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Advanced Multilayer Coatings for National Security

R. Soufli, R. Qiu, T. Pardini, C. Burcklen, J. Alameda, J. Robinson, C. Walton, E. Spiller, P. Mirkarimi, R. Negres, C. Harthcock, T. Lawrence, S. Ly, E. Feigenbaum, G. Gus, M. Menor, V. Peters, L. Zepeda-Ruiz, A. Martin, C. Stolz, H. Nguyen

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FINAL REPORT
Advanced Multilayer Coatings for National Security
Tom Pardini (17-SI-001)

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Abstract

This project advanced the state-of-the-art in multilayer interference coatings with custom-tailored properties for national security applications, by understanding and overcoming limitations in the physical properties of these coatings. We focused on improving the properties of two major types of multilayers: the reflectance of hard x-ray aperiodic multilayer coatings (MLs) and the laser damage resistance of dielectric multilayer coatings (MLDs). We developed a new class of hard x-ray MLs for imaging in the 17 – 59 keV photon energy range for applications including target diagnostics and astrophysics. We elucidated the physical and chemical properties of nanoscale layers of ML materials and their interfaces and developed generalized protocols for aperiodic ML design and deposition. We revealed the origin of important laser damage-prone precursors and the underlying mechanism upon exposure to high energy and intensity nanosecond (ns) lasers in the ultra-violet (UV) region. In both ML and MLD coatings, we investigated the relationships between deposition conditions and performance. We then applied deposition process modifications specific to each type of ML and MLD coatings to dramatically improve the ML reflective performance and the MLD laser-damage resistance.

Background and Research Objectives

Multilayer interference mirrors are enabling components in optical systems operating in a wide spectral range, from infrared to hard x-ray wavelengths. Multilayer mirrors consist of periodic or aperiodic structures of alternating thin-film layers of two or more materials deposited on an optical substrate. The constructive interference between the layers results in efficient reflectance at incidence angles ranging from grazing to near-normal. X-ray aperiodic MLs are components in imaging and illumination systems, reflective filters, grating spectrometers, and polarizers, in target diagnostics, high energy physics, astrophysics and free-electron laser applications. The aperiodic layer configuration enables operation in a wide spectral range, or a wide angular field of view. MLDs are found in high energy and intensity laser systems for beam combination, beam steering, wavelength separation, and diffraction gratings. However, the physical properties of multilayers can severely limit their performance. For example, the performance of hard x-ray MLs with sub-nanometer layer thickness is dramatically reduced by roughness and intermixing at the layer interfaces that cannot be easily predicted or controlled. This problem has seriously hindered the ability to produce MLs with high experimental reflective performance, that meets design expectations. The objectives of the x-ray ML effort in this project, are: (1) elucidate the physical and chemical properties of ultrathin layers and their interfaces, within each ML system (2) incorporate these properties in ML design and modeling (3) employ deposition process modifications to limit detrimental interfacial effects and improve ML reflective performance. The laser-induced damage in MLD coatings hinders future utilization of lasers for applications under extreme conditions, namely, the exposure to higher energy and intensity particularly at 351 nm. Coating defects such as inclusions, non-stoichiometric clusters and interface irregularities are hypothesized to be the important laser damage prone precursors.

However, the physical nature and origin of the defects as well as the underlying damage mechanism remain elusive. What is needed is a fundamental understanding of these precursors in order to develop transformative technologies that enable the fabrication of high performance MLD coatings with reductions in damage density up to a few orders of magnitude. The objectives of the MLD effort are two-fold: (1) gain fundamental understanding of damage precursors in MLD coatings, (2) develop strategies of fabricating coatings with improved laser damage resistance for demanding applications.

We have met all the objectives set for this project. To accomplish this work, we leveraged Laboratory expertise in multilayer thin-film science, laser–matter interaction science, the materials science and design of optical interference coatings, and computer simulations, along with the infrastructure in specialized deposition systems, laser testing capabilities, metrology, and diagnostics facilities.

