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Optical and Laser-Induced Damage Characterization of Porous Structural Silicon Oxide Film with Hexagonal Period by Nanoimprint Lithography

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Abstract: We designed and fabricated a porous nanostructured film with a hexagonal period for a high-power laser system. The proposed nanostructure exhibits polarization-independent, infrared, and antireflective properties. The measured transmittance of the structural film does not drop below 93% between 948 nm and 2500 nm (exceeding 95% from 1411–2177 nm), and this performance is maintained for incident angles ranging from 0–30°. The laser-induced damage threshold (LIDT) of the structural film (17.94 J/cm²) is much higher than that of the single layer of SiO₂ film (7.06 J/cm²). These results show that the preparation process is an effective technique to obtain a large-scale structural surface for high-power laser systems.

Keywords: antireflection; structural film; polarization independence; laser-induced damage threshold (LIDT)

1. Introduction

The optical components of high-power laser systems need coating in order to feature the antireflective (AR) properties required to ensure high laser transmission efficiency. Traditionally, optical antireflection has been accomplished using single or multiple layers of antireflection laser film with appropriate refractive indices and thicknesses [1]. However, the laser output power is limited by the laser-induced damage threshold (LIDT) of the laser thin film, thereby hindering the development of high-power laser systems. Structural surfaces, such as sub-wavelength grating and optical dielectric metasurfaces, exhibit some excellent optical properties. Anti-reflective gratings have been studied extensively with the aim of combining desirable optical properties with a high LIDT [2–6]. The optical properties of the grating are determined by the structural parameters [7–10]. Furthermore, the laser damage resistance of optical elements is related to the manufacturing process. The smooth surface of the optical element helps to improve its LIDT [11]. In the past, various preparation methods, such as e-beam evaporation [12], plasma-enhanced chemical vapor deposition [13–15], atomic layer deposition [16,17], and the sol-gel method [18], were used to fabricate laser films, but these methods are not suitable for the preparation of large-area nanostructured surfaces with high-precision patterns. Laser surface treatment can be used to process some functional surfaces, but large-area nanoscale patterning is difficult to fabricate. Recently, some metasurfaces [19,20] with novel optical properties were designed using all-dielectric materials, composed of specifically designed sub-wavelength units in a two-dimensional plane. This low-cost method, which provides fast throughput and high-resolution nanoimprint [21–23] technology, was used to fabricate these metasurfaces. Nanoimprint combined with electron beam lithography or inductive coupled plasma reactive ion etching (ICP-RIE) may be a high-throughput and lower-cost processes for highly customizable optical components [19]. Previous research on the laser damage...
2. Materials and Methods

2.1. Design

We used RCWA to design the grating [24,25]. The structure of the 2D grating is shown in Figure 1. The geometric model is designed for a single-side substrate. A quartz glass substrate sits below a SiO$_2$ film layer with a thickness of 800 nm. The structure is defined by several parameters: $\Lambda$ is the period of the 2D grating, and $d$ and $h$ are the diameter and depth of the holes, respectively. The coordinate axes relative to the structure are also indicated in Figure 1: an incident plane wave propagates along the negative direction of the $z$-axis, that is, the direction of the wave vector ($k$). An incident wave with an electric field, whose $y$-component is parallel to the $y$-axis is a TE (or $y$-polarized) wave. By contrast, an incident wave with an electric field $y$-component perpendicular to the $y$-axis it is a TM (or $x$-polarized) wave. The angle $\theta$ is defined as the angle between the $y$-axis in the plane formed by the $z$-axis and the incident light.

![Figure 1. Scheme of the 2D grating structure: (a) side view, (b) top view.](image)

To obtain desirable low-order optical properties, the structural parameters of the grating should satisfy the diffraction equation [26]:

$$n_s \sin(\alpha) + n_0 \sin(\beta_m) = m \frac{\lambda}{\Lambda}$$

(1)

where $\lambda$ is the wavelength, $m$ is the diffraction order ($m = 0, \pm 1, \pm 2,\ldots$), $n_s$ and $n_0$ are the refractive indices of the substrate and air, respectively, and $\alpha$ and $\beta_m$ represent the angle of incidence and the angle of the $m$-order diffracted beam, respectively.

For $m = 0$, the angle of refraction is described by Snell’s law.

Furthermore, because sine functions can vary between $+1$ and $-1$ only, the existence of higher diffraction order requires that

$$-(n_s + n_0) < m \frac{\lambda}{\Lambda} < (n_s + n_0)$$

(2)
Higher-order diffraction modes are not conducive to realizing transmittance across the entirety of the infrared spectrum [27]. Consequently, only the diffraction orders 0, 1, and $-1$ can be released, which means that

$$2\lambda > \Lambda (n_s |\sin(\alpha)|+n_0)$$  \hspace{1cm} (3)

Here, to account for large incident angles, we take the absolute value of the sine of the incident angle as 1. In accordance with Equation (3), the grating period was chosen to be less than the short-wavelength-end of the infrared spectrum. Thus, for initial substrate and SiO$_2$ thin-film refractive indices of 1.45 and an initial $\lambda$ of 800 nm, $\Lambda$ cannot exceed 653 nm.

