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Anti-Reflective Fluoride Coatings for Widely Tunable Deep-Ultraviolet Diode-Pumped Solid-State Laser Applications

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An anti-reflective (AR) fluoride coating in the 170–230 nm spectral range is prepared by the thermal evaporation method for the applications of widely tunable deep-ultraviolet diode-pumped solid-state lasers. The transmittance of an AR coated calcium fluoride (CaF_2) window in thickness 3 mm is measured to be in the range of 95.8% at 170 nm to 97.1% at 230 nm, with the maximum transmittance 99.2% and the minimum residual reflectance 0.04% appeared at 195 nm. The experimental results indicate that treating the AR coated window and the bare substrate with ultraviolet irradiation can significantly improve their optical performance.

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The development of deep ultraviolet (DUV) diode-pumped solid-state lasers has attracted great interest in recent years due to the discovery of a novel nonlinear optical crystal $KBe_2BO_3F_2$(KBBF)[1] by Chinese scientists and the promising applications of DUV laser sources in semiconductor photolithography, photo-luminescence, photochemical synthesis, high-resolution DUV laser spectroscopy, and photoemission spectroscopy, etc.[2] By using a KBBF prism-coupled device (KBBF-PCD), a coherent emission with over 10 mW power at 177.3 nm was realized by directly frequency-doubling the third harmonic (354.7 nm) of an Nd:YAG or Nd:YVO_4 laser,[3] that is, the sixth harmonic generation of a 1064 nm source. On the other hand, a widely tunable DUV emission was obtained by a direct second harmonic generation (SHG) of a frequency-doubled Ti:Sapphire laser, corresponding to the fourth harmonic generation (FHG) of the Ti:Sapphire laser. By using a nanosecond Q-switched Ti:Sapphire laser, a continually tunable DUV light with wavelength range from 175–210 nm was generated.[4] Most recently, the tunable wavelength range was further expanded from 175–210 nm to 170–232.5 nm by employing a femtosecond pulsed Ti:Sapphire laser as the light source.[5]

The successful applications of these widely tunable DUV lasers require DUV optics to manipulate the laser beams. Both optical windows and lenses, which are normally coated with anti-reflective (AR) coatings to enhance their transmittances, are among the most commonly used optical components in laser systems. Up to now, the researches on AR coatings in the DUV spectral range are focused on AR coatings at two excimer laser wavelengths 193 nm and 157 nm, and major efforts were put at wavelength 193 nm, due to the lithographic applications of argon fluoride excimer lasers. By employing different material combinations (MgF_2/LaF_3, MgF_2/GdF_3, AlF_3/LaF_3, and AlF_3/GdF_3, etc.) and different deposition techniques (such as thermal evaporation,[6] ion beam sputtering,[7] rf magnetron sputtering,[8] and ion assisted deposition,[9] etc.), the measured maximum transmittance values of AR coated DUV windows at 193 nm were in the range 99.4–99.7%. On the other hand, the research on AR coatings at 193 nm in China was recently reported by Sang *et al.*[10] By using an MgF_2/LaF_3 combination and thermal evaporation technique, the transmittance of a one-side AR coated fused quartz substrate was measured to be 93.5% at 193 nm, with a minimum residual reflectance of 0.16%. No research on the optical coatings for DUV solid-state lasers has been reported up to date.

In this Letter, we report on the preparation of an AR coating for applications in the widely tunable DUV solid-state laser sources. By using MgF_2 and LaF_3 as low- and high-refractive index materials and UV irradiation treatments, the transmittance of an AR coated calcium fluoride (CaF_2) window is measured to be in the range of 95.8% at 170 nm to 97.1% at 230 nm, with a maximum transmittance of 99.2% appeared at 195 nm.