Scientific Approach and Accomplishments

The ML coating effort focused on the development of multilayer prescriptions for operation at a fixed hard x-ray photon energy (17, 22, 35, 59 keV) and for a wide angular acceptance. The selected photon energies of operation include the Mo, Ag and W Kα emission lines which are of interest in target diagnostic experiments. The ML material systems studied in this work include Mo/Si, W/Si, W/SiC, Ir/SiC, W/B4C, Mo/B4C, Ir/B4C. The starting point in our algorithmic approach for designing these ML structures was found in the literature (Kozhevnikov et al. 2001), where the ML structure is assumed to be composed of two different alternating materials (a bilayer), the bilayer thickness is monotonically varying across the ML stack ("depth-graded"), the thickness ratio of the two materials in the bilayer is assumed to be constant across the stack, and the interface roughness is assumed to be the same at every interface. This approach numerically searches for a ML coating design (recipe) that most closely matches the target spectral response. When the selected coating recipe was deposited however and the ML coating was measured, the experimental spectral response (peak reflectivity and shape of reflectivity curve) was found to differ significantly from the design, thus indicating that the above-mentioned 2-layer model used for the ML structure is insufficient. This issue was addressed by a dedicated experimental study of interfacial effects (roughness, interdiffusion) for each ML system we developed. The interfacial layers that were determined after this study, were included in a customized 3- or 4-layer ML model, i.e: by treating each interface as a separate layer in the ML structure. ML coatings designed and deposited using this approach showed a dramatic improvement in agreement between model and experimental performance. The ultimate step that we introduced, was a layer-by-layer fit of experimental reflectance data to our ML model, to refine the layer thickness parameters and obtain the exact ML design prescription that will produce the goal reflectance. This method was generalized to each ML material system we studied and was extended to fully aperiodic (vs. depth-graded) ML structures (Figure 1), resulting in remarkable agreement between design and experimental performance (Burcklen et al. 2018). Furthermore, in each ML system we studied, after we understood the physics behind interfacial effects that are the driving factors for reducing reflectance in ML structures, we employed the appropriate process modifications to minimize or eliminate them. These process modifications include the introduction of: (i) interface barrier layers, e.g: B4C barrier layers in Mo/Si MLs (Burcklen et al. 2019) (ii) reactive (N2) sputtering during the deposition process (employed for example in W/B4C and Ir/B4C MLs), to limit interdiffusion and lower thin film stress

with the introduction of N2-containing compounds in the ML structure (iii) reduction of process gas (Ar) pressure to increase adatom mobility during deposition, thus reducing layer roughness and interdiffusion, employed in Mo/Si MLs. Among the surprising findings in this research was the discovery that Mo/Si MLs with B4C barrier layers on the Mo-on-Si interface have higher reflectance at 17 keV than Mo/Si with B4C on both Mo-on-Si and Si-on-Mo interfaces (Burcklen et al. 2019).

