Femtosecond laser processing of crystalline silicon

D. V. Tran(a), Y. C. Lam(a),(c), H. Y. Zheng(b), V. M. Murukeshan(c), J. C. Chai(c), D. E. Hardt(d)

(a) Singapore-MIT Alliance, Nanyang Technological University, Singapore 639798
(b) Singapore-MIT Alliance & Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(c) Singapore Institute of Manufacturing Technology, 71 Nanyang Drive, Singapore 638075
(d) School of Mechanical and Production Engineering, Nanyang Technological University, Singapore 639798

Abstract—This paper reports the surface morphologies and ablation of crystalline silicon wafers irradiated by infrared 775 nm Ti:sapphire femtosecond laser. The effects of energy fluences (below and above single-pulse modification) with different number of pulses were studied. New morphological features such as pits, cracks formation, Laser-Induced Periodic Surface Structures (LIPSS) and ablation were observed. The investigation indicated that there are two distinct mechanisms under femtosecond laser irradiation: low fluence regime with different morphological features and high fluence regime with high material removal and without complex morphological features.

Index Terms—crystalline silicon, femtosecond laser, morphology, ablation, incubation effect.

I. INTRODUCTION

 Silicon is an important material in semiconductor industry and useful for MicroElectroMechanical Systems (MEMS) devices. Laser processing of silicon (Si) has received significant attention in the last several decades. In the past, one of the interests in laser processing of Si is the “laser annealing” process in which lattice damage by ion implantation of dopants such as Boron (B) or Phosphorus (P) into the crystalline Si could be removed and electrically activated [1].

Laser annealing of Si has been demonstrated to offer advantages over furnace annealing such as exceeding the solid solubility limit of dopants in Si and having less defects after annealing, leading to the improvement in the electrical properties and hence the function of the junction subjected to ion implantation. Different laser sources with wavelengths from far infrared to ultraviolet (UV), for example, continuous wave (CW) CO2 laser (λ = 10.6 μm) to pulsed lasers such as ruby (λ = 0.694 μm), Nd: YAG (λ = 0.1064 μm), and excimer (λ = 0.249 μm) lasers have been used [1]. The fundamental frequency, for example, Nd:YAG laser (λ = 0.1064 μm), could be doubled, tripled and quadrupled to 0.532 μm, 0.353 μm and 0.265 μm respectively to enhance absorption on crystalline Si (indirect band gap ≈ 1.13 μm).

One of the important parameters in laser processing is the laser pulse width (or pulse duration). The first laser invented in 1960 by Maiman [2], based on a ruby crystal and pumped by a xenon flash discharge, created a laser pulse lasting between millisecond to microsecond. New laser generation techniques such as Q-switching and mode-locking has been developed since the first ruby laser reduced the pulse width to nanosecond (1 ns = 10−9 s), picosecond (1 ps = 10−12 s), femtosecond (1 fs = 10−15 s) and recently attosecond (1 as = 10−18 s) [3] duration. Among these pulse durations, fs laser has been attracted many interests in the last decade. By shortening the pulse width to fs duration (sometime called ultrashort or ultrafast pulses) it follows the studies of ultrashort phenomenon in matters and laser-induced phase transformations. The former related to the capability to use fs laser to observe phenomenon with fs time resolution, for example, the energy transfer from electrons to the lattice in solids [4]. New subfields of science have been created, namely femtochemistry [5] and femtobiology [6] in which the phenomena could be resolved on ultrashort time-scale resolution. The focus of this paper is the capability of an ultrashort laser pulse to induce a novel phase transitions on matters, for example Si.

