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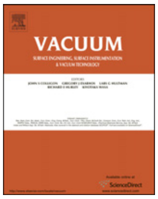

Mechanical stress in 355 nm LaF_3/MgF_2 high reflectors with various layer-pair number and methods for reduction

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ABSTRACT

Layer-pair number ranged from 9 to 22 of 355 nm LaF_3/MgF_2 high reflectors were deposited by boat resistant heating onto substrates of fused silica and K9 glasses, and the total stress was obtained by curvature measurements. The stress increased with incremental layers until crazing happed because of huge tensile stress at higher layer-pair number. Two methods called post-heat treatment in vacuum and double stack design with combination of LaF_3/MgF_2 and HfO_2/SiO_2 coatings were found to be effective to reduce the stress and avoid crazing. Especially in the double stack designed coatings, both low stress and high optical properties with transmittance smaller than 0.4% at 355 nm were obtained. Substrates and age effects were also discussed.

1. Introduction

In the UV region, fluoride coatings usually possess attractive higher laser induced damage thresholds than oxide coatings because of their initial wider band gaps [1,2], but at the same time they own huge tensile stress which always restricts their application in high reflectors in the form of crazing and destruction.

The stress in thin films is generated in the process of condensation [3], which is complicatedly affected by factors such as substrate and initial materials (such as thermal expansion coefficient listed in Table 1), deposition process (substrate temperature, base pressure, rate, etc.). Other factors as defect, morphology and environment (moisture) also influence the stress properties of thin films [4–7]. For the origin mechanism of stress, references [3,8–10] can be resorted to.

So it's necessary to discuss the stress in UV fluoride coatings and find some effective methods to reduce it. In this paper, firstly, various layer-pair number of LaF_3/MgF_2 high reflectors were deposited by boat resistant heating aiming to comprehend the development of stress with layer-pair number. Secondly, two methods called post-heat treatment in vacuum and double stack design with combination of LaF_3/MgF_2 and HfO_2/SiO_2 coatings (deposited by electron beam evaporation) were adopted to reduce the total stress in high reflectors. Finally, substrate (fused silica and K9 glasses) and age (mainly caused by water adsorption) effects on stress were also discussed.

2. Experiments

For the preparation of LaF_3/MgF_2 high reflectors and double stack designed coatings of $HfO_2/SiO_2/LaF_3/MgF_2$, fluoride and oxide coatings were deposited by boat resistant heating and electron beam evaporation, respectively, in the same facility which covers the two deposition methods, as is shown in Fig. 1. A base pressure below 1.5×10^{-3} Pa was obtained by the refrigerator cryopump system before deposition, ultrahigh purity of O_2 (99.99%) was used to raise the background pressure to 2×10^{-2} Pa when depositing oxide coatings. The substrates (fused silica and K9 glasses) were all heated to around 180 °C before deposition, the WZK silicon controlled temperature control system was used to measure the substrate temperature. The film thickness was controlled optically (Fig. 1) by a single wavelength turning point method with a wavelength of 360 nm, in which a deuterium light source was used. Other detailed deposition parameters are shown in Table 2.

When the deposition was finished, post-heat treatment was caught on as followings: the temperature in the vacuum chamber (1×10^{-1} Pa) was firstly reduced to 120 °C and kept it still for two hours, then to 70 °C for another two hours, at last to ambient temperature. For comparison, some samples were taken out without being processed by this kind of post-heat treatment.

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Table 1
Refractive indexes, thermal expansion coefficients of films materials and substrates.

Films materials and substrates	n at 355 nm	Thermal expansion coefficient (/K)
LaF_3 (M)	1.6	8.6×10^{-6} [5]
MgF_2 (A)	1.4	16.5×10^{-6} [5]
HfO_2 (H)	2.1	1.4×10^{-6} [5]
SiO_2 (L)	1.5	0.7×10^{-6}
K9	1.56	7.1×10^{-6}
Fused silica	1.56	0.55×10^{-6}

Table 2
Detailed deposition parameters of $(AM)^a$ and $(HL)^b$ H $(AM)^c$ and some comments.

Designs	Layers	Rates (nm/s)	Crazing
Sub/$(AM)^a$	$a = 9,12,16,18,22$	0.4 for A, 0.1 for M	$a \geq 18$ for coatings on K9 $a \geq 16$ on fused silica
Sub/$(HL)^b$ H $(AM)^c$	$b = 4$, $c = 12$; or $b = 8$, $c = 8$	0.6 for H, 0.2 for L	none for coatings on K9 partially on fused silica

After the samples were out, Perkin–Elmer Lambda 900 UV/VIS/NIR spectrophotometer was employed to measure the transmittance spectrum aiming to indirectly and qualitatively assessment the reflectance variation trend of the high reflectors. The total stress was obtained by curvature measurements, a ZYGO Mark III-GPI interferometer was used to measure the radii of the substrate before (R_1) and (R_0) after deposition, then the total stress $\sigma_{tot}$of all the samples could be given by Stoney's equation [11]:

$$\sigma_{tot} = \frac{E_S}{6(1-\nu_S)} \frac{t_S^2}{t_f}\left(\frac{1}{R_1}-\frac{1}{R_0}\right) \tag{1}$$

Where $E_S/(1-\nu_S)$ is the biaxial modulus of the substrate, t_s and t_f are the thickness of the substrate and films, respectively.

