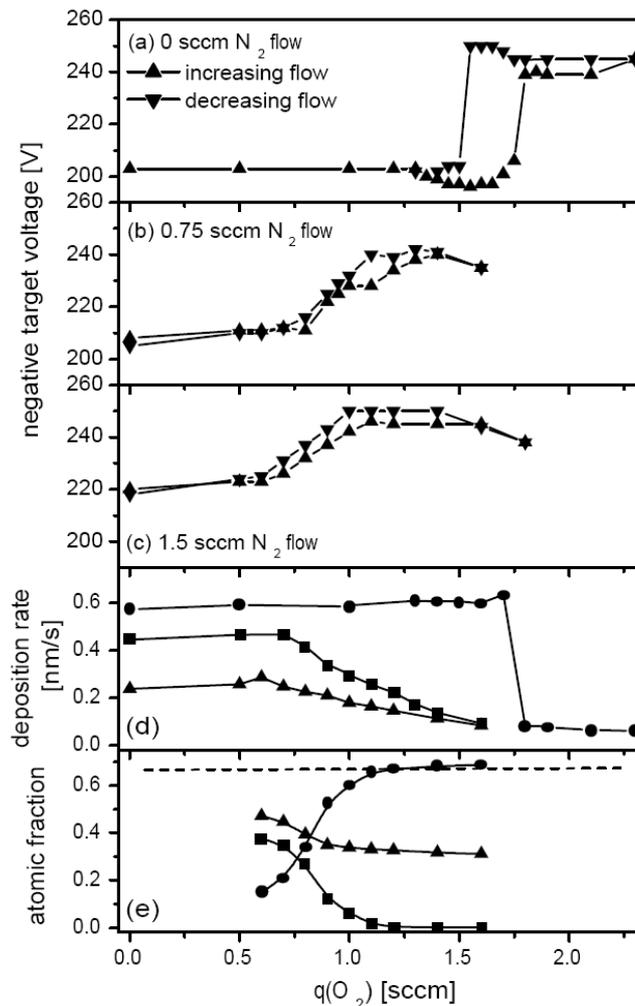
Fig.3a-c: Measured negative target voltage at three different fixed flows of nitrogen addition for increasing and decreasing oxygen flow. Fig. 3d: Deposition rate (circle: 0 sccm, square: 0.75 sccm, triangle: 1.5 sccm nitrogen addition). Fig. 3e: Amount of zirconium, nitrogen and oxygen content in the films sputtered at 0.75 sccm nitrogen addition (triangle: zirconium, circle: oxygen, square: nitrogen). The oxygen content for the nominal stoichiometry of ZrO_2 is indicated by the dashed line.

Reactive sputtering using a reduced erosion area and a compositional modification

The method above stabilizes the process but gives small amounts of nitrogen in the deposited films. If this is not acceptable there are other approaches that can be used. By reducing the size of the target sputter erosion zone below a certain critical value, simulations predicted that it should be possible to completely eliminate the hysteresis, see Fig. 4 which shows simulations for different target areas or erosion sizes. Details of the simulations are given in ref. [11]
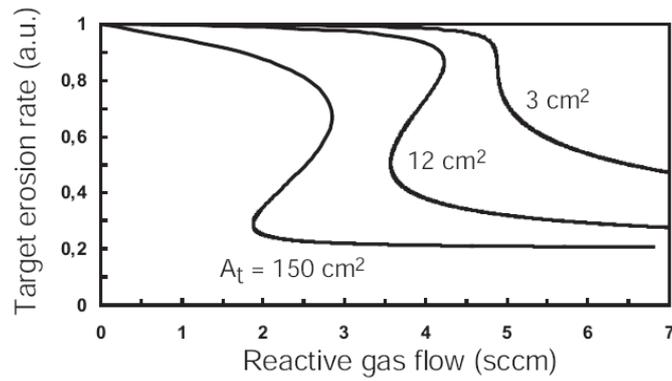
Fig. 4 Calculated sputter erosion rates vs. supply of the reactive gas for different target (= effective sputter erosion) areas.

The curves in Fig. 4 clearly indicate that the hysteresis be eliminated by decreasing the target size. As a consequence, hysteresis behaviour will be eliminated for all other parameter as well. In addition to eliminating the hysteresis effect, the small sized target also very positively affects the target sputter erosion rate. Note, in Fig 4, that the sputter erosion rate stays relatively high for quite high flows of reactive gas until it smoothly decreases to a lower value. This effect favours operation with a small sized target.

The reason for these effects is that the compound formed at the target surface is effectively sputter removed at reactive gas pressures high enough to form compound films at the substrate. Beyond these pressures, a compound is inevitable built up at the target surface. Simulation results of the target- and substrate surface composition vs. reactive gas flow, for different target sizes, are shown in Fig. 5. From these curves, it is possible to see that compound films can be deposited at the substrate while the target stays metallic. It should be pointed out that similar effects cannot be obtained if the ion current density is increased by increasing the total ion current. Consequently, the beneficial effects are obtained only when the target erosion area is reduced.
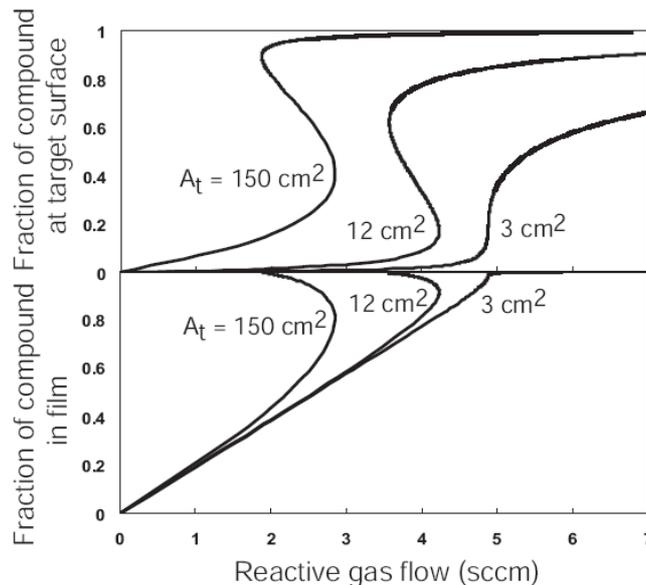