In the late seventies, one of the studies created many
interests is on the phase transformation processes by laser on Si in the laser annealing process as mentioned above. Most of the studies have been carried out on ns laser pulses. This ns laser pulses provide fluences (energy densities) high enough to melt a surface layer of amorphous Si created by ion implantation of dopants on single crystalline silicon. Resolidification of the molten silicon removed the lattice damage and electrically activate the dopants with free defects. Nanosecond laser pulses could also be used to recrystallize fine-grained polycrystalline Si films deposited on insulating substrate, for example, SOS (silicon-on-sapphire) with practical applications in silicon technology [1]. For ps laser pulses, when the laser irradiates on the materials, heating and cooling rates up to $10^{14} \text{C/s}$ could be obtained [7]. With cooling rate at these magnitudes, the kinetics of phase transitions may lead to new phenomena. Amorphization of single crystalline silicon or recrystallization of this amorphous layer could be carried out by controlling the energy density of the Gaussian laser pulse [7]. In a recent experiment, near-infrared fs laser-induced crystallization of amorphous silicon on insulator have been performed [8]. It is shown that large grains of polycrystalline silicon on oxidized silicon wafer deposited by low-pressure chemical vapor deposition (LPCVD) could be achieved when fs laser is scanned over the sample. Unlike ns laser annealing (linear annealing), fs laser annealing (FLA) was a nonlinear photoenergy absorption process where non-equilibrium between the electrons and the lattice dominates [9]. Amorphization of silicon by fs laser was also observed when studying ablation of crystalline silicon [10]. A layer of amorphous silicon around the ablated holes was found by using cross-sectional Transmission Electron Microscopy (TEM). This study was in contrast with the postulation that direct solid-vapor transition [11] and negligible hydrodynamic motion [9] were assumed on femtosecond laser ablation of materials.

One of the novel phase transformations in using fs laser is the ablation process. In the last decades, many interests focus on the fs ablation with potential applications in industry (high precision microfabrication) and in medicine [12]. With the advent of the Chirped Pulse Amplification (CPA) technique [13] to increase the average power for micromanipulating applications, a wide set of parameters, especially the pulse duration, could be varied while other parameters, for example, the focusing condition, are kept unchanged. With this capability, ablation materials with fs laser has been studied and compared to that of ns ablation in different materials (metals [11], semiconductors [14], dielectrics [15], and polymers [16]). Advantages of fs laser ablation over ns ablation have been demonstrated for high precision in micromachining applications. Some of the salient features of ablation with fs are (i) reduction of Heat-Affected Zone (HAZ) and defects (burr, micro cracks), (ii) deterministic ablation threshold, (iii) sub-micrometer processing and (iv) ability to machine transparent materials.

In this paper, we report the morphologies and ablation on crystalline silicon irradiated by fs laser. The experiment is studied with both low (below single-pulse modification threshold) and high (above single-pulse modification threshold). The effect of fs laser fluences with different number of laser pulses on Si will be presented. New features on morphologies of crystalline silicon are discussed.

II. EXPERIMENTAL

The experimental setup consisted of an amplified kHz Ti:sapphire femtosecond laser system (CPA-2001, Clark-MXR, Inc.) illustrated in Fig. 1. The laser emits pulses of 150 fs at Full Width Half Maximum (FWHM) with linearly-polarized light at a central wavelength of approximately 775 nm in the near infrared. The laser has Transverse Electromagnetic Mode TEM$_{00}$ and nominal repetition rate of 1 kHz. The total pulse energy $E_{\text{pulse}}$ was attenuated by a rotating half waveplate followed by a linear polarizer (attenuator in Fig. 1). The repetition rate of the laser was lowered to and kept at 250 Hz and synchronized with a mechanical shutter, which allowed control on the number of laser pulses on the target. The laser beam was made circularly-polarized by using a quarter waveplate in the beam path before the focusing lens (focal length $f = 50$ mm). The beam was directed perpendicular to the sample surface, forming an almost circular spot on it. The radius of the spot sizes $\omega_0$ (defined at 1/e$^2$ of peak intensity) was measured by the knife-edge technique [17]. Two silicon wafers, thickness of 100 $\mu$m and 460 $\mu$m, were subjected to different pulse energy fluences. The fluences were varied by changing the total pulse energy and the focusing spot size. At the given laser fluence, the same experimental condition was kept constant except for the number of laser pulses. Each data point was repeated 5 times with a fixed number of pulses. A computer-controlled xyz-stage allowed positioning of the wafer at the desired location. The experimental results were reproducible. Using an optical microscope and a Scanning Electron Microscope (SEM), the laser-induced surface damage morphologies and ablation of the crystalline silicon wafers were analyzed. We defined surface damage as a sudden change in surface damage morphology, i.e., modification, not necessarily ablation, when observed under optical

![Fig. 1. Schematic of the experimental setup](image-url)
microscope or SEM.

