Nanogratings and nanoholes fabricated by direct femtosecond laser writing in chalcogenide glasses

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Abstract: We report on the fabrication of sub-wavelength nanostructures on the surface of As_2S_3 chalcogenide glasses by appropriately controlling the irradiation condition of single-beam direct femtosecond laser writing. Nanogratings with a period of 180 nm were realized by multipulse irradiation. More importantly controllable nanoholes as small as 200 nm in diameter (one quarter of the illumination wavelength) were, for the first time, achieved in As_2S_3 using direct laser writing by single-pulse irradiation.

OCIS codes: (140.3390) Laser materials processing; (220.4241) Nanostructure fabrication; (160.2750) Glass and other amorphous materials.

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1. Introduction

In recent years, chalcogenide glasses (ChGs) have gained extensive interest not only because of their high refractive index, wide transparent window and ultrahigh Kerr nonlinearity but also their rich physicochemical properties, such as phase changing and photopolymerization, upon light exposure [1]. These unique properties have made ChGs an excellent candidate for diverse applications including nonlinear and reconfigurable photonic chip devices [2,3], high density optical data storage [4], biophotonic devices [5] and the fast expanding metamaterials [6].

Among these applications, the precise generation of nanometric structures, in particular nanoholes with the maximum achievable refractive index manipulation, holds the key to functional devices in the optical regime. This, at the moment, largely relies on the sophisticated electron beam or focused ion beam fabrication facilities, which are expensive and time-consuming. In comparison, direct laser writing (DLW) based on a femtosecond pulse induced multiphoton process is a fast, flexible and simple approach for micro-scale and nano-scale fabrication [7]. Waveguides and photonic crystal structures have been demonstrated in ChG films [3,8]; however the achievable minimum structures were still on the order of the illumination wavelength (λ_i) or larger, which in turn restricts the operation wavelength of the devices to near infrared or infrared region. So far, using the DLW method, it has remained challenging to achieve elemental structures with consistently controllable sizes at least half of the illumination wavelength ($\lambda_i/2$) or smaller, which are essential to achieve functional photonic devices in the telecommunications or visible wavelength ranges.

In this paper, through careful manipulation of the fabrication condition, in particular the exposure pulse number from an ultrafast laser amplifier, we not only demonstrated the fabrication of nanogratings (period = 180 nm) with multipulse irradiation but also consistently generated 200 nm ($\lambda_i/4$) nanoholes on the surface of As_2S_3 glasses using the DLW method with tailored single pulse irradiation.

2. Experiment and results

2.1 Experimental setup and sample preparation

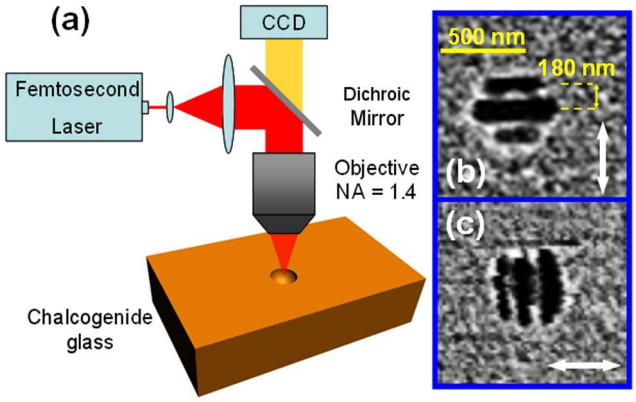

Fig. 1. (a) Experimental setup for the nano-fabrication experiment. SEM images of the nanogratings fabricated by multipulse irradiation with laser beams polarized along (b) vertical and (c) horizontal directions.

The bulk As_2S_3 glass sample was prepared by the conventional melt-quench method and cut into $2 \times 2 \times 10$ mm^3 pieces with the large faces polished for the nanofabrication [9]. The laser modification was induced by focusing a femtosecond laser beam at a wavelength of 800 nm with a repetition rate of 1 kHz and a pulse width of 100 fs from a regenerative amplifier (Spitfire, Spectra-Physics, USA) through an oil immersion objective (NA = 1.4, 100 × ,

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Olympus) on the surface of the sample, as shown in Fig. 1(a). A shutter was used to control the exposure time. No chemical etching or post process was used after fabrication.

2.2 Nanograting formation with multipulse irradiation

Figure 1(b) presents the scanning electron microscopic (SEM) image of the fabricated structure with 10 ms (10 pulses) exposure time at an energy level of 1.3 nJ. It is interesting to see that a grating-like periodic structure rather than a hole corresponding to the focal spot is formed. The periodicity of the grating is approximately 180 nm and the entire laser modified region is approximately 500 nm in diameter. We noticed that the normal direction of the gratings is parallel to the direction of the laser polarization and rotates as the polarization direction changes, as shown in Figs. 1(b) and 1(c); however the periodicity remains almost unchanged.

