Doping transition metal ions as a method for enhancement of ablation rate in femtosecond laser irradiation of silicate glass

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We present a doping method to improve the femtosecond laser ablation rate and promote ablation selectivity. Doping transition metal ions, Co^{2+} or Cu^{2+}, in silicate glass apparently change absorption spectroscopy and induce resonant absorption at wavelengths of 600 and 800 nm, respectively. Comparing with femtosecond laser processing of the same glass without doping, we find that the threshold fluence decreases and the ablation rate increases in resonant absorption in doped silicate glass. Resonant absorption effectively increases multiphoton ionization for seed-free electron generation, which in turn enhances avalanche ionization.

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In micro/nanomachining, femtosecond lasers are very promising for the fabrication of transparent dielectrics for photonic and optoelectronic devices[1–4], due to their high intensity and ultrashort pulse width. However, typical femtosecond laser ablation is low throughput with a high photon cost, which is not suitable for industrial applications[5,6]. One effective way to improve photon absorption efficiency is by resonant absorption where photon energy, $h\nu$ (or multiphoton energy, $N h\nu$), is equal to the difference between the energy levels involved in electronic transition. Resonant absorption has been widely applied in different research areas[7–9], especially in ultrafast laser ablation. Liu *et al.* realized resonance-enhanced multiphoton ionization in photoelectron spectroscopy in which ammonia was first excited by resonant absorption of two 267 nm photons and then ionized by a 401 nm probe pulse[10]. Zhao *et al.* found that a resonant enhancement effect in nonlinear photon absorption happened during laser ablation of neodymium glass when the laser wavelength was 586 nm[11].

However, in the aforementioned studies on laser resonant ablation, the band structures of the experimental materials were well defined and fixed. A common resonant absorption practice is to tune the laser wavelength to achieve a resonant transition by exciting an atom or molecule. But for transparent dielectric material, such as silicate glass, there is no controllable energy level in the forbidden band to realize the resonant absorption of a photon within the wavelength tuning range by a commercial tunable laser source. Doping proper elements in dielectric materials can adjust the material band structures and the corresponding optical properties[12,13]. Therefore, we considered the use of a doping method to achieve resonant absorption at specific photon energy and enhance the material removal rate of silicate glass.

In this work, the transition metal ions, Co^{2+} and Cu^{2+}, are selected as dopants to mix into the silicate glass, which induce photon resonant absorption in the visible to near-infrared band. We find that doping can selectively improve the material removal rate in the enhanced absorption band, and the amount of improvement strongly depends on the doping concentration level and absorbed intensity.

The experimental setup was a commercial optical parametric amplifier (OPA, Light Conversion) coupled to an amplified Ti:sapphire laser system (Spectra-Physics) with a pulse width of 50 fs (full-width at half-maximum) and a repetition rate of 1 kHz. The OPA could tune laser wavelengths from 290 to 2600 nm. A combination of a half-wave plate and a polarizer

allowed the laser energy delivered onto the sample to be controlled. A mechanical shutter was applied to get the desired pulse numbers. The laser pulse was focused normally on the sample surface with a 20×, numerical aperture = 0.45 microscope objective to a Gaussian spot radius ($1/e^2$) of 2.9 μm. The Rayleigh length of the laser beam was calculated to be 6.4 μm. The sample was installed on an XYZ translation stage allowing the precise positioning of the sample between the irradiation points. A charge-coupled device (CCD) camera was used to visualize the surface of the sample and to position the sample surface at the beam focus.

The Co^{2+} or Cu^{2+} doped silicate glass samples were prepared by the normal melt-quenching technique. Reagent grade chemicals of SiO_2, Na_2O, CaO, and CoO/CuO were used in this work as starting materials. They were carefully mixed in appropriate proportions and melted in an alumina crucible at 1500 °C by an electrical muffle furnace for 3 h. After complete melting, the melts were cast into a stainless steel mold before being annealed at 500 °C for 3 h to relieve any residual stress. Finally, the samples were cooled down to room temperature, cut, and fine polished to a dimension of 40×20×2 (mm). The chemical compositions of the glasses in mass percent with the name of the samples are summarized in Table 1. Absorption spectra of the glass samples were measured by a UV-VIS-NIR spectrophotometer (Varian) at room temperature.

