PNL-SA--9859

DE82 007163

CONF-820107--6

RECENT DEVELOPMENTS IN REACTIVELY SPUTTERED OPTICAL THIN FILMS

MASTER

W. T. Pawlewicz
P. M. Martin
D. D. Hays
I. B. Mann

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

December 1981

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ef

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Recent developments in reactively sputtered optical thin films

W. T. Pawlewicz, P. M. Martin, D. D. Hays and I. B. Mann

Materials Department, Pacific Northwest Laboratory
P. O. Box 999, Richland, Washington 99352

Abstract

Highlights of a multiyear effort to develop new or improved thin film optical coating materials through the use of reactive sputtering techniques are presented. Reactive sputtering is shown to be an extremely versatile technique capable of synthesizing broad classes of materials in a straightforward manner. The exceptional utility of sputtering for preparation of hard coatings such as oxides, nitrides and novel materials based on Si and Ge is described. Some of these coating materials cannot be made by conventional evaporative techniques. Reactive sputtering is shown to allow precise control of coating composition, microstructure and the resulting optical properties. Supporting data are presented for TiO_2 , for which record high damage thresholds were obtained, and for Si-based coatings, for which record low infrared absorptance was achieved. Transparent conductive ITO coatings with low sheet resistance and high visible and near infrared transmission can also be made. These coatings have many electro-optic contact and electro-magnetic shielding applications. Examples of multilayer coatings such as all-dielectric and dielectric-enhanced mirrors made from reactively sputtered materials are included, and simple yet elegant fabrication techniques are introduced. The reactive sputtering technique and equipment used specifically for optical coatings are briefly described, and comparison is made with the conventional evaporative approach.

Introduction

Thin film deposition by sputtering employs large-area flat-plate sources which are bombarded by inert gas ions when an rf or dc potential is applied to the source. Bombardment results in "sputtering" or atom-by-atom removal of material from the source and subsequent transfer to a substrate usually located in plane-parallel proximity. Thin films of virtually any metal (Ag, Ti, Mo, etc.) or elemental dielectric (Si, Ge, etc.) can be deposited by sputtering from a source of the same material using Ar or Kr inert gas. Addition of a reactive gas such as O_2 , N_2 or H_2 to the Ar or Kr permits deposition of oxides, nitrides and hydrides from metallic or elemental dielectric sources. For example, a Si source can be used with Ar, Ar + O_2 , Ar + N_2 and Ar + H_2 to deposit thin films of Si, SiO_2 , Si_3N_4 and Si:H alloys. Compared to conventional evaporative techniques for depositing thin films, sputtering generally provides improved control over the properties of conventional coating materials. Sputtering also makes possible the deposition of new coating materials with complex compositions that cannot be made by evaporation.

The use of sputtering specifically for the improvement of optical coatings has been under development at Pacific Northwest Laboratory for the past five years. During this time many significant gains have been made in control of the optical, structural and compositional properties of optical coatings, and several exciting techniques have been developed for synthesis of new materials and fabrication of complex multilayer coatings. The purpose of this paper is to report highlights of these developments. The wide range of oxide, nitride and elemental semiconductor materials investigated to date is reviewed, and specific examples of structure or composition control that resulted in significant coating performance improvement is presented for TiO_2 , Si:H alloys and ITO conductive coatings. Novel techniques for fabricating multilayer coatings are described, and performance results for all-dielectric and dielectric-enhanced reflectors are presented. In addition, general features of the sputtering apparatus are described, and comparison is made with conventional evaporative approaches.

