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Laser processing of silicon at submicron scale using photochromic films

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Abstract

Laser fabrication at submicron scale is experimentally demonstrated with the nonlinear optical switching effect of photochromism. The effect, which is a result of change in the optical properties of the photochromic material between the open-ring and closed-ring isomers during the photoisomerization, effectively reduces the laser beam size.

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The ultrafast response of the molecular photocyclization and cycloreversion reactions at a time scale of a few picoseconds ensures the instantaneous realization of the effect. Utilizing a photochromic film of cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethane as the mask layer, laser processing of a silicon wafer demonstrated submicron scale feature size with improved surface quality as compared to the smallest features achievable using direct laser ablation without the photochromic film.

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Keywords: Laser processing, organic films

1. Introduction

Laser processing, virtually applicable to all kinds of materials, has received significant attention over the past few years for their applications in optoelectronic devices, biomedical components and various industrial products [1-3]. For applications in photonic crystals [4,5], optical lithography [6], and ultrahigh density optical data storage [7], continued efforts are being expended in trying to achieve smaller laser microfabricated features to meet the device design requirements. However, due to the diffraction of light, which limits the attainable spot diameter, it is difficult to reduce the feature size any further through direct laser ablation process. Microfabrication techniques, including lithography and reactive ion etching, can produce microstructures. However, these processes are costly and tend to be either limited in their resolution or slow in their throughput. It is considerably more

effective to use direct laser writing techniques with the added advantages of high efficiency and applicable to all kinds of materials with features of arbitrary shapes or forms. In the literature, the optical near-field effects have been reported to be capable of achieving resolution exceeding the diffraction limit in some applications [8-10]. However, generation of optical near-field through a near-field scanning optical microscope (NSOM) has the inherent difficulty in the fabrication of the tapered fiber, lack of reproducibility in the performance of the fiber tip, fragile aspects of the optical fiber and the complexity in the precision to control the near-field distance between the fiber tip and the sample surface at nanometer scale.

Since it is quite difficult to obtain diffraction-limited laser output from a given laser, the resulting machined features are

much larger. Investigation on new techniques to shape the laser beam to realize features as submicron scale has been a challenging task in laser microprocessing.

Recently, super-resolution effect of a thermoreversible organic film was demonstrated to effectively shape the laser beam to realize recording byte size of a few hundred nanometers in a phase change optical disk [11]. In this letter, nonlinear optical switching effect of a photochromic film was utilized to achieve laser fabrication at submicron scale on a silicon wafer. The ultrafast nature of the photoisomerization of the photochromic film in the switching process has superior time response than that of a slow thermal process in a thermoreversible film.

2. Experimental details

Illustrated in Fig. 1, a silicon wafer (thickness ~380 μm), as the target material to be machined, was covered with a photochromic film (thickness 0.41 μm). In this study, one of diarylethene derivatives, cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethane (CMTE) (TCI America), was used. For laser machining, a focused laser beam from a frequency-tripled UV output of a diode-pumped solid-state YAG laser (355 nm, pulse width ~40 ns, AVIA, Coherent Inc.) was used. The laser was operated in a single pulse mode and focused by a microspot focusing objectives (NA of 0.32, Optics For Research, Inc.) before irradiating the samples. The theoretical focal spot diameter, as specified by the manufacturer, was of the order of 1 μm. For comparison, a same type of Si wafer without photochromic film was prepared for the direct laser ablation under similar experimental conditions. The samples were mounted into a fixture, fitted to a computer-controlled *X*-

Y translation stage, while the focused laser beam irradiated the sample at normal incidence. The machining experiments were conducted in ambient environment. The depth information of the machined features was obtained from interferometric measurements (WYKO interferometric microscope, NT-2000). The WYKO interferometric microscope was operated in vertical scanning interferometry (VSI) mode with a depth resolution limit of 3 nm for measurements. The morphology of the samples was observed by a scanning electron microscope (SEM, Hitachi S-3500N).

3. Results and discussion

As illustrated in Fig. 1, the nonlinear optical switching film was prepared on the sample surface, that exhibits rapid change in its optical properties upon exposure to laser irradiation and effectively reduces the beam size as the beam propagates

through the film thickness towards the interface of the film and the surface to be machined. The applicability of the film as an effective nonlinear optical switching layer may be evaluated by using *ABC* parameters [12]:

$$A = \frac{1}{d} \ln[T(\infty)/T(0)]. \tag{1}$$

$$B = -\frac{1}{d} \ln[T(\infty)]. \tag{2}$$

$$C = \frac{A+B}{AI_0 T(0)[1-T(0)]} \frac{dT}{dt}. \tag{3}$$

where d is the thickness of the film, $T(0)$ is the initial transmittance of the film before exposure to the incident laser light, $T(\infty)$ is the saturated transmittance of the film after complete exposure to the laser light, and I_0 is the intensity of the light just in close proximity to the film. To achieve maximum effect, the change in transmittance between $T(\infty)$ and $T(0)$ must be as large as possible. With regard to the *ABC*

parameters, a large A parameter and a small B parameter are required. Time response factor dT/dt is also important in increasing parameter C to ensure the switching effect to be effective in machining the target surface as well as to improve the microprocessing efficiency.

