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High aspect ratio nanoholes in glass generated by femtosecond laser pulses with picosecond intervals

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ABSTRACT

Because of its potential uses, high aspect ratio nanostructures have been interested for last few decades. In order to generate nanostructures, various techniques have been attempted. Femtosecond laser ablation is one of techniques for generating nanostructures inside a transparent material. For generating nanostructures by femtosecond laser ablation, previous studies have been attempted beam shaping such as Bessel beam and temporal tailored beam. Both methods suppress electron excitation at near surface and initiate interference of photons at certain depth. Recent researches indicate that shape of nanostructures is related with temporal change of electron density and number of self-trapped excitons. In this study, we try to use the temporal change of electron density induced by femtosecond laser pulse for generating high aspect ratio nanoholes. In order to reveal the effect of temporal change of electron density, secondary pulses are irradiated from 100 to 1000 ps after the irradiation of first pulse. Our result shows that diameter of nanoholes is increasing and depth of nanoholes is decreasing as pulse to pulse interval is getting longer. With manipulating of pulse to pulse interval, we could generate high aspect ratio nanoholes with diameter of 250–350 nm and depth of 4~6 μm inside a glass.

1. Introduction

Generation of high aspect ratio nanostructure has been attempted by various research groups for last decades. Since it can affect to propagation of light, it has been applied to photonic devices [1,2], photovoltaic devices [3], and even nanocell surgery. [4,5]

For generating nanostructures, several methods were attempted. Which are electron beam (E-beam) lithography [1], metal assisted chemical etching [3], focused ion beam (FIB) milling [6], and femtosecond laser ablation. [7–16] In particular, femtosecond laser ablation has been highly interested in generating nanostructure in transparent material.

When femtosecond laser pulses are irradiated in transparent material, carrier excitation is induced by absorption of photons that includes multiphoton absorption and avalanche ionization. Simultaneously, carrier-carrier scattering and carrier-phonon scattering occurs. Those events occur within few tens of picoseconds and followed by thermal/structural events such as shock-wave emission, thermal diffusion, re-solidification at few nanoseconds after irradiation of femtosecond laser pulse [17]. The amount of excited carrier depends on intensity of laser pulse and it affects to thermal/structural events. When electron density exceeds critical value, permanent structural change occurs.

In order to control the size of permanent structural change in transparent material, manipulating of electron density by spatial and temporal beam shaping were attempted such as Bessel beam [16] and temporally tailored beam [10]. Through beam shaping, it is possible to suppress electron density at near surface below critical density [10]. Then photons can penetrate into transparent material with relatively low loss. At target depth, electron density induced by photon absorption exceeds critical value due to interference. Thus, nanoholes with high aspect ratio could be generated.

In this study, we try to generate high aspect ratio nanoholes by using of temporal change of electron density. Here, photons of the first pulse induce excitation of electrons and it decays and diffuses temporally. In order to induce temporal interference between excited electrons and photons, secondary pulses are irradiated from 100 to 1000 ps after the first pulse irradiation. With manipulation of pulse to pulse temporal interval, we could acquire high aspect ratio nanoholes with diameter of 250–350 nm and depth of 4~6 μm.

2. Experimental

The experiments were performed by fiber based femtosecond laser (Amplitude systemes, Satsuma HP3, full width half-maximum pulse du-

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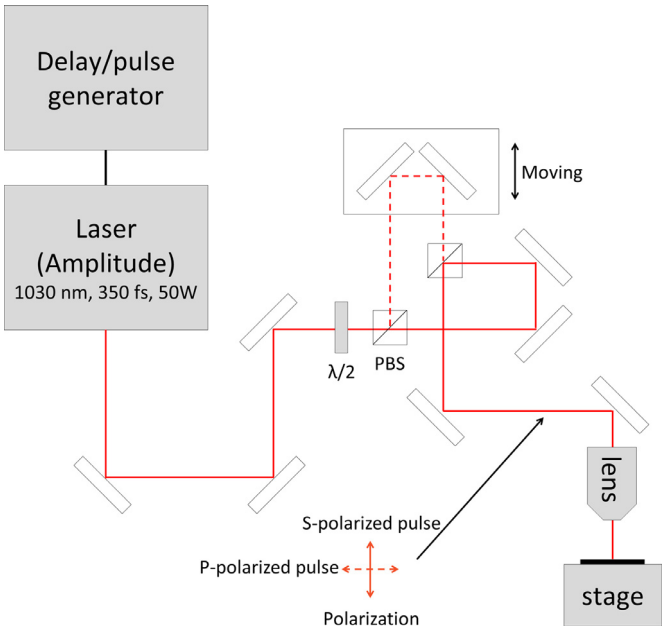

Fig. 1. Schematics of experimental set up.

