Mid-Frequency Dual Magnetron Reactive Co-Sputtering for Deposition of Customized Index Optical Films

D.J. Christie, W.D. Sproul, and D. Carter, Advanced Energy Industries, Inc., Fort Collins, CO

Key Words: Sputter deposition, Power supplies, Reactive deposition, Partial pressure control

ABSTRACT

Reactive co-sputtering is a means to create films of customized or graded index of refraction. This gives the optical coating designer new options, and enables practical realization of new classes of coatings. Two neighboring targets may be sputtered such that material from both targets and reactive gas are incident on the workpiece, depositing a film consisting of a compound. For example, if one target is Si and the other Ti, with oxygen as the reactive gas, then the index of the film may be adjusted over a range of approximately 1.5 to 2.4 by varying the power to each magnetron. Factors limiting application of reactive co-sputtering include the disappearing anode effect when DC supplies are used, and difficulty adjusting the relative power to the magnetrons when mid-frequency AC supplies are used in dual magnetron sputtering. However, current source pulsed supplies can independently regulate power delivered to each magnetron (in dual magnetron sputtering), while eliminating disappearing anode effects. This enables reactive co-sputtering of optical films. We present optical films, having a customized index of refraction deposited by mid-frequency dual magnetron reactive co-sputtering, with independent target power regulation and show the ability to create films with a range of indexes.

INTRODUCTION

It is possible to configure a sputtering system such that two different target materials are sputtered, with the power to each of the targets controlled independently, as shown in Figure 1. This is called co-sputtering. When co-sputtering is performed in the presence of a reactive gas, it is called reactive co-sputtering. The motivation is creation of controlled mixtures of materials in the film deposited by the process. Reactive co-sputtering is appealing because it can deposit films otherwise unrealizable. It allows, for example, the creation of films with customized or graded indexes of refraction. For example, SiO_2 can be deposited with a refractive index of about 1.5 and TiO_2 can be deposited with a refractive index of about 2.4. If a co-sputtering arrangement is configured with one Si target and one Ti target, the ratio of Ti to Si can be varied by controlling the power to each of the magnetrons. Therefore, in principle, it is possible to "dial" the refractive index anywhere between 1.5 and 2.4.

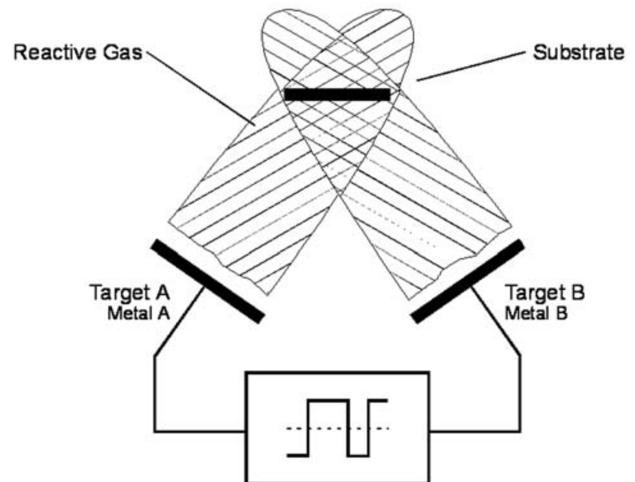

Figure 1: Mid-frequency dual magnetron reactive co-sputtering arrangement.

Co-sputtering of two different materials has typically been accomplished with ion beam sputtering or the use of RF or DC supplies to deliver power to sputtering targets in diode or magnetron configurations [1, 2]. The advent of pulsed supplies, which can reliably regulate the power delivered to each magnetron, is a key enabling technology for reactive co-sputtering in a conventional dual magnetron sputtering (DMS) arrangement. Pulsed supplies inherently offer more flexibility in control of the process. They provide the capability of independently regulating the power delivered to each magnetron. Independent regulation enables the creation of controlled mixtures of materials in the film when dissimilar materials are used for the magnetron targets. This allows the creation of films with customized or graded indexes of refraction.

Recently, development effort has focused on pulsed current source supplies [3, 4]. Commercial availability of high power pulsed current source supplies at the 120-kW level began in early 1998. The first commercial 200-kW unit was shipped in early 2000 [5]. Similar supplies at the 20-kW level were available in 1996 [6, 7].