Sputtering Apparatus

Figure 1 is a schematic diagram of the type of diode sputtering apparatus used for most optical coating work to date. Sputtering sources are made from high-purity metal plates, vacuum-cast or melt-grown semiconductors, or hot-pressed oxides. Sources are metal brazed or epoxy bonded to an rf or dc electrode which is water cooled during deposition. Source diameters are presently 6 inch and 9 inch, and a 16-inch-source system is being designed. The substrate table is generally the same diameter as the source, is water cooled and/or electrically heated, and is located about 1.5 inch from the source in a plane-parallel arrangement. A shutter is used to preclean and condition the source surface before coating deposition. Coating thickness uniformity is controlled primarily by the ratio of source diameter to source-substrate spacing. Thickness uniformity of $\pm 1\%$ is achievable over substrate diameters of 4 and 7 inches for source diameters of 6 and 9 inches, respectively. Uniformity of $\pm 1\%$ is expected over 14 inches for the 16-inch system. No substrate rotation or movement is necessary. This situation contrasts markedly with that of point-source evaporative approaches where substrate rotation/movement is often necessary and where thickness uniformity is determined by the ratio of substrate diameter to source-substrate spacing. Scale-up to larger diameters is also conceptually simpler for sputtering than for evaporation. In sputtering, only the source diameter changes while the source-substrate spacing remains essentially fixed. In evaporative approaches, substrate rotation/movement becomes increasingly difficult for larger substrates.

Any variety of inert gases such as Ar or Kr or reactive gases such as N_2 , O_2 , H_2 can be introduced from a manifold and valving arrangement such as that shown in Figure 1. Gas purity is usually 99.999% or better. Capacitance manometers must be used in place of gauges with hot filaments whenever O_2 is used. Gas flow meters are also frequently used. Operating pressures range from 1 to 150 mTorr, but pressures between 1 and 20 mTorr are most common by far. With evaporative approaches operating pressures are much lower, but source-substrate spacing is much larger. Recall that the probability of collisions between gas atoms and atoms omitted from the source is proportional to the product of gas pressure and source-substrate spacing.

The sputtering systems used for this work are mounted on conventional mechanical and oil diffusion pumps. High efficiency liquid nitrogen cold traps are used between the chamber and diffusion pump to increase the pumping speed for water and to minimize diffusion pump backstreaming. A variable orifice is used between the diffusion pump and the cold trap so that the pump inlet can be throttled when the sputtering gas is introduced without decreasing the pumping speed for water. With the orifice fully open the chamber pumps to a pressure near 10^{-7} torr.

The structure, composition and properties of any optical coating material deposited depend greatly on the exact deposition conditions used. As with evaporative approaches, substrate temperature and deposition rate are important conditions for sputtering. However, several other conditions are also important to sputtered coatings. These include the sputtering gas pressure, sputtering gas composition and potential of the substrate relative to the plasma ("bias voltage"). The large number of conditions that can be controlled with sputtering permits greater control and flexibility in coating structure, composition and properties. On the other hand, systematic variation of many deposition conditions sometimes complicates coating optimization.

Materials sputtered to date

Table 1 is testimony to the tremendous versatility of sputtering. Tabulated here are optical coating materials successfully deposited to date by sputtering at PNL. Also included are the useful transmission range, the mid-range refractive index and other important physical properties of each coating material.

Note the wide range of oxide materials that can be readily deposited by sputtering. Oxides range from low refractive index materials such as SiO_2 , GeO_2 and Al_2O_3 to high index materials such as TiO_2 , ZrO_2 and Nb_2O_5 . Also note that complex intermediate compounds such as $\text{Y}_4\text{Al}_2\text{O}_9$ and MgAl_2O_4 are readily made by sputtering from mixed oxide sources such as $(2)\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$ or $\text{MgO} + \text{Al}_2\text{O}_3$.

Included with the oxides is ITO which is sputtered from a mixed oxide source of $\text{In}_2\text{O}_3 + \text{SnO}_2$ or from a In:Sn alloy source. Conductive coatings with resistivity as low as 4×10^{-4} Ohm cm (sheet resistance of 10 Ohms/square for a 4000 Å thickness) are routinely made with high transmission in the visible and near infrared spectral regions.