The AR coating was designed with a three-layer structure of non-quarter-wave optical thicknesses. The three-layer design was selected to minimize the total physical thickness of the coating and therefore the optical absorption loss, and to improve the laser-induced damage threshold of the coating. This is due to the high extinction coefficients of the fluoride films in the short wavelength range ($<$ 180 nm). The design was a sub/L'H'L"/air structure, optimized by the

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commercial Essential Macleod design software to maximize the transmittance from 175 nm to 215 nm with a target transmittance of 100%. Here L' and L" are the low-index layers and H' is the high-index layer of non-quarter-wave optical thickness. The physical thicknesses of the L', H', and L" layers are 7.77 nm, 28.44 nm, and 34.07 nm, respectively. In the three-layer design, the refractive indexes of the L and H layers are determined from the spectroscopic ellipsometry (in the spectral range of 240 nm to 500 nm) and spectrophotometry measurements (in the spectral range 190–500 nm)[11] of single-layer samples prepared with the same deposition parameters as that used in preparation of the AR coating. The extinction coefficients were obtained from the literature.[6,12] Figure 1 shows the refractive indexes n and extinction coefficients k of MgF_2 and LaF_3 layers, respectively, used in the design, in the spectral range 170–240 nm. Figure 2 shows the theoretical transmittance and reflectance spectra of a CaF_2 window coated with the designed AR coating on both sides. In the design, the optical loss of the substrate was neglected. From Fig. 2, the maximum transmittance of 99.78% occurring at 194 nm, and the transmittances at 170 nm and 230 nm are 96.0% and 96.7%, respectively. The minimum residual reflectance is 0.09%, which occurs at 193 nm.

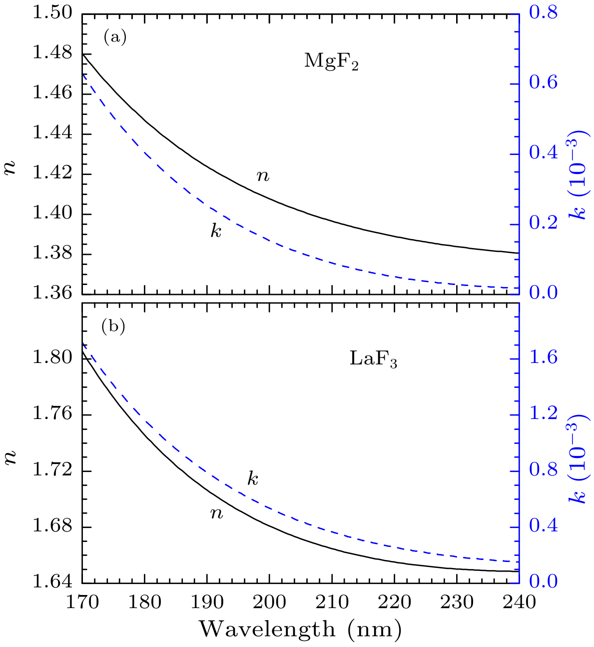

Fig. 1. Refractive indexes n and extinction coefficients k of the L (MgF_2) and H (LaF_3) layers used in the design, respectively.

Experimentally, the AR coating was deposited using the molybdenum boat evaporation method. Before the evaporation process, the deposition chamber was pumped down to a base pressure of less than 1.5×10^{-4} Pa by a cryopump set. The work pressure was around 1.7×10^{-4} Pa. The deposition rates were controlled and optimized by a quartz monitor, and were set to 0.2 nm/s and 0.04 nm/s for MgF_2 and LaF_3 layers, respectively. The nominal substrate temperature was set to 400°C. The high substrate temperature was used in order to reduce the absorption loss of the coatings at wavelength shorter than 180 nm. A 3-mm-thick CaF_2 plate was used as the substrate, which was cleaned by a commercial UV photo-cleaner for 40 min before deposition to remove hydro-carbon contaminations at the surfaces.