Figure 2 shows reflectivity averaged over the spectral range of 800~2500 nm calculated with respect to the diameter of the pore $d$ and the depth of the pore $h$ with $\Lambda = 640$ nm, when the structure is illuminated from air in normal incidence. It can be seen that the high transmittance ranges of 800~2500 nm are $h$ range of 250~350 nm with $d$ range of 100~400 nm.

![Figure 2](image)

**Figure 2.** Reflectivity averaged over the spectral range of 800 nm~2500 nm calculated with respect to the diameter of the hole $d$ and the depth of the hole $h$ with $\Lambda = 640$ nm, when the structure is illuminated from the air in a normal incidence.

The mechanisms of laser-induced damage in optical materials are numerous. They are roughly classed into two categories: the inherent damage mechanism of materials and the preparation and treatment methods [14,16,17]. The inherent damage mechanism of dielectric materials is related to the localized enhancement of the electric field intensity (EFI) [28,29], with damage resulting from localized temperature rises [4,30,31]. For silica films under the irradiation of nanosecond pulsed laser, the local electric field enhancement in the sub-surface is a main factor in laser-induced damage [28].

In order to understand the distribution of local electric field intensity caused by the structure, the incident EFI of the laser is unit 1 (V/m), and the incident wavelength of the laser is 1064 nm. The intensity distribution of the laser is a Gaussian distribution. The pulse width is 10 ns and the incidence angle is 0 degrees. The electric field distribution (EFD) of the structure at the center of the energy is simulated when the laser is incident on the surface of the structure.

Figure 3 shows the electric field intensity of the hole wall (blue curves), the interface between the film and the substrate (magenta curves), and the structure surface (green curves) for 1064 nm in normal incidence. Asterisk, circle, diamond, and square represent pore diameters of 100, 200, 300, and 400 nm, respectively. In Figure 3, it can be seen that the maximum electric field intensity of the pore wall is the highest among three positions at the same diameter of the pore for $h$ range of 250~350 nm. Furthermore, the larger diameter of the hole, the lower the electric field intensity for diameter $d$ range of 100~400 nm.
Considering the optical properties, we obtained an appropriate range of grating sizes: \( \Lambda = 640 \text{ nm}; h = 250 \text{ nm} - 350 \text{ nm}; d = 350 \text{ nm} \).

Figure 3. The electric field intensity at the surface of the grating, the hole wall, the interface between the film and the substrate, and the surface when the structure is illuminated from the air in a normal-incidence 1064 nm laser.

2.2. Sample Preparation

The 2D grating was fabricated on a quartz wafer with a six-inch diameter coated with an 800-nanometer-thick SiO\(_2\) thin film. Periodic hexagonal pore arrays were prepared on the same SiO\(_2\) film batch using nanoimprint lithography, while the SiO\(_2\) films were deposited via plasma-enhanced chemical vapor deposition (PECVD). The PECVD-deposited SiO\(_2\) films presented an extremely high degree of homogeneity, both in thickness and in distribution. The average thickness of each SiO\(_2\) film was 800 nm. Figure 4 gives a simplified overview of the various manufacturing steps, which are described in the following paragraph.

![Process flow for the fabrication of the 2D grating.](image)

Figure 4. Process flow for the fabrication of the 2D grating.

We started with dry etching for creating a master on the Si-wafer (ICP-RIE plasma etcher SI 500, SENTECH, Berlin, Germany) for nanoimprint lithography (NIL) steps. It had structure depths of 1 \( \mu \text{m} \), which was confirmed with AFM measurements. We used vapor deposition of Perfluoro decyl trichloro silane (FDTS) to imbue the surface of the master with an anti-sticking property. We yielded the PDMS stamp after the baking process. Next, the NIL-resist GD-NIL 201 was spin-coated to obtain a 1.1-micrometer layer of UV-resist
on top of the wafer, which was a quartz glass coated with an 800-nanometer SiO2 film, as shown in step 3. This was followed by the imprinting process, as shown in step 4. The wafer with the NIL-resist layer was pressed against the stamp in the nanoimprinting device GD-N-03. The pattern from the stamp was transferred under UV lighting to the resist layer. After curing, we removed the PDMS stamp from the NIL-resist wafer master. Next, the NIL-resist wafer master was treated with an ICP-RIE process. After dry etching, we obtained the final structure in the substrate coated with SiO2 film.