Also included in Table 1 are several nitride materials, a carbide and two hydrides. In most cases the same elemental metal or semiconductor source used for reactive sputtering of the oxides of that element can also be used to deposit the nitride, carbide or hydride by substitution of N_2 , CH_n or H_2 for O_2 in the sputtering gas. Particularly exciting cases are Si and Ge. With a single Si source, five different optical coating materials can be made by simple exchange of the reactive gas component. These materials include Si, SiO_2 , Si_3N_4 , Si:H and SiC. Their refractive indices cover a very wide range from 1.45 to 3.6 and their useful transmission ranges span the spectrum from the ultraviolet to the far infrared. With a Ge source, coatings of Ge, GeO_2 , Ge_3N_4 and Ge:H have been made. For this materials system, refractive indices range from 1.61 to 4.08 and high/low index pairs are available for use throughout the infrared.

II-VI Compounds such as CdS, CdTe and ZnSe have also been sputtered. In these cases, deposition takes place entirely by physical sputtering since no reactive species is added to the inert sputtering gas.

Much of the versatility sputtering provides to coating material selection arises from the atom-by-atom nature of the momentum-transfer process. Virtually any inorganic material can be sputtered by ion bombardment. This situation contrasts markedly with evaporative approaches for which a material must be heated to temperatures sufficient to produce a significant vapor pressure. Reaction between the crucible and the starting material does not occur with sputtering. In addition, deposition rate control is inherently superior since with sputtering the rate is essentially linear in power applied to the source, while with evaporation the rate varies exponentially with the temperature to which the crucible is heated electrically or by electron bombardment.

Structure and composition control

TiO₂ Coatings

An excellent example of the structure and microstructure control possible with sputtering is provided by recent accomplishments^{1,2} with TiO₂ optical coatings. In this work sputter deposition was shown to permit excellent control and reproducibility of the phase composition and grain size, allowing rapid optimization of refractive index and laser damage resistance.

Figure 2 shows that TiO₂ phase compositions ranging from 40% rutile/60% anatase to 100% rutile can be reproducibly obtained by sputtering. Phase composition is controlled by substrate temperature and O₂ partial pressure, as shown in this phase composition diagram. Intermediate substrate temperatures yield mixed-phase coatings with rutile contents given by the numbers in the circles. Rutile content increases with the O₂ partial pressure. Rutile coatings are obtained for lower temperatures and higher temperatures. The occurrence of the rutile phase over a wide range of temperatures when high O₂ pressures are used permits variation of the grain size from 10 to 60 nm by appropriate selection of the substrate temperature. For mixed-phase coatings, grain sizes are restricted to 10 to 30 nm since mixed phases are obtained over a narrower temperature range.

Figure 3 shows how the substrate temperature can be used to control the average grain size of rutile coatings. Grain sizes near 10 nm are obtained for lower temperatures, increasing to about 30 nm near 600°C. Larger grains are obtained by taking advantage of plasma heating of the substrate at higher target power levels, as shown in the inset for a nominal substrate temperature of 450°C. Grain size increases with power density to 60 nm near 8 W/cm². At still higher power levels, grain size decreases due to inhibition of lateral grain growth by high deposition rates. The data in this figure were obtained by both x-ray diffraction and TEM techniques. Agreement between the two is good for the larger grain sizes and fair for the smaller.

Coatings with a predominantly glassy structure, or a grain size much smaller than 10 nm, are obtained by applying 5 to 10% of the rf power to the substrate. With substrate bias, glassy coatings are obtained regardless of the substrate temperature used. Thus by using substrate bias, substrate temperature and target power in the right combination, microstructure can be controlled from glassy to 60 nm grain size.

The influence of phase composition on refractive index and laser damage threshold was investigated by depositing TiO_2 coatings with different phase compositions, but identical grain sizes, using the deposition conditions prescribed by Figure 2. Results are summarized in Figure 4 and Table 2.