© 2003 Society of Vacuum Coaters 505/856-7188

46th Annual Technical Conference Proceedings (2003) ISSN 0737-5921

Co-sputtering has typically been reported on a small scale. A constant concern in the large-area coating community is scaling to large substrates, with sizes appropriate for architectural and automotive glass, as well as large web coaters. Results for large-scale inline coaters were reported in 1991 [8, 9, 10]. Several issues of scaling, such as thickness uniformity and film quality, were addressed.

The potential of reactive co-sputtering has motivated several workers to address process models. An early attempt at modeling co-sputtering processes focused on process voltage and current as model outputs [11]. Almost ten years later, an extension of the Berg model [12] was introduced which showed that the process curves look qualitatively like those for simple reactive sputtering [13].

A detailed investigation of co-sputtering, based on process modeling, has shown that more than one enabling technology is required. Pulsed dual-magnetron sputtering with independent regulation for each magnetron is the required base. However, a closer look shows that both the composition of the film and the deposition rate are in fact functions of the partial pressure of the reactive gas. This result indicates that partial pressure control will allow operation in the transition region, and may also be required in order to achieve high quality films of consistent composition and thickness.

MODELING

The notion of reactive co-sputtering is fundamentally simple. Two different target materials are sputtered in the presence of a reactive gas, such as oxygen or nitrogen. If either target material is reactively sputtered alone the result is a transparent dielectric film with a distinct index of refraction (the choice of target material and reactive gas to yield a dielectric is assumed here, since the paper is on optical films, but is not always the case). These two possible indexes represent the extremes. It seems reasonable to expect that any index between the two extremes could be obtained by varying the relative fraction of each target material. It may also seem that the relative fraction of the target materials in the deposited film could be varied by controlling the power to each target. A process model was used to explore these expectations, and the results were surprising. Modeling indicated that not only deposition rate, but also relative composition of the film is a strong function of partial pressure, for realistic reactive gas partial pressures in the transition region. This implies the need for reactive gas partial pressure control to successfully deposit high quality films by reactive co-sputtering, particularly in the transition region.

The model used was based on one due to Moradi, et al. [13]. This model is essentially an extension of the static Berg model [12]. The calculations are performed in a single pass by an Excel spreadsheet. The model shows that important process outputs such as deposition rate and process composition are single-valued functions of the reactive gas partial pressure. However, those process outputs may have multiple values with respect to flow in some process regions.

The model is shown schematically in Figure 2. The variable F denotes the flux of reactive gas to the surfaces of Target 1 and Target 2 and the Chamber Surfaces. Variables J_1 and J_2 are the sputtering ion fluxes to the surfaces of Target 1 and Target 2, respectively. The fractions of Target 1 and Target 2 covered by the reactive compound are represented by Θ_{1t} and Θ_{2t}, respectively. These are the so-called coverage fractions. The ion flux tends to reduce the target coverage fraction by sputtering the compound molecules away. In contrast, the reactive gas flux tends to increase the coverage fraction by forming more compound molecules on the surface. The sputtering yields are typically quite different for the compound and the target material. When everything is considered, there is a unique equilibrium condition for the coverage fractions of the two targets which is calculated by the model [12, 13]. The chamber surfaces are conceptually divided into two sections. The first section is impacted by F_{M1}, the metal flux from Target 1, and F_{C1}, the compound molecule flux from Target 1. The fraction of the Chamber Surfaces occupied by Metal 1 is designated by y. The fraction of y occupied by reactive compound is represented by Θ_{1s}. The second section of the Chamber Surfaces, occupied by Metal 2, is impacted by F_{M2}, the metal flux from Target 2 and F_{C2}, the compound molecule flux from Target 2. This section is represented by (1-y), and the fraction of it covered by reactive compound is denoted by Θ_{2s}. The notion of a compound molecule flux was introduced as an effective simplification to the model [12, 14], although it does not capture the exact physics of the process. The model calculates a unique equilibrium for y, Θ_{1s}, and Θ_{2s} based on F, F_{M1}, F_{C1}, F_{M2}, and F_{C2}. The final step is to calculate the input reactive gas flow. A continuity equation equates input reactive gas flow to the cumulative consumption mechanisms in the process. These include getter pumping at Target 1, Target 2, and the Chamber Surfaces in addition to the reactive gas removed by the system pump.

