Abstract

Application of laser direct writing to the fabrication of microchannel networks for tissue engineering applications was presented. Using a Q-switched Nd:YAG laser with fundamental wavelength, multi-depth, multi-width microstructures on silicon were machined without photolithography-based methods. The molten material inside the microchannel was ejected with a modified assist gas and thus the amount of laser ablation was increased. The debris build-up due to the strong thermal reaction of silicon to the nanosecond IR laser pulse was cleaned up with chemical wet etching in HF and HNO$_3$ solution. The etching of laser ablated silicon surface was studied to measure the etching rate and see the evolution of surface morphology. Using the laser machined silicon structures as a mold, a Poly(dimethylsiloxane) (PDMS) replica was molded. Flow visualization was carried out with the patterned PDMS.
Introduction

Laser direct writing has proven to be a flexible tool for micromachining with simple and inexpensive operations. A variety of lasers can be used for micromachining, from nanosecond lasers to ultrafast lasers or from IR lasers to UV lasers, depending on the materials to be fabricated and desired applications. Although the use of ultrashort pulse lasers or UV lasers has been highlighted for micromachining due to minimal peripheral thermal damage and associated debris, nanosecond non-UV lasers are still most commonly available. Thus, it is necessary to estimate what extent nanosecond non-UV lasers can be used for micromachining.

This paper describes laser direct writing of microfluidic structures on silicon using a Q-switched fundamental Nd:YAG laser for tissue engineering applications such as cell culturing. By rapid prototyping of a multi-depth multi-with microchannel network with a 3D tapered inlet which is almost impossible with conventional photolithograph based technology, the utility of laser direct writing was demonstrated. The laser machined silicon structure was used as a mold for making microfluidic patterns on PDMS which is optically transparent, nontoxic, and gas permeable, and thus widely used in biomedical devices.

Silicon is known as difficult material to fabricate in laser machining. There are several different strategies to fabricate silicon structures. Femtosecond or UV laser micromachining have most commonly used for fabricating silicon structures [9-11]. Otherwise, chlorine-assisted laser micromachining of silicon has been reported [12]. However, femtosecond lasers have relatively low productivity compared with their relating costs, although they improve the quality and resolution significantly which very important for multi-generation bio-mimetic channels. UV laser requires specially designed optics, beam delivery, and diagnosis. Chlorine-assist laser micromachining needs complicated chlorine gas circulating systems. Therefore, direct laser writing of silicon using commonly available nanosecond IR laser would have significant impact.

The nanosecond laser micromachining of silicon is a substantial challenge since the roughness of the laser ablated surface is caused by strong thermal reaction of irradiated silicon. Explosive boiling for each pulse and overlap of the pulses are not only two main processes in nanosecond laser ablation but also two main reasons for the roughness problem. Solidified molten material and splashed debris in the craters created by laser pulses initiates the surface roughness. In addition, the overlapping of the pulses aggravates the surface roughness. In this study, methods to improve the quality of nanosecond laser ablated silicon surfaces were presented. Modified assist gas injected in a cutting direction instead of a conventional coaxial gas stream was introduced to eject molten mass out of microchannels. Since the silicon wafer is thin and fragile, the coaxial assist gas injection to the cutting zone is not appropriate for the laser ablation of silicon. A chemical wet etching in a mixture of HF and HNO₃ solution was applied as post processing to remove the debris build-up consisting of solidified molten material. Etching tests showed how the morphology the laser ablated silicon surface evolves to be smooth.

The laser machined silicon structure was used as a mold to make microvasculature patterns on Poly(dimethylsiloxane) (PDMS). PDMS is one of most commonly used materials in the fabrication of microfluidic structures. Fluid flow visualization was carried out using the microchannel network on PDMS copied from the laser machined silicon structures.

Experimental

A Q-switched Nd:YAG laser (TRW DP-11) operating at 1064nm was used as the ablation laser. In this study, the laser was set to operate at a repetition rate of 500Hz and a pulse width of 100µs (duty cycle of 5%). In order to perform laser micromachining in the nanosecond regime the laser beam was further modulated. The average power of the incident beam on the silicon sample was controlled with a half-waveplate without changing the laser setting. The incident beam was also circularly polarized with a quarter-waveplate. Within the Rayleigh range, the beam shape was near-Gaussian, with a symmetric diffraction spot pattern surrounding a bright central lobe. After these diffraction spots surrounding the bright central lobe were filtered off by a pin-hole, the resulting beam, passing through the spatial filter to the workpiece, was a clean-cut symmetric near Gaussian beam. The beam spot size at focus was about 15µm in radius.