3. Results and discussions

3.1. Optical properties

The transmittance results of $(AM)^a$ high reflectors on K9 glass with different layers are shown in Fig. 2, which shows decreasing trend as the layer-pair number increasing, and transmittance of 1.5% is attained in $(AM)^{22}$ high reflectors, but crazing occurs when a is above 18. Fig. 3 gives the transmittance results of double stack designed coating of $(HL)^b$ H $(AM)^c$ on K9 glass substrates, minimum transmittance below 0.4% is gotten in samples of $(HL)^4$ H $(AM)^{12}$ without showing crazing.

As is shown in Table 1, small difference of refractive index between LaF_3 (1.6) and MgF_2 (1.4) making it need more layer pairs to get higher reflectance such as 99%, but the initial high tensile stress always make it fragile and destructive [5] as the layer-pair number increasing to an extreme. It shows a larger refractive index difference between HfO_2 (2.1) and SiO_2 (1.5), less pairs of stacks are needed to attain high reflectance in these multi-layers, so it seems a good idea to pack lower number of layer pairs of fluoride coatings onto oxide coating of HfO_2/SiO_2, through which high reflectance can be attained without crazing happening and high laser resistant ability can also be guaranteed by the outer fluoride coatings [1,2,5,12].

3.2. Stress properties

Total stress in films can be written as the sum of intrinsic stress σ_{intr}, thermal stress σ_{therm}, and extrinsic stress σ_{ext}, and the physical–chemical induced stress sometimes is also considered which is caused by adsorption phenomena such as the incorporation of water into a porous columnar structure or grain boundary oxidation [13]. So the total stress in coatings can be written in a formula as:

$$\sigma_{tot} = \sigma_{ext} + \sigma_{therm} + \sigma_{intr} + \sigma_{phys\text{-}chem} \tag{2}$$

$$\sigma_{therm} = \left(\frac{E_S}{1-\nu_S}\right)\left(\alpha_{sub} - \alpha_{film}\right)(T_a - T_d) \tag{3}$$

The extrinsic stress σ_{ext} is due to crystalline or volume transformations within the coating. Intrinsic stress σ_{intr} is always thought to be related to the chemical composition of the film, to the morphological and crystalline structure developed in the coating and to the substrate-coating bonding. Intrinsic stress σ_{intr} is

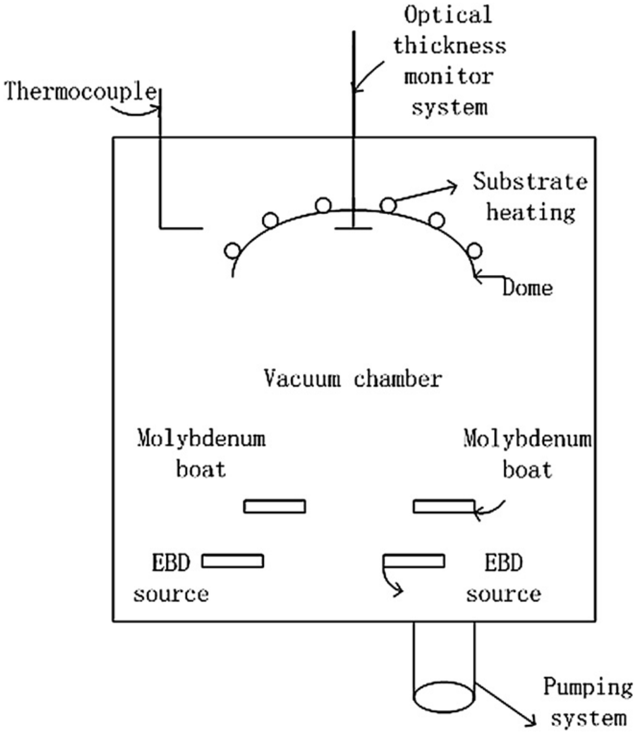

Fig. 1. Deposition device for fluoride and double stack designed coatings.

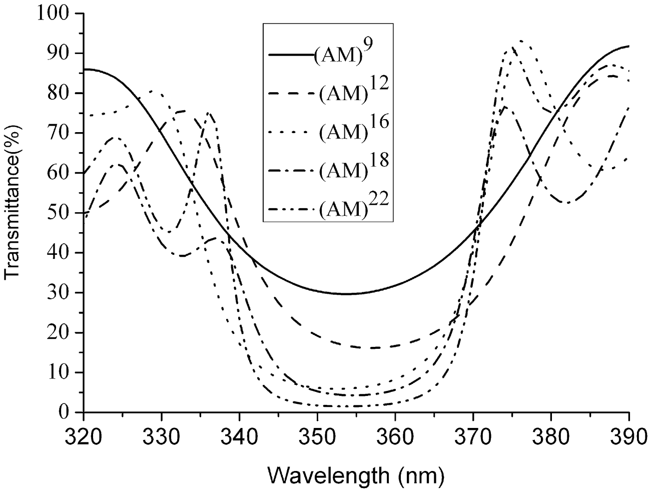

Fig. 2. Transmittance spectra of $(AM)^a$ on K9 glass substrates.