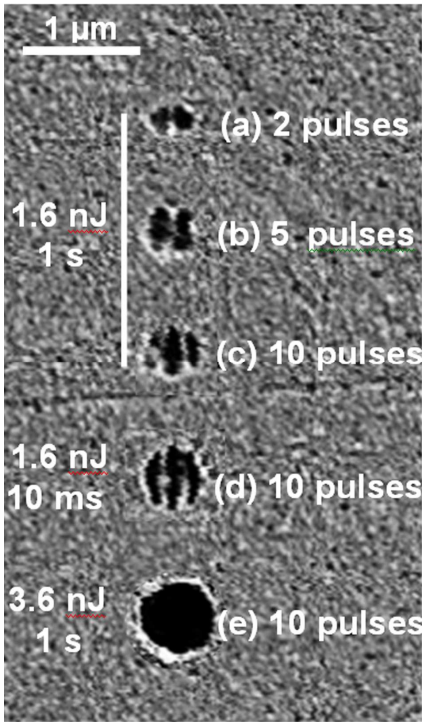

Fig. 2. (a) to (c) SEM image of nanogratings produced at an energy level of 1.6 nJ under 2 to 10 pulse irradiation (pulse interval: 1 s); (d) SEM image of nanogratings produced at an energy level of 1.6 nJ with 10 pulses and a 10 ms pulse interval; (e) SEM image of nanoholes produced at an energy level of 3.6 nJ with 10 pulses and 10 ms pulse interval. Scale bar: 1 μm.

The similar nanograting formation has recently been reported extensively in silica [10,11], semiconductors [12], diamond and graphite [13]; however the mechanism responsible for this phenomenon is still under debate. Two theoretical models have been proposed. Shimotsuma and associates proposed that the interference of the incident laser field with the electron plasma density wave leads to a periodic modulation of the electron plasma concentration and the structural changes in material [10]. It this model, the periodicity of the nanograting is related to the temperature of the plasma which is determined by the number of irradiation pulses, the separation of each pulse and the power of the laser. However, the model proposed by Bhardwaj *et al.* pointed out that nanogratings were formed by the inhomogeneous breakdown caused by the inhomogeneous growth of plasma [11]. They proposed that the growth of underdense nanoplasmas into sheets would cause light to adopt modes similar to those in planar waveguides, leading to a $\lambda_i/2n$ period, which is constant under different laser intensity irradiance.

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To validate the theoretical models, we first investigated the influence of the number of pulses on the formation of the nanograting. Figures 2(a-c) present the resultant nanogratings produced at a given energy level of 1.6 nJ under 2 to 10 pulses irradiation (pulse separation: 1 s, which is long enough for the relaxation of the heating effect of the previous pulse). It is seen that with an increasing pulse number, the laser modified area increases; however, the periodicity of the nanograting remains almost the same.

To compare the influence of the laser pulse separation on nanograting formation, we fabricated structures under the same pulse energy (1.6 nJ) with 10 pulses and a 10 ms pulse interval, as shown in Fig. 2(d). Comparing Figs. 2(c) and 2(d), we can find that the two nanogratings have almost the same periodicity for 1 s and 10 ms pulse interval. The only difference is the overall size of the laser modified area. Other combinations of the irradiation energy, the number of pulses and pulse intervals were also tested. It was found that when the irradiation energy is lower than the "clear hole" threshold, where no fine grating structures can be preserved in the central part of the laser modified area (Fig. 2(e)), the periodicity of the nanograting is independent of the irradiation pulse number and the pulse interval.

We also investigated the nanogratings generated at different laser energy levels ranging from 1.3 nJ to 2.0 nJ as shown in the inset of Fig. 3. It clearly shows that the periodicity is not dependent on the laser power either. These results indicate that the interaction between the incident light beam and the electron plasma density wave may not be the main reason for the formation of nanogratings on the surface of As_2S_3 because the periodicity of the nanograting is independent on the plasma temperature and density [10]. In fact our periodicity (180 nm) is very close to $\lambda_i/2n$ (n is the refractive index of ChGs), which matches well with the theory proposed by Bhardwaj and associates [11]. Under such a circumstance, the dependence of the nanograting periodicity on the laser energy is not expected. In addition, the orientation of the nanogratings (perpendicular to the incident laser polarization) also agrees with the Bhardwaj's model.