The system modeled was Ti and Al, with O_2 as a reactive gas, yielding compounds TiO_2 and Al_2O_3 at the extremes and $TiAl_xO_y$ in the middle. The expected range of possible indexes is approximately 1.66 to 2.4. Parameters used for the model calculations, with references and comments where appropriate, are listed in Table 1. The model was configured to provide rate versus flow, flow versus pressure, composition versus pressure, and rate versus pressure.

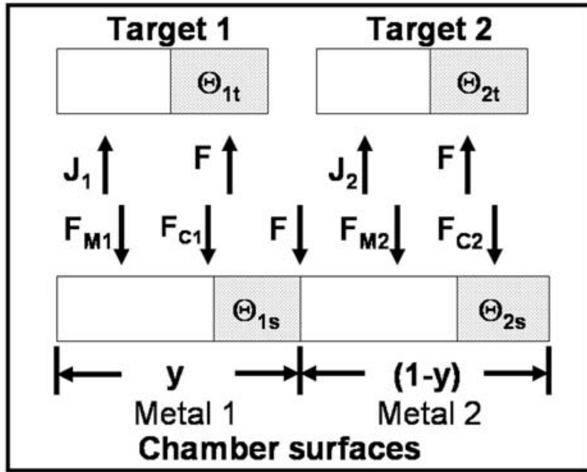

Figure 2: Reactive co-sputtering model diagram.

Table 1: Reactive co-sputtering model parameters.

Parameter	Value	Comments
Ti sputtering yield	0.5	[14]
TiO_2 sputtering yield	0.017	[14]
Al sputtering yield	0.8	[15]
Al_2O_3 sputtering yield	0.025	[15]
Sticking coefficients	1	[12, 13]
Ti target area	0.068 m^2	Estimated
Al target area	0.068 m^2	Estimated
Chamber area	1.46 m^2	Estimated
Ti target current density	294 A/m^2	1 kW, 500 V
Al target current density	367 A/m^2	1 kW, 400 V
Pumping speed	465 l/sec	Measured
Gas	O_2	
Temperature	300 K	Estimated

Figure 3 shows the rate versus flow curve. Even though there are two targets with two metals, there is only a single s-curve, similar to the classic s-curve for reactive sputtering with one target material. This suggests that the process could behave similarly to a standard reactive sputtering process, and shows that simple flow control will not allow access to the part of the process space with a positive slope.

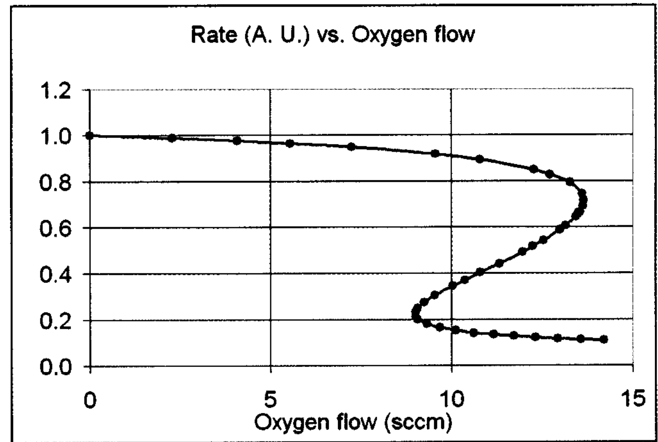

Figure 3: Model calculation of rate versus flow.

Figure 4 shows the flow versus pressure curve which accompanies Figure 3. The transition region is the decreasing portion from about 0.01 mTorr to 0.09 mTorr. Flow decreases monotonically with pressure in this region, suggesting the possibility of partial pressure control.

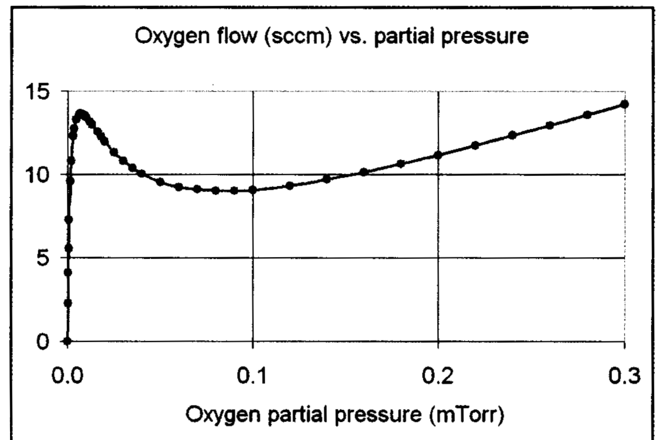

Figure 4: Model calculation of oxygen flow versus oxygen partial pressure.

