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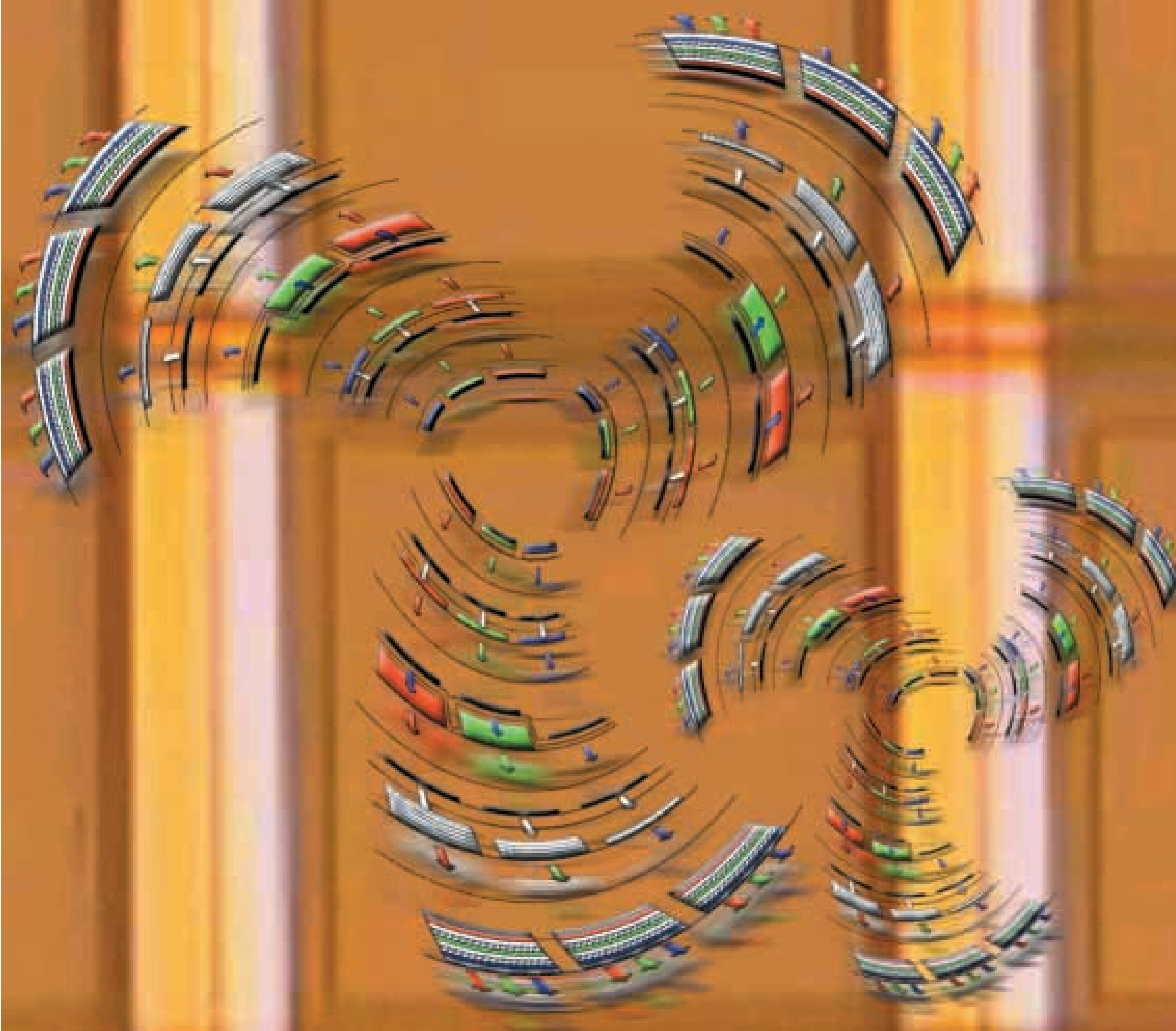

