

# Direct patterning of silicon oxide on Si-substrate induced by femtosecond laser

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**Abstract:** In this study we report for the first time a method for direct patterning of silicon oxide on a silicon substrate by irradiation with a femtosecond laser of Mega Hertz pulse frequency under ambient condition. Embossed lines of silicon oxide with around 3~4  $\mu\text{m}$  width and less than 100 nm height were formed by controlling the parameters such as laser pulse power and frequency rate. A Scanning Electron Microscope (SEM), an optical microscopy and a Micro-Raman and Energy Dispersive X-ray (EDX) spectroscopy were used to analyze the silicon oxide layer.

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**OCIS codes:** (140.3390) Laser materials processing; (140.6810) Thermal effects; (350.5340) Photothermal effects; (320.7090) Ultrafast lasers; (160.6000) Semiconductor materials.

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## 1. Introduction

Silicon Oxide is one of the most important semiconductor materials which plays crucial role in nanoelectromechanical systems (NEMS) and microelectromechanical systems (MEMS) [1–4], it also has some characters which cause its extended use in producing semiconductor and lab On a Chip Systems [5–7]. Patterning of dielectric layers of silicon oxide on Si-substrate is one of the most important issues in modern micro and nano electronics which is often accomplished through a photolithography [8,9]. This technique requires a photomask for replication. The fabrication of photo masks is normally very expensive and time consuming due to the fact that there are several steps involved in the fabrication process [10–12]. Some approaches based on atomic force microscope have been proposed for maskless patterning of silicon oxide on Si-substrate [13–18]. These techniques include scanning probe oxidation [13–16], Tribo nanolithography (TNL) [17,18] and dip-pen lithography (DPL) [18]. In contrary to the conventional photolithography methods for patterning silicon oxide on Si-substrate, the advantages of these techniques are that no photomask is needed, features in nano scale can be obtained and any redesign can be easily done. However, it determined that these approaches that employ AFM are slow processes and only applicable to micron-sized devices, the speed of an Atomic Force Microscope (AFM) scanning probe is normally set to be around 300 nm/s and the scanning field (X × Y) of an AFM is typically around 100 μm × 100 μm. For large scale manufacturing, cell stitch must be performed and it could be very challenging due to the small dimension of each cell.

In the present work, we attempted to develop a new method for the generation of silicon oxide pattern in micro-scale based on high frequency pulses of femtosecond laser. The proposed approach enables a direct (single-step) generation of an oxide layer on a silicon substrate. In comparison with previous methods, the direct oxidation of silicon induced by femtosecond laser is a maskless single-step technique which offers a higher flexibility and

reduced processing time. In addition this method allows for large-area patterning (in mm-scale) at fast writing speed under ambient condition.

## 2. Experimental setup and fabrication process

An undoped <100> oriented silicon samples were rinsed in acetone and then treated in pure water. The Femtosecond laser used in the study was a diode-pumped, Yb-doped system. This laser emits pulses of 214 fs pulse duration. Using a harmonic generator, the laser beam is frequency doubled from 1030 nm to 520 nm. The theoretical diameter of the focused laser spot is calculated to be 1.02  $\mu\text{m}$ . Samples were irradiated with laser beams of power ranging from 0.2 W to 1 W at pulse frequency ranging from 8 MHz to 26 MHz (8, 13 and 26 MHz) and a speed of scanning of 500 mm/s. Irradiated samples were observed using a scanning electron microscopy (SEM), an optical microscopy and a Micro-Raman and Energy Dispersive X-ray (EDX) spectroscopy to analyze oxide layer generated on the silicon surfaces.

## 3. Results and discussion

Although a wide range of laser power at various pulse frequencies were used for irradiation, micro scale embossed lines were only evident at two points: laser power of 1 W at a pulse frequency of 13 MHz and 0.35 W at 26 MHz. In other instances, the irradiated area was either completely ablated or slightly modified. As shown in Fig. 1, at 8 MHz, the line on the left presents no material breakdown but color-change, whereas at 26 MHz, the line on the right clearly shows material removal. The embossed line can only be generated at 1 W at 13 MHz (middle line).

With carefully controlled laser parameters, embossed lines can be created consistently, as shown in Fig. 2. It is also noticed that this process has much better repeatability at 26 MHz than at 13 MHz.

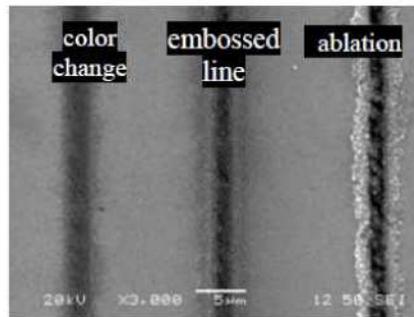


Fig. 1. SEM image of Silicon surface after irradiation with Femtosecond Laser pulses at 1 W at the various pulse frequency (left to right: 8, 13 and 26 MHz)

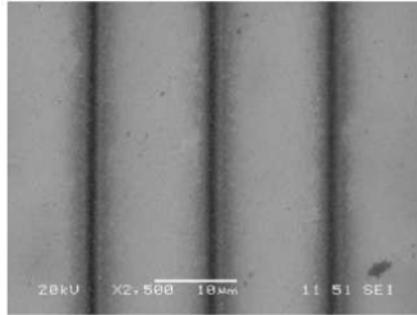


Fig. 2. SEM image of silicon surface after irradiation with Femtosecond Laser pulses at 0.35 W at the pulse frequency of 26 MHz.