III. RESULTS AND DISCUSSION

The surface damage morphologies and ablation of crystalline silicon depend on the energy fluences and the number of pulses. As shown later, the surface morphologies of silicon were different for energy fluences below and above single-pulse modification threshold. The effect of number of pulses will be discussed.

The relationship between the total pulse energy, \( E_{\text{pulse}} \), and fluence is derived as follows. For a Gaussian beam, the spatial and temporal profile of the laser intensity is [18]

\[
I(r,t) = I_0 \exp\left(-2 r^2 / \omega_0^2\right) \exp\left(-2 t^2 / \tau^2\right)
\]

(1)

where \( I_0 \) is the peak intensity at the center, \( \omega_0 \) and \( \tau \) are the spatial radius and temporal radius, respectively, at the \((1/e^2)\) intensity contour, \( r \) is the radial coordinate of distance from the propagation axis and \( t \) is the time variable. The spatial distribution of the energy fluence

\[
E(r) = \int_0^\infty I(r,t) dt = E_0 \exp\left(-2 r^2 / \omega_0^2\right)
\]

(2)

where \( E_0 \) is the peak fluence at the center of the beam. The peak fluence relates to the total pulse energy as

\[
E_{\text{pulse}} = \int E(r) 2 \pi r dr = \int_0^\infty E_0 \exp\left(-2 r^2 / \omega_0^2\right) 2 \pi r dr
\]

\[
= \frac{\pi \omega_0^2 E_0}{2}
\]

(3)

or

\[
E_0 = \frac{2 E_{\text{pulse}}}{\pi \omega_0^2}
\]

(4)

From equation (4), the peak fluence \( E_0 \) of the laser could be varied by changing the total pulse energy \( E_{\text{pulse}} \) or the spot size \( \omega_0 \). We will investigate surface morphologies and ablation of Si from low energy fluence to high fluence with different number of pulses.

A. Fluence below single-pulse modification threshold

We have studied damage morphologies of crystalline silicon at energy fluence as low as 0.03 J/cm² (pulse energy \( \approx 0.24 \text{ mJ} \), spot size \((1/e^2)\) diameter \( \approx 1.4 \text{ mm}\)) [19]. SEM images of silicon at this fluence regime are shown in Fig. 2.

For a single pulse, we did not observe any surface damage at the processed region on the silicon surface under optical microscope or SEM. When the sample was subjected to 10 pulses, no trace of surface damage was observed as well, see Fig. 2(a). The SEM image was identical to that of the original phase. For 20 laser pulses, surface damage appeared as shown in Fig. 2(b). Surface damage was not easily recognizable since the phase change of the treated region was nearly identical with the original phase, which was crystalline. However, as can be observed later, the surface damage at this low number of pulses was important for surface damage evolution at subsequent laser pulses.

The surface damage in Fig. 2(b) at sub-threshold pulses shows the incubation effect, i.e. accumulation of energy, of materials when irradiated with multiple pulses. This effect was observed in many materials for ns, ps and fs lasers [20]–[24]. Jhee et al. [20] observed this incubation effect on silicon irradiated with ps laser pulses. They suggested that damage precursors by multiple pulses were due to the long-lived excitations or accumulation of permanent states. The incubation period of these states could last as long as 3 seconds and independent of the repetition rate. They showed that there existed a multiple pulse damage threshold or fatigue limit below which no damage was supposed to occur at an infinite number of laser pulses. They calculated this fatigue limit for silicon to be about 0.32 J/cm².

One of the characteristics differentiating fs to longer laser pulses (including ps laser pulses) is that fs laser has lower fluence damage threshold. It was demonstrated that fluence breakdown threshold \( F_{\text{th}} \) did not follow the scaling of \( F_{\text{th}} \approx \sqrt{\tau} \) (where \( \tau \) is the pulse duration) when the pulse duration was shorter than 10 ps [25]. For long laser pulses, heat diffusion could involve a much larger volume than the laser focus. As the pulse width decreases, the heat-affected volume due to conduction was smaller. As a result, a lower fluence was sufficient to create surface damage or ablation on materials with fs lasers.

