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Micropatterning of the SiO$_2$ coated Si surface using femtosecond laser diffraction

Y Fukami, M Okoshi and N Inoue
Department of Electrical and Electronic Engineering, National Defense Academy
1-10-20 Hashirimizu, Yokosuka 239-8686, Japan
E-mail: fukami@nda.ac.jp

Abstract. Dot-array patterns with a-few-$\mu$m period were formed on oxidized-Si substrates by Fresnel diffraction of Ti:sapphire femtosecond laser radiation. Si wafers were coated with thin SiO$_2$ films in order to prevent the surface degradation during laser processing. SiO$_2$ layers with various thicknesses from 0 to 1.2 $\mu$m were grown by thermal oxidation, and exposed to several laser conditions. The modified surface morphology and the depth of the dots were characterized, revealing periodic fine patterns of 3-$\mu$m depth for 0.2-$\mu$m SiO$_2$/Si samples irradiated for 30 s at 130-mJ/cm$^2$ laser fluence.

1. Introduction
Micro patterning by laser processing using diffraction or interference of the incident beam has been studied by several groups [1-4]. Fresnel diffraction [5], which also generates interference fringes in the near-field behind beam obstacles or masks, is another phenomenon potentially useful in laser micropatterning. The fringe size in Fresnel diffraction can be much smaller than the size of the beam obstacle or open aperture. Hence, micropattern processing is available without a complicated beam shaping system. Furthermore, the Fresnel irradiation pattern may be readily manipulated by controlling simple mask properties such as open size, aperture shape, and mask thickness.

In surface studies that aim to improve surface reactions, for example, photocatalytic performance, it is highly desirable to increase the surface area [6]. Roughening or texturing of the reacting surface of catalytic materials such as TiO$_2$ may benefit from a low-cost laser micro patterning based on Fresnel diffracted beam delivery.

In this paper, proximity masks have been used to generate Fresnel diffraction patterns of femtosecond laser light and induce periodic micropatterns on the surface of Si substrates. An oxide layer was grown on Si substrates to improve the contrast and quality of the surface textures, which have been characterized as a function of SiO$_2$ film thickness.

2. Experimental
Both Si (100) and SiO$_2$-coated Si wafers were tested. SiO$_2$ films up to 1.2-$\mu$m thickness were grown by a thermal oxidation, in O$_2$ flow under 1000 $^\circ$C heating.

Laser irradiation was carried out in air ambient at room temperature. The light source was a Ti:Sapphire laser (Spectra Physics, Tsunami and Spitfire/TSA-10 Hybrid system) providing 130-fs pulse width, 790-nm wavelength and 1-kHz repetition rate. A neutral density filter and a focusing lens ($f$=150 mm) was used to set the laser fluence to 130 mJ/cm$^2$, which slightly exceeds the silicon
ablation threshold of 100 mJ/cm². The irradiation time was varied in the range of 0.25-30 s. The samples were affixed with 20-μm-thick nickel transmission electron microscope (TEM) grids to serve as proximity masks. The grid size (aperture) was 30μm x 30μm square, which was significantly smaller than the ~500 μm beam diameter. Hence, the intensity distribution of the incident beam on one aperture can be regarded as uniform.

After laser irradiation, ablation sediment, which adhered weakly to the surface, was removed by ultrasonic cleaning in ethanol. The sample was then soaked in 1 wt. % hydrogen fluoride (HF) solution for 5 minutes. The surface morphology of as-irradiated, ultrasonically cleaned and HF soaked samples were characterized by a scanning electron microscope (SEM, Hitachi, S-4500), and a laser microscope (LM, Lasertec Corp., LLM21).

3. Results and Discussions

SEM images of the sample surface after a series of 10-s laser exposures, ultrasonic cleaning and HF etching, are shown in figure 1. The thickness of the SiO₂ layer was (a) 0 μm, (b) 0.1 μm, (c) 0.2 μm, (d) 0.4 μm, (e) 0.5 μm and (f) 1.2 μm, respectively. The mask-to-sample spacing corresponds to the SiO₂ thickness. A clearly defined grid containing an array of micro-holes was observed in figure 1(a)-(d). However, the dot pattern of the sample shown in figure 1(a) was randomly cracked and very rough. No fine patterns were observed in figures 1(e) and 1(f). The best defined pattern was observed in figure 1(c). Figure 1(g) shows the calculated beam intensity profile based on Fresnel diffraction theory [5, 7] for a mask-sample spacing of 0.2 μm, to match the expected irradiation condition in figure 1(c). The theoretical pattern closely matches the observes structure in figure 1(c), indicating that local micro ablation was induced by the intensified micro beam patterns produced by Fresnel diffraction.

The samples were classified into three groups: (i) samples with no SiO₂ layer (No-SiO₂/Si) which showed random and rough dot patterns, (ii) samples with thin SiO₂ layers (0.2 μm-SiO₂/Si) which had fine deep dot patterns, and (iii) samples with thick SiO₂ layers (>0.5 μm-thick SiO₂/Si) which had patterns with poor contrast.