The ions Co^{2+} and Cu^{2+}, when introduced into glass, caused resonant absorption in their electron clouds under white-light irradiation. Usually, discrete amounts of energy were taken up in certain wavelength ranges so that the irradiated light lost large portions of wavelengths in the form of defined absorption bands[14]. As shown in Fig. 1, compared with the undoped silicate glass, the glasses doped with transition metal ions exhibited strong absorption bands centered around 600 and 800 nm, respectively[15]. These two bands were identified with electronic transitions in the d–d levels of Co^{2+} and Cu^{2+}[16]. For the Co^{2+} doped silicate glass, the absorption at 600 nm corresponded to two states of Co^{2+} (one initial state of $^4A_2$ and one intermediate excited state of $^4T_1$)[17]. The absorption for Cu^{2+} doped glass was at a wavelength of 800 nm, corresponding to the ^2E and $^2T_2$ of Cu^{2+} states[18]. Thus, the photons could be resonantly absorbed when the laser wavelength was tuned to the enhanced absorption band of the doped glass.

Table 1. Chemical Compositions of Glasses

Sample	Glass Composition (mass%)
Silicate Glass	$70SiO_2$–$20Na_2O$–10CaO
S70Co3.0	$70SiO_2$–$20Na_2O$–10CaO–3.0CoO
S70CuX	$70SiO_2$–$20Na_2O$–10CaOXCuO

Note: X = **0.**5–4.0 (mass%).

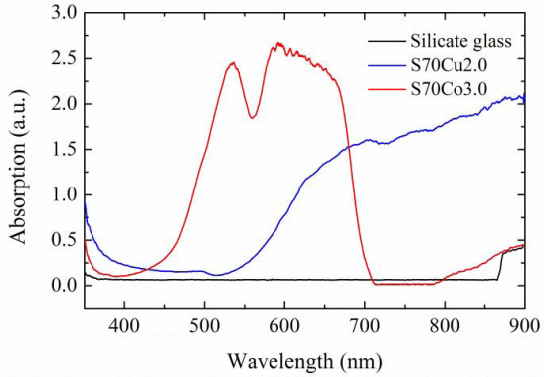

Fig. 1. Optical absorption spectra of the glass samples with different doping types. The most prominent absorption bands are around the wavelengths of 600 nm for Co^{2+} doped glass and 800 nm for Cu^{2+} doped glass.

To determine the ablation rate enhancement in femtosecond laser processing of doped glass by resonant absorption, microholes were drilled at different wavelengths and energy fluences. In the experiment, the concentrations of CoO and CuO in the doped silicate glass were 3.0 and 2.0 mass%, respectively. According to the optical absorption characteristics of the glass samples shown in Fig. 1, the laser wavelengths of 600 and 800 nm were selected for comparison. After processing, the depth was measured using a confocal microscope (Olympus) by adjusting the focus point on the edge and the bottom of the hole, respectively.

In Figs. 2(a) and (b), the maximum hole depth of the glass is plotted as a function of the applied laser fluence at wavelengths of 600 and 800 nm. The average

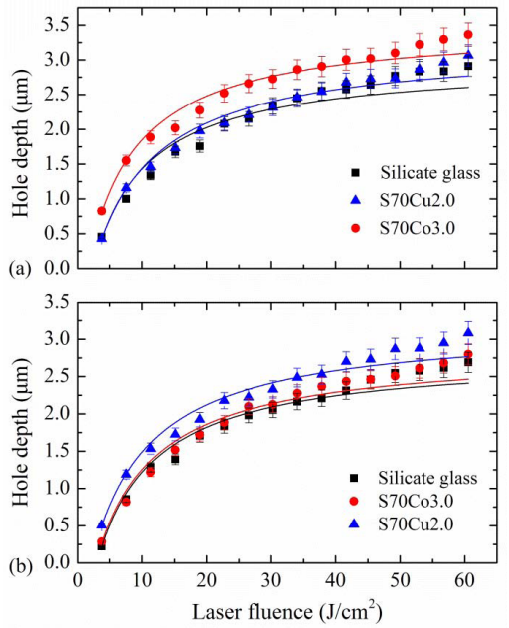

Fig. 2. Laser fluence dependence of hole depth for processing three glass samples at wavelengths of (a) 600 and (b) 800 nm, with a pulse number of 50 and a laser fluence range of 3.78–60.55 J/(cm^2). The solid lines are the fit according to Eq. (1).

for each point was determined using three measured data with a standard deviation from 5% to 10%, which is depicted by error bars. The ablation depth appeared to follow a logarithmic dependence on the applied laser fluence; and at high fluences, the ablation depth tended to reach saturation and was in the range of less than 3.5 μm.

Compared with undoped silicate glass, the ablation depth was deeper for glasses doped with Co^{2+} or Cu^{2+}; but this phenomenon only existed at the enhanced absorption band. At the non-resonant absorption wavelengths, the difference in ablation depth between doped and undoped glass almost disappeared. The ablation rate, average ablation depth per pulse, was obtained by dividing the hole depth by the pulse number and the hole depth was measured before reaching saturation at 50 pulses. At lower laser fluence, resonant absorption can enhance ablation rates by up to 81.5% for Co^{2+} doped glass, and 128.9% for Cu^{2+} doped glass.

