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Coating Materials News

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Optical Interference Coatings Conference 2007

This international conference, held every three years, assembles the world's leading researchers in thin film optics from academic and industrial facilities. Colleagues from several countries in Europe, Russia, Asia and North America gathered in the desert to present their latest results. General optics topics included design, deposition and monitoring, coating properties and measurement techniques. This edition of CMN summarizes those research items that readers might be interested in following up on.

"Nano-scale" was the word of the day at this conference! A world-wide effort is currently directed to lithographic optics, and their coatings, for wavelengths shorter than 193 nm (VUV) and 30 nm and 13.5 nm (EUV or soft X-ray). To this end, materials, their deposition processes and property characterization techniques and results were emphasized in more than one session. Film microstructural growth problems that might lead to scattering or absorption losses are an important consideration in producing efficient and stable UV coatings. Measurement of scatter properties at these short wavelength regions presents a new set of problems, and deposition techniques that minimize optical scatter and absorption are still in the development states. Two examples are mentioned. Only fluoride compounds exhibit sufficiently low absorption for the VUV region, and resistance-heated and E-beam evaporation techniques (without IAD) produce the highest damage thresholds for the transmitting multilayers. Coatings for EUV optics are multi-layer designs consisting of many very thin layers of Silicon, Molybdenum, and other metals that reflect these short wavelengths at grazing incidence.

Coatings for Nano-scale Applications

The generation and patterning of nano-structures of scale determined by EUV wavelengths is of interest for 3-D micro-machining. Precise nano-scale ablation of surfaces is now possible through ultra-fast laser pulse technologies being developed in labs and research centers world wide. The technology is based on the localization of energy by tight focusing, thereby avoiding bulk thermal damage. Among the applications are: nano-structuring of polymeric surfaces, optical device construction and integration, high-density data storage, optical waveguide production for communication devices, biological specimen assay and toxin detection, and laser treatments with minimum damage to surrounding tissues. An advantage provided by the pulsed laser deposition of thin films for optical and electronic purposes is the preservation of material composition. Pulse widths have decreased from micro-second to femto-second (10^{-15}) and repetition rates are in the MHz range. When VUV or EUV wavelengths are employed, structures smaller than 100 nm can be laser ablated. At pico-second and shorter pulses, condensation into droplets of the small quantity of material evaporated in each pulse is inhibited, thereby eliminating contamination by microparticulates that previously limited the application of laser ablation technology for critically small device generation. Examples requiring the highest quality optical surfaces are optical waveguide devices.

Femto-second lasers span the wavelength range UV (excimer) to near-IR (Ti:sapphire, λ 800 nm and Nd:YaG, λs 355 nm, 532 nm and 1064 nm), and present new requirements for the coating industry. The energy densities are extremely high within the very short pulse widths and high repetition rates. While the average power is not excessively high, thin film coatings applied to the optics

Figure 1

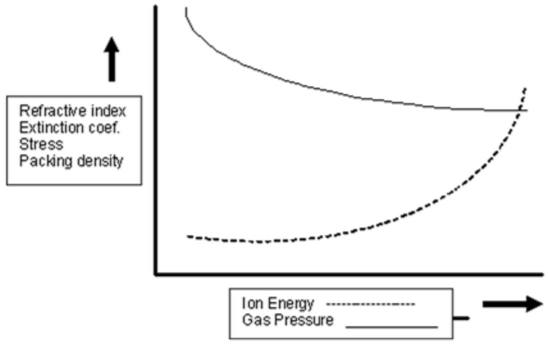

Figure 1. General relationships between film characteristics and the deposition parameters: ion energy and gas pressure, in IAD and reactive deposition processes. (Note: these are trend curves i.e., they are independent of each other and are on different scales).

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involved must possesses high damage thresholds. Damage thresholds are lower for multi-pulse exposure than for single pulses because the defects created that lead to absorption accumulate with pulse count. The damage threshold for multiple shots does not depend on the pulse rate within the range 1 Hz to 1 kHz [1]. Increasing pulse duration increases damage threshold: with femto-second pulses, materials tend to fracture and vaporize; longer pulse lengths lead to melting.