The photochromic film, which undergoes a reversible phototransformation of chemical species between two forms (open-ring isomers and closed-ring isomers) upon irradiation with UV and visible light [13], is the nonlinear optical switching layer in this study. Diarylethenes are newly emerged photochromic materials with outstanding fatigue resistance and thermal irreversibility [14-16]. Figure 2 shows the photoisomerization and the absorption spectra of CMTE film prepared using spin-coating. An absorption peak around 526 nm upon UV light irradiation can be seen (closed-ring

isomers). This absorption peak disappears after visible light irradiation (open-ring isomers). The process is a reversible photochromism between the open-ring isomers and the closed-ring isomers of the CMTE molecules with the accompanying change in the refractive index. The dynamics of cyclization and cycloreversion reactions of diarylethenes studied using pico- and femtosecond laser photolysis experiments revealed that both reactions take place very rapidly in less than a few picoseconds [14,15,17-19]. The ultrafast response of the photoisomerization process is crucial to ensure the effectiveness of the switching effect of the film upon irradiation of laser pulses with a pulse width of ~40 ns. The thickness of the film as a mask layer was selected to maximize the change in transmittance between the two photoisomerization states. For CMTE films having a thickness of 0.41 μm, used in this study, the transmission of

the film was found to increase from 0.13 to 0.26 at 355 nm during the photocyclization process upon UV light irradiation. The values of *A* and *B* parameters were calculated as 1.7 and 3.3, respectively.

After laser microfabrication, the CMTE film was dissolved using acetone solvent. Both samples were cleared in deionized water in an ultrasonic bath for 20 minutes. Figure 3 gives the scanning electron microscope images of laser microfabricated features on Si wafer at different pulse energies. Figure 3 (a), (b), and (c) correspond to the direct laser ablation on silicon wafer without the photochromic film while (d), (e), and (f) correspond to the laser fabrication on silicon wafer with the photochromic film. A careful investigation of the relationship between the diameter and the depth of the microfabricated features on Si wafers with the pulse energy is shown in Fig. 4

for the laser microfabrication with and without the photochromic film, respectively.

For laser microprocessing of silicon, the laser energy was initially absorbed by the carriers of Si, which undergo interband transitions. Depending on the laser fluence, five characteristic fluence regions were identified based on the observed surface morphology and debris patterns, following the interpretation of the dynamic studies [1,20]. (1) For the lowest fluence range (pulse energy < 3.0 μJ), the Si wafer did not melt. The hot carriers relax via carrier-carrier and carrier-phonon scattering, recombining on a time scale of several picosecond and transferring most of the absorbed energy to the lattice. (2) In the second fluence region, very small features can be found where the laser pulse energy (3.0 to 4.0 μJ) was near damage threshold. The surface morphology observed by

SEM (Fig. 3a) shows the melting of Si followed by re-solidification. Features as small as 2.0 μm could be found under optimal focusing conditions with only the intensity over the central part of the beam exceeded the damage threshold. (3) Significant material displacement was observed in the third fluence region with pulse energy ranging from 4 to 10 μJ. In this region, the craters were quite symmetric, and well defined with clear rims at the periphery. Less debris could be found in areas outside the crater region. Craters typically have a diameter between 7 to 10 μm and a depth of 2.2 to 4.6 μm. Figure 3b illustrates a feature fabricated with laser energy of 4.4 μJ. (4) With further increase in the pulse energy (10 to 60 μJ) for the fourth fluence region, violent and explosive removal of material was observed, which was accompanied with the re-deposition of Si droplets inside and outside the craters. Large debris of frozen material in micron size could be

found far beyond the outer rim. For a typical feature in Fig. 3c fabricated with pulse energy of 12.0 μJ, the diameter and depth of the crater were about 11.2 and 5.6 μm, respectively. (5) For direct laser ablation at pulse energy greater than 60.0 μJ, cracks were developed due to strong laser fluence and the stresses within the Si wafer, resulting in non-circular features. These results are in excellent agreement with a recent report by Borowiec *et al.* on the direct laser ablation of silicon wafer using nanosecond laser pulses [21].