Figure 3 represents optical microscope topography images of the irradiated areas. Cross sectional optical microscope images show embossed lines around 100 nm high and 3.5  $\mu\text{m}$  width induced with femtosecond laser pulses with a power of 0.35 W supplied at 26 MHz (Fig. 3(a)) and 40 nm high and 3  $\mu\text{m}$  width when the laser power is 1 W operating at 13 MHz. (Fig. 3(b)). Increasing pulse frequency results in the increased line height.

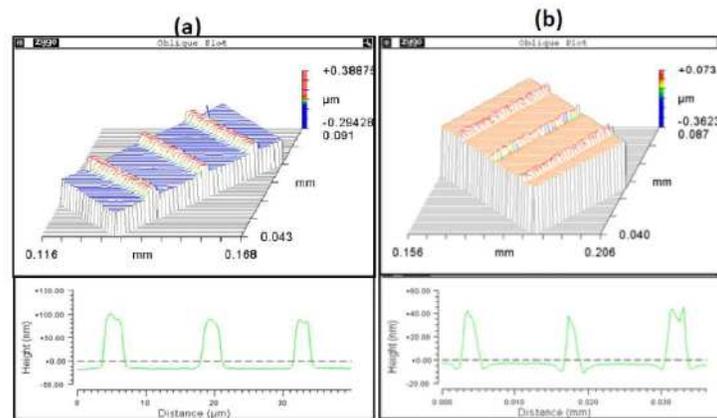


Fig. 3. (a) Optical microscope topography and cross sectional image (26 MHz, 0.35 W), (b) optical microscope topography and cross sectional image (13 MHz, 1 W).

In Fig. 4(a), EDX result clearly shows the presence of oxygen in irradiated lines which are believed to be due to Si-O-Si bounds. In an effort to verify the elemental composition of the embossed lines, a micro-Raman spectroscopic analysis was conducted. Back scattering microraman analysis was performed at room temperature using 532 nm line of Ar ion laser source. The Raman spectroscopic measurements on the processed samples showed a sharp peak at the wavenumber of  $519\text{ cm}^{-1}$ , which is the characteristic peak of silicon. Also, a hump was observed at the wavenumber of  $954\text{ cm}^{-1}$  indicating the existence of silicon oxide [19]. (See Fig. 4(b)). Therefore, it can be concluded that the irradiated zone was converted into silicon oxide.

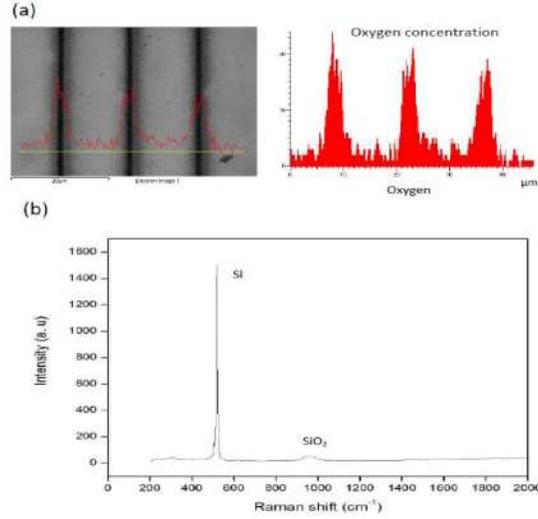


Fig. 4. (a) Graph of EDX spectroscopy analysis (b) Graph of Micro-Raman spectroscopy analysis.

The growth of an oxide layer can be explained by a fundamental thermal model [20]. Recent simulations using various thermal models have shown that thermal oxidation of silicon takes place at temperatures in the range of 700~1300 °C [20–24]. In the following analysis, it is assumed that if the temperature of the silicon surface is brought up and kept in the range of 700~1300°C (1000~1600 K), oxidization occurs.

In the analyses of the heat accumulation, the surface temperature at the end of a laser pulse,  $\Delta T$ , can be approximately calculated by the following formulas [25].

$$\Delta T = \frac{I_a \tau_l r^2}{4kt\sqrt{\pi Dt}} \quad (1)$$

Where  $I_a$  is the absorbed laser light intensity,  $r$  is the radius of the focal spot,  $\tau_l$  is the pulse duration,  $k$  is thermal conductivity,  $D$  is thermal diffusivity of the silicon and  $t$  is the pulse interval. Pulse interval  $t$  is given by  $t=1/f$  ( $f$  is the pulse frequency).