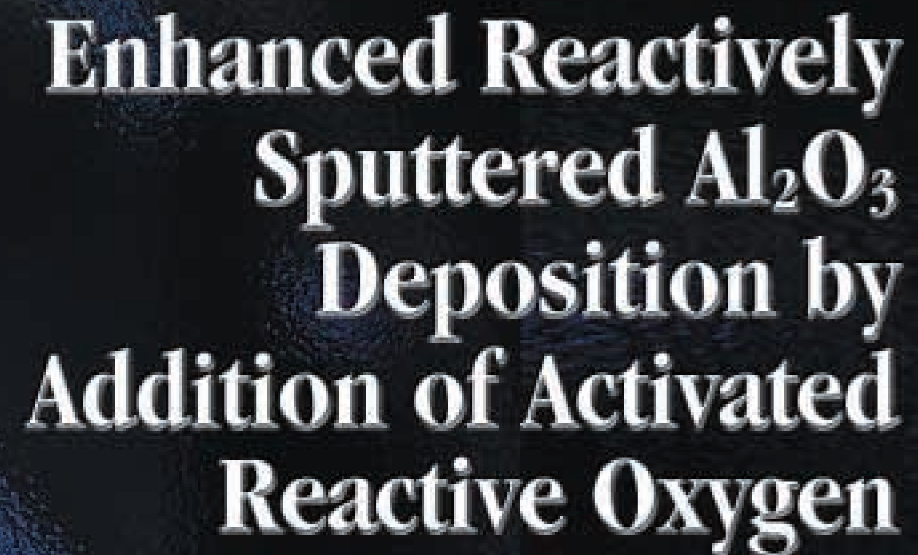

Enhanced Reactively Sputtered Al_2O_3 Deposition by Addition of Activated Reactive Oxygen

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Reactive sputter of dielectric materials has been a subject of study and process improvement research for many years. The deposition of insulating materials presents obvious issues in a traditional DC type sputter reactor for the simple reason that the films being processed do not conduct current and therefore are not supportive for the direct current circuit required to sustain a DC discharge. Many high dielectric constant materials such as aluminum oxide are especially problematic for sputter deposition for the issues stated above and also because many of these tend to readily form stable oxides in a reactive sputter process leading to target poisoning or a phenomena known as the disappearing anode [1]. Techniques to circumvent this issue are available [2,3] but are not without inherent costs. High frequency (RF) sputtering from a dielectric target is possibly the most straightforward practice but due to low and differential sputter yields, this technique suffers from very low deposition rates and target depletion issues. Reactive sputtering from a metallic target is the preferred choice for high rate deposition, but here the controllability issues of target and anode oxidation must be addressed. Because of these issues, the search continues for a solution providing high throughput, reproducible reactive sputtering results for materials like aluminum oxide.

Two of the most promising techniques for delivering production worthy deposition of difficult films are pulsed DC reactive sputtering [4,5,6] and dual magnetron AC reactive sputtering [7,8]. Both of these techniques when combined with a closed feedback loop for active process control have shown promise and with proper setup can represent viable solutions for many in need of a higher throughput sputter deposition of insulating oxides [7,8]. Still, as with all AC or discontinuous wave applications, both these approaches suffer from reduced throughput, or deposition rate, when compared DC power application of comparable power densities.

Inherently, the unipolarity of DC power provides a distinct advantage in a sputter process from a sputter yield and deposition rate standpoint [9]. As discussed, however, the challenges of depositing insulating films in a DC environment are significant and require proper reactor design and process methodology. Preferential application of reactive species to the substrate has been discussed as an approach to mitigate some of the effects of target oxidation in a DC sputter process [10,11], however, by itself, this technique is subject to the flexibility of the existing reactor design as a determinant of effectiveness. This paper discusses a new technique for enhancing such an approach through the use of preactivation of the reactive species prior to direct delivery to the substrate. Preactivation provides enhanced reactivity at the substrate providing added margin to the gas delivery and protection from typical process instabilities. Through proper reactor design and the added benefit of preactivation, a repeatable process for depositing quality aluminum oxide films is defined employing the benefits of DC power application without the added costs of elaborate closed loop control systems.