Phase composition is found to have a small but significant influence on coating refractive index. Figure 4 shows the index at 1000 nm plotted as a function of rutile content. Since grain sizes in mixed-phase coatings are restricted to 10-30 nm, the data point shown for 100% rutile is the average index observed for these grain sizes only. Only a small variation of the index with phase composition is observed, due to the closeness of the refractive indices of rutile and anatase. The apparent variation of the index is only 3%, which is approximately equal to the scatter in the data points.

Phase composition does not appear to influence laser damage resistance. Table 2 summarizes damage thresholds for coatings having grain sizes between 10 and 15 nm. All laser damage measurements were made at Lawrence Livermore National Laboratory. Note that for grain sizes in the range of 10 to 15 nm, little difference in damage threshold is apparent for 100% rutile coatings compared to coatings with a significant anatase content. Thus any phase composition may be selected for TiO_2 optical coatings without compromising resistance to laser-induced damage.

Grain size on the other hand, has been found to have a very significant influence on both the refractive index and the damage resistance of TiO_2 coatings. Figure 5 shows the influence of grain size on the refractive index at 1000 nm for 100% rutile coatings. For large grain sizes the ~ 2.5 index of bulk material is obtained. With decreasing grain size, the index

drops to values as low as 2.0 for glassy coatings. The discovery of this relationship explains the wide range of index values reported in the literature for TiO_2 coatings. Knowing this relationship, it is possible to preselect the refractive index of a coating for a particular application by choosing deposition conditions that give you small, intermediate, or large grain size. Alternatively, by measuring the refractive index of a coating one can determine the grain size.

The influence of grain size on the laser damage resistance of TiO_2 coatings is shown in figure 6. There are two key results. First, damage resistance increases with decreasing grain size. Second, damage thresholds of 7 to 10 J/cm^2 are obtained for glassy coatings. It is also interesting to note that damage threshold increased consistently with the amount of bias applied to the substrate. Thresholds of 7 to 10 J/cm^2 are excellent for single-layer coatings since the usually harmful effects of contamination at the substrate-coating interface are not masked as they are in high reflector designs frequently used for laser damage testing. These sputtered coating thresholds are twice as high as those observed for evaporated single layers.

Si_{1-x}H_x Coatings

An excellent example of how the precise composition control achievable with the reactive sputtering approach can be used to improve the optical properties of some coating materials is provided by recent work^{3,4} with Si_{1-x}H_x alloys. Si_{1-x}H_x is made by sputtering from a Si source in reactive Ar + H₂ gas mixtures. It is interesting to note that these materials cannot be made by conventional evaporation techniques. Molecular hydrogen (H₂) will not react with Si. A plasma or discharge such as that employed for sputtering is required to first form atomic hydrogen (H) which will react chemically with Si.

The chemical composition of Si_{1-x}H_x (atom % H) is controlled primarily by the deposition rate and the partial pressure of H₂ in the sputtering chamber during deposition^{3,4}. As shown in Figure 7, low H contents are achieved at high deposition rates and low H₂ partial pressures. High H contents are obtained at low deposition rates and high H₂ partial pressures. H contents are determined by infrared spectrophotometric measurement of the Si-H stretching vibrational modes which absorb strongly for wavelengths near 5 μm. Vacuum fusion or gas evolution determinations can be used to corroborate the infrared findings. Details of the measurements have been described elsewhere⁵.

The addition of H to Si coatings significantly reduces the absorption of the coatings at infrared wavelengths. Reduced absorption results in improved transmission and higher laser damage threshold. Figure 8 shows the absorption coefficient at 1.06 μm wavelength plotted as a function of the H content from 0 to 35 atom %. These absorption measurements were deduced from spectrophotometer data for many coatings. Note that conventional pure Si coatings (0 atom %) absorb strongly at 1.06 μm with a coefficient near 7000 cm⁻¹. Addition of H results in an exponential decrease in absorption. For 35 atom %, the coefficient is reduced two orders of magnitude to about 100 cm⁻¹. This reduced absorption could make possible the use of Si coatings at near infrared wavelengths previously not possible.

