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Picosecond laser ablation for silicon micro fuel cell fabrication

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Abstract

We have investigated laser ablation as a microfabrication approach to produce micro fuel cells (MFCs) in silicon. Picosecond pulses (15 ps) at a wavelength of 355 nm are used to make all of the MFC structures. To assess the benefits and drawbacks of laser ablation, reference cells have been produced by deep reactive ion etching (DRIE) using matching geometries. Ablated and etched cells have been evaluated and compared side by side. Our conclusion is that picosecond laser ablation is very well suited for MFC fabrication. The ablated cells match or excel DRIE-microfabricated cells in terms of current and power densities. Ablated MFCs achieved 47.6 mW cm⁻² of power density and 121 mA cm⁻² current density.

S Online supplementary data available from stacks.iop.org/JMM/23/055021/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Currently, portable electronic devices are powered with Liion batteries, but the quest for longer battery life is ongoing. Micro fuel cells (MFCs) have the potential to increase the energy storage for these portable devices [1]. If the MFCs are microfabricated from silicon, mature silicon microsystems technology can be used [2–4].

In recent years, laser ablation has gained some popularity [5–7] in microfluidics fabrication. The advantages of laser ablation include rapid prototyping, maskless multilevel material removal and noncontact operation. Laser ablation has also seen minor adoption in MFC microfabrication [8–15]. This includes chip dicing [8], flowfield ablation [9, 10], inlet hole drilling in steel, silicon and nickel [11–13], patterning of a hard mask for a subsequent reactive ion etching (RIE) step [14] and membrane-electrode assembly (MEA) segmentation [15].

While laser pulses with a duration of around a nanosecond offer good micromachining speeds for silicon and metals and, under the right conditions, can be used to ablate wider bandgap dielectrics [16–20], they produce a large heat-affected zone (HAZ) and droplets in and around the ablated area. Femtosecond lasers overcome these issues due to nonlinear optical phenomena at high light intensities and the short duration of femtosecond pulses, which cause crystal lattice nonthermal disordering. Furthermore, the thermal penetration depth of femtosecond pulses is very small, leading to a minimized volume in which energy is deposited by each pulse [19–25]. Unfortunately, femtosecond laser systems are more expensive than nanosecond systems of matching ablation performance (in terms of material removed in unit time).

Picosecond lasers offer an interesting compromise for material ablation that has been studied by several authors [17, 20, 24–28]. Whereas nanosecond ablation has high energy per pulse and high ablation rate, and femtosecond lasers have small thermal penetration depth and high

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Figure 1. Left: exploded view of a MFC. Right: construction of a flowfield/current collector silicon chip.

precision, picosecond ablation offers reasonable rates with good dimensional control and a small HAZ.

In this paper, we present the first prototype of laser-ablated silicon MFC. To determine the viability of replacing the plasma etching steps of silicon with laser ablation techniques, we have fabricated MFC chips using both technologies and compared their microstructures and cell performance.

2. Experimental methods

2.1. Construction and operation

The MFCs described in this work are composed of two silicon chips that function simultaneously as flowfields and current collectors. The basic design is similar to the perforated or mesh-like structures introduced a decade ago [29–31], with the difference being that the device in this work relies on highly conductive silicon ($\rho = 0.01 \ \Omega$ cm) to aid in current collection rather than thick gold metallization or gold mesh.

For the MEA, a commercial product (GoreTM Primea[®]) is used, based on Nafion[®] membrane, with Pt loadings of 0.3 mg cm⁻² on the cathode and 0.1 mg cm⁻² on the anode side. The MEA is clamped between two chips. In figure 1, on the left, we show an exploded view of an MFC with the two chips and the MEA separated. On the right, a single chip with the flowfield is depicted and some dimensions are noted. The reactant gases enter the flowfield through one inlet hole and leave from the diagonally opposite one. All of the dimensions pertaining to a single chip are summarized in table 1. For reactant gases, we used hydrogen as the fuel and oxygen as oxidant.

We studied four different chip designs with different channel geometries (summarized in table 1); these geometries were identical in both the plasma-etched and laser-ablated chips. The most important difference between ablated and plasma-etched channels is the cross section at the bottom: the ablated channels are expected to have a triangular or Gaussian cross section while the plasma-etched channels had a rectangular one.

