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Aging effect of AlF_3 coatings for 193 nm lithography

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ABSTRACT

As important part of components for 193 nm lithography, AlF_3 coatings deposited by resistive heating method acquire advantages like lower optical loss and higher laser damage threshold, but they also possess some disadvantages like worse stability, which is what aging effect focuses on. AlF_3 single-layer coatings were deposited; optical property, surface morphology and roughness, and composition were characterized in different periods. Owing to aging effect, refractive index and extinction coefficient increased; larger and larger roughness caused more and more scattering loss, which was in the same order with absorption at 193.4 nm and part of optical loss; from composition analysis, proportional substitution of AlF_3 by alumina may account for changes in refractive index as well as absorption.

1. Introduction

Rapid development of 193 nm ArF excimer laser in microlithography, semiconductor process, surgical procedures and other applications promotes the requirement for specified optical components, especially thin film coatings [1–3]. Low loss, high laser induced damage threshold (LIDT), good stability and long lifetime are some excellent properties that we desire [3–7]. In deep ultraviolet and vacuum ultraviolet (DUV/VUV) spectral region, restricted to band gap, only a few oxides and fluorides can be used [8–17]. Fluorides are sensitive to the environment, which may cause bad stability, and shorter wavelength always means more losses and sensitivity [6,18]. As a routinely used material, AlF_3 has low optical loss and high LIDT [19]. Preparation, characterization and application of AlF_3 coatings have been done a lot [20–23]. Optical property of AlF_3 films at different substrate temperatures owing to aging effect has been compared [20]. Optical property of components stored in different environment owing to aging effect has been discussed as well [24]. However, they just showed us the optical phenomena that spectra moved to longer wavelength and reflectance of components declined but without intensive study about the changes and their culprit. So our research on aging effect of AlF_3 material in DUV/VUV spectral region focused on more characterizations of AlF_3 films in more periods and combined calculation and analysis of results. Our work can play an important role in two aspects. First, with optical characterization of AlF_3 coatings about aging effect, we could extract optical constants in different periods and use it to analyze aging effect of more complicated film stacks. Second, characterizations of different aspects were combined to study the mechanism of aging effect for AlF_3 material, from which we can take some measures to improve property of AlF_3 coating material and components composed of AlF_3 coating material.

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2. Experiments

2.1. Preparation

AlF_3 coatings were deposited on $\phi 30\,mm \times 3\,mm$ super polished fused silica substrates by a resistive heating coating machine Leybold Optics SYRUSpro 1110 with a Mo boat. Before deposition, the chamber was pumped down to a base pressure of less than 4×10^{-6} mbar by a cryopump. The substrate temperature and deposition rate are shown in Table 1 [25].

To minimize the influence of different substrates on properties of the films in the same batch, the substrates with identical spectra and root mean square (RMS) roughness were selected. Moreover, prior to deposition, the substrates underwent standard ultrasonic cleaning process. In order to reduce degradation and deterioration from ever-changing environment, the deposited films were kept in a desiccator, where the temperature and humidity are comparatively stable.

Table 1
Deposition parameters of AlF_3 single-layer coatings.

Material	Thickness	Deposition rate	Substrate temperature
AlF_3	702.33 nm	~0.3 nm/s	250 °C

2.2. Characterization

The spectra were measured by LZH ML 6500 VUV spectrometer whose measurable wavelength range could be from 115 nm to 310 nm. When the measured wavelength is from 170 nm to 250 nm, the measurement error will be less than 0.05%. Transmittance of AlF_3 coatings on two-face polished substrates was measured. To exclude measured inaccuracy due to incomplete detection of light from back side of substrates, AlF_3 coatings on one-face polished and one-face roughened substrates were used to measure the reflectance. As we know, roughened side of substrate can make light reflect diffusely and polished side can make light reflect fully. As a result, reflected light from polished interface can be detected, but that from roughened interface can't. That is to say, when we measure the reflectance of one-face roughened and one-face polished substrates with films, only the light reflected by films medium can be measured and the exactness is more convincible. As the measured transmittance and reflectance were not from the same film, uniformity of the same batch was firstly ensured when films were newly deposited.