A similar decrease in absorption occurs at all infrared wavelengths between 1 and 3 μm . Figure 9, shows calorimetry measurements made with an HF laser operating near 2.7 μm wavelength. Shown for reference are absorption coefficient measurements⁶ previously reported for pure Si coatings prepared by several different techniques. Note that the coefficient for pure Si coatings is normally in the range of 20 to 80 cm^{-1} . A pure Si coating made by reactive sputtering was found to have a coefficient of 41 cm^{-1} , in good agreement with results for coatings made by other techniques. Addition of 12 atom % H, however, reduced the absorption coefficient to 3 cm^{-1} , a record low value for Si coatings. Further reduction in absorption at higher H contents appears likely.

Achievement of low absorption in $\text{Si}_{1-x}\text{H}_x$ coatings does require, however, that some compromise be made on refractive index. As shown in Figure 10, pure Si Coatings exhibit an index of about 3.6 for wavelengths near 2 μm . Addition of H results in a reduced index. For H contents near 35 atom % the index is reduced to about 2.0. However, even for 20 atom % H the index is still greater than 3.0, and for 30 atom % H the index is greater than 2.5. These index values compare very favorably with values for other infrared coating materials such as ZnS , As_2S_3 and As_2Se_3 which are typically in the range of 2.0 to 2.5.

ITO conductive coatings

A third example of the very useful coating materials which can be controllably made by reactive sputtering is ITO. ITO is a popular acronym for tin-doped indium oxide or $\text{In}_2\text{O}_3:\text{Sn}$. Very high conductivities can be achieved in transparent ITO coatings by proper selection of the Sn content and by careful control of a small oxygen deficiency relative to stoichiometric In_2O_3 .

Figure 11 shows both transmission and reflection spectra spanning the visible and near infrared spectral regions for an ITO coating with a resistivity of 4×10^{-4} Ohm cm. Transmission of the bare glass substrate is indicated by the upper dashed curve. Transmission in the visible range, as shown by the solid curve, is about 80% for the coated substrate. This transmission is remarkable in view of the fact that the coating resistivity is only about 50 times higher than that of pure indium metal. At wavelengths longer than $1 \mu\text{m}$ transmission drops due to free carrier absorption associated with the metallic properties of the coating. The transmission drop is accompanied by a rise in reflectivity as indicated by the lower dashed curve. The reflectivity rises to about 90% for wavelengths of 5 to $10 \mu\text{m}$. Higher visible transmission can be achieved through the use of thinner coatings or higher resistivities. For example a resistivity of 4×10^{-3} Ohm cm results in about 90% visible transmission and shifts the infrared absorption tail to wavelengths longer than $3 \mu\text{m}$. Note that a resistivity of 4×10^{-4} Ohm cm and a coating thickness of $0.4 \mu\text{m}$ is equivalent to a sheet resistance of 10 Ohms/square. These low sheet resistance values make ITO coatings very attractive for applications such as contacts in electro-optic devices, coatings for electromagnetic or rf shielding, or for other situations where both conductivity and optical transmission are required. It is also important to point out that sputtered ITO coatings have been shown to exhibit unexpectedly high laser damage thresholds.

Figure 12 shows that the resistivity of ITO coatings can be controlled from 4×10^{-4} to about 10^4 Ohm cm when the source composition is In_2O_3 + 9 mole % Sn and glass substrates are used. High resistivities are obtained at high O_2 partial pressures and low rf power densities applied to the source. Low resistivities are obtained at low O_2 partial pressures and high power densities. The power density controls deposition rate and thus the time available for In and Sn to fully oxidize. The power density and the O_2 partial together thus control the oxygen deficiency necessary for conductive coatings.