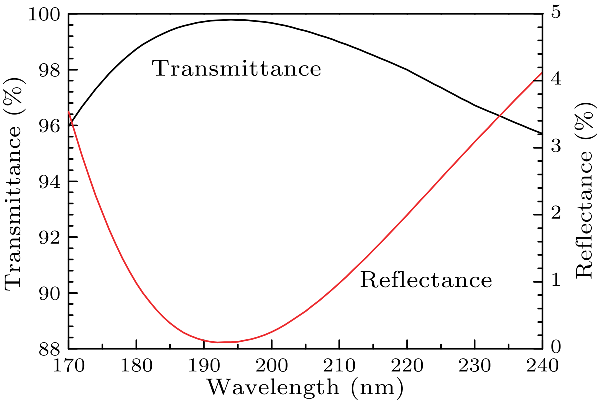

Fig. 2. Theoretical transmittance and reflectance spectra of a CaF_2 window coated with AR coatings on both sides. The optical loss of the substrate is neglected.

The transmittance and reflectance of the prepared AR-coated CaF_2 window were measured by a high-precision DUV spectrophotometer[13] under high-purity nitrogen purging condition, and the results are presented in Fig. 3, together with the transmittance of a bare CaF_2 substrate. The nominal measurement accuracy of the DUV spectrophotometer was 0.3% for the transmittance and 0.5% for the reflectance. Both the AR-coated window and the bare substrate were treated by a UV photo-cleaner for one hour before the measurements. The maximum transmittance of the AR-coated window was measured to be 99.2%, which occurred at approximately 195 nm. The maximum transmittance was determined by statistically averaging the measured transmittance values from 194 nm to 196 nm (with 21 data points), and the standard deviation was ±0.25%, which was within the range of the nominal measurement accuracy. The statistical result was $99.16 \pm 0.30\%$ from 192 nm to 197 nm. The maximum transmittance value was indicated by the dashed lines in Fig. 3 with an error margin of ±0.3%. The transmittance values at 170 nm and 230 nm were 95.8% and 97.1%, respectively. The minimum residual reflectance was only 0.04%, which occurred at 195 nm. On the other hand, the transmittance of the UV-treated bare CaF_2 substrate was measured to be 91.2% at 170 nm. The transmittance increased monotonically with the wavelength, and reached 93.0% at 240 nm. In comparison of the results presented in Figs. 2 and 3, the measured performance of the AR-coated window is in good agreement with the theoretical design, taking into account the difficulty to determine accurately the values of the refractive indexes and extinction coefficients of the layer materials used in the design in the deep UV spectral range.

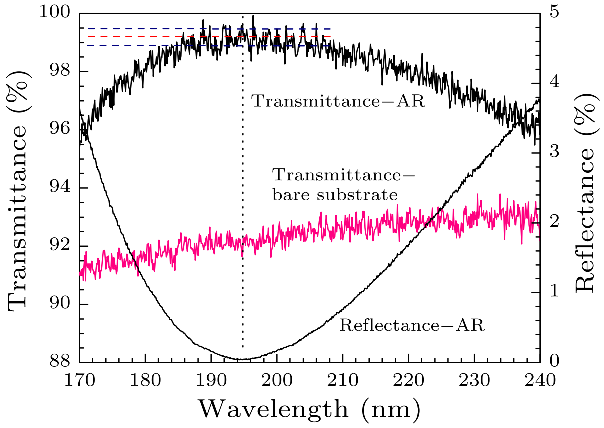

Fig. 3. Transmittance and reflectance spectra of the CaF_2 window coated with AR coatings on both sides, measured by a DUV spectrophotometer. The transmittance at 195 nm is indicated by the dashed lines with an error margin of ±0.3%. For comparison, the transmittance of a bare CaF_2 substrate is also presented.