Experimental Set-Up

Film depositions discussed in this work were performed in a Balzers PLS 500 vacuum sputter system pumped with a Pfeiffer Vacuum TMP 520 turbo-molecular pump backed with a Balzers PKD44 rough pump. A six inch 99.995% pure aluminum target mounted on a Balzers Torus 10 magnetron served as the sputtered aluminum source. Power to the sputter cathode was applied using an Advanced Energy Pinnacle™ 10kW DC power supply operated in a power regulation mode. Power regulation was chosen in these experiments simply as a monitor of process stability. By allowing the voltage to the cathode to drift, the level of poisoning could easily be monitored by tracking the target voltage.

Argon was used as the sputter gas in all deposition tests. The argon was fed to the chamber independent of the reactive oxygen via a dedicated gas entry manifold. Flows for both argon and oxygen were regulated using MKS 2179 mass flow controllers operated by an MKS 647B process control unit. Pressure monitoring in the sputter chamber was accomplished using a Balzers PKR250 Pirani/Cold Cathode gauge while pressures within the ICP source were monitored using an MKS 627 capacitance manometer. Partial pressure measurements were made using a SPECTRA Microvision 0-200 AMU quadrapole mass spectrometer.

Oxygen for the reactive sputter was delivered through an Advanced Energy Inductively Coupled Plasma Source (ICP) and then to the sputter chamber for all depositions. The ICP source was toggled "OFF" or "ON" (at the desired power level) depending on the deposition conditions of interest. A Pyrex delivery tube was used for all tests where direct delivery of the reactive gas to the substrate was desired. In the direct delivery tests, the total path from ICP source to the substrate surface was approximately 60 cm. A schematic of the ICP connection to the chamber and the general design of the sputter apparatus used is shown in **Figure 1.**

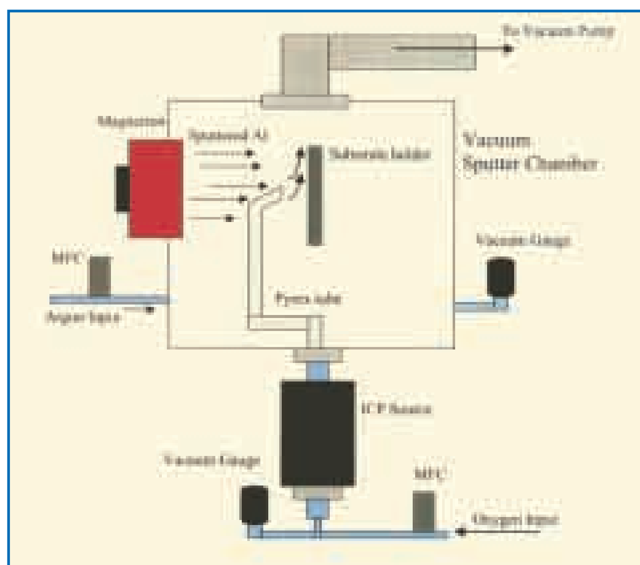

Figure 1. Vacuum apparatus used in aluminum oxide reactive sputter testing.

Glass substrates, cleaned with isopropyl alcohol, were mounted on a rotatable, shielded fixture allowing multiple depositions per pumping cycle. Depositions were performed after pumping to a base pressure of $4x10^{-5}$ Torr or less. No bias was applied to the substrates and no temperature control to the sample holder was employed. Target to substrate distance was approximately 18 cm for all depositions and substrates were carefully positioned such that the Pyrex nozzle did not block the path of sputtered aluminum.

Transmission data presented were taken either on a Perkin Elmer Lambda 9 NIR/UV/VIS Spectrophotometer or a Filmetrics Thin Film Spectrometer in the transmission mode. Hardness measurements were performed on a Nano Technology Nano-Indentation system.