2.3. Structural Characterization

The grating morphology was observed using a scanning electron microscope (SEM, Hitachi S-4800 FE-SEM, Hitachi, Japan). Incident light is incident vertically on the sample surface. The perpendicularity error of the incident angle was less than 10°.

Figure 5 presents SEM micrographs of the 2D grating, with Figure 5a showing the grating surface from a normal overhead view of the surface, while Figure 5b shows the cross-sectional view. The high precision of the array etching process used to pattern the SiO2 resulted in an almost vertical hole profile and an expected diameter error of no more than 8 nm. The verticality of the sidewalls (92.29°) confirms this slight tapering. Using the SEM images, the average values of $\Lambda$, $h$, and $d$ were measured as 642, 320, and 345 nm, respectively. The grating period, the etching depth, and the pore diameter all followed the design well.

Figure 5. (a) Overhead and (b) cross-sectional SEM micrographs of the 2D grating. The grating array pattern was fabricated in the SiO2 thin film layer, comprising a hexagonal arrangement of cylindrical holes.

2.4. Spectra Test

The transmittance of the 2D grating and the SiO2 film were measured by a spectrophotometer (Lambda 950, Perkin Elmer Company, Waltham, MA, USA).

2.5. Laser-Induced Damage Test

The LIDT testing was conducted at normal incidence using a wavelength of 1064 nm. The LIDT of the sample was tested using the “one-on-one” method according to ISO standard 21254-1 [32], using a Q-switched Nd: YAG pulsed laser in TEM00 mode with a pulse duration of 10 ns. The laser system provided a Gaussian beam profile with a beam diameter ($1 \times 10^{-2}$) of 800 µm. The error of the laser energy was controlled within ±2%, with 10 points measured at each fluence level. The morphology images of the sample before and after laser irradiation were acquired by a high-precision CCD camera, and the different images were processed by software (V1.0) to remove background. According to the principle of the image adjudication method, it was considered that the sample was damaged when the change number of pixels exceeded five. At least ten laser shots were tested at separate sites for perfluence. The probability of damage was defined as a percentage of the number of damaged versus the total number of irradiated sites for perfluence. We repeated this procedure for other sources of pulse energy to develop a plot.
of damage probability versus laser fluence. Linear extrapolation of the damage probability data to zero damage probability yielded the LIDT for each sample [32,33].

2.6. Simulations

The performance of the optical and electric field distributions was simulated using the finite element method (FEM). Rigorous coupled-wave analysis (RCWA) was exploited to obtain transmittance spectra for the 2D grating and SiO$_2$ film. A one-order diffraction and periodic boundary conditions were set for the diffraction efficiency in the RCWA calculation. The measured structural parameters of the sample were used in the simulation. The real part of refractive indices of the substrate medium and the air were set as 1.45 and 1, respectively, with SEM-derived values of 642, 320, and 345 nm used for the period ($\Lambda$), depth (h), and width (d) of the grating array, respectively. To reduce computing costs, the thickness of the quartz substrate was not considered in our simulations.

3. Results and Discussion

3.1. Optical Performance

Figure 6a shows a comparison of the measured and simulated transmittance spectra of the samples as a function of wavelength at normal incidence. Figure 6b shows the simulated transmittance of the 2D grating as a function of the incident angle. In Figure 6a, the magenta, cyan, and red curves represent the simulated TE, simulated TM, and total measured transmittance spectra for the grating, respectively. In addition, the blue and green curves represent the simulated and the measured transmittance spectra for the SiO$_2$ film, respectively. The measured transmittance curve of 1400~2200 nm for the grating is presented in Figure 6a. In Figure 6b, the marked and unmarked blue, green, red, and cyan curves represent the simulated TE and TM total transmittance spectra for the grating, respectively, at several typical incident wavelengths as the incident angle increases from 0° to 55°.

![Figure 6. Transmittance of the samples. (a) Comparison of measured and simulated transmittance spectra of the samples as a function of wavelength at normal incidence. The inserted curve is the measured transmittance of the grating. (b) Simulated transmittance of the 2D grating as a function of incident angle.](image)

In Figure 6a, the simulated TE and TM curves are almost identical, indicating that the transmission behavior of the 2D grating was insensitive to polarization. From 696.3 to 840.6 nm and 981.5 to 2500 nm, the simulated transmittance of the 2D grating was higher than that of the SiO$_2$ thin film. This response was mirrored in the measured spectra between 703 and 2500 nm, with the slight deviation due to the incident light during the experiment not being exactly normal to the sample. The perpendicularity error of the incident angle was less than 10°. Fabry-Perot (FP) oscillations were visible in both the TM
and TE curves during short wavelengths. Furthermore, the simulated transmittance of the grating exceeded 97% of 936.1 nm to 2500 nm in both the TE- and TM-polarized cases. In comparison, the measured transmittance of the grating did not fall below 93% from 948 nm to 2500 nm, exceeding 95% between 1411 and 2177 nm. The differences between the measured and predicted values were about 4% for both the grating and the SiO₂ film in the wavelength range of 800 nm–2500 nm. In order to reduce the computational cost, the thickness of the optical glass substrate was not considered in the simulation, so the reflectivity of the back of the optical glass substrate was not calculated. However, the reflectivity of the back of an optical glass substrate is 4% in practice. This accounts for the difference between simulated and measured transmittance.

