High-Rate Reactive Sputtering Deposition of TiO_2 Thin Films

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ABSTRACT

A more than 10 times improvement of the reactive sputtering deposition rate has been achieved for TiO_2 films using microwave downstream plasma atomic oxygen source. The microwave plasma was maintained outside the sputtering deposition chamber and excited radicals were delivered to the main deposition area using pyrex tubing. The total amount of oxygen gas flow in the chamber was significantly reduced as compared to conventional magnetron reactive sputtering of the same cathode power. The magnetron cathode was run in metallic mode, while atomic oxygen and excited oxygen molecules created in the microwave plasma provided for complete oxidation of the growing film. The films grown are characterized by good transmission and small absorption values similar to ones obtained by a conventional reactive sputtering. The adhesion and durability of the films were also good.

I. INTRODUCTION

Magnetron sputtering is a widely used technique for reactive sputtering deposition of thin films in both experimental and production scales. It allows to achieve a very high deposition rates reaching up to several hundreds of Angstroms per second for some materials. For an exception of conductive oxides, the sputtering deposition of oxide films is usually done in reactive mode, when a metallic target is used and molecular oxygen is added to the working gas mixture to provide for an oxidation of the growing film. This technique, though being fairly simple and straightforward, has some limitations. They come mostly from the fact, that during reactive sputtering the target itself also gets partially oxidized. This leads to several important consequences:

- The deposition rates for oxides is typically 3 - 20 times smaller than for corresponding pure metals. For a number of practically important oxides such as TiO_2 and SiO_2 the maximum achievable deposition rate is often less then 10 - 20 A/s.
- Arcing is a serious problem for a number of most important oxides, including SiO_2, Al_2O_3, TiO_2 and others.
- For production scale systems, where a long non-stop operation is required, the problem of "vanishing" anode can be serious, caused by anode oxidation in the oxygen plasma with a relatively high partial pressure of oxygen in the deposition chamber. The oxydation of the anode and/or chamber walls can be responsible for increased arcing as well.

The deposition rate for oxides is reduced because the sputtering yeild for oxides is much lower then for metal surfaces [1]. This problem is important in the applications were fairly thick films are required, such as anti-reflection coatings and dielectric mirrors, for example. In the production environment, the lower deposition rates mean a larger number of cathode positions in the deposition line (larger and more expensive system) or lower line speed and throughput. The arcing limits the maximum power applied to the cathode which, in turn, limits the deposition rate and the throughput of the system. In addition, even very small arcing often renders film quality unacceptable and can mean extra down-time for target change and clean-up.

The importance of these problems has drawn a persistent attention of researchers on both basic research and large scale production level. Among the recent approaches for arcing problem is the sputtering in the pulsed DC mode [2,3] with a typical frequency being in the 10 - 100 kHz range. The periodically terminated discharge helps to kill any possible arc that can develop during sputtering. AC sputtering is another alternative [4], which proved to be quite effective in reducing arcing. It can be done between the two cathodes or between the cathode and the grounded dark space shield around it. Various arc detection and arc suppression circuitry can be used with conventional DC sputtering [see for example 5]. This circuitry terminates the plasma each time when an arc is detected. As a matter of fact quite a few of various pulsed DC / AC sputtering power supplies as well as arc-killer units are being offered by several manufactures of sputtering equipment lately.

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Still another approach is to use a different design of magnetron sputtering deposition in which the target is made in the shape of rotating cylinder and the stationary magnets are placed behind it [6]. In this approach the fresh areas of the target are being exposed to plasma all the time. The major advantage of this approach is better utilization of the target material, however it was also reported to somewhat improve the other sputtering parameters, such as figher deposition rate and reduced arcing. The whole device, however is quite mechanically complicated. Some research efforts were published on using etching gases like CF_4 or CCl_4 in the working gas mixture during sputtering deposition of optical oxides such as SiO_2 and TiO_2 [7]. The rate enhancement of up to several times have been observed. Unfortunately, in this technique the properties of the film are also affected due to Cl and F atoms incorporation into the growing film. This leads to decreasing refractive index of the film, increased optical absorption and reduced mechanical durability. All these problems need to be solved before this approach can be successfully used.

The analysis of various approaches being used in addressing the problem shows that considerable success has been indeed achieved. However, the problem of low rate in reactive sputtering has not been solved yet, and the current solutions for the arcing problem still leave a lot of room for improvements.

Completely different approach can be realized, if one could decouple the oxidation of the growing film from the oxidation of the cathode. Then the target can be run in metallic mode, but the growing film is still fully oxidized. This would give a great enhancement in deposition speed and can allow to eliminate the arcing problem as well because the target surface is pure metal now. Unfortunately, in conventional magnetron reactive sputtering, the oxidation of the film is strongly coupled with the oxidation of the target.