Process Baseline

To properly evaluate the affects explored in this study it is important to establish a baseline for the process to serve as a reference for comparison. Additionally, a survey of the process space adds to the understanding of the inherent instabilities that exist and aids to demonstrate the effectiveness of the enhancement technique. To satisfy this interest, a series of hysteresis curves were generated to illustrate the issues encountered when reactively sputtering aluminum oxide thin films. For these initial tests oxygen was introduced into the sputter chamber through an open ICP port without the Pyrex delivery tube installed.

Figure 2 shows the typical oxygen partial pressure hysteresis

characteristic of this process. Reported many times in literature [2,8,9,11,12], this graph clearly shows the dynamic effects that take place in a reactive sputter process of aluminum as the oxygen partial pressure is increased. At low flows the pumping of oxygen is aided by the reaction with aluminum on surfaces within the deposition chamber. Beyond a critical point where the stoichiometric compound is produced [3,12], the gettering process within the reaction chamber is saturated and the pumping capacity is overwhelmed leading to a rapid increase in oxygen partial pressure.

In the oxygen saturated region of the curve all surfaces in the reaction chamber (including the target) are covered with an insulating layer of alumina. Most noteworthy is the condition of the target in this region as it is said to be "poisoned" due to the presence of an oxide layer on the surface. When poisoning occurs, deposition rates drop dramatically [2,9,11], arcing increases and severe instabilities may exist. This is explained by the increase in secondary electron emission from the oxide surface illustrated in the complimentary target voltage hysteresis curve shown in **Figure 3**. Here, voltage to the target is monitored as power to the cathode (2500 W) is regulated. In this scenario, as the oxygen flow is increased and chamber surfaces become oxidized, the target transitions from being metallic (~450V) in characteristic to being insulating (~250V) very rapidly.

At this transition point, secondary emission from the target increases dramatically leading to increased plasma current and reduced target voltage. This results in the aforementioned reduction in sputter rates and the increased susceptibility to arcing and plasma instabilities.

The issues with this behavior are obvious when considering the usability of this type of process. Only by reliably avoiding the target poisoning transition can one repeatedly deposit high quality reactively sputtered aluminum oxide films at high deposition rates. To achieve stable operation, one can employ sophisticated feedback control systems [7,8,11] or as in this study, modify the sputtering environment to increase the *effective* oxygen partial pressure in the deposition zone. The ultimate goal being to achieve the desired conditions at the substrate while operating the target in a more favorable environment, removed from the "poisoning" condition.

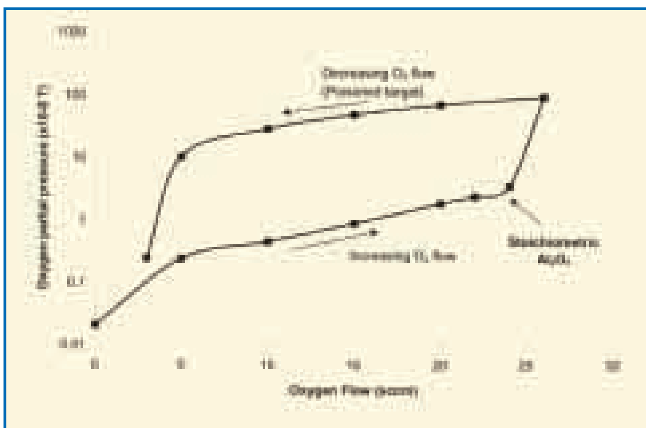

Figure 2. Oxygen partial pressure hysteresis behavior in a reactive aluminum oxide sputter process at 4.5 mT.

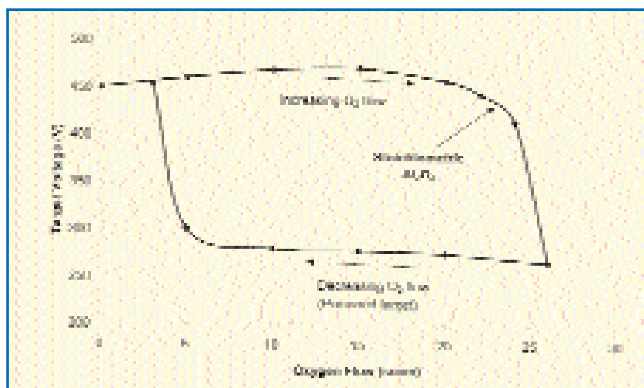

Figure 3. Target voltage hysteresis behavior in a reactive aluminum oxide sputter process at 4.5 mT.

