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Characterization of single LaF_3 and MgF_2 films on spherical substrate by planetary deposition

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ABSTRACT

LaF_3 and MgF_2 films were prepared upon witness plates distributed on a steep spherical substrate by thermal evaporation and planetary deposition. Micro-structures and optical properties of the films at different locations of the spherical substrate were comprehensively investigated. Column slanting angles of the films are experimentally revealed to increase from the center to the brim of spherical substrate, as interpreted by a flux vector theory. Accompanied by the increased column slanting angles, the average refractive indices of the films decrease while the refractive index inhomogeneities increase from the substrate center to the brim. Influence of the position-dependent refractive index and refractive index inhomogeneity on the optical spectra of 193 nm interference antireflective coatings is experimentally demonstrated. This investigation is helpful for optimizing the spectral uniformity and minimizing the wave-front aberration of 193 nm interference coatings used in micro-lithography systems.

1. Introduction

With the development of 193 nm micro-lithography systems towards high numerical aperture (NA), at least some elements of the optical projection systems present large clear aperture (CA) exceeding 300 mm and/or steep surfaces as characterized by ratio of CA to radius of curvature (CA/RoC) approaching 2 [1,2]. Antireflective (AR) coating for these large-CA/RoC elements has been a challenge for decades. On the one hand, coating materials are limited as most materials are strongly absorbing at wavelength below 200 nm. AR coatings for 193 nm micro-lithography systems generally consist of lanthanum fluoride (LaF_3) [3–7] and magnesium fluoride (MgF_2) [8–10] as high- and low-refractive index materials, respectively. Thermal evaporation was conventionally used as deposition method as it produced low-absorption films at deep ultraviolent (DUV) wavelength. On the other hand, it is difficult to achieve high and uniform transmission over the surfaces of optical elements with large diameters as well as large CA/RoCs. High film thickness uniformity over the whole spherical substrates is required primarily for such purpose, which was achieved by shadowing mask correction during planetary deposition [11–13]. Nevertheless, the transmission uniformity also relates with the micro-structures and optical properties of the fluoride films over the spherical substrates.

Comprehensive investigations on micro-structures and optical performances of LaF_3 and MgF_2 films are clearly necessary for spectrum optimization of 193 nm interference coatings. Investigation of the LaF_3 film deposited upon large spherical substrates by thermal evaporation has revealed remarkable structural difference between the center and the brim of spherical substrates [7]. The structural non-uniformity was responsible for the position-dependent spectra of 193 nm AR coatings on steep surfaces, as revealed by Kelkar et al. [2]. To meet the challenging spectral uniformity and polarization control requirements of 193 nm coatings, the coating design should be carefully optimized taking into account the position-dependent optical constants of the single films. However, many parameters such as substrate shapes, coating geometry, and shape of shadowing masks have influences on the characteristics of the films. As a result, general depictions of the structures and optical properties of the single films on the spherical surfaces would be greatly helpful for the performance optimization of the AR coatings.

In this paper, micro-structures such as column slanting angles and optical properties of LaF_3 and MgF_2 films deposited upon steep spherical substrates by thermal evaporation with planetary system are comprehensively investigated. A flux theory is developed to interpret the column slanting angle profile along the radial direction of the spherical substrate. Optical properties such as refractive indices and refractive index inhomogeneities of LaF_3 and MgF_2 single films at 193 nm are

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reversely engineered from the measured spectra. Strong influence of the position-dependent refractive index and refractive index inhomogeneities on the spectral performance of 193 nm AR coatings is experimentally demonstrated.

2. Experiment details

LaF_3 and MgF_2 single films were prepared by thermal evaporation with a SYRUSpro-DUV coating plant (Leybold Optics, Germany) equipped with a planetary system without planet inclination. The planetary system consists of four substrate holders with spin around its center approximately 60 rpm and revolution around the center of the coating plant approximately 10 rpm. The vertical distance (h) between the evaporation source and the substrate holders was 700 mm. The radius (ρ) of the revolution orbital was 300 mm. Evaporation sources (T) were located vertically below the planet orbital. The coater chamber was pumped down to a base pressure lower than 2.0×10^{-6} mbar and heated at 280 °C for 2 h before deposition. LaF_3 films were evaporated by resist heating Mo boat at a deposition rate of 0.4 nm/s. MgF_2 films were evaporated by electron beam gun at 0.3 nm/s. The spherical substrate was represented by a convex jig with CA 200 mm and RoC 140 mm. During film deposition the jig was placed at the center of the substrate holder. Fused silica plates with diameter 25.4 mm were distributed at four locations of the jig: the center, the radial positions 45 mm, 65 mm, and 85 mm from the center, referred as S1–S4 respectively, as shown in Fig. 1. The locations of S2–S4 were different azimuthally. Due to the small size of the plates, the properties of the films on the plates approximately represent the properties of the films at the specified positions of the spherical substrate. This approach has been conventionally utilized for film thickness uniformity investigation on spherical substrates [11–13]. The plates were manually cleaned with mixed ethanol and ether, and were subject to in-situ ion bombardment before film deposition. Correcting masks positioned 10 mm below the substrate were utilized to improve the film thickness uniformity [11].

