Microstructure related properties of gadolinium fluoride films deposited by molybdenum boat evaporation

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Abstract: In order to optimize the performance of fluoride thin films in wavelength of Deep Ultraviolet (DUV), GdF3 single layers are prepared by thermal evaporation at different deposition temperatures on Fused Silica. Optical and structure properties of each sample are characterized. The results that the refractive index increased gradually and the crystallization status becomes stronger with the temperature rising, the inhomogeneous of the thin films present linearity. The decrease total optical loss with deposited temper-ature is attributed to the higher packing density and lower optical absorption.

1 Introduction
In the past few decades, excimer lasers such as ArF (193nm) and F2 (157nm) have been increasingly applied in semiconductor exposure, material microstructure and medical surgeries because of its high power, high homogeneity and high stability. These excimer lasers are developed for higher output power, frequency and enhancements on beam homogeneity and pulse stability [1, 2]. Therefore, optical thin film devices which applied in laser and its corresponding optical system have played an important role. However, according to the technical requirements of low loss and high damage threshold for optical thin film components, only very little fluoride materials can be employed in the deep and vacuum ultraviolet region [3, 4]. The high refractive index material is very limited because it must have a large energy bandgap. Besides LaF3, gadolinium fluoride (GdF3) exhibit relatively low optical loss as well as high stability and LIDT. It is a potential candidate for further development in the excimer lasers application area [5, 6].

2 Experiment
2.1 Film preparation
GdF3 thin films were deposited using the molybdenum boat evaporation method in a coating machine (SYRUS 1110, Leybold Optics, Germany). The chamber was pumped out to a base pressure less than 2×10⁻⁶Pa before the evaporation process. The substrate and the chamber were conditioned with reactive plasma pretreatment. This pretreatment was applied to remove residual water vapour and hydrocarbons. The deposition temperatures were 150°C, 250°C, 300°C, 350°C, deposition rates controlled by a quartz crystal sensor was 0.2nm/s, the thickness of single layers was settled to 70nm.
2.2 Film characterization

The transmittance and reflection of the samples was measured by a spectrometer (Lambda950 UV/VIS/NIR Perkin-Elmer, USA). The microstructure of GdF\textsubscript{3} single layer was assessed by x-ray diffraction (XRD), equipped with a Cu-K\textalpha{} radiation source ($\lambda$=0.15418 nm). Diffraction angle $2\theta$ varied 20°-60°, step by 0.05°. The average crystal diameter of the thin film was estimated from the Scherer’s equation, where $\beta$ was the full width of peaks at half maximum intensity. The surface roughness RMS (Root Mean Square) of GdF\textsubscript{3} were evaluated by Atomic force microscopy (AFM) with sampling range 5\textmu{}m×5\textmu{}m and sampling points 256×256. The 1-on-1 damage test was according to IOS 11254 standards, He-Ne scattering method was adopted to the on-line monitoring of laser damage, in order to determine the occurrence of the damage, the standard method of Nomarski microscope was used, the laser pulse produced by the ArF excimer laser form Coherent (IndyStar-193nm), the pulse duration was 12ns, average power of 8mW, and repetition rate up to 1000Hz [7], the experimental apparatus for the investigation of DUV laser damage threshold is schematically shown in Fig. 1.

![Fig. 1 Schematic of the laser damage measurement setup.](image)

3 Results and Discussions

The transmittance spectra of the single layer of GdF\textsubscript{3} thin films at different deposition temperatures are shown in Fig. 2. The maximum transmittance was higher than that of the bare substrate [8]. This indicates that the refractive index of the film was negatively inhomogeneous. The refractive index decreased as the film thickness increased, that was in accordance with the theory of optical interference coating microstructures [9, 10]. The inhomogeneous was obvious in the films produced when the substrate temperature were lower than 300°C. At a substrate temperature of 350°C [11], the phenomenon of inhomogeneous was much less.