Experimental Method and Results

To achieve a stable environment for aluminum oxide deposition and to provide control margin to the reactive deposition process the effective oxygen partial pressure at the substrate was modified using two techniques. First, preferential delivery of the reactive gas to the substrate surface (see **Figure 1**), this technique, used elsewhere [10,11], acts to increase the oxygen partial pressure at the substrate and by the inherent pumping characteristics in our chamber protects from poisoning by maintaining a lower oxygen partial pressure at the target. Secondly, and of primary interest for this work, is the pre-activation of the reactive gas using the independent radio-frequency inductively coupled plasma source. The theory behind this technique is to deliver gas of a heightened reactivity to the substrate further increasing the effective oxygen partial pressure in the deposition zone and thereby increasing the operating margin by maintaining the target in a more stable range on the hysteresis curve.

The effect of preferential delivery of the reactive gas is shown in **Figure 4**. Oxygen, via the Pyrex tube, was delivered directly to the substrate surface and through diffusive flow, away from the sputter target. The result of this was a slight shift in the hysteresis curve where by transparent, stoichiometric films can be deposited at a flow range below that required to poison the target. By itself, this technique may be limited in its effectiveness by the design and pumping capabilities of the deposition system. In our case the effect was to move the knee of the hysteresis by an amount representative of 2 sccm of oxygen flow, not enough to bring the process to the "flat" portion of the curve.

The effect of ICP pre-activation of the oxygen on hysteresis behavior is shown in **Figure 5**. For these tests, the same gas delivery set-up was employed but here the gas was "activated" via dissociation in the ICP plasma source prior to introduction into the Pyrex delivery tube.

The effect of the ICP on the target hysteresis is negligible under these conditions. This lack of impact is due to the magnetron discharge being the dominant contributor to ionization and dissociation in the proximity of the cathode. At the substrate, however, the effects of the magnetron are decreased and the impact of the ICP must be assessed based on film deposition results.

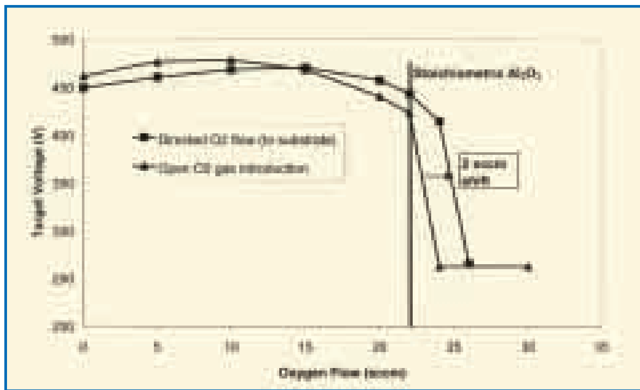

Figure 4. Target voltage hysteresis and the effect of directed oxygen flow at 4.5 mT.

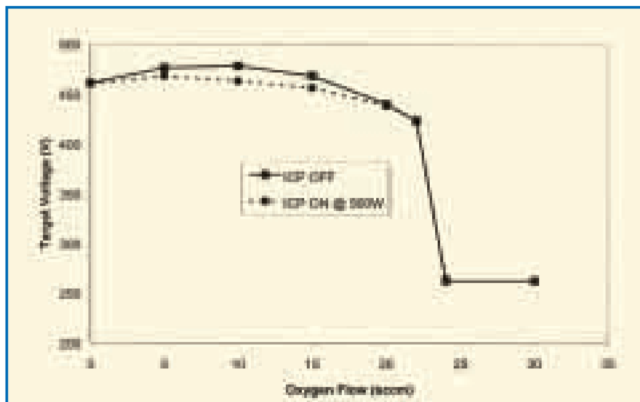

Figure 5. Target voltage hysteresis and the effect of pre-activated oxygen flow at 4.5 mT.

