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

Y.H. Chang, C.Y. Wang, L.Q. Qi, H. Liu

College of Opto-Electronic Engineering, Changchun University of Science and Technology, Changchun, Jilin, China

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 refrac-tive 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 F_2 (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 LaF_3, gadolinium fluoride (GdF_3) 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*

GdF_3 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^{-6}Pa before the evaporation process. The substrate and the chamber were conditioned with reactive plasma pretreatment. This pretreatment was applied to remove residual watervapour and hydrocarbons. The deposition temperatures were 150℃, 250℃, 300℃, 350℃, 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_3 single layer was assessed by x-ray diffraction (XRD), equipped with a Cu-Ka radiation source (λ=0.15418 nm). Diffraction angle 2θ varied 20°-60°, step by 0.05°. The average crystal diameter of the thin film was estimated from the Scherer's equation, where β was the full width of peaks at half maximum intensity. The surface roughness RMS (Root Mean Square) of GdF_3 were evaluated by Atomic force microscopy (AFM) with sampling range 5μm×5μm 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.

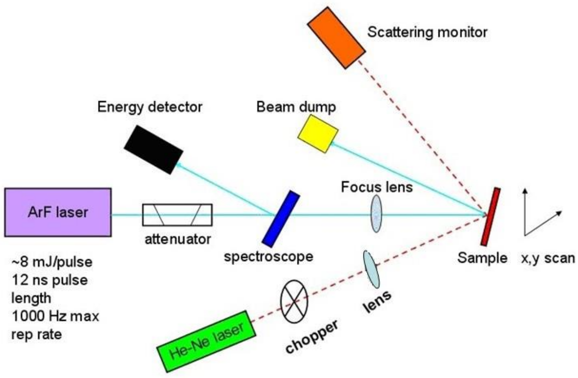

Fig. 1 Schematic of the laser damage measurement setup.

3 Results and Discussions

The transmittance spectra of the single layer of GdF_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℃. At a substrate temperature of 350℃ [11], the phenomenon of inhomogeneous was much less.

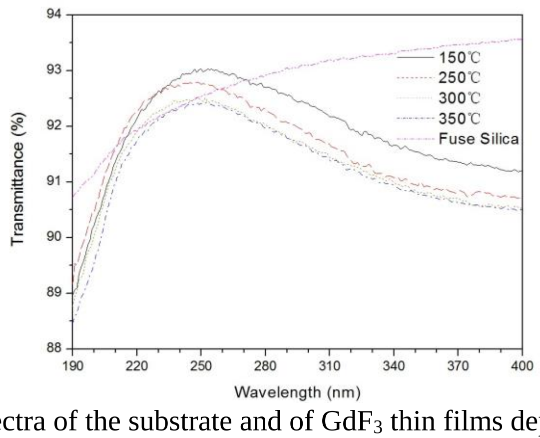

Fig. 2 Transmittance spectra of the substrate and of GdF_3 thin films deposited at different temperatures.

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℃. 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].

Table 1. Optical properties of GdF_3 thin films deposited at different temperature.

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℃ to the fourth at 300℃, when the diffraction peak (020) disappeared at 350℃. 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℃) to 27.6nm (350℃) [15, 16]. The body scattering happens when the grain size is increased, thus we obtain crystallization structure at a certain deposition temperature.