Figure 5 shows the fraction of the metal atoms in the film that is Ti. This fraction would correlate to index of refraction. It is a strong function of partial pressure in the transition region, and is relatively constant in the poisoned region, greater than about 0.08 mTorr.

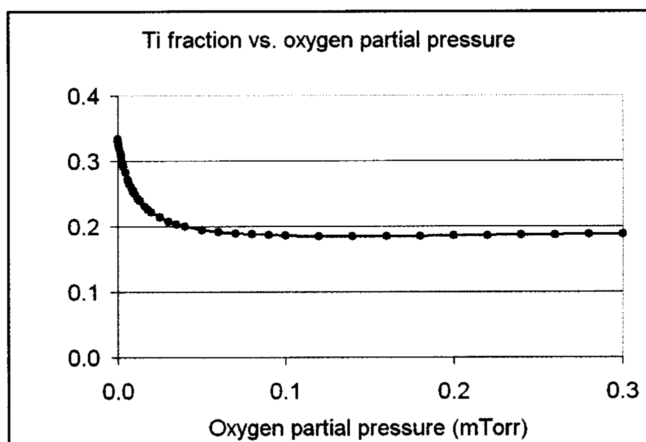

Figure 5: Model calculation of film composition (fraction of metal that is Ti) versus oxygen partial pressure.

Figure 6 shows the rate in arbitrary units (A. U.). This is actually calculated as the rate at which metal atoms are removed from the two targets, including the metal in the compound sputtered from the targets. Rate decreases strongly with pressure in the transition region. However, rate continues to decrease significantly with pressure in the poisoned region, where composition is relatively constant. This suggests the desirability of partial pressure control for stabilization of the deposition rate.

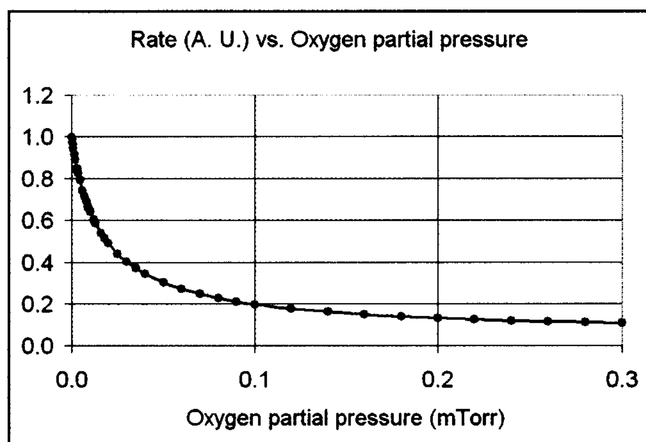

Figure 6: Model calculation of rate versus oxygen partial pressure.

EXPERIMENT

Data were generated in a medium-sized, open-volume, cylindrical vacuum chamber (about 0.75 m diameter x 0.45 m deep) with two 0.15-m Kurt Lesker Torus 10 balanced-field magnetrons. Uniform distribution of reactive gas was achieved using rather simple diffusers. The chamber was turbo-molecular pumped to base pressures below $5x10^{-6}$ Torr prior to deposition runs. Aluminum and titanium targets were sputtered using an Advanced Energy® Astral™ 20-kW pulsed-dc power supply system. Reactive gas partial pressure was controlled by an Advanced Energy® IRESS partial pressure control system, utilizing an Inficon Transpector mass spectrometer for partial pressure sensing. Film thicknesses were measured on glass substrates using a Tencor P200 profilometer and a Gaertner L116 ellipsometer. Index of refraction was measured on a Gaertner L116 ellipsometer. Deposition system parameters are listed in Table 2. Films with indexes of refraction from about 1.7 to 2.3 were deposited in the course of the experimental campaign.

Table 2: Experimental deposition system parameters.