(i) Samples without SiO₂ (No-SiO₂/Si): SEM images of 0-μm SiO₂/Si samples are shown in figure 2 for the irradiation time of (a) 1 s and (b) 30 s. The images are taken after laser-irradiation (top), ultrasonic cleaning (middle), and etching in the HF solution (bottom). As-irradiated sample surfaces were covered with a layer of sediment. Also a slight swelling was observed. After ultrasonic cleaning and etching in HF solution, the micro-hole pattern appeared. This indicates the growth of oxidized silicon compounds during the laser irradiation. Since such silica oxide is expected to be transparent to the laser radiation, one expects the formation of deeper structures in the Si substrate with further irradiation. However, as the irradiation continued, the oxidization layer appears to scattered the light and form rough surfaces without the expected near-field patterns. Thus, for non-oxidized Si samples,
fine micro-dot pattern could be maintained only at the beginning of the irradiation, and both drilling and roughening proceeded with the irradiation time.

(ii) Samples with thin SiO$_2$ layer (~0.2 μm-SiO$_2$/Si): SEM images of the 0.2-μm SiO$_2$-coated Si samples are shown in figure 3 for irradiation times of (a) 1 s and (b) 30 s. The images are recoded before (upper) and after (lower) ultrasonically cleaning and HF etching. Although formation of oxidized sediment is apparent (upper images), the amount generated was less than in the case of non-oxidized Si substrates. The SiO$_2$ layer contained numerous cracks and also swelled up. These observations suggest that the incident beam had transmitted the SiO$_2$ layer to reached the SiO$_2$/Si boundary where Si ablation led to both micropatterning and ablation plume pressure to crack the SiO$_2$ layer. The Si micropatterns were not apparent after ultrasonic cleaning, although the sediment layer was cleanly removed. The fine dot pattern appeared only after the HF etching step. This further suggests the sediment overlayer is a silicon oxide, possibly formed by reactions of ablated Si species with air as ablation products escape through the cracks in the original oxidization layer. Further, since the original oxide layer is transparent to the laser, additional laser irradiation may encapsulate Si ablation produces, which reacting with ambient oxygen through the microcracks, lead to formation of a relatively homogeneous and dense oxide medium under the flat SiO$_2$ layer. Such a transparent layer would enable continuous drilling of micropatterns in the silicon.

(iii) Sample with thick (>0.5 μm) SiO$_2$ layers: SEM images of the 1.2-μm thick SiO$_2$-coated Si samples are shown in figure 4. The irradiation time was (a) 1 s and (b) 30 s while the sequence of laser irradiation, ultrasonic cleaning and HF etching is similar to figure 2. Higher irradiation yield more sediment, but overall amounts were much less than generated in the case of 0-μm thick SiO$_2$-coated Si. This sediment was removable by ultrasonic cleaning. However, the original silica film was retained and remained crack free and mostly flat with only weak evidence of underlying patterning in the silicon substrate. Only faintly-visible micropatterns were observed after HF etching, with little difference on pattern contrast between the low and high exposures (1 s and 30 s). The thick SiO$_2$ layer has likely remained intact during laser irradiation, resisting cracking by the silicon ablation pressure and preventing air from oxidizing the potential Si ablation products that might impede laser transmission into the Si substrate.

The depths of microdots were measured by LM and are plotted in figure 5 as a function of laser irradiation time. Values are average depth of the four corner dots as viewed in figures 1 - 4. The etch...
depths increased most rapidly with increasing irradiation for the samples with 0 to 0.4-µm thick SiO₂ films, yielding a maximum 3-µm depth after 30-s irradiation. On the other hand, the micro-hole depth hardly increased for the samples with SiO₂ layers thicker than 0.5 µm.

The above evidence shows the formation of fine and deep microhole patterns in Si substrates was aided by a thin SiO₂ film coating. An optimum silica thickness coating layer appears necessary to reduce generation of thick oxide ablation sediments that otherwise scatter the laser radiation and prevent detailed beam patterning in non-oxidized silicon. The oxide films help retain optically flat surfaces to minimize laser beam distortion, while also enabling crack formation to induce Si oxidation for continuous drilling. These properties will be further influenced by film tension in the SiO₂ layer which decreases with increasing layer thickness and the fluence-dependent ablation pressure generated by the Si substrate. These factors are the subject of future work.

4. Conclusions
In this paper, the effect of SiO₂ thin-film coatings were studied on femtosecond laser drilling of Si wafers with the aim to generate fine micro-hole array patterns. We found that 0.2-µm thick SiO₂-coated Si provided the finest patterned surface structures, yielding 3-µm deep microholes after 30-s irradiation of 130-mJ/cm² laser fluence and 1-kHz repetition. The optimum silica film thickness requires further study of the physical strength and tension of the SiO₂ layer during laser irradiation and ablation dynamics. The results further show that Fresnel diffraction patterns can be simply manipulated by proximity distance, controlled here by film thickness (mask-to-silicon distance), and thereby offer relatively high accuracy laser micropatterning on Si substrates.

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