Multilayer coating fabrication

In spite of the excellent control of the materials and optical properties achievable for many optical coatings with reactive sputtering, the sputtering approach would not be useful unless multilayer coatings consisting of two or more alternating materials could be made with precise control of the individual layer thicknesses and optical properties. Accordingly, several examples of successfully fabricated multilayer structures are provided here and the methods for making them are described.

Figure 13 shows the reflectance of an all-dielectric mirror (high reflector) made from Si:H and SiO₂ for use at the infrared iodine laser wavelength of 1.315 μ m. The mirror was made using the apparatus of Figure 1. The mirror has nine coating layers and consists of the structure S(HL)⁴H where S is the fused silica substrate, H denotes a Si:H layer with quarter wavelength thickness at 1.315 μ m, and L is a quarter wave of SiO₂. Alternating layers of quarter wave thickness for high and low index materials are well known to result in high reflectance by constructive interference of appropriate wavelength light reflected from the various layer interfaces. The Si:H layer has 8 atom % H and was made using the techniques described in a previous section. Preparation and properties of SiO₂ have been described elsewhere⁸. Multilayers of this type can be made simply and elegantly by continuously sputtering from a pure Si source while alternating the introduction of H₂ and O₂ reactive gases at precise time intervals using the manifold and valve arrangement of Figure 1. Note that very high reflectance and a broad, flat reflectance peak are obtained with only nine layers because of the very high refractive index contrast between SiO₂ and Si:H.

Figure 14 shows that similar high reflectors can be made at visible wavelengths using the same gas-switching techniques if N₂ is substituted for H₂ to form Si₃N₄. Figure 15 shows both reflection and transmission spectra for a thirty-one layer structure consisting of SLL(HL)¹³HLL where S is the fused silica substrate, H is a quarter wave of Si₃N₄ at 540 nm wavelength, and L is a quarter wave of SiO₂. Visible high reflectors of this type are useful for many lasers operating at these wavelengths and in particular for He:Ne laser gyro applications.

Finally, Figure 15 shows the reflection spectrum for a $\text{ZrO}_2/\text{SiO}_2$ high reflector tuned for use at the Nd:YAG laser wavelength of $1.06\text{ }\mu\text{m}$. This mirror consists of nineteen layers in the structure $\text{S}(\text{H},\text{L})^9\text{H}$ where S is the substrate, H is a quarter wave thickness of ZrO_2 at $1.06\text{ }\mu\text{m}$ wavelength, and L is a quarter wave of SiO_2 . Excellent agreement of the measured reflectance spectrum shown in Figure 16 with that calculated numerically on a computer demonstrates the level of coating refractive index and thickness control achievable with sputtering. Structures of the type displayed in Figure 16, which consist of two alternating coating materials that are fabricated with different source materials, are fabricated in a sputtering system containing two sources and a substrate holder that can be rotated to face one source and then the other. For example, the system used to fabricate the mirror of Figure 16 contained a Zr source and a Si source and the sputtering gas consisted of an $\text{Ar} + \text{O}_2$ mixture which was not changed during multilayer fabrication. Between layers, sputtering is briefly stopped as the substrate is rotated from one source to another. Two-source systems permit use of very many coating materials combinations selected from those compiled in Table 1.

Summary

Reactive sputtering is shown to be a very promising new technique for optical coating fabrication. Sputtering allows precise control of coating structure and composition, leading to rapid property optimization and in many cases coating performance better than previously achieved with conventional evaporative techniques. New materials with complex compositions not synthesizable by traditional approaches can also be made by reactive sputtering, providing a second avenue to improved coating performance. Examples are provided from recent PNL research on reactively sputtered coatings of TiO_2 , $\text{Si}_{1-x}\text{H}_x$ and ITO. Techniques for the fabrication of useful multilayer structures by sputtering have been developed, and reflection/transmission spectra are presented here to demonstrate multilayer coating performance. Specific details of the sputtering process and equipment are presented for comparison with conventional approaches.