Figure 6b shows simulated TE (marked) and TM (unmarked) transmittance curves for the 2D grating at several typical incident wavelengths. It is clear that the simulated transmittance between 0° and 30° did not fall below 93.7%, irrespective of polarization. Therefore, the measured curve of the transmittance can represent the transmittance at vertical incidence.

3.2. Results of LIDT

The LIDTs of the 2D grating and non-patterned SiO₂ film were tested. The least squares method was used to fit the data, as shown in Figure 7, where the dashed blue line represents the fitting line for the non-patterned SiO₂ thin film and the solid red line represents the fitting line for the 2D grating. The LIDTs of the 2D grating and the non-patterned SiO₂ thin film were measured as 17.94 and 7.06 J/cm², respectively. The LIDT of quartz glass was 22.47 J/cm² (1064 nm, 10 ns) [34].

![Figure 7. The LIDTs of the samples.](image)

To analyze the mechanisms of laser-induced damage in the 2D porous nanotextures, the distribution of EFI was simulated by averaging the TM/TE polarization. The input power of the Gaussian beam was normalized, and the distribution of the electric field intensity on the surface of the 2D hexagonal array grating for 1064nm un-polarized waves is shown in Figure 8. Figure 8a shows the volume distribution of the EFI at normal incidence, and Figure 8b is the EFI of the grating surface (blue), the bottom of the hole (green), and the wall of the hole (red) as a function of the incident angle. To simplify the calculation, the thickness of the substrate is not taken into account in the simulation. The simulation results of the EFD for the 2D grating clearly show that the stronger EFI was concentrated in the walls of the holes comprising the hexagonal array. The lowest EFI was located at the bottom of the hole. The greater the incidence angle, the greater the maximum electric field intensity. Due to the presence of the surface structure, the constructive interference between the incident beam and the reflection beam led to the modulation of the electric field intensity.
field near the structured surface. This is the main reason why the LIDT of grating was higher than that of the unstructured silicon oxide film.

On the other hand, the influence of the preparation and treatment methods cannot be ignored. Some defects were inevitably introduced into the silicon oxide films deposited by the PECVD method. The defects were incorporated during the deposition process of the SiO$_2$ film. The laser-damage resistance of the 2D grating patterned on SiO$_2$ film is limited by the presence of defects embedded in the coating structure during the manufacturing process or subsequent handling and exposure to the operational environment [33]. These defects are responsible for reducing anti-laser damage performance. The LIDT of the material can be further improved by etching or reaction ion etching process [35,36]. Therefore, the removal of defects in the film layer was associated with the NIL and RIE process used to generate the grating, comprising a periodic hexagonal hole array patterned on a SiO$_2$ thin film. The NIL and RIE processing method could be an additional reason for this. The surface of the grating layer was very smooth and clean, as shown in Figure 5. These processes can decrease the density of defects in the damage precursor, and finally improve the laser damage resistance of the 2D grating compared to the SiO$_2$ film.

4. Conclusions

We designed and prepared an antireflective structured film with 2D hexagonal and porous array based on a SiO$_2$ film. The optical properties of the 2D grating and the EFD on its surface in response to laser irradiation at a wavelength of 1064 nm were simulated using FEA. The desirable optical properties of the 2D grating design included high transmittance (i.e., anti-reflectance) at 800 nm–2500 nm with low-order diffraction, and polarization independence. From 948 nm–2500 nm, the measured transmittance of the grating sample remained above 93% (exceeding 95% from 1411 nm–2177 nm). In addition, this high-transmittance performance was maintained for incident angles ranging from 0°–30°. The LIDTs of the 2D grating and SiO$_2$ film samples were 17.94 J/cm$^2$ and 7.06 J/cm$^2$, respectively. Although the LIDT of the 2D grating was lower than that of the LIDT of the quartz glass, the LIDT of the grating was two times that of the single-layer SiO$_2$ film. The distribution of the electric field intensity caused by the surface structure was the main reason why the LIDT of the structured film was higher than that of the unstructured film. Moreover, the processing technology of the structural film is also a factor that cannot be ignored. The results show that the combination of the NIL with the RIE process may be effective at creating large-area high-quality AR structures resistant to laser radiation, and that this large-area process has the potential to prepare dielectric structured surfaces for high laser damage resistance.
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