In comparison to the direct laser ablation, smaller and shallower features were obtained on Si wafer with the photochromic film (Fig. 3d-f). The smallest feature achievable in this case was approximately 0.5 μm in diameter with a depth of 0.2 μm (Fig. 3d), which is much smaller than the diffraction limit and a clear indication of super-resolution

effect. The small change in depth profile versus the laser power in the case of CMTE film shown in Fig. 4 was due to the absorption of the film, which reduced the laser intensity while significantly reducing the spot size. The rapid increase in feature diameters for pulse energies beyond 27.0 μJ implies nonlinear optical switching layer at the interface may have been damaged due to the presence of high laser fluence. Noticeably, there is no significant re-deposition of droplets around these features. High quality circular and reproducible features were obtained for pulse energies < 27 μJ. This could be explained by the fact that molten Si and CMTE may have mingled together and re-deposited on the Si surface with much less adhesion, and was easily removed by the chemical solvent than the refreezing of pure Si after melting. The improved surface quality of the fabricated features is of significance for their applications.

The use of film structures to realize feature resolution beyond the diffraction limit was also realized in the work of Tominage *et al.* and Tsai *et al.*, [11, 23-27]. The application of their approach in optical data storage, known as super-resolution near-field structure (super-RENS), has been demonstrated. The films are nonlinear optical layers which control the near-field optical aperture. Detailed studies also revealed that an ensemble of the localized surface plasmons and their photothermal energy transfer within the near-field distance was the underlying mechanism [26]. One advantage is that the near-field distance is well controlled by a solid layer of film, which ensures the near-field effect produced at the interface without the complicated feed-back control and the degradation of the near-field probe. Furthermore, the solid layer could be an inorganic or organic films prepared by a variety of

techniques, including vacuum techniques (thermal evaporation, sputtering, pulsed laser deposition, etc.), sol-gel, and spin-coating techniques, with the possibility to control the film thickness precisely at nanometer scale. In this study, we have demonstrated an approach with a reversible photochromic film achieving an ultrafast optical switching effect and the use of an organic material provides advantages of large material variety and ease of sample preparation.

4. Conclusion

A nonlinear optical switching material, photochromic film of cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethane (CMTE), has been demonstrated to be effective in achieving laser fabrication at submicron scale, which has the advantages of versatility, high efficiency, and the ease of operation. The resolution limit of this technique could be improved if the

material properties of the nonlinear optical switching layer could be further optimized. The technique presents a unique approach, which has the merits of large variety, low cost, and the potential to develop applications in laser materials processing, laser beam shaping, and optoelectronic devices.

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Figure captions:

Figure 1. Laser fabrication at submicron scale using a nonlinear optical switching layer. The beam propagation and narrowing of laser beam profile have been schematically outlined: 1, laser beam profile at waist without the photochromic film; and, 2, effective beam profile after the photochromic film.

Figure 2. Photoisomerization of cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethane (CMTE): (a) photocyclization and cycloreversion reactions; (b) reversible switching in the absorption spectra of CMTE film.

Figure 3. SEM images of laser microfabricated features on Si wafer at different pulse energies: (a), (b), and (c), direct

ablation without the photochromic film at pulse energy of 3.0, 4.4 and 12.0 μJ, respectively; (d), (e), and (f), laser fabrication with the photochromic film at pulse energy of 1.3, 5.4, and 12.0 μJ, respectively.

Figure 4. Relationship between the diameter and the depth of the microfabricated features on Si wafers with the pulse energy: (a) without the photochromic film; (b) with the photochromic film.