Table 1. Characteristic dimensions of the MFC silicon chips for designs A, B, C and D.

Feature	Dimension	А	В	С	D
Flowfield area Chip thickness	$\frac{10 \times 10 \text{ mm}^2}{400 \ \mu \text{m}}$				
Number of channels	·	5	10	5	10
per mm Flowfield channel width	(µm)	30	30	60	60
Pitch Inlet hole diameter	(µm) 1 mm	200	100	200	100

2.2. Laser ablation microfabrication process

A single-side-polished, highly doped silicon wafer was ablated with a picosecond laser system consisting of a Lumera HYPER RAPID 50[®] laser source of 355 nm wavelength, with a pulse duration of 15 ps and a galvanometric scanning system. The Lumera laser source is capable of repetition rates from 400 kHz with pulse energy of 46 μ J up to 1 MHz with pulse energy of 6.25 μ J. The minimum and maximum repetition rates were used to test the effect that the larger (46 μ J) versus smaller (6.25 μ J) pulse energies would have on the microchannel quality and ablation speed. The 1/e² beam waist (beam diameter at focal distance) was 36 μ m in both cases, producing a beam intensity of ~300 GW cm⁻² and ~40 GW cm⁻² for the 400 kHz and 1 MHz cases respectively.

The silicon wafer was placed on a static stage with the polished side up, facing the scanning laser beam. A vacuum hose was placed in the vicinity of the ablated wafer to suck away airborne silicon particles. To create the inlet holes, the beam was scanned in repeated concentric spirals to fully cover the surface of a 1 mm diameter circle. A total of 32 chips could fit on a 10 cm diameter wafer.

After the ablation, the wafer was immersed for 1 min in an isotropic wet etchant for silicon and SiO₂–HNO₃:NH₄F:H₂O in 44:1:18 volume ratios to remove silicon oxide and loosely attached silicon particles from the burr area at the top of the channels. 40 nm of chromium was sputtered over the flowfield to increase long-term stability and electrical conductivity of the



Figure 2. Apparatus for MFC performance characterization. Picture (a) and diagram (b).

fuel cell and 200 nm of aluminum was sputtered on the back for electrical contact. Finally, the wafer is diced to separate the chips.

2.3. Deep reactive ion etching (DRIE) microfabrication process

We used a traditional process flow that consisted of the following: A highly boron-doped, 400 μ m thick silicon wafer was thermally oxidized with wet oxidation at 1050 °C to form a 500 nm thick oxide layer. The layer was patterned with photolithography and wet etching in a buffered HF solution, followed by resist strip to define the flowfield channels. The flowfield channels were etched with a cryogenic inductively coupled plasma (ICP) RIE device to a depth of 50 μ m. The use of thermal oxide as an etch mask was necessary, as stress causes photoresist to crack at the cryogenic temperatures used in the DRIE step. To create the inlet holes, through-wafer DRIE etching was performed from the back, with 200 nm sputtered, lithographically patterned aluminum as a hard mask. The final steps of 40 nm thick chromium sputtering and dicing were identical for both the DRIE and ablated processes. More information on the process flow can be found in [2].

All RIE processing was done in a cryogenic ICP reactor (Oxford Instruments Plasmalab System $100^{(\text{R})}$). This device allows for the plasma and the plate RF powers to be separately adjusted. The process parameters were substrate temperature -110 °C, SF₆ flow 100 SCCM, O₂ flow 15 SCCM, ICP power 2000 W, RF power 3 W. With the given parameters, the etch rate for the anisotropic etching of the channels and through-wafer was 7 μ m min⁻¹. Because of the ICP RIE's circular clamp, only 16 chips could fit on one 10 cm diameter wafer.

2.4. MFC performance characterization

The MFCs were characterized by assembling and clamping them in a custom-built aluminum jig (figure 2). The electric connections were made with the jig's aluminum blocks, as they are in contact with the aluminum-metalized back of the chips. Gases were introduced into the cathode and anode flowfields through appropriate fittings threaded into the aluminum blocks. The flow was kept constant with the use of a Brooks Instrument[®] mass flow controller at 50 ml min⁻¹. Current and voltage loading and data logging were performed with a computer-controlled Metrohm Autolab PGSTAT100[®] potentiostat equipped with a current and voltage booster (Autolab BSTR10A[®]). The fuel was hydrogen, and the oxidant was oxygen.