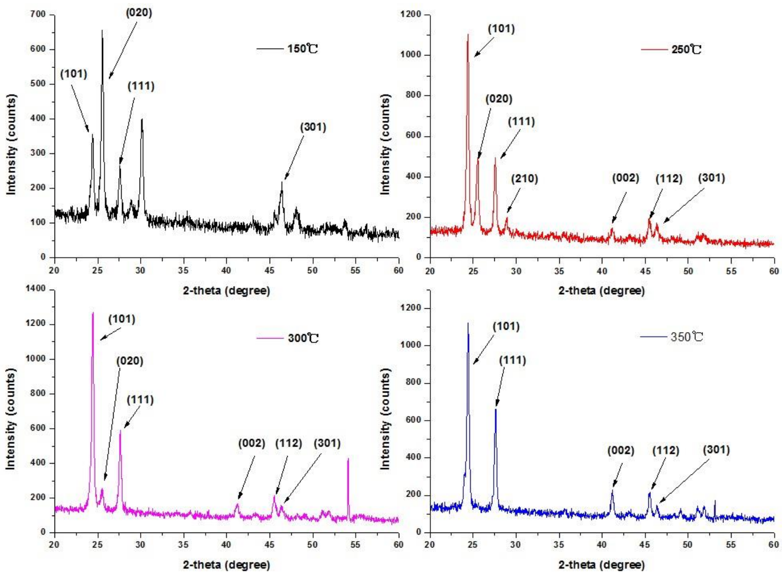

Fig. 3 XRD patterns of GdF_3 thin films deposited at different temperature.

Fig. 4 exhibits AFM images of GdF_3 films at different temperature over 5μm×5μm 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.

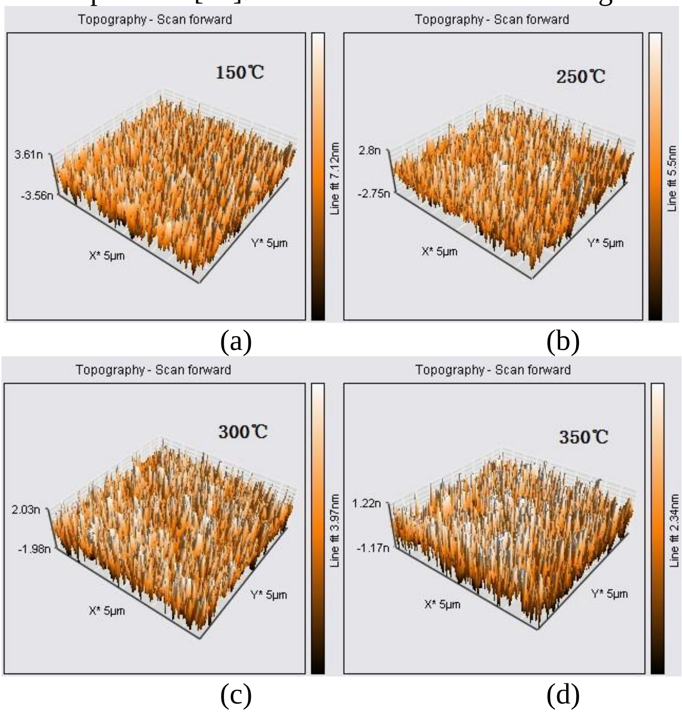

Fig. 4 AFM images of GdF_3 thin films deposited at different temperature.

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.

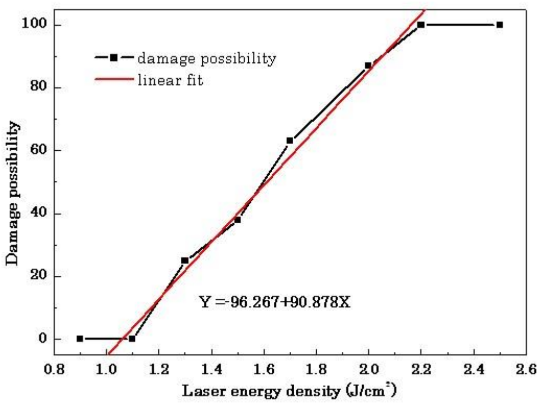

Fig. 5 Damage possibility of different energy density and fitting LIDT of the GdF_3 film.

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.

Acknowledgement
This work is supported by the Changchun University of Science and Technology Foundation under Grant No. XQNJJ-2015-05.