The accumulation of sub-threshold laser fluence when employing fs laser resulting in damage, i.e. incubation effect, were also observed on dielectrics [22] and tissue [23]. The damage on dielectrics could be explained by F-center formation during excitation by first or subsequent laser pulses. The optical break down in dielectrics occurred when local stress created by these F-center formations was built up [26] and created damage at a certain number of laser pulses. The surface damage on tissue, on the other hand, could be explained by cumulative thermal effect [23] when the material was irradiated with high repetition rate laser pulses.

As such, although the laser fluence employed here was of 0.03 J/cm², one order of magnitude lower than the fatigue limit reported by Jhee et al. [20] for long pulse laser, it was not surprising to have observed surface damage with increasing number of laser pulses as shown in Fig. 2(b).

Although our experimental conditions were not exactly the same as Bonse et al. [24], we expected our results to be similar to theirs as they also employed fs laser to irradiate on crystalline silicon. Their single pulse threshold for surface modification was 0.26 J/cm². They employed the same equation in Jee et al. [21] to describe the incubation effect for multiple pulses. Using the same constants and equation of Bonse et al., it could be calculated that for 20
laser pulses, the surface modification threshold would be 0.16 J/cm². Alternatively, it could be obtained that for a laser fluence of 0.03 J/cm², the number of pulses required for surface modification would be approximately 7x10⁶. Thus, with our laser fluence of 0.03 J/cm², it was expected that no damage could be observed for a single pulse, or for ten pulses. However, as compared with Bonse et al. [24], our observation of surface damage for 20 pulses was rather low either for the value of the fluence, or the number of pulses. The differences in observations could be because of the differences in experimental conditions as will be elaborated later, and we could not rule out the possibility that the equation employed by Bonse et al. might not hold for our experimental conditions.

After surface damage occurred (Fig. 2(b)), increasing number of laser pulses at the same laser fluence created different surface damage morphologies on silicon, as seen in Fig. 2(c). After 20 pulses (Fig. 2(b)), the surface damage was hardly recognized under SEM. However, at 50 pulses, the surface damage became easily recognizable under SEM, see Fig. 2(c). The effect of previous pulses had changed the properties of the materials and hence the absorption of laser energy. At this pulse number, the overall image of the surface damage was similar to that of Fig. 2(b). In addition, some cracks were observed on the surface.

At higher number of pulses, the surface damage area became larger, see Fig. 2(d) and Fig. 2(e) after irradiation with 100 and 500 pulses respectively. The surface damage areas were larger at higher number of pulses because of the effect of previous pulses. At 500 pulses, many pits began to appear (Fig. 2(e)). The formation of pits at this number of pulses was analogous to previous observation by Jhee et al. [20] at the beginning of the surface damage of silicon using ps laser pulses and could be explained by the evaporation of silicon by the accumulation of laser energy. As shown later, more pits were created at higher number of pulses in contrast to that reported by Jhee et al. [20] that these pits were grown and were the seeds for the formation of ripples and crater-like structures with increasing number of pulses. The diameters of these pits were larger at the crack positions compared to the surrounding regions, as can be seen in Fig. 2(f) and Fig. 2(g). In Fig. 2(f) and Fig. 2(g), more re-deposited materials appeared and were located at the boundary between the damaged and undamaged regions. At 5000 pulses, Fig. 2(h), the surface damage developed at the pit positions. Interestingly, center region had not developed any pits, see Fig. 2(h).

In contrast to reports on formation of ripples and columnar structures when irradiated with multiple pulses [20]–[23] we did not observe these self-organized structures at this fluence with multiple pulses (from low number to high number of pulses). Instead, many pits were created and formed the seed for the development of surface damage, as clearly seen in Fig. 2(h). In the fs regime, the different observation of surface damage morphologies on silicon from previous reports [20]–[27] might be explained by the differences in the experimental set up as follows.