2.5. Micro-Raman characterization of laser ablated chips

Raman spectroscopy is a powerful analytical tool used to characterize the chemical composition and crystallinity of matter [32]. Based on the detection of in-elastically scattered light caused by molecular or lattice vibrations, it is a very sensitive method to determine the intrinsic stresses in the crystals that appear during their growth and/or in the device fabrication process [33–35]. When compared to the most used techniques for stress measurements, such as x-ray diffraction, high-resolution transmission electron microscopy and convergent beam electron diffraction, the main advantages of Raman spectroscopy are nondestructive behaviour with a submicron resolution, operation under air conditions and simplicity in sample preparation.

Raman measurements were performed using a confocal Raman system (NTEGRA Spectra[®], NT-MDT) in an upright configuration. A 20-mW DPSS laser (532 nm, LCM-S-111-20-NP25) was used to excite the sample. The system was equipped with a 100×0.7 numerical aperture objective, resulting in a spot diameter of 0.5 μ m at focal distance and a controlled XYZ stage capable of scanning samples in a lateral direction over a 130 μ m \times 130 μ m area. The typical laser powers at the focus were controlled with a resolution of 5 μ W. A laser power of 0.5 mW was applied to avoid heating the samples. The scattered signals were collected by the same objective and then focused through a 100 μ m pinhole. A 532 nm ultrasteep long-pass edge filter rejects residual backscattered laser light, and the signal is directed into a spectrometer (MS5004i, SOL instruments) equipped with a CCD camera thermoelectrically cooled to -60 °C $(1024 \times 127 \text{ pixels}, \text{DV401-BV}, \text{Andor Technology}^{\text{TM}})$. An

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Table 2. Laser ablation parameters.

Parameter	High pulse energy	Low pulse energy
Pulse frequency	400 kHz	1 MHz
Average power	18.4 W	6.25 W
Pulse energy	$46 \ \mu J$	6.25 μJ
Passes for channel ablation	270	1000
Scan speed for channel ablation	4 m s^{-1}	10 m s^{-1}
Resulting channel width	$\sim 60 \ \mu m$	$\sim 30 \ \mu m$
Passes for through-hole ablation	5	28
Scan speed for through-hole ablation	0.4 m s^{-1}	4 m s^{-1}

Echelle grating with ultrahigh dispersion was used, resulting in a spectral resolution of 0.22 cm^{-1} . White light microscope images were captured by another CCD camera.

For the Raman mapping procedure, fresh cuts/cleaves of silicon chips were prepared immediately before the measurements and then mounted perpendicularly to the incident p-polarized laser light. A full Raman spectra map was recorded for a scan area of $129 \times 129 \ \mu\text{m}^2$ with a step of 1 μ m between two points, resulting in a map of 129 \times 129 spectra. The acquisition time was 3 s for each spectrum. The Raman data acquired was processed using the NT-MDT software package (Nova 1.0.26).

3. Results and discussion

3.1. Laser ablation process

The laser process parameters were adapted to obtain flow fields with channel widths of 30 μ m and 60 μ m (tables 1 and 2) and a minimum depth of 50 μ m.

As mentioned before, the selected repetition rates were 400 kHz and 1 MHz, and the beam waist was 36 μ m. These parameters were fixed while the number of scans (passes) and scan speeds were varied. Laser on and off delay times were also optimized. Since these parameters are specific to the model and laser system type (laser source, control card and galvanometric scanner head), the optimization work for the on–off delay times have only been briefly mentioned.

Experiments to determine suitable scanning speeds were performed for both of the 400 kHz and 1 MHz repetition rates. Figures S1 and S2 (in supplementary data, available at stacks.iop.org/JMM/23/055021/mmedia) show SEM images of cross sections of channels ablated in silicon at different scan speeds. Due to the different available pulse energies, for 400 kHz, the channels were scanned seven times, while for 1 MHz they were scanned 20 times (see table 2). The intention was to obtain an approximately similar and measurable ablation depth for both cases.

To obtain the necessary channel depth, a large number of scans were required. Rather than repeating the scan for each channel individually, all channels were ablated consecutively with each scan—distributing the generated heat more homogeneously and minimizing the HAZ.