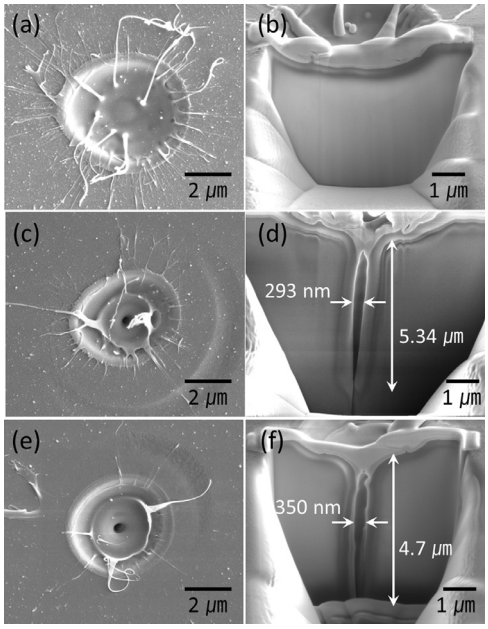

Fig. 2. Nanoholes in AN100 glass generated by femtosecond laser pulses energy of 13.4 and 14.2 μJ: (a) Top view and (b) Cross section view of double pulse irradiation with zero interval, (c) Top view and (d) Cross section view of double pulse irradiation with 300 ps interval, (e) Top view and (f) Cross section view of double pulse irradiation with 1 ns interval.

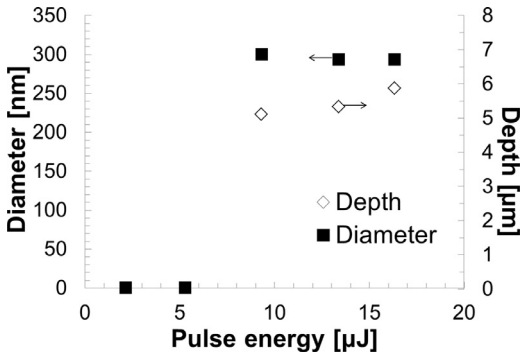

Fig. 3. Diameter and depth of nanoholes at 300 ps pulse to pulse interval.

ration: 350 fs, center wavelength: 1030 nm). Laser pulses were triggered by external TTL signal of delay/pulse generator (Stanford Research Systems, DG535). Emitted single pulse is divided by combination of half wave plate ($\lambda/2$) and polarization beam splitter (PBS). S-polarized component of pulse is reflected and p-polarized component of pulse is transmitted at PBS, additionally rotation of $\lambda/2$ can change intensity of each component. Thus, with $\lambda/2$ and PBS, it is possible to control an intensity ratio between divided pulses. After dividing, s-polarized pulse experiences fixed optical path and p-polarized pulse experiences variable optical path. The length of variable optical path is controlled by precise motion stage (Thorlabs, DDS220). Both s-polarized and p-polarized pulses are combined at another PBS. After combining, both pulses experience the sole optical path with certain time intervals. Finally those pulses are tightly focused on sample by objective lens (NA 0.55, Mitutoyo M Plan Apo 50X). Fig. 1 shows schematics of our experimental set up.

Since we tried to use a temporal change of electron density in transparent material, it is important to define an origin of time (time zero). At the time zero, both pulses are simultaneously irradiated on the target surface. In this study, in order to find the time zero, autocorrelator (A.P.E., PulseCheck USB 15) is adopted. The autocorrelator can only detect horizontal polarized pulse. Thus, $\lambda/2$ is placed on optical path to the autocorrelator for filtering horizontal polarized components of both pulses. Considering temporal detection range of the autocorrelator, length of variable optical path and fixed optical path is matched. When temporal interval between two pulses is below 10 ps, autocorrelator can detect both pulses. Once both pulses are detected by the autocorrelator, it is possible to find the time zero with manipulating of precision stage at variable optical path. After finding the time zero, temporal interval between pulses are converted from distance of precision stage from the time zero location.

3. Results and discussion

As aforementioned, when electron density initiated by laser pulse is higher than critical density, most photon energy is absorbed at near surface [10]. However, if it is below critical density, photon can penetrate into the material. The typical order of critical electron density in glass is ~10^{21} cm^{-3} [18]. In this study, we found the condition that photon penetrates into the glass (AN100, Asahi glass company) and generate high aspect ratio nanoholes with secondary pulse irradiation. When two pulses are irradiated on the glass without temporal interval, a crater is formed. In this case, we could not observe any high aspect ratio nanoholes inside a glass. (Fig. 2(a) and (b)) However, when pulses with few hundreds picoseconds interval is irradiated, nanohole is generated inside the glass. (Fig. 2(c), (d), (e), (f)) Here, first pulse has 13.4 μJ of energy and followed by secondary pulse with 14.2 μJ of energy. We observe that the nanoholes are generated by laser pulses with temporal intervals of from 100 ps to 1 ns. Generated nanoholes has diameter of 150~350 nm and depth of 4.7~6.3 μm. Fig. 2(c) and (d) shows the generated nanohole when the pulse to pulse interval is 300 ps. As we can see in the image, irradiation of pulses with 300 ps intervals can generate nanoholes with diameter of 293 nm and depth of 5.34 μm. The aspect ratio of this nanohole is 18.2. In order to do further understand of generating mechanism, we try to change pulse energy of secondary pulses and temporal interval between each pulses.

