Optics & Laser Technology 46 (2013) 77–80

Contents lists available at SciVerse ScienceDirect

Optics & Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

New damage behavior induced by nanosecond laser pulses on the surface of silica films

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ARTICLE INFO

Article history:
Received 20 February 2012
Received in revised form
23 April 2012
Accepted 23 April 2012
Available online 28 May 2012

Keywords:
Subwavelength periodic stripe
Nanosecond laser etching
Silica films

ABSTRACT

The discovery of subwavelength periodic stripes with similar grating structures is currently only associated with femto-/picosecond laser ablation experiments. A nanosecond laser is generally accepted as incapable of etching out subwavelength periodic stripes. While in this paper, the subwavelength periodic stripes on the surface of silica films induced by nanosecond laser pulses have been observed. The silica films have a particle accumulation structure. This laser damage behavior promotes the industrial production advancement of laser etching subwavelength periodic stripes. The microstructure and spatial period of the periodic stripes under different film structures and radiation energy densities were studied.

1. Introduction

Nanofabrication techniques have resulted in widespread interest on the novel electronic, optical, and mechanical properties of various nanostructures. Among the physical, chemical, and mechanical nanofabrication techniques, laser-assisted methods are efficient and environmentally friendly [1]. In laser ablation, the remarkable formation of laser-induced periodic surface structures occurs in various materials under diverse irradiation conditions [2].

It can be seen from an earlier study on laser ablation that laser irradiation can facilitate the formation of periodic structures on a material surface [3]. Before the advent of the femtosecond laser, a long-pulse or continuous laser was used to obtain stripes with large periods. In a normal-incident situation, the intervals of the stripes are generally close to the laser wavelength. These are called as "classic stripes" [4]. In contrast, ultrashort pulse laser-induced novel stripes have spatial periods considerably less than the laser wavelength [5]. These stripes are strictly perpendicular to the laser polarization direction. Their structures are similar with those of grating, wherein a steep edge exists between the slot and ridge parts. This kind of "subwavelength periodic stripes" has opened a new avenue for laser micro–nano production. Consequently, subwavelength periodic stripes have become an important topic in laser studies and related fields.

The femtosecond laser-etching process of subwavelength periodic stripes has been studied for over 10 years. Numerous theories, such as those on scattering waves, organization, secondary harmonics, as well as laser and plasma interactions, have been proposed [6–10]. Huang et al. [10] have systematically researched the laser and plasma interaction theory. The surface plasma interference-formed standing wave is shown to determine the initial spatial period of subwavelength stripes. The main etching mechanism is a nanoscale Coulomb explosion in the grooves of the stripes. The subwavelength stripe orientation depends on the cavity mode and surface plasma transverse mode (TM) wave characteristic.

Thus far, only femtosecond and picosecond laser experiments have focused on subwavelength periodic stripes [11]. In the case of nanosecond laser irradiation [12–15], damage is mainly induced by the strong, random absorption of impurities or defects in a material. There is no clear pulse fluence boundary between material damage and non-damage, which limits the development and application of the nanosecond laser microprocessing technology. The heat action process is the main distinction between nanosecond and femtosecond laser damages. The local areas of the material may reach a sufficiently high pressure and erupt. The eruption process takes away the periodic stripes that the surface plasma has etched. Therefore, a nanosecond laser is considered not suitable for etching subwavelength periodic structure stripes [8].

While, plasma flash is generally observed in the nanosecond laser-induced material damage process. The core part of the

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http://dx.doi.org/10.1016/j.optlastec.2012.04.032

subwavelength stripe etching mechanism that Huang et al. [10] have proposed does not repel a nanosecond laser if some unfavorable factors of the damage process can be overcome. Such factors include the local area absorption and high-temperature material eruption. Hence, it is possible to use a nanosecond laser to etch subwavelength periodic stripes.

2. Experiment details

2.1. Experimental design

In the present study, an experiment using nanosecond laser to irradiate sol–gel porous silicon dioxide films with a particle accumulation structure was designed based on the following observations. First, the sol–gel method can considerably improve film purity and decrease the probability of film damage. Second, visible or infrared light cannot directly instigate the production of a material surface plasma wave, but the particle structure of a sol–gel silica films can scatter incident light. The incident laser can then be aided to stimulate a surface plasma wave. Third, when porous materials melt or gasify, they can expand and penetrate to some extent. This process can reduce the pressure in a high-temperature area, and delay or prevent local high-temperature material eruption. The local temperature of the material can also be decreased to the extent that the material can be restored to its solid form, and the laser etching of the periodic stripe structure can be maintained.