The effective number of pulses, i.e. the number of times laser pulses hit the same area, is given in formula (1) below [19], where f is the repetition rate, d is the beam waist and v is

the scanning speed. Note that this equation is an approximation and does not take into consideration the pulse duration. It remains correct as long as the pulse duration multiplied by the scanning speed is much smaller than the beam waist (i.e. the spatial enlargement of the illuminated area of a moved single pulse is negligible), which is the case for 15 ps pulses and tens of m s⁻¹ scan speeds.

$$N_{eff} = \sqrt{\frac{\pi}{2}} \cdot \frac{f \cdot d}{v}.$$
 (1)

The effective number of pulses ablating the same spot N_{eff} decreases with increasing scanning speed, since the overlap between pulses is reduced.

In figures S1 and S2, we can clearly observe that lower scanning speeds produce deeper channels. Ablation at a 400 kHz repetition rate (pulse energy of 46 μ J) produces a channel that better approximates a Gaussian curve than that at the 1 MHz repetition rate (6.25 μ J pulse energy). In the latter case, as can be seen from figures S2 (b), (c), (d), (e), (f) and (g), the bottom of the channel is flat, whereas in figure S2 (h), we see that the ablation depth has suddenly increased, and the profile is roughly triangular.

Based upon these results, scanning speeds of 4 m s⁻¹ for the 400 kHz repetition rate and 10 m s⁻¹ for the 1 MHz repetition rate were chosen to ablate the flowfield. At these scan speeds, the overlap was 3/4th of the spot size, which was suitable for the creation of smooth sidewalls. These higher scan speeds also resulted in shorter process times. For the required depth, a large number of scans were required. According to Crawford *et al* [19], it also leads to a reduction of burr height, as the amount of material ablated from the bottom of the channel tends to decrease with the increase of channel depth while the removal of burr by the beam edge remains constant.

To form the 1 mm diameter inlet holes, helical drilling was used. The laser beam was scanned in a spiral starting from the center of the circle toward its circumference. The spiral step was 10 μ m. For the inlet holes, the sidewall quality was of lesser significance than for the flowfield. Scanning speeds 0.4 m s^{-1} for 1 MHz repetition rate, and 1 m s⁻¹ for 400 kHz repetition rate were chosen, because they offer the highest ablation rates, albeit poor sidewall quality and significant redeposition. At these scanning speeds, the number of passes (spirals) necessary to ablate through a 400 μ m wafer was 28 for the 1 MHz case and 5 for the 400 kHz case. The number of passes was much smaller than one would expect from the SEM characterization of the channels ablated at the 0.4 m s⁻¹ (figure S1 (h)) and 1 m s⁻¹ (figure S2 (h)) scan speeds. One reason for the fewer passes was the overlap between spiral steps (spot size, minus 10 μ m), which is in addition to the overlap between consecutive spots. Another possible reason is that, because HAZ minimization was not an issue, the holes were ablated with all the passes at once instead of distributing them like was done with the channels. As a consequence, silicon in the hole area was still at a high temperature when the next spiral was scanned, which increased absorption. Yahng and Jeoung [22] report a high dependence on temperature of the amount of ablated material. Moreover, ablating a more absorbing material should lead to a larger proportion of the expelled



Figure 3. SEM micrographs of flowfield structures ablated at 1 MHz, 200 μ m pitch (type A). (*a*) Top view, (*b*) higher magnification top view and (*c*) cross-sectional view. The burr on the sidewalls is highly regular.

material to be in the form of molten droplets ejected at lower velocities [24].

A very large number of SEM observations were performed, and it was found that the shapes of the channels and the top of the pillars are highly consistent. Figures 3-6show SEM images of the laser ablated chips' flowfields. The cross-sectional SEM images of the cleaved chips (figures 3(c), 4(c), 5(c) and 6(c)) show the amount of redeposition on top of the sidewalls. At 1 MHz ablation rate and 1000 passes (table 2) the burr is uniform (figures 3 and 4), while it is more irregular with 400 kHz repetition rate and 270 passes (figures 5 and 6). This burr is more prominent with type B chips compared to type A. This is consistent with type B channels being 10 μ m deeper in average than type A. This could be due to the type B pitch being half of that of type A, which causes higher local temperatures during type B ablation. Therefore, a similar phenomenon as the one present in accelerating the throughhole ablation (described above) should also be in place for this case [22, 24].