![Fig. 2 Transmittance spectra of the substrate and of GdF\textsubscript{3} thin films deposited at different temperatures.](image)
Optical constants (refractive index and extinction coefficient) are obtained from the measured transmittance (T) and reflectance (R) spectral curve, the optical loss (L) is defined by L (%) = 1 - T (%) - R (%). It is evaluated by a first order bulk inhomogeneous model (Schroeder model), this model implies that the film refractive index changes linearly from the film substrate side to the film ambient side, and the OptiChar module of thin film software Optilayer is used to calculate. The optical properties of the GdF$_3$ samples are shown in Table 1. It is found that the refractive index increased gradually with the temperature rising. It can be explained that the deposited molecule obtains larger kinetic energy and higher mobility when the deposition temperature increases. The great amount of molecules makes sufficient surface diffusion and the packing density increases [12, 13]. As the temperature rises, the optical loss and extinction coefficient have a same trend, the largest optical loss of GdF$_3$ thin film is obtained at the 350°C. Because the chemical bond between Gd and F are weak or unstable, the stoichiometry of the GdF$_3$ is locally disordered, the fluorine deficiency responsible for larger absorption loss at the UV region [14].

| Deposition temperature (℃) | 150 | 250 | 300 | 350 |
|----------------------------|-----|-----|-----|-----|
| Refractive index (@193nm)  | 1.659 | 1.673 | 1.685 | 1.691 |
| Extinction coefficient (@193nm) | 0.00205 | 0.00211 | 0.0023 | 0.00274 |
| Optical loss (% @193nm)    | 0.881 | 0.902 | 0.907 | 1.166 |
| Inhomogeneous (%)           | -3.6 | -3.26 | -1.58 | -1.14 |

The crystalline structure of the GdF$_3$ films on fused quartz substrates prepare at different temperature by XRD as shown in Fig. 3, are polycrystalline. The diffraction peaks become stronger gradually with the rising of the substrate temperature. On contrary, the diffraction peak (020) weakens little by little, from the strongest one at 150°C to the fourth at 300°C, when the diffraction peak (020) disappeared at 350°C. High heat energy leads to a more oriented crystalline structure. Besides, the grain sizes are evaluated of GdF$_3$ films by Scherer formula. Obviously, the average crystal diameters increases with the temperature increasing from 24.2nm (150°C) to 27.6nm (350°C) [15, 16]. The body scattering happens when the grain size is increased, thus we obtain crystallization structure at a certain deposition temperature.

Fig. 3 XRD patterns of GdF$_3$ thin films deposited at different temperature.
Fig. 4 exhibits AFM images of GdF$_3$ films at different temperature over 5$\mu$m×5$\mu$m scanning size with a RMS of 1.37nm(a), 1.0nm(b), 0.78(c) nm and 0.56nm(d). Sample (d) shows the least RMS roughness. This might have been due to the surface migration well in the thin films when the film is prepared at high substrate temperature [17]. It makes the surface scattering of the sample to improve.

![AFM images of GdF$_3$ films](image)

Fig. 4 AFM images of GdF$_3$ thin films deposited at different temperature.

Fig. 5 shows the LIDT testing results of the GdF$_3$ film in 1-on-1 mode. In the measurement, different energy density levels of ArF laser were adopted to irradiate on the sample. The LIDT value of the sample was obtained by extrapolating the curve of damaged possibility with energy density to zero damaged possibility [18, 19]. Due to the thin film thickness was settled to 70nm, the LIDT of GdF$_3$ single layer prepare under different temperature as same as the vale obtained when the substrate were measured, the LIDT of the film was 1.06 J/cm$^2$.

![Damage possibility curve](image)

Fig. 5 Damage possibility of different energy density and fitting LIDT of the GdF$_3$ film.

4 Conclusion
GdF$_3$ single layers were prepared by thermal evaporation at different deposition temperatures on Fused Silica. The film has better crystal structure, high refractive index, small RMS roughness and low inhomogeneous as the substrate temperature increased. However, the largest optical loss of GdF$_3$ thin
film is obtained at the 350°C because of the fluorine deficiency, thus we obtain optimal the performance of fluoride thin films at a certain deposition temperature.

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