First, the pulse energy is changed from 2 to 20 μJ. The nanoholes are generated when pulse energy exceeds 10 μJ. Thus, we could claim that interference of excited electrons and photons enhances an electron density and it reaches at critical density when the secondary pulse energy exceeds 10 μJ. (Fig. 3) As pulse energy is increasing, depth of nanohole is also increasing, however we could not observe significant

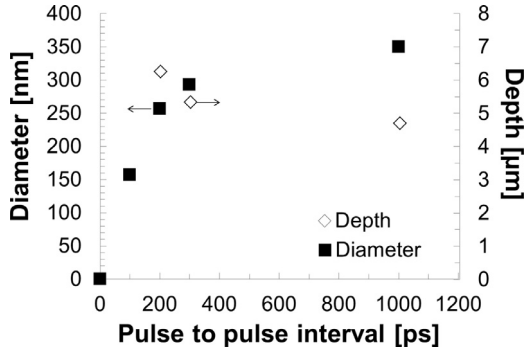

Fig. 4. Diamter and depth of nanoholes according to pulse to pulse interval. An energy of first pulse is 13.4 μJ and second pulse is 14.2 μJ.

change of diameter. Even though pulse energy rarely affects to diameter of nanoholes, the result shows that electron density affects a depth of nanoholes. It quite well explains our hypothesis. Normally, radial distribution of electron density is affected by beam shape and size. In addition, it is limited by focusing lens. Without change a focusing optics, radial distribution of electron density is rarely changed as pulse energy. However, axial distribution of electron density is different. It is affected by pulse energy. When the pulse energy is increasing, propagating direction of voxel is also increasing. Therefore, the result shows a possibility of manipulate size of nanohole via electron density change.

Second, the pulse to pulse interval is changed from 0 to 1000 ps. Since electrons diffuse temporally, the shape of nanoholes can be changed as intervals. The result shows that diameter of nanohole is changed according to intervals as well as depth. (Fig. 4) Diameter is fast increasing and saturating. This behavior is similar to diffusion. Furthermore, depth is decreasing as interval. It may relate with decay of excited electrons. Therefore, we may claim that it is possible to control the shape of nanohole. We successfully observe final structure of nanoholes according to pulse energy and pulse to pulse interval, however it is still ambiguous the physical principles underneath of nanohole generation.

There are several candidates for explaining a high aspect ratio nanohole generation. First possible phenomenon is self-trapping of photons followed by filamentation [19,20]. When the pulse energy of Gaussian beam exceeds critical power, self-focusing and plasma defocusing occurs in the material. If the pulse energy is high enough, repetition of self-focusing and plasma defocusing can elongate focusing depth [20]. In our case, nanohole is not generated at the time zero, therefore we cannot claim that nanoholes are generated by filamentation. (Fig. 2(a) and (b)) Second possible phenomenon is spatial interference induced by Bessel beam [15,16]. However in order to initiate interference at the focal plane, donut beam should be irradiated into focusing optics. In our case either axicon or spatial light modulator (SLM) have not be placed on the optical path. Furthermore, measuring result of spatial intensity profile shows the Gaussian shape for both pulses. Thus we cannot claim that nanoholes are generated by spatial interference. Third possible phenomenon is temporal change of electron density inside a glass. When laser pulses are irradiated on the material, electron density increases due to absorption of photon energy. Then electrons in conduction band are rapidly decayed into self-trapped exciton (STE) state. The typical lifetime of STE in glass is $\sim 10^{-3}$ s [21,22]. These electrons can interact with photons and eventually transfer its energy to phonon on time scale of few hundreds of picoseconds [23,24]. Thus, it is possible to interact electrons with photons of secondary pulse in time scale of few hundreds picoseconds. The result supports possibility of interaction between electrons at STE state with photons at secondary pulse. It indicates that diameter of nanoholes are increasing as temporal interval getting longer. The trend of it is similar with diffusion, thus we may claim that the electrons induced by first pulse interacts with secondary pulse. Furthermore, depths of nanoholes are decreasing as temporal interval getting longer. It is possible to explain our result with the electron density distribution. Because of absorption, an electron density is decreasing as propagating of photons. Thus, extinction of excited electrons in deeper location occurs relatively fast. When the secondary pulse is irradiated before the extinction of excited electrons, then it is possible to initiate avalanche ionization.

4. Conclusion

In summary, we performed a double pulse irradiation of femtosecond laser and generates high aspect ratio nanoholes with diameter of 250–350 nm and depth of 4~6 μm. When the first pulse is irradiated on AN100 glass, electrons are excited and may rapidly decay to STEs. Then photons of secondary pulse interact with these STEs or excited electrons and increase electron density inside a glass. As a result, high aspect ratio nanoholes can be generated. In order to explain our result, further studies have been conducted, which include change of pulse energy and pulse to pulse intervals. Both initiates change of electron density distribution. The nanoholes are generated when pulse energy exceeds 10 μJ. In addition, diameter of nanoholes is increasing and depth of nanoholes is decreasing as temporal interval getting longer.

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