In a recent study, Popovic *et al* [28] ablated silicon with a picosecond laser while heating the surface with a continuous wave laser. They found that heating causes the median of ablated particle size distribution to shift toward larger sizes, when compared to unheated substrate. Larger particles would more readily redeposit rather than be airborne and sucked

away by the vacuum hose. This is also consistent with the more prominent burr of type B ablated channels compared to type A. The pitch of type D flowfield, being half of that for type C, would also explain most of the 17 μ m difference in depth between the respective ablated channels.

In figures 6(*b*) and (*c*), where a type D (400 kHz repetition rate and 100 μ m pitch) laser-ablated flowfield is visible, the redeposition does not actually form a burr because the channels are not spaced apart far enough. Instead, the ablated material is partially redeposited on top of the pillars, which finally results in jagged domes. Because of this redeposited silicon, the pillars obtained are higher than in the case of type C.

The curved channels at the edges of the flowfields visible in figures 3(a), 4(a), 5(a) and 6(a) were created due to the inertia of the galvanometric scanner. Careful adaptation of delays between laser trigger and scanner movement was required to remove these artefacts.

Figure 7 shows laser scanning microscope (LSM) measurements of the same chips, which give better quantitative information about both the burr formed at the top of channel sidewalls and the channels' depth. The x and y-axes shown in figure 7 have been rescaled to obtain a 1:1 aspect ratio for easier comparison with SEM images (the original, unmodified scans are provided as figure S3 in the supplementary materials, available at stacks.iop.org/JMM/23/055021/mmedia). The





Figure 4. SEM micrographs of flowfield structures ablated at 1 MHz, 100 μ m pitch (type B). (*a*) Top view, (*b*) higher magnification top view and (*c*) cross-sectional view.

actual depth of the obtained channels is 52 μ m for type A, 62 μ m for type B, 63 μ m for type C and 80 μ m for type D ablated chips. As you can see, type B channels look similar to type A, apart from the difference in depth. Burr height and channel depth can be measured in this way, without cleaving the substrate first. The line scans were positioned across the center of the pillars to obtain a cross section of several channels.

Since the samples for SEM were prepared by cleaving along the channels, the SEM images appear to show channels that are shallower than in the LSM scans. This is caused by redeposited silicon at the crossing of the ablated channels. There is also a noticeable slant of the channel visible in figure 7(a). This is the result of the ablating laser beam inclination angle; it becomes larger the further the chip is from the wafer's center. The jagged dome shape of the pillars for type D ablated chips is confirmed by the LSM scan in figure 7(d).

Table 3 lists the times necessary to ablate a whole wafer using the parameters described in this work. The larger number of passes used to ablate type A and B chips (1 MHz, 1000 passes) contributes to the process taking more than twice the time when compared with the ablation of type C and D chips (400 kHz, 270 passes). Going from type A to type B or type C to type D, where the number of channels doubles, does not

Table 3. Total laser ablation times p	per wafer (32 chip	s)
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MFC type	Total number of channels per wafer	Ablation time (h, min)
A	3200	1 h, 45 min
В	6400	2 h, 29 min
С	3200	45 min
D	6400	58 min

cause the processing time to double. This is because the time necessary to ablate the through-holes in the wafer remains the same, regardless of the total number of channels.

By approximating the cross section of the ablated channels as an isosceles triangle and setting up two systems of equations (one each for the 400 kHz and 1 MHz repetition rates), we obtain a rough figure for the silicon removal rate of 77.4 $10^6 \ \mu m^3 \ s^{-1}$ for the 400 kHz and 8.8 $10^6 \ \mu m^3 \ s^{-1}$ for the 1 MHz case.

3.2. DRIE processing

SEM micrographs of DRIE-etched channels for type A and type C MFCs are presented in figure 8. The sidewalls are slightly receding.