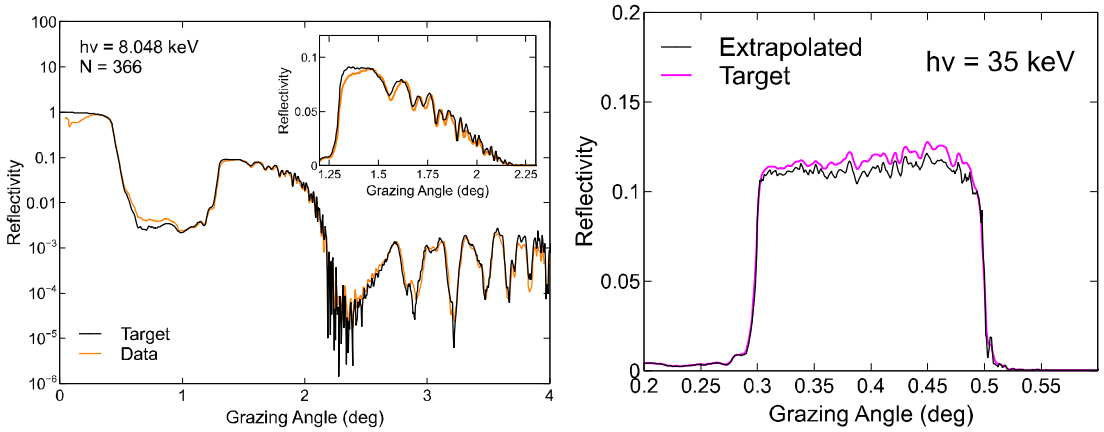


Figure 1 (Burcklen et al. 2018a). Left: Predicted (target) and measured (data) reflectivity of an aperiodic W/SiC multilayer (ML) at 8 keV (lin-log scale). The remarkable agreement between the two curves was achieved with our approach in just one coating iteration. Right: The reflectivity of the same W/SiC ML is plotted in linear scale at 35 keV, which is the intended photon energy of operation. The "extrapolated" curve was calculated using the model built from the measurements at 8 keV shown on the left.

All ML coatings in this work were deposited via magnetron sputtering at LLNL and were measured via x-ray diffraction at 8 keV (Cu Kα source). Selected ML coatings were also measured at 17 keV (Mo Kα source) at Rigaku Corp. (Auburn Hills, MI). For ML coatings designed to operate at photon energies higher than 17 keV, the model constructed from experimental data at 8 and 17 keV was used to calculate the performance at the photon energy of operation. The physics of the layers and their interfaces in each ML system were studied by fits to x-ray diffraction data, cross-sectional transmission electron microscopy (TEM) analysis of the ML thin film (Figure 2), Rutherford backscattering spectroscopy (RBS) to determine density and composition and x-ray photoelectron spectroscopy to obtain chemical state information. The thin film stress of all ML coatings was measured at LLNL and was found to be in the 0 to -0.7 GPa range (compressive), which is in the low to moderate range, making these ML coatings suitable for deposition on actual optics for applications.

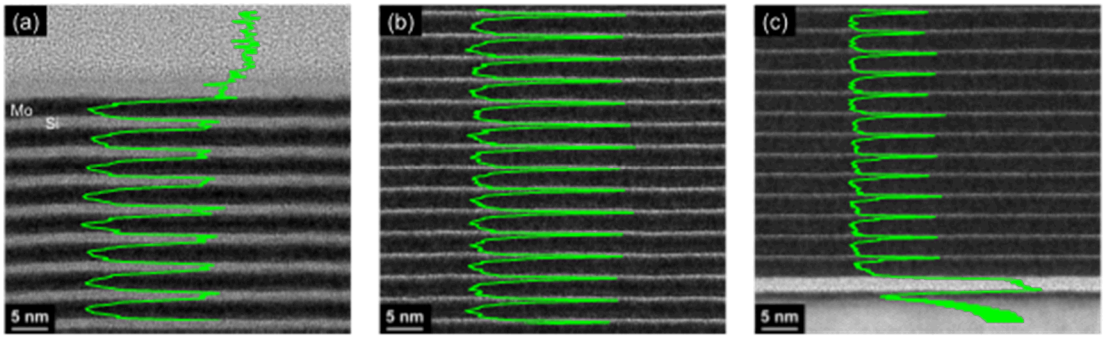


Figure 2 (Burcklen et al. 2019). High-resolution, 440k magnification transmission electron spectroscopy (TEM) images of a cross-section of a depth-graded Mo/Si multilayer (ML) designed for operation at 17 keV photon energy. The dark layers are Mo and the bright layers are Si. (a) top, (b) middle and (c) bottom of the ML. The averaged profiles of Mo or Si concentration (green lines) are over-plotted on the corresponding TEM images.

The MLD coating effort focused on the understanding of laser damage precursor and the laser-defect coupling mechanism upon ns UV laser exposure. Dense coatings of silica/hafnia by ion beam sputtering (IBS) were selected for their bulk-approaching physical properties and environmental stability. Three potent UV laser damage precursors, i.e. nanobubbles, sub-stoichiometry, and rough interfaces were identified.