2.2. Preparation of silica films

Based on a 1.0: 2.0: R: 37 ratio of tetraethylorthosilicate (TEOS), H_2O, NH_3, and C_2H_5OH (R=0.1, 0.2, 0.4, 0.6, and 0.8), the reagents were combined, completely sealed, and fully mixed at 50 °C by stirring 4–5 h. The solution was then filtered at a low pressure using a filtration membrane with a pore radius of 0.8 μm. At 20–25 °C and relative humidity of 60%, the pulling method was used to prepare the coatings. The cleaned substrate (B270 glass with the dimension of 25 mm × 75 mm × 2 mm) was dipped in the solution for 60 s before being smoothly, uniformly, and vertically lifted at a speed of 1.5 mm/s. The heat treatment was performed in a furnace in the following scheme: from room temperature to 100 °C at approximately 2–5 °C/min and maintained for 30 min under 100 °C; from 100 to 250 °C at approximately 2–5 °C/min and maintained for 1 h at 250 °C; as well as from 250 to 450 °C at approximately 2–5 °C/min and maintained for 0.5 h at 450 °C. Subsequently, the furnace was closed and the samples were allowed to cool to room temperature. Before annealing, a beaker filled with ammonia was placed in the muffle furnace to allow the film to be heated under an ammonia atmosphere. The final film thickness was detected by a step profiler and it is about 200 nm.

2.3. Laser etching

The laser etching experiment was performed in the “1-on-1” regime of laser damage testing according to International Organization for Standardization 11254-1.2. The “1-on-1” regime means only one laser pulse will be imposed on a test point on the specimen surface. The schematic of the experimental setup for laser etching is shown in Fig. 1. The Nd: YAG laser system was operated at the TEM00 mode. The laser beam was focused on the target plane normally with 1 mm diameter spot ($1/e^2$) by a nonspherical lens of 250 mm focal length. The laser pulse width was 12 ns, and the laser wavelength was 1064 nm. A total of 100 sites were tested for each sample and every site was exposed to one laser pulse. Every ten sites, in a line, were exposed to the same fluency, and the portion of the damaged sites was recorded. A Nomarski microscope was used to determine the damage to the radiation sites at 100 × magnification. The laser pulse energy was adjusted by an attenuator comprising a half-wavelength plate and a polarizer. The polarization direction of the irradiation light was determined by the polarizer, and it was independent on the laser pulse energy. Before testing, a marking line which was parallel to the polarization direction of the irradiation light was made on the specimen. This marking line is helpful for judging the relationship between the polarization direction of the irradiation light and the orientation of the formed subwavelength ripples.

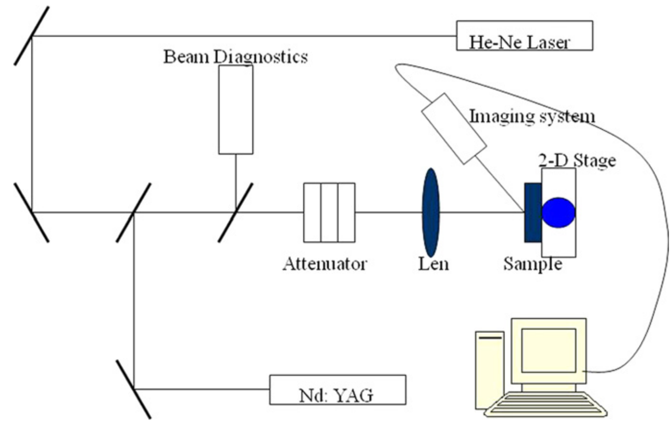

Fig. 1. The schematic of the experimental setup for laser etching Ref. [16].

3. Results and discussions

3.1. Films structure and laser damage threshold

Fig. 2 shows the scanning electron microscopy (SEM) image of the SiO_2 film when R=0.8. It can be observed that the SiO_2 film has particle accumulation structure and numerous cracks exist in it. Based on the cracking trend, the cracks are deduced to be caused by the preparation process and not by the sample preparation for the SEM test, which could have affected the integrity of the etching stripes. Besides, when NH_3/TEOS=0.1, 0.2, 0.4, 0.6, and 0.8, the radii of SiO_2 particles are 5, 7.5, 12.5, 20, and 30 nm, respectively. The particle radii are the average value of more than twenty measurement particles radii from the SEM images such as Fig. 2.

The laser damage thresholds have been fitted according to the damage probabilities under different irradiation energy densities [16]. The damage threshold is corresponding to the highest pulse fluence which will cause zero probability damage. When the radii of SiO_2 particles are 5, 7.5, 12.5, 20, and 30 nm, the laser damage thresholds are 11.2, 11.7, 16.8, 14.3, and 13 J/cm^2, respectively. Compared with the silicon oxide film prepared by electron beam evaporation, the sol–gel film has higher laser damage threshold. The higher purity of the sol–gel film can account for this finding. The sol–gel film is also a loose microstructure that can ease local thermal stress caused by laser irradiation [17–18].

3.2. Structure of periodic stripes

In Fig. 3, the periodic stripes in the sol–gel films damage spots are shown as they emerge. The spatial periods of the periodic stripes in every picture are less than the laser wavelength of 1064 nm. The orientations of the stripes in a picture are the same and they are vertical to the polarization of the laser irradiation.