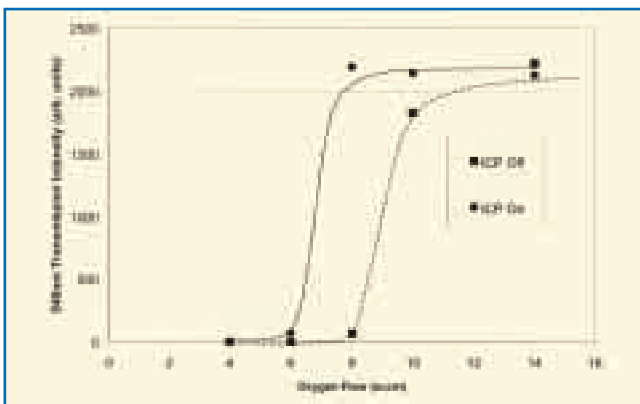

Figure 6. Reactively sputtered aluminum oxide films deposited at Pressure = 4.0 x10^{-3} Torr; ICP OFF and ON @ 500W.

All films were deposited using 2500 W of DC power to the sputter cathode, chamber pressures of 3 to 5 mT, oxygen gas flows of 4 to 20 sccm (delivered to the substrate) and ICP powers from 0 to 1500 Watts. Reflected power in the ICP was maintained at less than 5% of the power to the load. For films deposited in the flat region of the hysteresis, deposition rates varied with chamber pressure and target to substrate spacing. Deposition rates for the films tested range from 50 to 100 nm/min.

Incorporation of ICP pre-activation had the effect of producing clearer films at lower oxygen flows than those produced without the aid of pre-activation. **Figure 6** shows the effect of

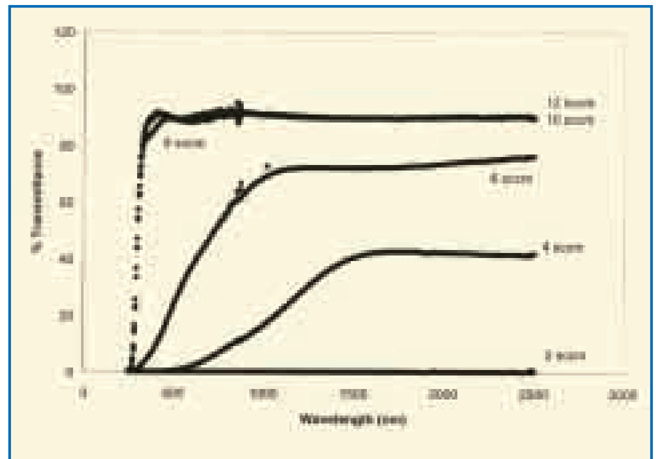

Figure 7a. Broad band transmission of films deposited at 4.0mT and oxygen flows from 2 to 12 sccm with ICP turned off.

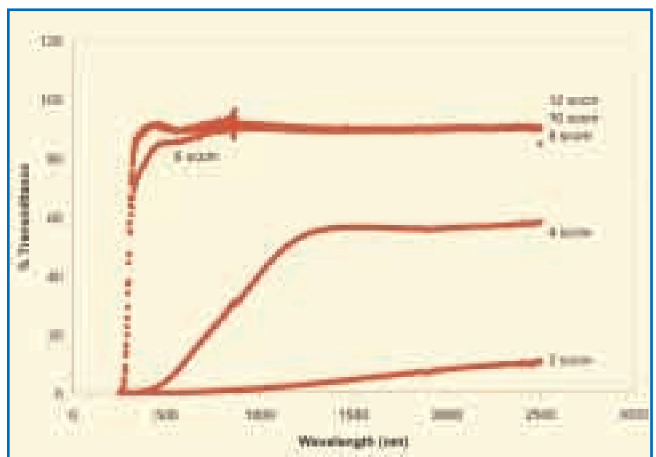

Figure 7b. Broad band transmission of ICP enhanced films deposited at 4.0mT and oxygen flows from 2 to 12 sccm.