Table 1: Relationship Between Band gap and LIDT for Pure Oxide Compounds

Pure Material	Index (λ 600 nm)	Absorption Gap (eV)	LIDT (J/cm^2)
TiO_2	2.44	3.48	0.25
Nb_2O_5	2.30	3.62	0.09
Ta_2O_5	2.11	3.87	0.35
SiO_2	1.49	**5.30**	2.7 (bilk)

Other papers in the conference revealed that laser induced damage thresholds are not changed by changes in irradiating beam size, but only the slope of the threshold curve is affected. Nodular defects growing from micro-particulates imbedded in a coating are points of enhanced electric field intensity, and therefore sites for damage initiation.

Film Microstructure

Several papers were presented on the control of film microstructure through the use of energetic deposition techniques, such as variations on conventional magnetron sputtering (MS) that include high-power pulsed MS (Fraunhofer Institute for Surface Engineering), closed field MS (Applied Multilayers Ltd, UK), and plasma ion assisted deposition, PIAD (Leybold Optics GmbH and Carl Zeiss AG). For high-energy femto-second (fs) laser applications, ion beam sputtering has been shown to produce coatings with high laser damage thresholds for visible wavelengths. Those coatings are very stable because of the high packing density characteristic of IBS.

A very practical paper that discussed the optimum O_2 pressure for achieving high quality TiO_2 films from Ti_3O_5 starting material was presented (2). CERAC Ti_3O_5 as the starting material, as opposed to other TiOx compositions, has been shown to produce the most reproducible film composition and index (3). Using reactive E-beam evaporation, films were grown on substrates at 200° C at a rate of 2 Å/s. An index of 2.41 was achieved at 550 nm wavelength for a 5 sccm oxygen flow rate. When the flow rate was changed to either side of this optimum rate, either 4 or 6 sccm, the index decreased to $\leq$ 2.39. Extinction coefficient, k, was ~0 to wavelength 400 nm. No particulate ejection is experienced from the melted source. This study emphasizes the importance of determining the optimum background pressure value and control to achieve complete and homogeneous oxidation, and maximum index with low absorption.

Figure 1 illustrates the general dependencies of film packing density, index, absorption, and stress on background pressure and ion energy in IAD and reactive deposition processes. As background (reactive) gas pressure increases, more gas molecules are incorporated in the film structure than are reactively consumed, leading to lower density and consequently lower index. However, stress and absorption are lower. Increasing ion energy causes compaction, increased reactivity, and higher stress. Extinction coefficient generally increases perhaps due to defect –induced absorption.

An investigation of the morphology, index, and crystal structure of Yttria, (Y)ZrO_2, and CeO_2 layers was reported by R. Thielsch using substrate temperature and IAD as variables [4]. Differences in growth and crystal alignment were noted: all three materials exhibited a fibrous (columnar) structure and negative index inhomogeneity on high temperature ($\geq$350° C) substrates. This is due to selective polycrystalline growth rate and orientation. When Ar IAD (4 keV, 10 mA/cm^2 and oblique incidence) is applied, the film layers assumed a more homogeneous structure with a preferred crystalline orientation aligned with the ion direction at low growth rates. Apparently, the randomly growing grains are sputtered more rapidly than the crystalline grains that are aligned in a preferred direction.

Table 2. Results of AR combinations for the 193nm Lithography Applications

Combination	Roughness (nm)	Loss (%)	Stress Mpa)	LIDT (mJ/cm^2)
MgF_2 / LaF_3	0.65	0.05	440	2700
MgF_2 / GdF_3	1.2	0.12	350	2250
AlF_3 / LaF_3	0.4	0.07	275	3000
AlF_3 / GdF_3	0.5	0.1	150	2900

Mixing Techniques

The deposition technique Ion Beam Sputtering (IBS) received much attention at the conference. IBS has the primary advantage over other techniques of depositing dense film layers with minimum optical absorption. Therefore IBS coatings find appropriate application where absorption and scatter losses must be reduced to ppm values. Such applications are ring-laser gyros and high-energy laser optics. A favorite technique for depositing the high- and low-index oxide compounds is to build the sputter target with half covered with each material (“zone target”). The appropriate target material is moved into and out of the beam as required. Advantages are: mixtures can be generated that provide otherwise unavailable refractive indices intermediate between the H and L values by partially exposing both targets to accomplish the desired mixing ratio. Low percentage “doping” of either material can be provided for stress control, and discrete interfaces between layers can be eliminated to reduce scatter.