Firstly, comparing to the work of Bonse et al. [24], the laser fluence employed here was lower and the spot size was larger. As a result, the surface damage morphology was not observed at single pulse or even at 10 pulses (Fig. 2(a)) while it was not the case in their experiments. Secondly, the laser was made circularly-polarized instead of linearly-polarized as in their work. It was expected that polarization of the laser beam affected the surface damage similar to what has been observed recently in the laser drilling process with ultrashort laser pulses [28]. Finally, it
was also expected that the surface orientation of the silicon influenced the surface damage morphology. The surface orientation employed here was (100) rather than (111) as in Bonse et al. [24]. Experiments with ns pulses had demonstrated that [21] the accumulative damage by multiple pulses depended on the surface orientation. Differences in laser fluence, polarization, and surface orientation might explain the differences in observation of surface damage morphologies. These factors would contribute to the differences between our observations.

In Fig. 3, we show SEM images at fluence of 0.25 J/cm² (pulse energy ≈ 0.36 mJ, and spot size (1/e²) ≈ 300 µm in diameter) [29]. Similar to morphologies in Fig. 2., for a single laser pulse, no trace of surface damage morphology could be detected when the processed region was observed under optical microscope and SEM. However, after irradiating with 5 pulses, surface damage morphology appeared; see Fig. 3(a). The phenomenon is similar to the incubation effect discussed above for fluence of 0.03 J/cm². However, in this case since the fluence is higher the surface damage of silicon starts at lower number of pulses i.e., surface damage starts at about 5 pulses at 0.25 J/cm² whereas it starts at 20 pulses at 0.03 J/cm².

When the number of laser pulses was increased at constant fluence (80 consecutive pulses) different surface damage morphologies were observed, see Fig. 3(c). At this number of pulses, the surface damage area became larger compared to that of low shot numbers as in Fig. 3(a) (note the scale bar on the SEM images). Obviously, the effect of previous pulses had changed the surface microstructure and morphology and hence the absorption. To qualitatively illustrate the different surface damage morphologies on Fig. 3(c), Fig. 4 was used to schematically characterize different damage regions with respect to the energy fluence distribution and thresholds of the Gaussian beam profile [29]. As shown later, the patterns of damage morphologies schematically illustrated in Fig. 4 were repeatable with increasing number of pulses. The only difference is that these damages were more distinguishable with higher pulses.

Different surface damage morphologies in Fig. 4 could be qualitatively explained (from center to outermost regions of damages). At the center region where the laser fluence was highest (denoted as ablation in Fig. 4), ablation was expected to occur along with Laser-Induced Periodic Surface Structure (LIPSS) patterns, which were clearly observed. This was not surprising since the material in this region was irradiated with the highest energy fluences of the Gaussian beam. A similar pattern was observed recently with femtosecond pulses by other researchers [24]. The major difference was that our peak fluence was below the single-pulse surface damage threshold while the patterns observed previously were at peak fluence above the single-pulse damage threshold [24]. The next annulus region was the re-deposited materials because of the ablation at the center. This could be similar to the “rim” in the recent study on indium phosphide (InP) irradiated by single and two fs pulses. The formation of the rim may presumably due to either the momentum transfer from the ablated material (at the center region) to the molten surface layer or the surface tension gradients [30].

The next two annulus regions (one inside the border of the “rim” and other outside the border of the rim, denoted as central modification region in Fig. 4) was attributed the modification region. These two annulus could be expected to be in the amorphous states or polycrystalline silicon since there was a difference in reflectivity when observed under SEM. As discussed in the introduction, amorphous
or polycrystalline silicon was observed on crystalline silicon when irradiated with proper energy fluence with both long and ultrashort pulses. The formation of amorphous or polycrystalline silicon on single crystalline silicon was a kinetic process of resolidification of materials from melting. The amorphous phase could be formed on crystalline silicon because of the cooling rate during the solidification process is fast (about 10¹⁴ °C/s [7]) and there is no time for the material to return to the crystalline phase. This phase change on crystalline silicon was confined only within a certain laser fluence range. With the laser fluence higher than this range (for example at the center of the Gaussian beam), the cooling rate on solidification was low enough to allow epitaxially re-crystalline from the substrate.