The accumulated temperature raise at the end of  $N^{\text{th}}$  pulse is  $T$  [25]:

$$T = N \times \Delta T = N \times \frac{I_a \tau_l r^2}{4kt\sqrt{\pi Dt}} \quad (2)$$

The light intensity,  $I_a$ , can be estimated by the reflection coefficient,  $R$ , at a wavelength of 520 nm and residual energy coefficient,  $K$  [26]:

$$I_a = K \times (1 - R) \times I_i \quad (3)$$

The incident light intensity,  $I_i$ , is calculated from laser power,  $P$ , pulse frequency,  $f$ , which is the reciprocal of pulse interval,  $t$ , and laser spot diameter,  $d$ .

$$I_i = \frac{4P}{\pi \tau_l d^2 f} \quad (4)$$

Substituting Eqs. (3) and (4) in Eq. (2), it is simplified to:

$$T = N \frac{K(1-R)P}{4k\sqrt{\pi^3}Dt} \quad (5)$$

Previous studies showed that the reflection coefficient of silicon during irradiation with femtosecond laser is 0.393 at a wavelength of 488 and 0.329 at the wavelength of 800 nm [27]. Thus, the reflection coefficient of silicon at a wavelength of 520 nm is calculated to be around 0.38. When the fluence is less than ablation threshold, experiments revealed that  $K$  is around 0.8 for silicon [28]. In our experiment, the speed of scanning is 500 mm/s, the thermal conductivity ( $k$ ) is  $155 \text{ W/(mK)}$  and the thermal diffusivity is  $8.5 \times 10^{-5} \text{ m}^2/\text{s}$  [29]. Fig. 5(a) shows the surface temperature at various pulse frequency and average power calculated from Eq. (4).

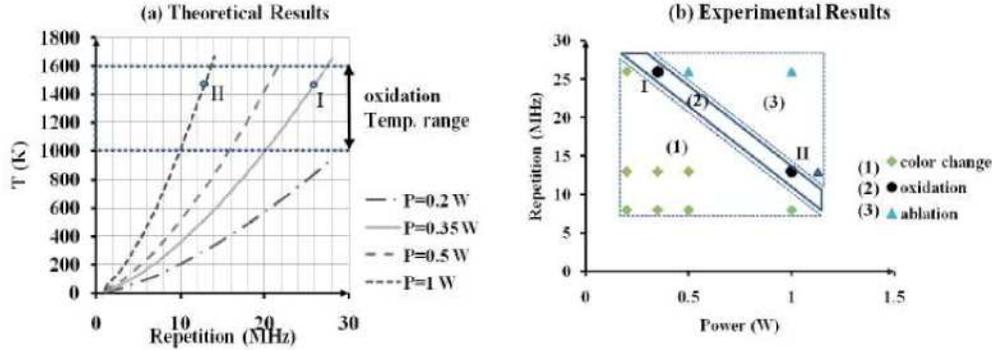


Fig. 5. (a) theoretical results based on Eq. (4) (Relation between  $T$  and frequency at various powers) and (b) Experimental results.

As shown in the Fig. 5(a), the temperature of silicon substrate can be brought up to 1450 K using 214 femtosecond pulsed laser light at 0.35 W with frequency of 26 MHz (point I) and at 1 W with frequency of 13 MHz (point II) which could lead to the formation of silicon oxide on the substrate surface. This calculation is in agreement with the results of our experiment. Figure 5(b) maps the range of laser parameters used for our experiments and the observed morphology alteration. Only two points, (I) and (II), fall into the oxidation temperature ranges in Fig. 5(a) and this is where we observed the embossed lines. Figure 5 (b) defines three zones (1), (2) and (3) which can be named as the color-change, oxidation and ablation zone, respectively. As Fig. 5(b) presents, oxidation occurs only at a narrow band of Zone (2), which is slightly below the border line of ablation. This means that direct oxidation with femtosecond laser requires a stringent parameters control. Even a slight deviation in laser parameters, for examples fluctuation in laser power, will result in surface temperature drift and will not result in oxidation. Therefore, higher pulse frequency is preferred for oxidation since at the same laser power the pulse energy fluctuation is lower at higher pulse frequency. This explains why we observed better repeatability at 26MHz during the experiments.

Increasing pulse frequency has noticeable influence in heat accumulation process; High pulse frequency results in both decreasing the heat dissipation between pulse intervals and increasing surface temperature at the end of  $N^{\text{th}}$  pulse. Therefore, with the same laser power, the surface temperature would be higher at 26 MHz in comparison with 13 MHz [30]. Consequently, increasing pulse frequency results in increasing the line height.

#### 4. Conclusion

In this study, we proposed a new method for laser direct patterning of silicon oxide on Si-substrate, using a Mega Hertz femtosecond pulsed laser. Embossed lines of silicon oxide around  $3\text{--}4 \mu\text{m}$  width and less than 100 nm height were generated by irradiated with laser at 1 W, at 13 MHz and 0.35 W, at 26. A Scanning Electron Microscope (SEM), a Micro-Raman and Energy Dispersive X-ray (EDX) spectroscopy and an optical microscope were employed to characterize the oxide layers. Using high frequency femtosecond pulsed laser which makes this technique particularly suitable for rapid prototyping and custom-scale manufacturing for a

wide variety of applications in MEMS, NEMS, fabrication of semiconductor and Lab On a Chip systems which demand for flexibility in re-design.

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