Each time after measurement of spectra, optical constants of the films were extracted via a software package called Essential Macleod [26]. After optical constants were extracted, value of them should be at acceptable range, so should film thickness and matching degree. Meanwhile, surface morphology and roughness of the films were revealed by a Nano-Scope III PSI atomic force microscope (AFM) in taping mode. Composition was measured by a Thermo K-Alpha X-ray photoelectron spectrometer (XPS) to seek for more changes in detail.

The spectra were measured many times in different periods, so were surface morphology and roughness and composition. Therefore, changes in different aspects can be combined to study the mechanism of aging effect for AlF_3 films.

3. Results and discussions

3.1. Optical property

As shown in Fig. 1(a), transmittance of AlF_3 coatings decreased monotonously in long term, while in Fig. 1(b), reflectance of aluminum fluoride coatings increased over time. In addition, in about 14 months after deposition, the spectra moved about 4.2 nm to longer wavelength. With the help of Essential Macleod, optical constants including refractive index and extinction coefficient were abstracted by a method known as envelope method, which makes use of two envelope functions about those extrema [19]. Then Cauchy dispersion equation $n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$ and index dispersion formula $k(\lambda) = D + E\exp(\frac{\lambda}{F})$ were utilized to fit the data output by the former step. Both refractive index and extinction coefficient increased with more stored time as shown in Fig. 1 (c) and (d). At 193.4 nm, refractive index altered from 1.391 as deposited, then 1.414 in about 5 months, finally to 1.421 in about 14 months, which evinced that newly deposited AlF_3 coatings underwent faster change.

Surface morphology was revealed by AFM in an area of 5×5 µm. From Fig. 2(a)–(d), grain size and distribution became more and more uniform, but the fluctuation from conical structure got bigger and bigger, as a result, roughness shown in Table 2 became larger and larger. The differences of RMS roughness among (b), (c) and (d) are mainly because of more and more sharp peaks as can be seen clearly in (c) and (d).

RMS roughness of high frequency may lead to scattering. As known to us, lights going through components will be divided into four forms, transmittance, reflectance, scattering and absorption, which can be expressed by formula (1). Because absorption of AlF_3 coatings at 193.4 nm was not so much, scattering could be calculated by total integral scattering calculation formula (2) about RMS roughness.

$$T + R + S + A = 1 \quad (1)$$

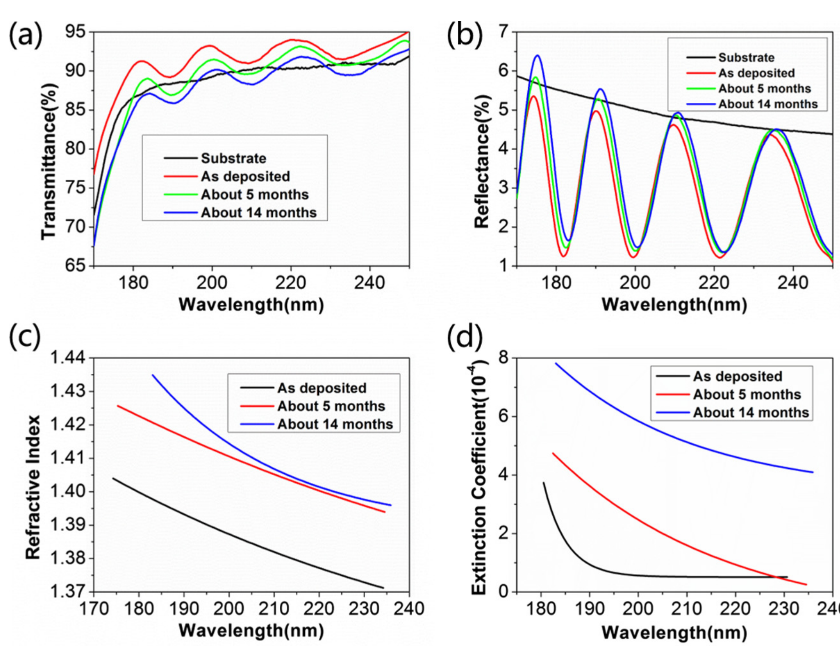

Fig. 1. (a) Transmittance of two-face polished substrates with and without deposited films. (b) Reflectance of one-face polished and one-face roughened substrates with and without deposited films. (c) Refractive index. (d) Extinction coefficient in different periods.

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