Acknowledgements

The research leading to this paper was performed for the Division of Materials Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy. Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830. The authors gratefully acknowledge W. Howard Lowdermilk and David Milam of Lawrence Livermore National Laboratory for the laser damage measurements on TiO_2 and ITO coatings, and also thank Major Ronald L. Lusk of the Air Force Weapons Laboratory for coordinating the HF calorimetry measurements on Si:H coatings.

References

1. Pawlewicz, W.T. and Busch, R., "Reactively Sputtered Oxide Optical Coatings for Inertial Confinement Fusion Laser Components", Thin Solid Films **63** (2), pp. 251-256. 1979.
2. Pawlewicz, W.T., Busch, R., Hays, D.D., Martin, P.M., and Laegreid, N., "Reactively Sputtered Optical Coatings for Use at 1064 nm", Laser-Induced Damage in Optical Materials: 1979; edited by H.E. Bennett, A.J. Glass, A.H. Guenther and B.E. Newnam, NBS Spec. Publ. 508, pp. 359-374. 1980.
3. Pawlewicz, W.T. and Martin, P.M., "Bonding and Composition Diagrams for Sputter Deposited a-Si:H," Solid State Communications, **39** (2), 337-339. 1981.
4. Martin, P.M. and Pawlewicz, W.T., "Influence of Sputtering Conditions on H Content and Si-H Bonding in a-Si:H Alloys," Journal of NonCrystalline Solids, **45** (1), 15-27. 1981.
5. Martin, P.M. and Pawlewicz, "Property-Composition Relationships in Sputter-Deposited a-Si:H Alloy," Solar Energy Materials, **2** (2), 143. 1979/1980.
6. Donovan, T.M. Reference to be provided later.
7. Pawlewicz, W.T., Mann, I.B., Lowdermilk, W.H. and Milam, D. "Laser Damage Resistant Transparent Conductive Indium Tin Oxide Coatings," Applied Physics Letters, **34**, 196. 1979.
8. Pawlewicz, W.T., Hays, D.D. and Martin, P.M., "High-Band-Gap Oxide Optical Coatings for 0.25 and 1.06 μm Fusion Lasers," Proceedings of the International Conference on Metallurgical Coatings, April 1980, San Diego, CA., Thin Solid Films, **73** (1), 169-175. 1980.

Figure Captions

1. Schematic diagram of rf sputtering apparatus for reactive deposition of optical coatings.
2. Phase composition diagram for TiO_2 coatings constructed from pertinent sputtering condition data. Diagram can be used to preselect the anatase/rutile composition of an optical coating.
3. Influence of substrate temperature on the grain size of rutile coatings. Inset shows grain size enhancement by plasma heating during deposition.
4. Influence of phase composition on the refractive index of TiO_2 coatings with intermediate grain sizes.
5. Influence of grain size on the refractive index of TiO_2 rutile coatings.
6. Influence of grain size on the laser damage threshold of rutile coatings. Highest thresholds are obtained for glassy coatings.
7. H content diagram for Si:H coatings constructed from pertinent sputtering condition data. Diagram can be used to select the composition of an optical coating.
8. Exponential decrease of absorption coefficient of Si:H coatings with increasing H content at $1.06 \mu\text{m}$ wavelength.
9. Record low absorption coefficient for Si:H coating at $2.7 \mu\text{m}$ wavelength and comparison with Si coatings made by other techniques.
10. Influence of H content on the refractive index and optical band gap of Si:H coatings.