In addition, the threshold fluences were measured to confirm the doping effects on the ablation enhancement. Threshold fluences were calculated based on the relationship between the maximum hole depth h and laser fluence ϕ. The solid lines shown in Fig. 2 fit the logarithmic expression

$$h(\phi) = h_0 \ln\left(\frac{\phi}{\phi_{\text{th}}}\right), \tag{1}$$

where ϕ_{th} and h_0 are the fit parameters[19]. The fit parameter h_0 represents the hole depth at fluence $e\times\phi_{\text{th}}$ ($e = 2.718\ldots$) for a pulse number of 50, and the value of it was approximately 900 nm. The multipulse threshold fluence $\phi_{\text{th}}(50)$ for silicate glass at 800 nm was 2.98 J/cm^2, which was in agreement with the value obtained in Ref. [20].

As shown in Table 2, sudden drop in the ablation threshold was observed at a wavelength of 600 nm in Co^{2+} doped glass and at 800 nm in Cu^{2+} doped glass. The threshold fluence also decreased slightly at the non-resonant absorption wavelengths, which was probably attributed to the decreasing band gap of the silicate glass after doping. In our experiment, the low doping concentration made the band gap decrease not so obvious.

The percentage decrease in the ablation threshold for doped glass, compared with the undoped silicate glass, is listed in Table 2. At the resonant absorption wavelengths, the threshold fluence of Co^{2+} and Cu^{2+} doped glass decreased 36.8% and 28.4%, respectively, than that of undoped glass. The reduction in threshold fluence was supposed to be related to the intensity absorbed by the material, as a higher absorbance of the doped glass (Fig. 1) led to a relatively higher drop in threshold fluence.

In order to analyze the relationship among ablation rate, threshold fluence, and absorbed intensity, we prepared the following Cu^{2+} doped silicate glasses with doping concentrations ranging from 0.5 to 4.0 mass%. The photographs and absorption spectra of Cu^{2+} doped glasses are shown in Figs. 3(a) and (b), respectively. With an increase in CuO concentration, the color of the transparent doped glass changed from colorless to dark blue, and the absorbed intensity of the band at 800 nm increased linearly.

In this experiment, the laser wavelength was held constant at 800 nm, and the dependence of the hole depth on the laser fluence was investigated at a pulse number of 50. As can be seen in Fig. 4, by adding CuO into the silicate glass, the hole depth increased gradually with the increase in CuO content at every laser fluence. Furthermore, the ablation threshold calculated using the above method was inversely proportional to the CuO concentration.

Assuming that the absorption was homogeneous as supported by Fig. 4, the absorption coefficient α can be calculated for each sample at a wavelength of 800 nm by

$$\alpha = \left(\frac{1}{d}\right)\ln\left(\frac{I_0}{I_t}\right), \tag{2}$$

where d is the thickness of the sample, and I_0 and I_t are the intensities of incident and transmitted radiations, respectively. The values of the absorption coefficient, the percentage of ablation rate increase, and the percentage of threshold fluence decrease are listed in Table 3. At the absorption coefficient of 14.5 cm^{-1}, the doped glass achieved a maximum threshold fluence decrease of 41.2% and ablation rate increase of 190.5%.

After irradiation by the femtosecond laser, the focused area in the Cu^{2+} doped glass was still blue as observed in an optical microscope. The absorption

Table 2. Comparison of Threshold Fluence Between Glasses at Wavelengths of 600 and 800 nm and the Percentage Decrease in Threshold Fluence for Doped Glass

Glass Sample	λ = 600 nm		λ = 800 nm	
	Threshold Fluence (J/cm^2)	Reduction (%)	Threshold Fluence (J/cm^2)	Reduction (%)
Silicate Glass	2.33	–	2.98	–
S70Co3.0	1.47	36.8	2.85	4.3
S70Cu2.0	2.24	3.5	2.13	28.4