Cross-sections of single LaF_3 and MgF_2 films were analyzed by scanning electron microscope (SEM) (S4800, Hitachi, Japan). The thickness of the witness plates for SEM measurements was 0.5 mm. Two perpendicular cross-sections, marked as A and B hereafter, were captured for each witness plate. For S2–S4 cross-sections A and B were along and perpendicular to the radial direction, respectively. The cross-sections were prepared by cutting the 0.5 mm plates from the uncoated surfaces of the plates. Two cross-sections of each sample were then coated simultaneously with evaporated gold (Au) film for SEM measurements. The optical spectra of single LaF_3 and MgF_2 films were measured with Perkin Elmer Lambda 1050 spectrophotometer at nearly normal incident angle. The error of the reflection and transmission measurements was approximately ±0.2%. The reflectance spectra of the two-side AR coated fused-silica plates were measured at an incident angle of 10° with a ML6500 spectrophotometer (Laser Zentrum Hannover, Germany) specified for DUV optics. The measurement error was approximately ±0.15%. DUV graded fused silica plates with the surface roughness of 0.3 nm and thickness of 4 mm were utilized for the spectral measurements. The samples for SEM and spectrum measurements were prepared with the same coating procedure.

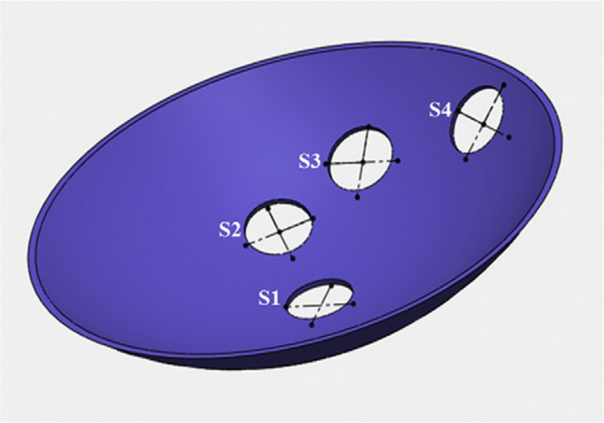

Fig. 1. Model of the spherical jig. Fused-silica plates are positioned in S1, S2, S3 and S4, respectively. Cross-sectional morphologies are obtained along two perpendicular lines in S1–S4, which is along and perpendicular to the radial directions.

3. Results and discussion

Fig. 2(a)–(d) shows the cross-sectional morphologies of single LaF_3 films for S1–S4 with film thickness uniformity correction, respectively. Columns in S1 are normal to the plate surface in both cross-sections A and B. For films S2–S4, the columns are slanted in cross-section A. The column slanting angle, defined as the angle between the column orientation and the substrate normal, increases as the witness plate location shifting towards the substrate brim. On the other hand, the columns are normal to the substrate surface in cross-section B. In addition, columns in cross-section B of S2 and S3 are relatively larger in size than those in cross-section A, indicating that the columns elongated perpendicularly to the column slanting plane during film growth. Such cross-sectional morphologies reveal the bundling effect during film growth, which is generally observed for oblique deposition. Similar behavior for single MgF_2 films are observed.

The micro-structures of the fluoride films without thickness correction have also been investigated. Fig. 3(a)–(d) presents the cross-sectional morphologies of the single LaF_3 films for S1–S4, respectively. Without thickness correction, the film thickness decreases gradually from the substrate center to the brim. Compared to the results presented in Fig. 2, the column slanting angles of the films prepared without the shadowing masks are somewhat larger for the same locations. Comparatively, the column slanting angles of the single MgF_2 films are slightly larger than the column slanting angles of LaF_3 for the same locations.

Previous studies have revealed that the formation of columns was resulted from the low mobility of the evaporated molecules [16]. The deposition temperature and melting temperature of the materials are of prominent importance for the molecular mobility. From the previous reports and our results, LaF_3 and MgF_2 films prepared by planetary deposition and oblique deposition presented similar columnar structures [8,14,15]. For oblique deposition, the substrates are hold at fixed positions, the molecular incident angles keep constant during the coating process. The columns are slanted towards the molecular incident angle. Generally the column slanting angles are smaller than the molecular incident angles, as described by the tangent rule [17]. On the other hand, for planetary deposition, the coating parameters r and θ change continuously during the coating process. For S1, the molecular incident angles are symmetric with respect to the substrate normal due to the spin of the substrate, therefore the films grow normally. For other positions S2 to S4, the molecular incident angles are not zero by average, as a consequence the columns are slanted accordingly.

A flux vector theory is applied to analyze the column slanting angle. The flux vector theory was firstly developed to describe the film growth by alternative deposition of segments with different incident angles in a PhiSweep coating machine [18,19], where the direction of the columns is determined by the vector summation of the segments. For the film growth during planetary deposition, the flux vector segment generated upon the surface element (S) at time t is equal to the deposition rate. For thermal evaporation the film deposition from the source to the substrate is essentially approximated as an illumination problem. For the geometry of planetary deposition as shown in Fig. 4, the value of the flux vector (f) is given by

$$f = K\frac{\cos\theta\cos^n\psi}{r^2}, \tag{1}$$