As previous studies have shown [8], the atomic oxygen produced in the magnetron plasma is the main source of oxidation of the growing film. The magnetic confinement of plasma by a set of magnets placed behind the target, used in magnetron sputtering, provides that the most dense plasma is in a fairly thin layer adjacent to the target surface. Therefore, the oxygen atoms created in magnetron plasma effectively oxidize the target surface as well.

The target and substrate oxidation can be decoupled if the additional remote plasma source is used to provide a flow of oxygen atoms on the substrate. This oxygen atoms will effectively oxidize all the sputtered metal atoms arriving to the surface of the growing film. If the flow of oxygen atoms is matched to the flow of sputtered metal atoms, the backstream flow of oxygen reflected from the substrate will be small, providing for the small partial pressure of oxygen in the chamber. Therefore, no significant oxydation of the target takes place, the target is run in metallic mode and high sputtering rate is achieved. As a remote plasma source in this wok we used a microwave downstream plasma source which is known for its highly effective dissociation of molecular oxygen reaching up to 70% for oxygen gas flows of 75 sccm [9].

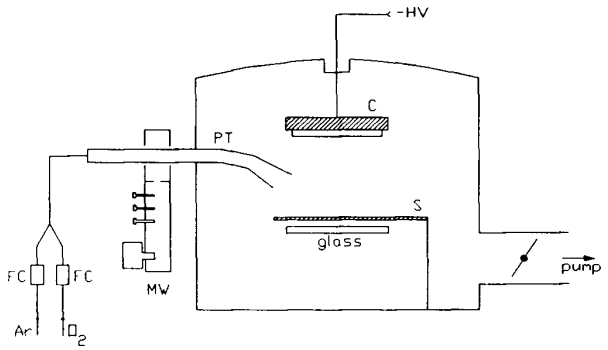

Fig. 1. Experimental setup of microwave plasma assisted reactive sputtering deposition. FC - flow controllers for argon and oxygen, MW - microwave plasma source, C - cathode, S - shutter, HV - high voltage power supply.

II. EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 1 Sputtering was done using 300 mm diameter round cathode placed horizontally above the substrate. Target was 6 mm thick round plate of 99.99% pure titanium. As a substrate, a 100 × 75 mm pieces of soda-lime glass were used. The distance between the cathode and the glass was 6 cm. Prior to sputtering the chamber was pumped down to the base pressure of 5.10^{-6} Torr. Then the target was pre-sputtered in the atmosphere of argon for 15 min. Sputtering was done in the atmosphere of argon and oxygen with the total pressure of 2 mTorr. The argon and oxygen gas flow was controlled by two mass flow controllers *FC*, the total gas pressure was measured with a capacitance manometer.

Just outside the vacuum chamber wall, the microwave plasma was created in the incoming gas flow. The plasma was confined within 1/2" pyrex tube *PT* carrying the gas flow. The tube went through the microwave resonance cavity *MW.* The microwave power was fed to the cavity from a 300 W, 2.45 MHz magnetron through a waveguide coupling section with matching stubs. All the incoming argon and oxygen was fed through thus created microwave plasma. The plasma source of this kind, although being fairly simple, is characterized by high efficiency of molecular oxygen dissociation reaching as

high as 70% as measured by NO_2 chemical titration technique [10]. The source is described in more details elsewhere [9].

The downstream flow of dissociated oxygen atoms and other excited molecules and radicals created in the plasma was delivered by the pyrex tube *PT* into the deposition area inside the chamber and directed towards the substrate.

III. EXPERIMENTAL RESULTS

The sputtering was done at the maximum DC sputtering power of 4 kW using argon flow rates in the range of 25 - 35 sccm. The total pressure was maintained at 2 mTorr. The amount of oxygen flow was varied from 3 to 20 sccm.

The type of sputtering mode could be easily identified in our case of titanium based on color of the plasma. The metallic mode has a characteristic blue color, while reactive mode has a pink color. In our experiments, at the values of oxygen gas flow in the range of 5 - 10 sccm, the sputtering was always done in metallic mode. With the increase of oxygen gas load higher than 15 sccm, the transition to reactive mode was observed. The plasma color changed to characteristic pink color.

Without the microwave plasma we found that clear films could only be obtained when the target was run in reactive mode. Fig.2 shows the transmission and reflection spectra for the films made in reactive mode without microwave plasma. The molecular oxygen flow rate was 20 sccm and the DC power was 4 kW. The films made in reactive mode have good transmission and exhibit general interference maxima and minima. The film thickness was 130 nm with a deposition rate of .38 nm/s. The spectra of the films made in metallic mode are presented in Fig.3. The DC power was the same, but the oxygen flow was 6 sccm. One can see that transmission of the films made in metallic mode (curve t1) is quite poor. The typical value for absorption in this case is about 50%.