Parameter	Value	Comments
Ar flow	50 sccm	
Ar pressure	≈ 1.5 mTorr	
Substrate angle	45 deg	To Ti and Al target surface normals
Ti target to Al target angle	90 deg	Angle between surface normals
Ti target to sample distance	0.254 m	
Al target to sample distance	0.185 m	
Frequency	50 kHz	
Duty Cycle	50 %	

Figure 7 and Figure 8 show experimental results with both targets in power control mode. The data points plotted correspond to seven process runs. The Ti target was operated at 1333 W and the Al target was operated at 667 W for a total of 2000 W. Partial pressure is indicated in Volts and has essentially a logarithmic relationship to the mass spectrometer Faraday cup current. Partial pressure was not absolutely calibrated for these experiments. In Figure 7, the rate has a significant dependence on partial pressure, while Figure 8 shows that the index of refraction has a relatively weak dependence on partial pressure. This could be expected, given the modeling results discussed in the previous section, and would suggest operation in or close to the poisoned region.

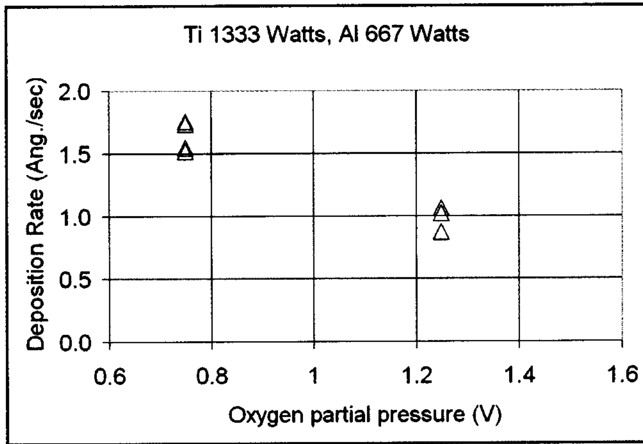

Figure 7: Experimental deposition rate versus oxygen partial pressure data (Ti 1333 Watts, Al 667 Watts).

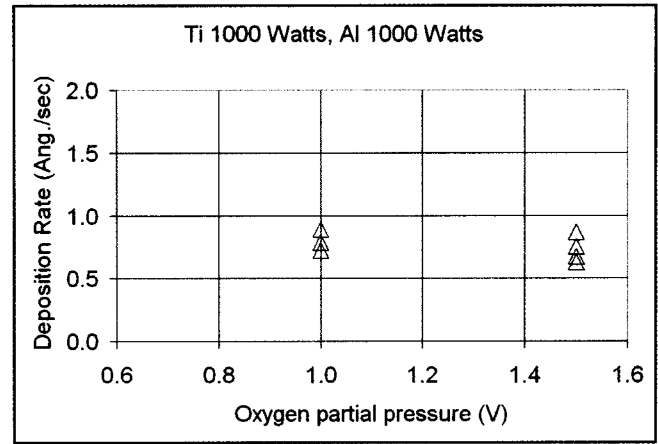

Figure 9: Experimental deposition rate versus oxygen partial pressure data (Ti 1000 Watts, Al 1000 Watts).

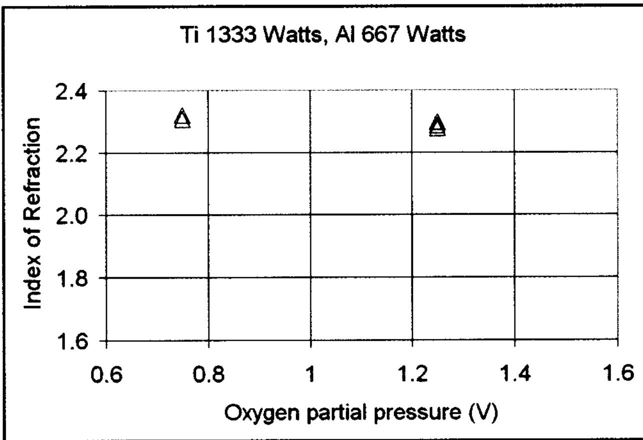

Figure 8: Experimental index of refraction versus oxygen partial pressure data (Ti 1333 Watts, Al 667 Watts).

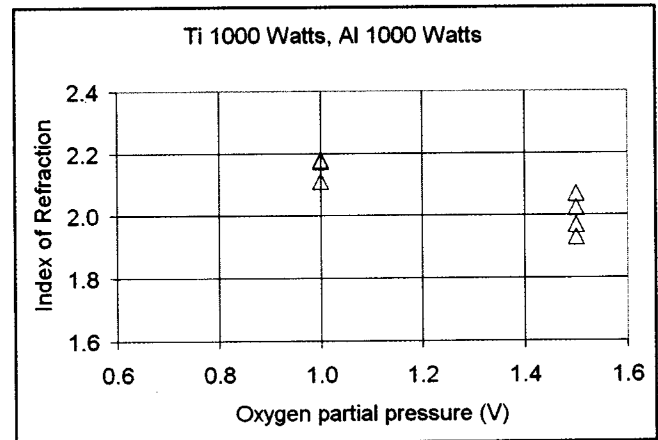

Figure 10: Experimental index of refraction versus oxygen partial pressure data (Ti 1000 Watts, Al 1000 Watts).