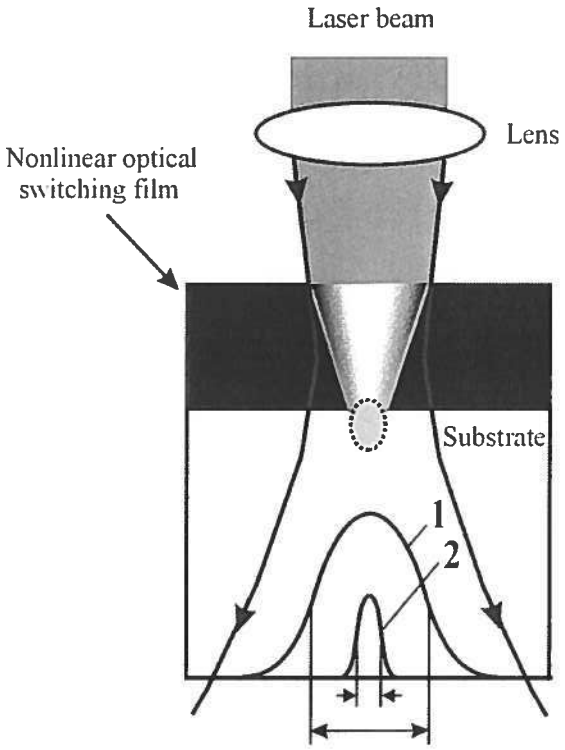
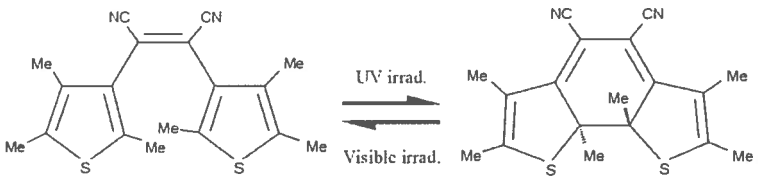
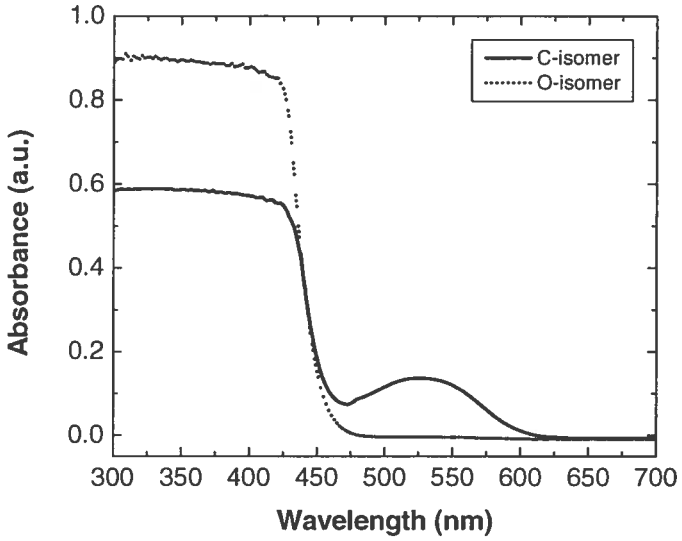


Figure 1. (Q. Chen and S. Nikumb, Laser processing of silicon at submicron scale using photochromic films)



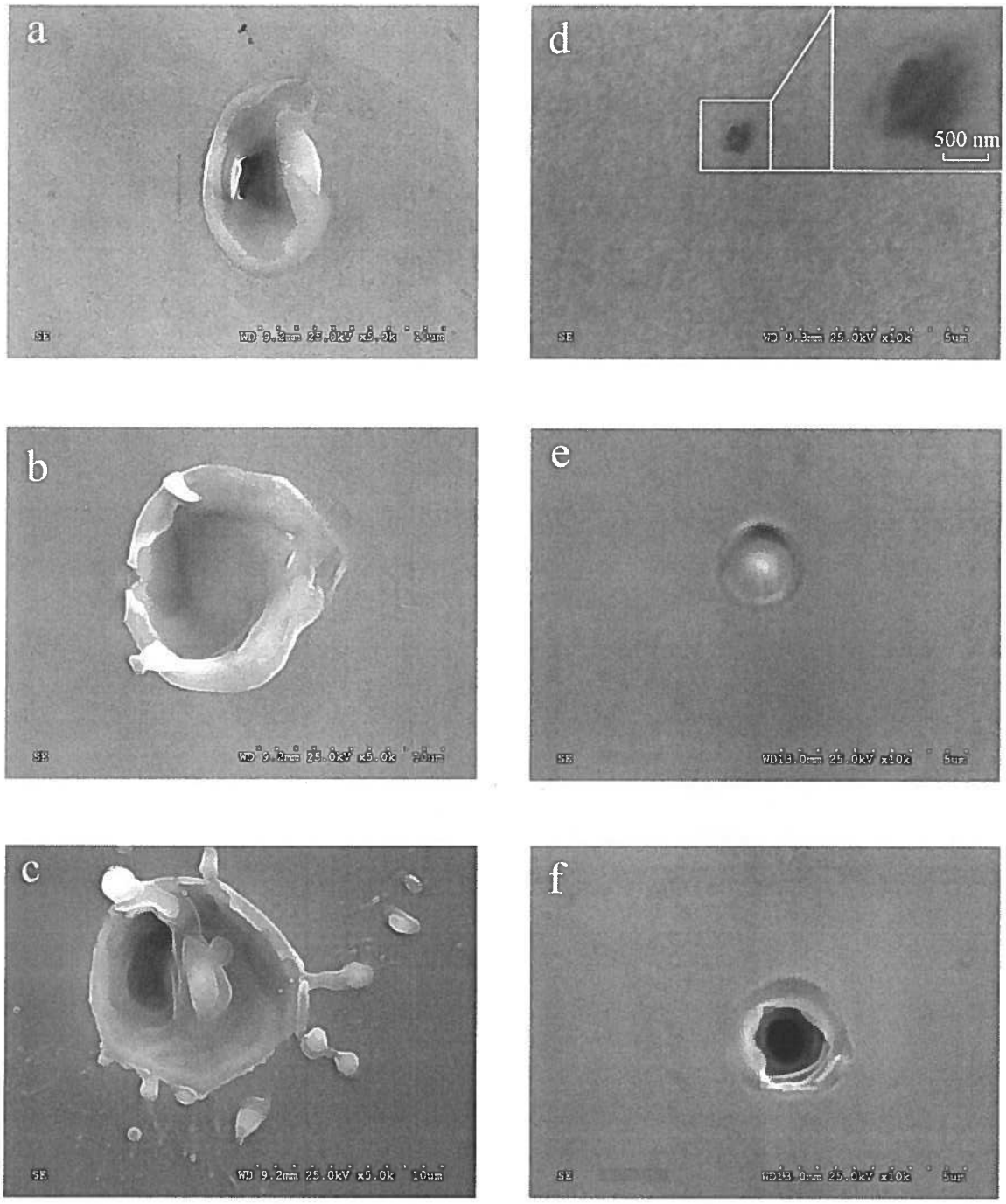
Open-ring isomer (O-isomer) Closed-ring isomer (C-isomer)