Fig. 5 Fraction of compound on target (upper) and substrate (lower) vs supply of reactive gas for different target sizes (A_t).

Experiments have been carried out to verify that the hysteresis disappear for small sized targets. Fig. 6 shows the reactive gas pressure as a function of reactive gas flow for the large (diameter of 9 cm) and the small targets (4.5 cm), respectively. The curves were taken under identical processing conditions (pumping speed, target current, target material, etc.). It is clearly seen that the hysteresis is eliminated for the small sized target. These results strongly support the theoretical predictions. Additional experimental details are given in ref. [11]. In addition to the elimination of the hysteresis effect, experiments indicate (not shown) that the smaller erosion area also offers the high rate all the way up to the point where stoichiometric films is deposited while the rate drops substantially for the large sized target.

The heating of the target may exceed the acceptable limits if the target power is focused onto a small erosion area. Therefore it is recommended to use a magnet behind the target that is moving relative the target. This will offer "virtual small size target" conditions for hysteresis free operation and the movement enables effective erosion and power distribution from the whole target.
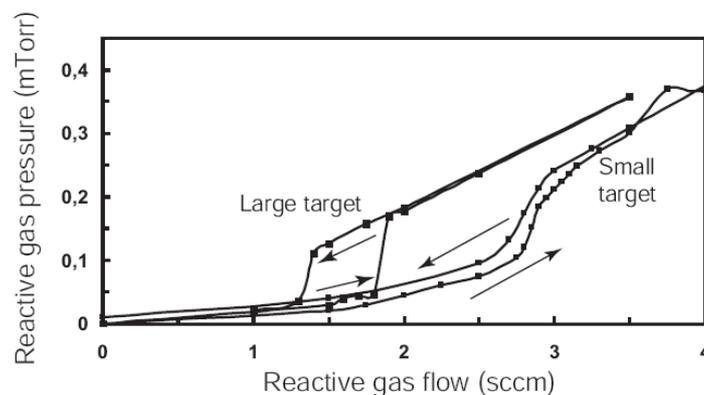

Fig 6. Experimental results for reactive gas partial pressure P vs supply of the reactive gas Q for a small and a large area target.

There are, however, physical lower limits to the smallest achievable size of a race track. Sometimes the smallest possible race track may not be enough for complete elimination of the hysteresis effect. Modelling has suggested that there exist other ways to further reduce the hysteresis effect if necessary. One possible way to achieve this would be the use of already partially compounded targets, where a larger compound fraction implies a smaller hysteresis, but unfortunately also a smaller deposition rate. It is therefore recommended that the compound fraction is large enough to completely reduce the hysteresis effect. There is no reason to make the compound fraction larger, since that would only reduce the achievable sputtering rate. In practice, the way to set up a hysteresis free deposition system is the following: 1) Increase the pumping speed as much as is affordable with respect to initial costs for pumps and running costs for maintenance of pumps and consumption of reactive gas. 2) Arrange the magnets behind the target in such a way that the erosion area becomes as small as possible 3) Add a fraction of compound to the metallic target, the fraction of compound being selected large enough to completely eliminate the hysteresis effect but not larger.

There might be some technical problems in manufacturing a target consisting of certain fractions of metal and compound. There exists, however, reports about substoichiometric TiO_{2-x} targets which have been used for reactive sputter deposition of TiO_2 films.[5] In those reports, the targets were substoichiometric in order to have sufficient conductivity for DC sputtering.

Conclusions

Two different ways of modifying the traditional reactive sputtering process have been suggested. The purpose of these modifications is to enable stable reactive sputtering without the need of feed-back control system or operating close to the point where the system might flip into low-rate compound mode.

First, it is shown that the addition of a constant flow of nitrogen during reactive sputtering of oxides can lead to stabilization of the process and to a reduction and ultimately elimination of the hysteresis effects. Furthermore, the deposition rate is increased due to the higher sputtering yield of the nitride compared to the corresponding oxide. This enables higher deposition rates at stable discharge conditions compared to sputtering of oxides without nitrogen addition. Moreover, the deposited films contain only low amounts of nitrogen.

Secondly, it is shown that a reduction of the target erosion area, may completely eliminate the hysteresis behaviour. A potential problem with this approach might be local melting of the target caused high current density. This problem is solved by moving the erosion area, e.g. by means of magnets behind the target. If the target erosion area cannot be made small enough to completely eliminate hysteresis, it is further suggested that the target is manufactured from a fraction of metal and a fraction of compound. If the fraction of compound material is large enough, the hysteresis is predicted to disappear. The fraction of compound material should be chosen large enough to eliminate hysteresis but not larger, since that will cause an unnecessary reduction of the sputtering rate.

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