ICP activation on transmission characteristics in the green region (540 - 550 nm) for films deposited at 4.0 mT for five minutes, films for this test were nominally 2500 A thick.

Full spectral characteristics of films deposited with increasing amounts of oxygen are shown in **Figure 7** indicating improved transmissivity at lower flows with the ICP on.

Dispersion of the reactive species was tested at increased pressure to illustrate its effect on film uniformity. Here, very low flow rates were adequate to begin to see transparent films but high non-uniformity was present due to shorter mean-free-paths. **Figure 8** shows transmission uniformity in the green region (540-550 nm) for films deposited at 4.8 mT. The effect of the ICP activation in this case is to increase the effective conversion zone where sufficient oxygen of adequate reactivity existed to form a transparent film.

The effect of ICP power on film transmission characteristics is shown in **Figure 9**. Films deposited at varying ICP input power indicate an observable and, as of yet, unexplained relationship between power and optical properties. Based on this, best results are achieved at ICP powers in the 600 to 900 watt range or at higher powers around 1500 watts. The reduced transmissivity between these ranges is not understood.

Deposition rate as a function of oxygen flow is shown in

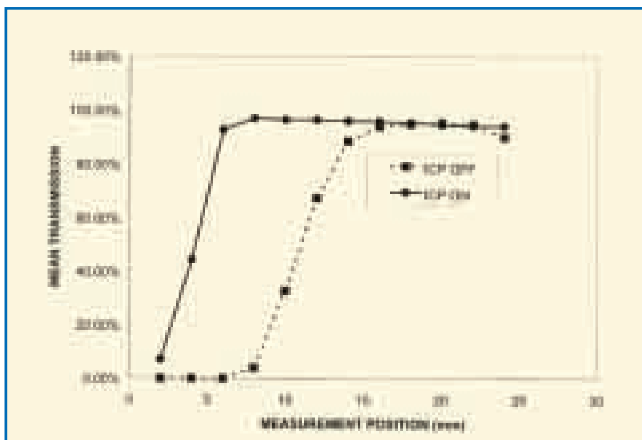

Figure 8. Green transmission (540 - 550nm) as a function of position on sample. Films deposited at 4.8mT; O_2 = 2sccm; ICP @ 400W.

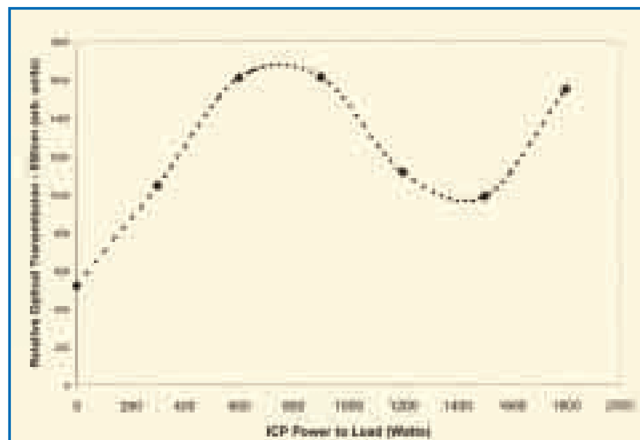

Figure 9. Optical transmission as a function of ICP power for films deposited at 8sccm of O2 flow.

Figure 10. While comparable rates are achieved regardless of ICP status, previous data indicating the ability to operate the target in a more metallic mode using the ICP indicates a rate advantage with this technique. The magnitude of this effect will depend on various chamber and process parameters, for this work, the attainable rate increase is estimated at 10%.

Nano-hardness tests were performed on films produced with and without the ICP ignited. Results in **Table I** indicate a general trend toward harder films being produced with the ICP on.

Oxygen incorporation in deposited films was measured using X-ray-Photoelectron-Spectroscopy. Due to contamination on samples, the calculated Al:O ratios suggested oxygen rich films for both ICP and non-ICP samples. A sputter back technique was used to remove the surface contamination and while the ratios were closer to that expected for stoichiometric Al_2O_3, the values still indicated some form of contamination. The one conclusion that can be drawn from this survey is that clear films produced by both techniques have comparable compositions allowing for the uncertainty of the XPS technique.