11. Transmission and reflection spectra for a highly conducting (4×10^{-4} Ohm cm) ITO coating on fused silica. Upper dashed curve is transmission of bare substrate.
12. Influence of target power density and O_2 partial pressure on the resistivity of sputtered ITO coatings.
13. Reflection spectrum for a Si:H/SiO₂ high reflector fabricated by reactive sputtering for use at the iodine laser wavelength of 1.315 μ m.
14. Reflection and transmission spectra for a Si₃N₄/SiO₂ high reflector fabricated by reactive sputtering for use at 540 nm wavelength.
15. Reflection spectrum for a ZrO₂/SiO₂ high reflector fabricated by reactive sputtering for use at the Nd:YAG laser wavelength of 1.06 μ m. Computer calculated spectrum is shown for comparison.

Table 1. Sputtered Optical Coating Materials Examined To Date
And Their Properties

Material	Useful Transmission Range (nm)	Mid-Range Refractive Index	Comments
SiO ₂	< 200 to 8000	1.45	
GeO ₂	280 to 8000	1.60	
TiO ₂	380 to 8000	2.1 to 2.7	Index depends on grain size and phase composition
ZrO ₂	240 to 8000	2.15	Monoclinic
ZrO ₂ •CaO	250 to 8000	2.10	Cubic-stabilized, 15 mole % CaO
ZrO ₂ •Y ₂ O ₃	250 to 8000		Cubic-stabilized, 15 mole % Y ₂ O ₃
HfO ₂	220 to 8000	2.00	
Ta ₂ O ₅	350 to 8000	2.03	
Nb ₂ O ₅	320 to 8000	2.20	
Y ₂ O ₃	220 to 8000	1.90	
La ₂ O ₃	250 to 8000	1.76	Hygroscopic
MgO	225 to 8000	1.69	
Al ₂ O ₃	< 200 to 8000	1.67	
Y ₄ Al ₂ O ₉	220 to 8000	1.76	
MgAl ₂ O ₄	225 to 8000	1.61	
ITO	400 to > 1000	1.8 to 2.0	Conductive, resist- ivity as low as 4 x 10 ⁻⁴ Ohm cm.
Si ₃ N ₄	250 to 9000	1.95	
Ge ₃ N ₄	800 to 9000	2.11	
TiN	500 to 8000	2.13	
BN	250 to	1.67	
SiC	2500 to > 11000	2.95	
Si	1000 to 9000	3.6	
SiO ₂	< 200 to 8000	1.45	
Si ₃ N ₄	250 to 9000	1.95	
Si:H	700 to 9000	2.0 to 3.6	H contents from 0 to 40 atom %
SiC	2500 to > 11000	2.95	

Table 1. Sputtered Optical Coating Materials Examined To Date
And Their Properties (Continuation)

Material	Useful Transmission Range (nm)	Mid-Range Refractive Index	Comments
Ge	1500 to > 11000	4.08	
GeO ₂	280 to 9000	1.60	
Ge ₃ N ₄	800 to 9000	2.11	
Ge:H	1200 to > 11000	2.88 to 4.08	H contents from 0 to 3 atom %
CdS	600 to > 11000	2.52	
CdTe	900 to > 11000	2.70	
ZnSe	500 to > 20000	2.42	

Table 2. Laser damage thresholds of TiO₂ optical coatings with the same grain size but different phase compositions. All coatings are single layers with half-wavelength thickness at 1064 nm (~ 230 nm) on fused silica substrates.

Phase Composition ^(a)	Grain Size (nm) ^(a)	Damage Threshold (J/cm ²) ^(b)
100% R	11	5.2 ± 0.8
"	15	3.9 ± 0.6
"	10	≤ 2.5
65% R/35% A	10/12	4.1 ± 0.7
60% R/40% A	10/10	2.3 ± 0.5
85% R/15% A	12/12	≤ 2.0

(a) X-Ray Diffraction.

(b) Measured at Lawrence Livermore National Laboratory, 1 nsec pulses, 2 mm beam diameter.

FIGURE 4.

FIGURE 5:

FIGURE 6. Influence of grain size on the laser damage threshold of rutile coatings. Highest thresholds are obtained for glassy coatings.