(a)



(b)

Figure 2. (Q. Chen and S. Nikumb, Laser processing of silicon at submicron scale using photochromic films)



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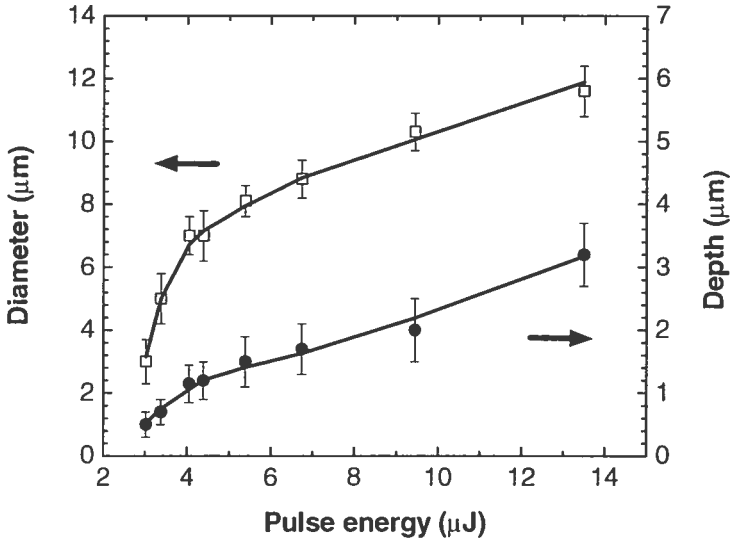
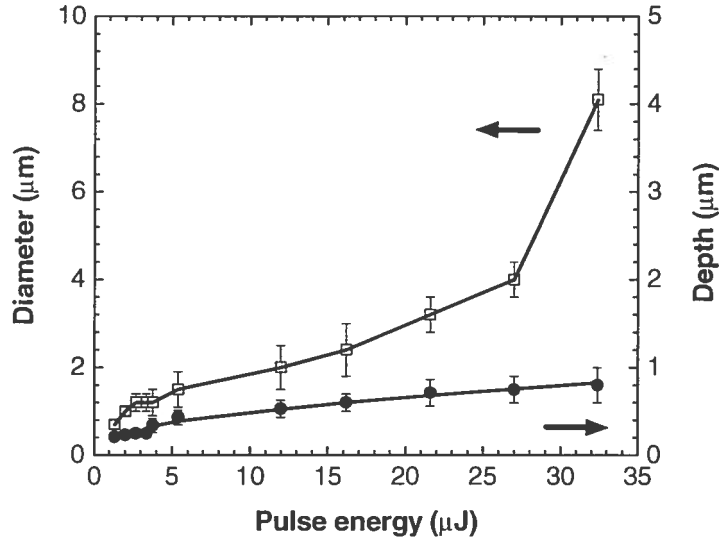


(a)



(b)

Figure 4. (Q. Chen and S. Nikumb, Laser processing of silicon at submicron scale using photochromic films)