The total cleanroom process time for a single wafer is one day, excluding the time to prepare the photomasks. Any change





Figure 5. SEM micrographs of flowfield structures ablated at 400 kHz, 200 μ m pitch (type C). (*a*) Top view, (*b*) higher magnification top view and (*c*) cross-sectional view.

in the flowfield topology would require a new mask or even a new maskset, the preparation of which can take anywhere from one to three days (if the mask printing is not done in-house). This is in contrast with changing the laser beam scan pattern, which can be done in minutes to a few hours.

3.3. Micro-Raman characterization

The change in the 520.5 cm⁻¹ Raman peak position of triply degenerate optical (LO+TO) mode of unstressed monocrystalline silicon (Si-I) provides information about the stress induced in the silicon lattice as a consequence of laser ablation [36–39]: the Si-I peak position shifts from 520.5 cm⁻¹ toward higher energies in the case of compressive stress and toward lower energies in the case of tensile stress. Thus, the phonon deformation potentials proposed in [39] can be used for stress (σ) evaluation, finally giving the equation: $\sigma \approx -435 \Delta \omega$, where $\Delta \omega$ is in cm⁻¹ and σ is in MPa. It is also possible to observe a Raman signal from hexagonal (Si-IV) and/or nanocrystalline silicon with a peak at 510 cm⁻¹ and a broad peak at around 490 cm⁻¹ caused by amorphous silicon (a-Si) [37, 38].

The micro-Raman mapping was done by cleaving the chips and choosing a cleavage line in such a way that both

the ablated sidewall of the channels and the bulk of the silicon could be mapped (figure 9(a)). In other words, the objective lens of the micro-Raman setup 'sees' both the sidewall of the channel as well as the bulk of the silicon chip. This way we successfully obtained Raman spectra of silicon both on the surface of the ablated channels as well as in the bulk near the surface. Figures 9(b) and (c) show optical microscope images of the cleaved samples used for our micro-Raman characterization.

As can be seen from the Raman maps in figure 10, the stress induced during 1 MHz laser ablation (figure 10(a)) is much higher than that in the case of 400 kHz laser ablation (figure 10(b)). Its average value is about 1–1.5 GPa (green areas); however, in some regions it can reach up to 2–2.5 GPa (blue areas). The result shows that, while a gentler ablation (larger number of pulses with smaller energy) would cause a smaller HAZ, it does not have a beneficial influence on minimizing induced stresses. We tried to measure the contribution of amorphous silicon (a-Si), nanocrystalline silicon and hexagonal silicon (Si-IV) to the Raman signal, to quantify the amount of nonmonocrystalline silicon. To this end, we introduced a measure of noncrystallinity, or deviation from crystallinity d, obtained by subtracting the center of mass position of the Raman spectrum in the range of





Figure 6. SEM micrographs of flowfield structures ablated at 400 kHz, 100 μ m pitch (type D). (*a*) Top view, (*b*) higher magnification top view and (*c*) cross-sectional view. Large amounts of redeposited silicon form dome-shaped pillars.



Figure 7. Profiles from the LSM measurements: (a) type A chip, (b) type B chip, (c) type C chip and (d) type D chip.



Figure 8. SEM micrographs of DRIE-etched channels in MFCs: (a) type A chip, (b) type C chip.



Figure 9. (*a*) 3D model of the cleaved MFC sample. (*b*) Optical micrograph of the cleaved chip ablated at 1 MHz repetition rate. (*c*) Same as (*b*) but for 400 kHz repetition rate.

(470–530) cm⁻¹ from the Si-I peak position. The center of mass x_{cm} was calculated using formula (2):

$$x_{\rm cm} = \frac{\sum_{x_1}^{x_2} x \cdot I(x)}{\sum_{x_1}^{x_2} I(x)}$$
(2)

where *x* is the Raman shift position in cm⁻¹, I(x) is the Raman intensity in counts, and x_1 and x_2 are the start and end points of the selected range. The deviation from crystallinity is then given as $d_c = x_{\text{Si-I}} - x_{\text{cm}}$.

In the case of monocrystal silicon (without the presence of a-Si or Si-IV) the position of the center of mass coincides with the Si-I peak position and $d_c = 0$. This coincidence persists even in the case of stress. When there is a-Si, nanocrystalline

Si and/or Si-IV, which produce peaks at 490 cm⁻¹ and 510 cm⁻¹ respectively, the center of mass x_{cm} of the Raman spectrum shifts to the left (lower energies) of the Si-I peak.