The optical losses of the bare CaF_2 substrate and the AR-coated window were also measured. By directly measuring the transmittance T and the reflectance R simultaneously, the optical loss was determined to be $1-T-R$. The measured results are shown in Fig. 4. The optical losses of both the bare substrate and the AR-coated window before and after the UV treatments are presented. Without UV treatment, the optical loss of the 3-mm-thick substrate is approximately 1.7% at 170 nm, and decreases monotonically to approximately 0.1–0.2% at 230 nm. The UV treatment significantly reduces the optical loss of the substrate at the short wavelength region (below 200 nm).[14,15] At 170 nm, the optical loss was reduced to only approximately 0.6%, and at 195 nm, the optical loss was reduced from 0.9% to 0.2–0.3%. On the other hand, at wavelength above 230 nm, the influence of the UV treatment on the optical loss of the substrate is negligible. The similar situation appears for the AR-coated sample. Without UV treatment, the optical losses at 170 nm and 195 nm are as high as approximately 3.3% and 1.7%, respectively, and are reduced to approximately 1.6% and 0.7% by the UV treatment. Below 190 nm, for both the bare substrate and the AR-coated window, the optical losses increase rapidly with the decreasing wavelength. By subtracting the optical loss of the substrate from the coated sample, the optical loss of the AR coatings alone is approximately 1.0% at 170 nm, 0.4% at 195 nm, and 0.1% at 230 nm, respectively. The mechanism for the reduction of optical losses of DUV optics by UV treatment is the removal of hydrocarbon-related contaminants by photosensitized oxidation processes.[16] In UV treatment, the hydrocarbon molecules are excited and dissociated by the absorption of bright line at 253.7 nm from a low-pressure mercury (Hg) lamp. Simultaneously, atomic oxygen O and ozone O_3 are produced when oxygen is irradiated by the Hg lamp with strong lines at 184.9 nm and 253.7 nm. The excited contaminant molecules and the free radicals produced by the dissociation react with atomic oxygen to form volatile molecules, such as CO_2 and H_2O.

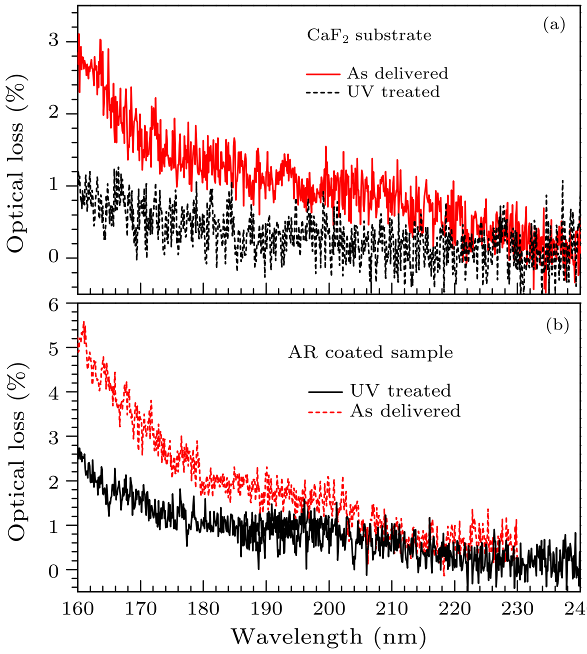

Fig. 4. Optical losses of (a) the CaF_2 substrate and (b) the broadband AR coating in the range 160–240 nm, without and with UV treatment, measured by a DUV spectrophotometer.

It is worth mentioning that for applications that require anti-reflective bands even wider than 60 nm, AR coating designs with more than three layers, for example, four- or five-layer designs, are appropriate with the compromise of increased absorption losses and reduced damage thresholds.

In conclusion, a deep-UV anti-reflective fluoride coating in the 170–230 nm spectral range has been prepared by the thermal evaporation method. With a three-layer AR coating design, the transmittance improvements of 4.6% at 170 nm, 7.1% at 195 nm, and 4.2% at 230 nm have been achieved as compared to the bare CaF_2 window. The experimental results have shown that the UV treatments significantly reduce the optical losses of AR coating and the substrate at wavelength below 200 nm, which should also greatly improve the damage threshold of the DUV coatings.

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