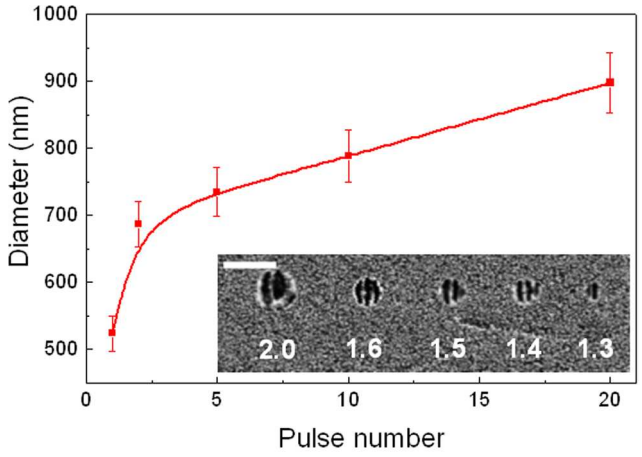

Fig. 3. Dependence of the nanohole diameter on the pulse number for multipulse fabrication at a pulse energy level of 3.6 nJ with a pulse separation of 0.5 s. Inset: SEM image of nanogratings produced for different pulse energy levels from 1.3 nJ to 2.0 nJ with 10 pulse irradiation. Scale bar: 1 μm.

2.3 Nanohole formation with single pulse irradiation

In many photonic applications, for example the two-dimensional photonic crystals and micro diffraction elements, nano/micro holes on the surface of bulk materials are required as the building blocks [14–16]. In our fabrication with multipulse irradiation, nanoholes can only be formed when a high laser energy level is used, which completely removes the central part of the laser affected area, as shown in Fig. 2(e). In Fig. 3 the diameter of the nanoholes generated at a pulse energy level of 3.6 nJ versus the pulse number is plotted. It is expected to see that

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the nanohole diameter reduces with decreased pulse number. The smallest nanohole that can be achieved under this irradiance condition is approximately 520 nm under single-pulse irradiation.

To find out the smallest nanohole we can achieve, we fabricated a series of nanoholes under single-pulse irradiation within a large energy range from 1.4 nJ to 8 nJ as shown in the SEM images in Fig. 4(a). It is interestingly to note that under single-pulse irradiance, the nanohole can be formed even under the low irradiation energy and no nanograting can be formed at any energy level. The nanoholes present well defined symmetric shape and the rims of the nanoholes are smooth. The smallest controllable hole induced by the femtosecond laser beam under a threshold fabrication condition is approximately 200 nm, which is only a quarter of the illumination wavelength (800 nm) and its depth is approximately 100 nm, as confirmed by the SEM and the topographic images shown in Figs. 4(b) and 4(c), respectively. Figure 4(d) shows the energy dependence of the diameters of nanoholes. This dependence can be fitted by the equation [17]:

$$D = P_1\sqrt{\ln\frac{E}{P_2}}, \tag{1}$$

where D is the diameter of holes (μm) and E is the energy (nJ). The fitting parameters are P_1 = 0.614 μm, P_2 = 1.25 nJ. The good fitting the experimental data and the curve suggest that under the single pulse fabrication condition, the size of the nanoholes is mainly determined by the Gaussian shape of the laser focal spot [17].

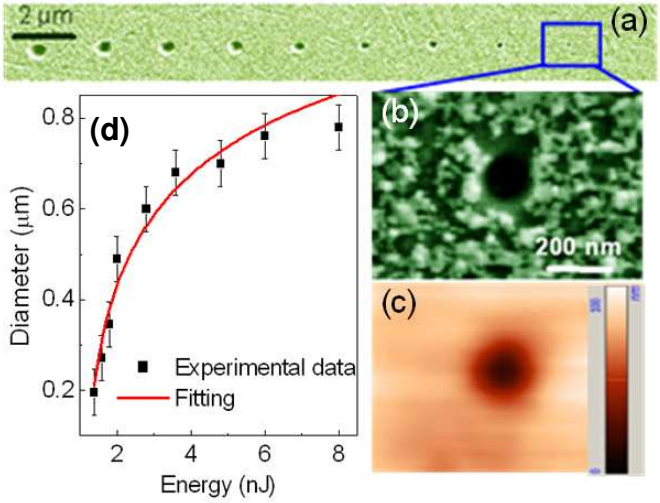

Fig. 4. (a) SEM images of the nanoholes at different energy levels; (b) SEM images of nanoholes with a diameter of 200 nm; (c) Topological image of the same nanohole as shown in (b) obtained from a scanning near-field microscope. (d) Dependence of the nanohole diameter on the laser energy for single-pulse fabrication.

3. Conclusions

In conclusion, using the single beam DLW method, we have demonstrated the creation of nanogratings (periodicity = 180 nm) in As_2S_3 by the multipulse irradiation from an ultrafast laser amplifier. It was found that the periodicity of the nanogratings is independent of the laser energy suggesting a complex formation mechanism. More importantly, by appropriate control of the irradiation pulse number down to a single pulse level, well controlled nanoholes with diameters of $\lambda_i/4$ was produced, for the first time, at the threshold fabrication condition, providing a useful, flexible and cheap alternative approach to fabricating functional nonlinear

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photonic devices in ChGs potentially operating in telecommunications and visible wavelength region.

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