Figure 9 and Figure 10 show experimental results with both the Ti and the Al targets operated at 1000 W, for a total of 2000 W. The data points plotted in these figures represent results from seven samples. Figure 9 shows a relatively weak reduction in rate with partial pressure, while Figure 10 shows a reduction in index with increased pressure. This suggests that the partial pressure is in a range where composition and rate are both changing. The existence of such a region is predicted by the model, and it would be the transition region.

CONCLUSION

Mid-frequency dual magnetron co-sputtering can be used to produce optical thin films with customized index of refraction. Modeling has been used to gain a insight into the process. Films with indexes from about 1.7 to 2.3 have been deposited using Ti and Al targets, with O_2 for the reactive gas. Refractive indexes in this range are useful for optical coatings. Pulsed current source power supplies provide independent power regulation for each magnetron. Reactive gas partial pressure controllers allow stable operation in the transition region, and stabilization of rate and index. Both are enabling technologies for mid-frequency dual magnetron reactive co-sputtering.

ACKNOWLEDGMENTS

The authors would like to express their gratitude to Fernando Tomasel for designing and fabricating the multiple sample holder, to Karen Peterson for performing experiments and measurements, and to John Accardo for assistance with the power supply system.

REFERENCES

1. J.-C. Hsu, et al., "Co-sputtering some materials in titanium oxides by ion-beam sputtering deposition," OSA Technical Digest Series 1998, Vol. 9: Optical Interference Coatings, Tucson, AZ, p. 63-65, 1998.

2. C. Misiano, E. Simonetti, "Co-sputtered optical films," *Vacuum* vol. 27 no. 4, p.403, 1977.

3. D. Kovalevskii, M. Kishinevsky, Low-frequency modulated current mode power supply for magnetron sputtering cathodes, US Patent 5,777,863, 1998.

4. R. A. Scholl, D. J. Christie, Pulsed direct current power supply configurations for generating plasmas, US Patent 5,917,286, 1999.

5. D. J. Christie, et al., "High performance pulsed current source supplies for large area dual magnetron sputtering," *Proceedings of the 3rd –ICCG*, ISBN 90-9014255-x, p. 107, 2000.

6. D. J. Christie, "The Astral™ bipolar pulsed power supply for dual cathode sputtering," 39th Annual Technical Conference Proceedings of the Society of Vacuum Coaters, p. 320, 1996.

7. Astral Accessory, Advanced Energy product data sheet, 2000.

8. A. Belkind, et al., "Co-sputtering of Alloys. I. Co-Sputtering of Oxides and Nitrides using Two Planar Magnetrons," *JVST A* 9, (3), p. 530, 1991.

9. A. Belkind, et al., "Reactive Co-Sputtering of Oxides and Nitrides using a C-Mag™ Rotatable Cylindrical Cathode," *Surface and Coatings Technology*, 49, 1-3, p. 155, 1991.

10. R. Laird, et al., "Co-Sputtered Films of Mixed TiO_2/SiO_2," *JVST A* 10 (4), p. 1908, 1992.

11. K. Steenbeck, E. Steinbeiβ, K.-D. Ufert, "The problem of reactive sputtering and cosputtering of elemental targets," *Thin Solid Films*, 92, p. 371, 1982.

12. S. Berg, et al., Modeling of reactive sputtering of compound materials, *JVST A* 5(2), p. 202, 1987.

13. M. Moradi, et al., "Modeling of multicomponent reactive sputtering," *JVST A* 9 (3), p. 619, 1991.

14. P. Greene, R. Dannenberg, "Modeling of production scale reactive deposition," 42nd Annual Technical Conference Proceedings of the Society of Vacuum Coaters, p. 23, 1999.

15. L. Jonsson, et al., "Dynamic simulations of pulsed reactive sputtering processes," *JVST A* 18 (2), Mar/Apr, p. 503, 2000.