Figure 11 shows maps of the deviation from crystallinity d_c , as defined above, for an interval (x_1-x_2) of (470–530) cm⁻¹. The chips ablated at 1 MHz repetition rate display a considerable amount of noncrystalline silicon (figure 11(*a*)) both on the sidewall of the channel as well as in the bulk, while the ones ablated at 400 kHz repetition rate have almost none. In [40] it was reported that silicon amorphization starts occurring at fluences of 0.2 J cm⁻² and up to about 0.26 J cm⁻² when ablated with a picosecond laser. After



Figure 10. Micro-Raman spectroscopy scans of the 520 cm⁻¹ peak position of cleaved silicon chips ablated at (*a*) 1 MHz repetition rate and (*b*) 400 kHz repetition rate. The green areas denote tensile stresses of about 1–1.5 GPa, while the blue areas are regions where tensile stress can reach up to 2–2.5 GPa. Ablation at 1 MHz repetition rate creates larger stressed areas, than with 400 kHz repetition rate.

the higher fluence threshold, silicon recrystallizes epitaxially. In our case, the fluence for the 1 MHz repetition rate was 0.61 J cm⁻² for a perpendicular beam, but at an angle like the ones visible in figures 7(*a*) and (*b*), it is lower. The measured angle of incidence for the type A and B MFCs is $\theta = (67^{\circ}-76^{\circ})$ (figure 12). The effective fluence is obtained as $F_{\text{eff}} = F_{\text{incident}} \cos(\theta)$, which gives a fluence interval of (0.15–0.24) J cm⁻², overlapping with the (0.2–0.26) J cm⁻² region where amorphization occurs. With the 400 kHz repetition rate, the fluence is 4.52 J cm⁻²—well above the upper threshold for amorphization by picosecond laser pulses, as reported by Liu *et al* [40].

Comparing figures 11(a) and (b) with figures 10(a) and (b), a correlation is noticeable between the noncrystalline areas and the areas with high stress. In a study on nanosecond-laser ablation of silicon [37] it was found that the stressed and amorphized areas largely coincide; however, their micro-Raman map analyzed the sample from the top and not the cross section. Also, the measure for 'level of amorphization' used in the study was the area under the a-Si peak at 480 cm⁻¹ divided



Figure 11. Micro-Raman spectroscopy scans showing the deviation from crystallinity $d_c = x_{\text{Si-I}} - x_{\text{cm}}$ of cleaved silicon chips ablated at (*a*) 1 MHz repetition rate and (*b*) 400 kHz repetition rate. The channels ablated at 1 MHz repetition rate show higher crystal lattice disorder compared to channels ablated at 400 KHz.



Figure 12. Illustration of the angle of incidence θ , of the laser beam to the sidewall.

by the surface under the 480 cm^{-1} (a-Si), 510 cm^{-1} (hexagonal, Si-IV) and 520 cm^{-1} peaks.

From the micro-Raman characterization of our samples, it appears that higher energy laser pulses induce less stress and better crystallinity than a larger number of lower energy



Figure 13. Polarization curves (*a*), and chronoamperometric measurements (E = 0.6 V) (*b*) of type A DRIE-etched (full line) and laser-ablated (dashed line) MFCs.



Figure 14. Polarization curves (*a*), and chronoamperometric measurements (E = 0.6 V) (*b*) of type B DRIE-etched (full line) and laser-ablated (dashed line) MFCs.

pulses. A possible explanation is that a larger HAZ promotes recrystallization, which in turn relaxes the residual stress and increases the crystallinity.

3.4. MFC characterization

Each geometry type (A–D) and both DRIE-etched and laserablated MFCs were characterized in terms of electrochemical performance. Polarization curves were obtained by measuring the current produced by the MFC while sweeping the voltage from open-circuit (OCV) down to 0.1 V. After the polarization curve measurement, the MFCs were subjected to a 72 h chronoamperometric measurement at a constant voltage of 0.6 V. Multiple measurements were performed and showed a high level of consistency (less than 10% standard deviation). A summary of all measurement results can be found in Table S2 in the supplementary data, available at stacks.iop.org/JMM/23/055021/mmedia.

Both the transient performance shown by the polarization curves and the long-term performance of the laser-ablated MFCs was better than the equivalent DRIE-etched ones (figures 13–16).