In the next annulus region, we expect that there was no phase change. The phase of this region was expected to be consistent with the original phase as observed under SEM. Although this annulus region was repeatedly illuminated by multiple pulses the accumulation of energy was not high enough to modify the surface. As schematically illustrated in Fig. 4, the energy fluence was presumably lower than the multiple-pulse modification threshold and hence do not create any phase change. Interestingly, there was a phase change to the annulus region next to the above no phase change region by multiple pulses the accumulation of energy was not high enough to allow epitaxially re-crystalline from the substrate.

B. Fluence above single-pulse modification threshold
At a higher fluence level, we have observed a different surface damage and ablation mechanism on crystalline silicon [32]. Fig. 5 shows SEM images of silicon when subjected to single-laser pulse with increasing laser. Comparing the SEM images of Fig. 5 when the silicon was subjected to single-pulse with increasing fluence level with Figs. 2 and Fig. 3, we could observe clearly the difference in surface damage and ablation mechanism. The surface damage and ablation was driven by more material ejected out of the center of the illuminated regions, i.e. at the peak fluence of the Gaussian beam. No features such as ripples and column formation were observed in this regime. This ablation mechanism in silicon could be analogous to the strong ablation phase in dielectrics [33] and the absorption mechanisms by heat penetration depth in metals [34] as reported recently.

From Fig. 5, one could observe that the radii or diameters of the damaged areas (at the center of the laser focus) increase with increasing laser fluence. If we assume that the laser pulse had a Gaussian distribution intensity profile, the development of the damaged features (e.g. ablated hole areas in Fig. 5) should be consistent with the distribution given by equation (2).

From equation (2), the radius r or diameter d of the damaged features relates to the peak fluence $E_0$ by

$$d^2 = 4r^2 = 2\omega_0^2 \left(\ln E_0 - \ln E(r)\right)$$

Since there is a linear relationship between the peak fluence and the laser pulse energy (equation (4)), and with equation (5), one can obtain a linear relationship between the diameter square of the surface damaged areas versus the logarithm of the laser pulse energy. The laser focus radius $\omega_0$ could be calculated from the slope of this plot. The peak fluence could then be calculated again using equation (4). From equation (5), one could obtain the fluence threshold (expressed in peak fluence of the beam) by extrapolating the linear line to the horizontal axis. This technique was first introduced by Liu et al. [18] when studying laser-induced damage solid-liquid transformation in silicon with ps laser pulses. Recently, the technique was used successfully even with pulses as short as 5 fs on dielectrics [35].

Using this technique we calculated the ablation threshold for single pulses (about 7.8 J/cm²) and the laser focus $\omega_0$ (about 33 µm) at 1/e² intensity) within the experimental error of the energy fluctuation of about 5%. Fig. 6 shows the relationship between the peak fluence and the diameter square of the ablated holes in Fig. 5. The value of the laser focus $\omega_0$ (obtained from the fitted line) was comparable to the value obtained when measuring by the knife-edge scanning method (about 30 µm). The ablation threshold in this regime was significantly different from the low fluence regime. As mentioned above, the ablation mechanism in this regime might be characterized by the higher removal of materials than in the gentle phase ablation regime. This could be verified by comparing the SEM images from Figs. 2 and 3.
IV. CONCLUSION

In this paper, we report surface damage morphologies and ablation of crystalline silicon interacted with femtosecond laser pulses at different energy fluences and number of pulses. At low energy fluence regime, we observed new features such as pits and cracks formation which exists even for a high number of pulses. We also have observed similar morphologies, for example, Laser-Induced Periodic Surface Structure (LIPSS) and columnar formation. At high fluence regime, we did not observe these morphologies but high removal of materials which left a crater consistent with a Gaussian distribution of the pulse.

**ACKNOWLEDGMENT**

D. V. Tran would like to acknowledge the financial sponsorship of the Singapore-MIT Alliance (SMA) in the form of a research scholarship. The technical support provided by SIMTech is also gratefully acknowledged.

**REFERENCES**