Papers reported on the success of TiO_2 / SiO_2 zone targets for increasing Laser Induced Damage Threshold (LIDT) for femto-second (fs) coatings by a factor of 2 [5], and extending the UV cutoff limit of co-sputtered Ta_2O_5 with differing ratios of SiO_2 films to shorter wavelengths [6]. The LIDT of pure materials is proportional to their absorption bandgap and the electric field strength established in the material layer, as shown in the table below [5].

Varying percentages of silica are “mixed” with the high-index component either by proportionally exposing the H and silica targets or by interposing thin layers of silica to create a graded average index decrease from the substrate toward air.

DUV Lithography Coatings

The generation of small structures using light of wavelength 193 nm has progressed, but coatings for this DUV region are required to have a high LIDT and low loss. Only fluoride compounds satisfy these requirements, and the candidate materials are: AlF_3 and MgF_2 for low-n, and LaF_3, and GdF_3 for high-n. Combinations of H & L for AR coatings at 193 nm were evaluated for microstructure, roughness, stress, loss, and LIDT [7]. Using resistance heated Mo boat, 300° substrate temperature, and deposition rates ≤ 2 Å/s, AR combinations were deposited and evaluated. The results are summarized in Table 2.

Except for AlF_3, all fluorides grew with a coarse columnar microstructure; AlF_3 appeared to be amorphous. This property is reflected in, and perhaps responsible for, the superior properties for the AlF_3-combinations shown in Table 2.

A paper on the deposition of LaF_3 films for DUV applications revealed the influence of the substrate polish on film quality. Substrates of polished single-crystal CaF_2 held at 150° were coated at 2 Å/s from a Mo boat. Dense amorphous films were grown for thickness ~50 nm, but a columnar structure develops for greater thicknesses, resulting in greater roughness and increasing inhomogeneity. Highest packing density, lowest roughness, and lowest absorption are obtained on super-polished substrates. Polycrystalline growth is produced on silicon substrates independent of film thickness. [8].

Conclusion

The conference exposed the international optical thin-film community to the issues currently receiving focused attention. We see that material and deposition topics remain important, especially as applications stretch the state of technology to shorter wavelengths and laser pulse widths. These and other papers will be presented in full in a future issue of *Applied Optics*.

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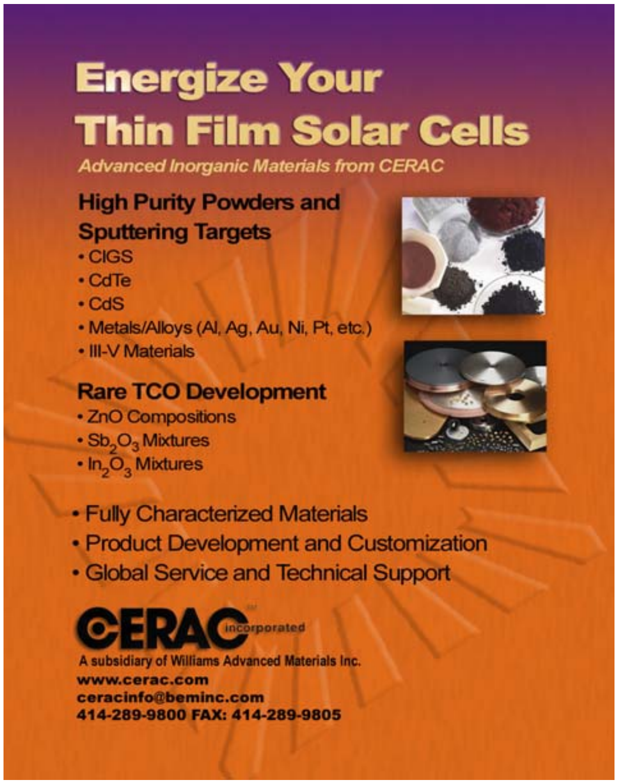

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