The precursor of nanobubbles was discovered (Harthcock et al. 2019) by correlating the laser-induced damage onset in hafnia films deposited by O assisted IBS to the physical nature of entrapped Ar and O. The laser damage onset depends strongly on the amount of Ar and excessive O entrapped in the films (Figure 3a). These entrapped gas species are found to create nanobubbles in the hafnia films by the small angle x-ray scattering (SAXS) analysis (Figure 3b). The size of the nanobubbles is 1.3 nm and 1.0 nm for the film deposited with- and without O assist, respectively. The presence of nanobubbles with entrapped gases is confirmed by the scanning transmission electron microscopy (STEM) and high-angle annular dark-field (HAADF) characterizations (Figures 3c-d). The over 100× of atmospheric pressure in the nanobubbles results in plasma formation at a laser fluence threshold that is consistent with the value displayed in Figure 3a. The thermal energy dissipation during- and post- the laser pulse leads to irreversible coating material damage.

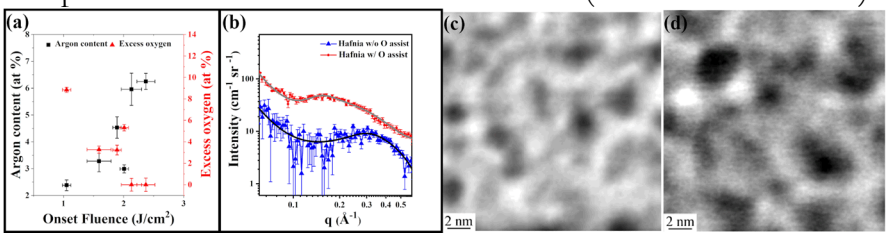


Figure 3. (a) Correlation between the laser damage onset and contents of Ar and excessive O in hafnia films. (b) Small angle x-ray scattering of hafnia films produced at zero and 350 V O assist voltages. (c-d) Scanning transmission electron microscopy (STEM) and high-angle annular dark-field (HAADF) images of hafnia films shown in (b).

The direct identification of sub-stoichiometry as a laser damage precursor was made possible from our revelation of the stark compositional contrast between hafnia films produced at two extreme planetary locations in the same deposition run (Harthcock et al. 2019). The hafnia films near the planetary edge exhibit the perfect stoichiometric oxygen (O) to hafnium (Hf) ratio and those at the center location are sub-stoichiometric (Figure 4a). The laser damage onset under UV irradiation is significantly higher (over 1 joule per square centimeter) for the stoichiometric (edge) film than that of the center film (Figure 4b). The sub-stoichiometry is the performance-limiting precursor for initiating the laser damage. The origin of the sub-stoichiometry is the exposure of high energetic reflected Ar neutrals from the sputtering working gas, which removes O in the film by preferential re-sputtering (Selinder et al. 1991). TRIM.SP Monte Carlo simulations (Biersack et al. 1984) confirm that the region of highest energetic reflected Ar neutrals (dark brown) coincides with the center of the planetary system (Figure 4c).

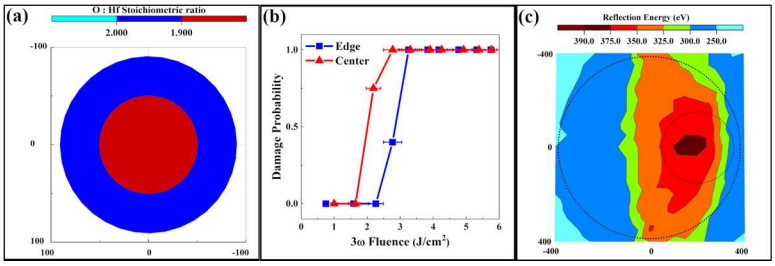


Figure 4. (a) The schematic showing the average distribution of O to Hf ratio on the planets from RBS analysis. (b) The laser damage probability as a function of fluence (355 nm, 8 ns, p-polarization) for hafnia at the two extreme locations. (c) Monte Carlo simulations of reflected Ar neutral energies at the planetary surface.