Mass transfer resistance can only be seen with type A ablated chips from the rapid voltage decay at high current densities of more than 100 mA cm⁻² (figure 13(*a*)) [41]. Even though the mass transfer resistance is due to the high area of MEA covered by the pillar tops (72%) and the flat top surface of the pillars, it is not visible in the case of the type A etched MFC, since high enough currents are not produced with them.

The ablated MFCs reached a stable or an improving performance in less than 10 h of operation, while the DRIE etched MFCs degraded steadily during the 72 h performance test. The only exception was the ablated MFC of type D



Figure 15. Polarization curves (*a*), and chronoamperometric measurements (E = 0.6 V) (*b*) of type C DRIE-etched (full line) and laser-ablated (dashed line) MFCs.



Figure 16. Polarization curves (a), and chronoamperometric measurements (E = 0.6 V) (b) of type D DRIE-etched (full line) and laser-ablated (dashed line) MFCs.

(figure 16(b)), which took about 50 h to stabilize, and during this time a significant decrease of current was observed. This could be due to the malformed pillar shape (figure type D SEM), which allows water to gather between the pillars and the catalyst layer and so hinders the mass and current transport.

It is known that increasing the gas pressure inside a fuel cell results in better performance [42, 43]. It is clear from the SEM images that the cross section of the ablated channels is smaller than the DRIE-etched channels. As the gas flow rates were kept constant in all experiments, the pressure inside ablated MFCs was higher, which at least partly explains the improved performance of the ablated MFCs compared with the DRIE-etched MFCs.

Another reason for the better performance of the ablated chips may be a thicker chromium layer formed on the V-shaped channels, that allows conformal deposition of chromium

during sputtering. In the case of DRIE-etched channels, the sidewalls are slightly receding (figure 10). Since sputtering is a partially directional deposition technology, and the sputtered chromium reaches the silicon wafer perpendicularly, it is likely that the chromium layer is thinner or even interrupted on the receding sidewalls of DRIE-etched channels. While our SEM investigation could not show this thin layer of chromium on the silicon sidewalls (only on the top of the pillars), its thickness can be calculated by assuming that the layer is uniformly distributed on the slanted sidewalls. The contribution of this layer to the conductance of the MFC pillars can be calculated by modeling the chromium layer and the silicon pillar as two resistors connected in parallel (table 4). Even though sputtered chromium will have a specific resistivity that is higher than that of bulk chromium, from table 4 we see that the contribution of sputtered chromium to a pillar's conductance is not insignificant.

Ablated MFC	Pillar/sidewall height (µm)	Chromium thickness (nm)	Conductance of Cr on sidewalls (S)	Conductance of Si pillar (no Cr) (S)	Total conductance of pillar + Cr (S)
A	52	11	1.2	5.6	6.8
В	62	9.4	0.36	0.8	1.16
С	63	17	1.3	3.1	4.4
D	80	14	0.23	0.2	0.43

Table 4. Contribution of chromium to silicon pillar conductivity.

4. Conclusions

In this work, MFCs were fabricated with laser ablation. As is visible from the SEM micrographs in figures 3–6 and the LSM in figure 7, the laser-ablated channels in this study present some degree of redeposition near the sidewalls. This is not a limitation for MFCs that have a polymer membrane pressed against the machined silicon. It would be a serious drawback for applications where a rigid material would be bonded. Our MFC characterization results show that cells fabricated by silicon laser ablation show significantly better performance than their identical counterparts made by silicon DRIE. Another result of this work is that the density of ablated channels per area will influence the efficiency of ablation, depth and shape of the microchannels and should be kept into consideration when designing microfluidic devices made by ablation.

Micro-Raman characterization of the laser-ablated samples produced with two different sets of parameters (at 400 kHz and 1 MHz repetition rates) revealed that the one where more silicon is removed per pass is both faster and leaves less residual stress in the silicon bulk. This makes the 400 kHz parameter set an unambiguously better choice for silicon MFC fabrication.

Given that laser ablation is a maskless microfabrication process characterized by fewer steps than the one based on lithography and DRIE, the method described in this work is suitable for the fast prototyping of MFCs. It is also a useful alternative for laboratories that do not have access to traditional microfabrication equipment.

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