With the microwave plasma on, clear films could be obtained in metallic mode as well as in reactive mode. In metallic mode, the oxygen gas load was kept at 6 sccm for DC power 4 kW, which is about 2/5 of the amount needed to cause the transfer to reactive mode. This way a steady metallic mode of operation was assured. The argon flow rate was 30 sccm. Fig. 3 shows the reflection and transmission spectra of the films obtained in metallic mode with the microwave plasma on and off. The DC sputtering power was 4 kW, the microwave power was 300 W. The film thickness was 212 nm. The deposition rate was 4.0 nm/s, which is more than 10 times rate enhancement as compared with conventional sputtering. This rate is close to the deposition rate of pure metallic titanium in our case.

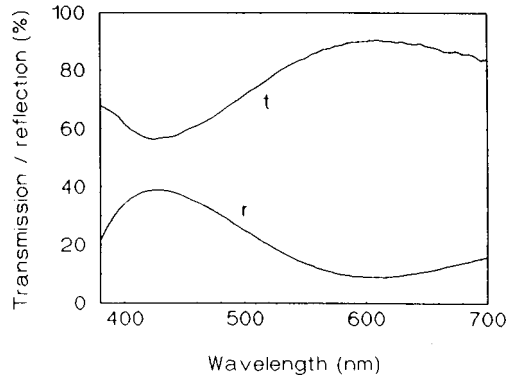

Fig.2. Reflection (r) and transmission (t) spectra for TiO_2 films made by conventional magnetron sputtering in reactive mode without microwave plasma.

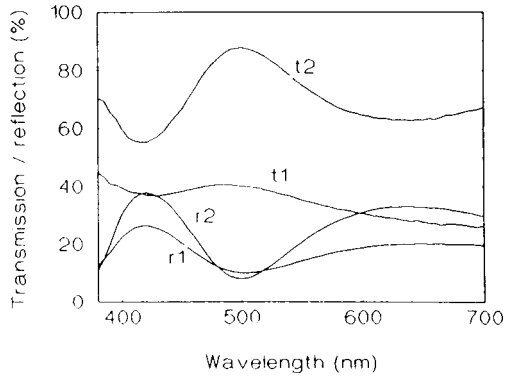

Fig.3. Reflection and transmission spectra for TiO_2 films made by microwave plasma assisted sputtering (curves r2 and t2). Curves r1 and t1 show the reflection and transmission spectra of the film made without microwave plasma, all other parameters being the same as for curves r2 and t2.

With the increase of the oxygen gas flow in excess of 15 sccm, the color of the plasma changes to pink even when the microwave plasma was on, which indicates that sputtering is now in reactive mode. The deposition rate drops down to the values closed to those obtained without microwave plasma.

IV. DISCUSSION

In conventional reactive sputtering the oxidizer is introduced as a molecular oxygen gas. This gas itself has fairly small chemical activity. For example, the probability for an oxygen molecule to stick to the pure Si surface as a result of collision with that surface is in the range of 0.01 - 0.03 [11]. This molecular oxygen, however, is excited and dissociated in the plasma, and the chemical activity of the radicals and excited species created in the plasma is much higher. The magnetron plasma, however is localized in the close vicinity of the target surface, because it is confined by a magnet assembly placed behind the target surface. Therefore, these chemically active radicals can easily go to the target surface and oxidize it. As a result, the conventional magnetron reactive sputtering is usually done with oxidized target surface.

In our approach, the active radicals are created outside the main deposition area by an additional microwave discharge. The flow of these atoms is delivered to the deposition area via the pyrex tube and directed onto the growing film effectively oxidizing it. The amount of oxygen supply is determined by the amount needed to oxidize the growing film. For TiO_2 film density ρ (g/cm³), substrate area A (cm²), and deposition speed S (nm/s), we have the required minimum molecular oxygen gas flow Q (sccm):

$$Q = 0.129\ \rho\ A\ S / m_a ,$$

where m_a is the atomic mass of TiO_2 molecule. For our case of A = 75 cm² and S = 4 nm/s we have Q = 2.06 sccm. This is about 1/3 of the amount we used in our experiments. The sticking probability of the atomic oxygen to metal surface is close to one, it somewhat declines for partially oxidized surface but still remains pretty high. Therefore, there is a good chance that the flow of oxygen atoms from downstream microwave plasma will effectively oxidize the growing film. Because the significant fraction of the total oxygen flow is absorbed on the substrate, the partial pressure of oxygen in the deposition chamber is reduced, which is very good for stable operation in metallic mode. Small oxydation of the target does occur, but it all is cleaned up by continuing sputtering. Therefore, the target stays clean, providing for high sputtering deposition rate.

V. CONCLUSION

It has been shown, that the use of microwave plasma source of atomic oxygen in the magnetron reactive sputtering can increase the deposition rate by more than 10 times without altering film properties. Results, obtained for TiO_2 films show that in this case the deposition rate is close to that of pure metal. It has been shown that the flow of oxygen atoms provides sufficient oxidation of the growing film, thus render its high optical transparency, but allows for the target surface to stay in clean metallic mode. This technique has a great potential for industrial applications, provided that its successful scale-up is done. The implication of this technique would mean a costeffective way of great throughput improvement of the current sputtering coaters.

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