A close examination of layer pairs of silica/hafnia coatings reveals random nano-roughness at the otherwise sharp interface (Figure 5a). The rough regions exhibit a ~10 nm transition with a structure that is very different from the two layers (Figure 5b). The sharp regions display clear structural transition at the interface (Figure 5c) as expected. Furthermore, there also exists a transition in composition between the two type of interfaces: a gradual change at the rough region (Figure 5d) and a sharp jump at the straight region. Figure 5e shows the cross-sectional view of a damage site at different steps of focused ion beam (FIB) carving on a layer pair coating upon UV laser exposure. The damage occurred at the interfaces as highlighted by the red arrows indicating interface is a potent laser damage precursor in dielectric coatings.

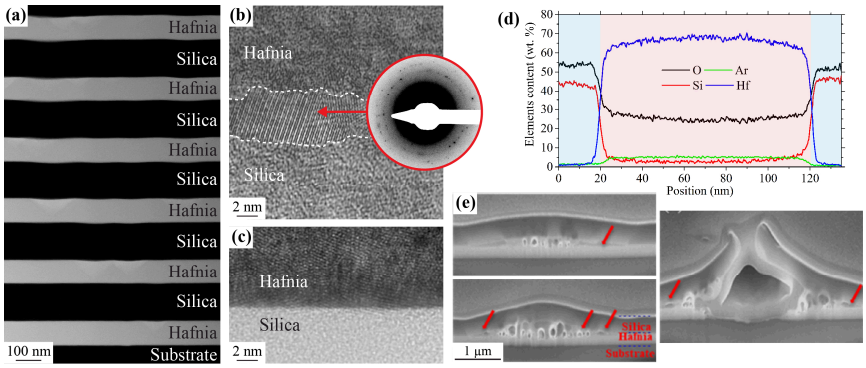


Figure 5. (a) STEM cross-sectional view of IBS coated silica/hafnia layers. (b) High resolution TEM (HRTEM) of a silica/hafnia interface containing a crystal defect. (c) HRTEM of a sharp interface. (d) Energy dispersive r-ray spectroscopy (EDS) line-analysis crossing the silica/hafnia/silica layers in wt. and at. %. (e) Cross-sectional scanning electron microscope (SEM) images of a damage site at different steps of focused ion beam (FIB) carving.

Our results provide insights into the mechanism of the laser-induced damage, the origin of defect formation and the development of laser damage resistance dielectric coatings for applications in national security. The exciting outcome is three-fold: i) defines a previously unrealized role for nanobubbles in dielectric coatings; ii) develops a novel approach for thin film defect isolation; iii) offers new pathways for future investigation of the role of interfaces on laser performance of dielectric coatings.

Impact on Mission

The ML effort in this project developed an entirely new capability at LLNL, for the design and deposition of high-performance, hard x-ray aperiodic MLs with tailored properties for national security and science applications. The knowledge gained and the capabilities developed can addresses ignition and stockpile stewardship challenges by helping provide a pathway to higher power and energy on NIF and other ICF experimental facilities, higher intensity optics for ARC and lasers for emerging directed energy systems. The results of this work impact the Laser and Optical Science and Technology, Advanced Materials and Manufacturing, High-Energy Density Science and Space Security core missions at LLNL. Two talented postdocs were hired and trained at LLNL as part of the ML and MLD tasks in this project and two additional postdocs were also shared to support the projects.

Conclusion

The new ML capabilities developed in this research will result in new projects from government (DOE, NA-22, NASA) as well as industrial sponsors. The results, deposition technologies and methodologies developed in this work are also useful for photon energy ranges and applications outside of those explored in this project. For example, MLs for the extreme ultraviolet/soft x-ray spectral range (0.02 – 1 keV) for solar physics, astrophysics, semiconductor photolithography, lasers and attosecond science applications, may greatly benefit from this research. This opens new opportunities for sponsored projects at LLNL. The accomplishments have set a scientific foundation for the development of laser damage resistant MLD coated optics for high power and energy lasers by suppressing or removal of the identified precursors. The knowledge gained is also being used to fabricate high performance dielectric coatings for developing new type of laser systems in DoDT programs. The capabilities developed will help collaboration between LLNL and US manufacturers for developing large laser optics for national security.

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Notes to the Editors

YBa2Cu3Ox. YBa(subscript)2Cu(subscript)3O(subscript)x.