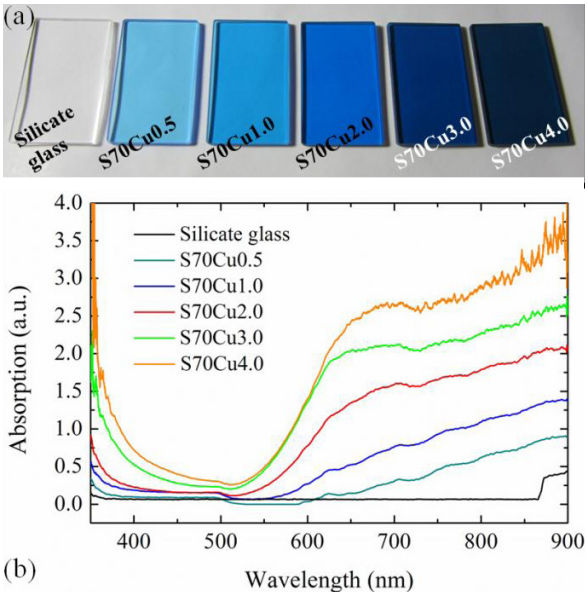

Fig. 3 (a) Photographs and (b) optical absorption spectra of Cu^{2+} doped silicate glasses with the doping concentrations increasing from 0.5 to 4.0 mass%.

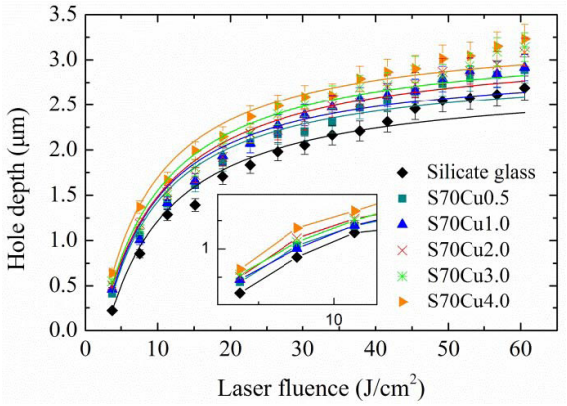

Fig. 4. Laser fluence dependence of hole depth for processing Cu^{2+} doped silicate glasses with laser wavelength of 800 nm, and pulse number of 50. Inset shows a local enlargement in laser fluence range of 3.78–11.35 J/cm².

spectra of the glass was the same before and after the femtosecond laser irradiation, which indicated that no changes were induced in the valence states of Cu^{2+} ions. In fact, we did not observe any variation for the absorption of the doped glass at room temperature even after months. Therefore, the doping effects were stable.

The ablation enhancement phenomenon is explained by the resonant absorption effect. By calculating the Keldysh parameter[21], we realized that multiphoton ionization was responsible for seed-free electron generation as silicate glass interacted with femtosecond pulses, as the Keldysh parameter was larger than 1 under the laser fluence used in our experiment. For the silicate glass whose band gap was about 3.5 eV[22], three-photon ionization occurred with irradiation by an 800 nm laser. After doping with Cu^{2+} ions, intermediate energy levels were induced in the forbidden band of the glass. The photon energy at a central wavelength of 800 nm was equal to an energy level difference of an electronic transition from ^2E to $^2T_2$ in a Cu^{2+} ion, which led to the resonant absorption. After the resonant absorption process, the electron ionization needed to absorb two more photons at 800 nm. Compared with the non-resonant absorption, the densities of free electrons contributed by photoionization were much higher due to the resonant absorption between the intermediate state and the ground state[10,23]. Subsequently, the impact ionization became dominant at relatively high free-electron densities, which led to more intense electron–electron collision and more free electrons generation. Ionization enhancement increased the ablation rate, and the degree of increase strongly depended on the absorbed intensity of the glass.

In conclusion, we demonstrate that the doping method can improve the ablation rate and possible selectivity in femtosecond laser micromachining of transparent dielectrics. We change the absorption of silicate glass by doping with transition metal ions, Co^{2+} or Cu^{2+}, and observe the threshold fluence decrease and ablation rates increase in the enhanced absorption wavelengths located at 600 nm for Co^{2+} doped glass and 800 nm for Cu^{2+} doped glass. In addition, the ablation enhancement is closely related to the doping concentration and absorbed intensity that determine threshold fluence and ablation rate differences between doped glasses. The ablation enhancement is mainly due to the resonant absorption effect, which enhances the multiphoton ionization and generates more free electrons during a laser–glass interaction.

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Table 3. Absorption Coefficient, Percentage Increase in Ablation Rate, and Percentage Decrease in Threshold Fluence for Cu^{2+} Doped Silicate Glasses at 800 nm

Glass Sample	**S70Cu0.5**	**S70Cu1.0**	**S70Cu2.0**	**S70Cu3.0**	**S70Cu4.0**
Absorption Coefficient (cm^{-1})	3.1	5.5	8.9	11.4	14.5
Ablation Rate Increase (%)	87.3	109	128.9	148.9	190.5
Threshold Reduction (%)	19.7	23.2	28.4	32.5	41.2

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