References

[1] Ullmann J, Mertin M, Zeiss Carl, et al (2000). Coated optics for DUV-excimer laser applications. *Proc SPIE*, *3902*, 514-527.
[2] Biro Ryuji, Sone Kazuho, Niisaka shunsuke, et al (2002). Development of low-loss optical coatings for 157nm lithography. *Proc SPIE, 4691*, 1625-1634.
[3] Finders Jo, Dusa Mircea, Nikolsky Peter, et al (2010). Litho and patterning challenges for memory and logic applications at the 22nm node. *Proc SPIE, 7640*, 76400C1-76400C10.
[4] Zaczek C, Mullender S, Enkisch H, et al (2008). Coatings for next generation lithography. *Proc SPIE, 7101*, 71010X1-71010X10.
[5] Uhlig H, Thielsch R, Heber, et al (2005). Lanthanide tri-fluorides: a survey of the optical, mechanical and structural properties of thin films with emphasis of their use in the DUV-VUV-spectral range. *Proc SPIE*, *5963*, 59630N1-59630N12.
[6] Roland Thielsch, Joerg Heber, Hein Uhlig, et al (2005). Optical, structural, and mechanical properties of gadolinium tri-fluoride thin films grown on amorphous substrates. *Proc SPIE*, *5963*, 59630O1-59630O12.
[7] Deng Wenyuan & Jin Chunshui (2013). Laser induced damage threshold testing of DUV optical substrates. *Chin. Opt. Lett.*, *11*, S107021-S107023.
[8] Tikhonravov A V, Trubetskov M K, Sullivan Brian T, et al (1997). Influence of small inhomogeneities on the spectral characteristics of single thin films. *Applied Optics*, *36*(*28*), 7188-7198.
[9] Wang Jue, Schreiber Horst, Davis Ronaldw, et al (2008). Structural comparison of GdF_3 films grown on CaF_2 (111) and SiO_2 substrates. *Appl. Opt.*, *47*(*23*), 4292-4296.
[10] Chang Yanhe, Jin Chunshui, Li Chun, et al (2012). Characterization of optical constants of ultraviolet LaF_3 films by thermal evaporation. *Chin. J. Lasers.*, *39*(*10*), 08070021-08070025.
[11] Gotzelmann Rainer, Hagedorn Harro, Zoller Alfons, et al (2005). Oxide and fluoride coatings for the excimer wavelength 193nm. *Proc SPIE*, *5963*, 59630L1-59630L7.
[12] Bischoff Martin, Gabler Dieter, Kaiser Norbert, et al (2008). Optical and structural properties of LaF_3 thin films. *Applied Optics*, *47*(*13*), C157-C161.
[13] Yu Hua, Shen Yanming, Cui Yun, et al (2008). Characterization of LaF_3 coatings prepared at different temperatures and rates. *Appl. Surf. Sci.*, *254*, 1783-1788.
[14] Liu Mingchung, Lee Chengchung, Kaneko Masaaki, et al (2006). Microstructure-related properties at 193nm of MgF_2 and GdF_3 films deposited by a resistive-heating boat. *Appl. Opt.*, *45*(*7*), 1368-1374.
[15] Liu Mingchung, Lee Chengchung, Kaneko Masaaki, et al (2005). Microstructure related properties of lanthanum fluoride films deposited by molybdenum boat evaporation at 193nm. *Thin Solid Films*, *492*, 45-51.
[16] Liu Mingchung, Lee Chengchung, Kaneko Masaaki, et al (2006). Microstructure and composition related characteristics of LaF_3 thin films at 193nm. *Opt. Eng.*, *45*(*8*), 0838011-0838016.
[17] Wang Jue, Maier Robert, Dewa Paulg, et al (2007). Nanoporous structure of a GdF_3 thin film evaluated by variable angle spectroscopic ellipsometry, *Appl. Opt.*, *46*(*16*), 3221-3226.
[18] Liu Jie, Zhang Weili, Cui Li, et al (2014). Study on high-reflective coatings of different designs at 532nm. *Chin. Opt. Lett.*, *12*(*8*), 0831011-0831013.
[19] Chang Yanhe, Jin Chunshui, Li Chun, et al (2013). Laser induced damage of fluoride coatings at 193nm. *Chin. J. Lasers.*, *40*(*7*), 07070011-07070014.