Discussion

Optical data presented here show that transparent aluminum oxide films can be deposited at oxygen flows below the target poisoning point simply by directing the reactive gas to the substrate and away from the cathode. According to the hysteresis curves, in this test, the optimum film is produced approximately 2 sccm removed from the flow required to poison the target.

Table I

Film Hardness (GPa) 5 min. deposition @ 4.0 mT		
Oxygen Flow	ICP Off	ICP On @ 1500W
2 sccm	8.66	14.22
4 sccm	11.73	12.35
6 sccm	15.61	18.09
8 sccm	17.57	23.51
10 sccm	15.87	17.61
12 sccm	19.75	18.44

While the magnitude of this effect will vary with other deposition parameters, considering the steep slope of the curve in this region, it is expected that this technique by itself may be inadequate to provide the margin desired for a production worthy process. A method for providing additional margin may be necessary in order to define a stable process capable of continuous uninterrupted operation.

Optical data presented in **Figures 6 through 8** indicate the additional margin gained by pre-activating the reactive gas prior to introduction into a directed flow apparatus. By incorporating both affects in this manner, it is possible to define a deposition process where highly transparent films are deposited in a range where target poisoning is reduced.

The ability to operate the target in a more metallic mode not only provides operating margin but will also result in improved rate without sacrificing film quality. In fact, data indicate that the incorporation of pre-activation into such a process may act to improve film properties such as hardness beyond that achievable through more traditional techniques.

Conclusion

To produce a fully oxidized aluminum oxide film and reliably avoid target poisoning in a DC magnetron reactive sputtering

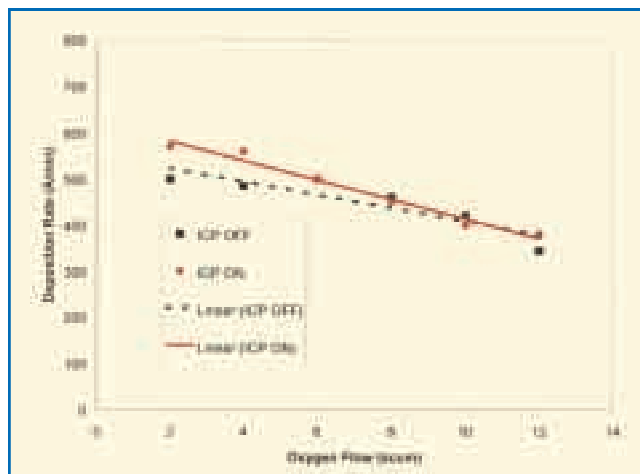

Figure 10. Deposition rate as a function of oxygen flow for films deposited at 4.0mT and oxygen flows from 2 to 12 sccm.

process one of two approaches must be taken. 1) Employ sophisticated feedback and control loops in the gas delivery system to maintain the oxygen partial pressure at a precisely specified level or 2) Modify the environment immediate to the substrate such that the oxygen partial pressure experienced at the target is measurably less than that required to cause poisoning but the partial pressure and reactivity at the substrate is adequate to produce the films of the desired properties. The former technique, explored in this study, was shown effective in producing high quality aluminum oxide films in a DC reactive sputtering environment without the issue of target poisoning. Using these enhancements, films deposited in the flat portion of the target voltage hysteresis curve displayed properties comparable, and in some cases, superior to those deposited near the knee of the curve without the aid of the mentioned enhancements.

While the results of this work appear promising, to fully understand the utility of this technique, further work is needed to accurately measure film stoichiometry and to better understand the relationship between ICP power, sputter power and optical film properties. Additionally, investigation into potential enhancement of pulsed DC reactive sputtering is of interest. Ultimately, the incorporation of this technique with a closed loop active flow control mechanism may prove to be a highly effective approach for delivering a high throughput, reliable, production worthy reactive sputtering process for traditionally difficult to manage thin films.

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