Two types of silicon wafer were irradiated with the laser beam, bare silicon wafer and nitride
coated silicon wafer. The nitride coating protects the silicon surface from a wet etching in acid. Both silicon wafers were N-type and <100> in the crystal orientation. CNC codes were programmed to control the movement of X-Y stage based on the desired structures.

Argon gas was injected in the axial direction of the cutting zone to remove molten material out of ablated channels as shown in figure 2. The angle of the nozzle was set at 45° to target surface, and the gas regulator was set at 60kPa. Considering a loss through the gas tube, the pressure of 60kPa at the regulator was enough to remove the molten material.

![Fig. 1. Schematic sketch to illustrate the role of Argon gas injected in the axial direction of a microchannel](image1)

As post processing, debris buildup in silicon structures was cleaned with wet etching in a mixture of 49% HF and 69% HNO₃ solution in the ratio of 10:1 after surface cleaning with 30% KOH for 10 min at room temperature.

In order to make PolyDiMethylSiloxane (PDMS) replica from silicon structures, Sylgard 184 pre-polymer base and Sylgard 184 curing agent were mixed with 10:1 ratio in weight and then air bubble in the mixture were removed in a vacuum chamber. To prevent PDMS sticking to silicon molds, the silicon mold surface was silanized in a vacuum chamber before pouring the PDMS pre-polymer liquid. The air removed PDMS pre-polymer liquid was poured onto the silanized silicon molds in Petri dishes and then cured for 3hrs at 60°C.

**Results and Discussion**

1. **The effect of modified assist gas**

   Generally, coaxial assist gas is injected in order to eject molten material and get deep penetration depth in laser cutting or drilling processes. However, silicon wafers are fragile, brittle and typically very thin, so the injection of assist gas in the coaxial direction of the nozzle is not applicable to laser machining of shallow microchannels on thin silicon wafers [2].

   In this study, Argon gas was injected in the axial direction of a microchannel at 45° from the coaxial direction as shown in figure 1. Figure 2 shows the morphology of laser-irradiated surfaces without gas injection (top) and with Argon gas injection (bottom). Obviously, the laser ablated
channel with Ar assist gas shows better ablation efficiency than the ablation without assist gas. The material escape in nanosecond laser ablation without assist gas relies on evaporation and splash of molten material due to explosive boiling. Thus, resulting ash is scattered around the ablated channel. Cast of remaining molten material inside channel blocks the transfer of laser energy to the target surface. Contrary to the ablation without assist gas, the hump on the edge of the ablated channel with the modified assist gas injection is created because the gas flow increases the cooling rate of the molten material ejected out of channel resulting accumulation of cast silicon on the edge.

2. Chemical wet etching in HF and HNO$_3$ solution

In order to solve the roughness problem due to the debris buildup composed of the solidified molten material, a chemical wet etching in 49% HF and 69% HNO$_3$ solution in the ratio of 10:1 was applied after cleaning the surface with 30% KOH for 10 min post processing.

Figure 3 shows the change of surface morphology of a micro-channel on bare silicon wafer with increasing the etching time. After dipping the laser ablated surface in 30% KOH solution for 10 min at room temperature splashed ash and particles are removed. However, the hump of molten mass on the edge of channel is not etched at all. After further etching in the solution of 49% HF and 69% HNO$_3$ for 2 min, as shown in the second SEM image of figure 3, the hump is etched out leaving good edge quality. Since the etching rate is proportional to the area in contact with the etchant, the hump having a larger surface area to volume ratio than other parts disappears first. The etching by the HF and HNO$_3$ solution is observed to occur in any normal direction of the surface without reference to crystalline of silicon. As the etching time increases, the size of the channel gets wider, but variation in the direction of depth was not great because the etching happens in the non-patterned surface outside the channel as well as the laser ablated surface. The periodic ruffling pattern on the bottom of the channel after wet etching is because the channel is created by periodic laser pulses. The etching rate of HF and HNO$_3$ solution decreases with time because the etchant neutralizes fast as it reacted with non-patterned large area of silicon sample as well as the laser ablated narrow region. The etching rate depends on the amount of solution and silicon pieces so that a qualitative profile of the temporal etching rate was not measured.

![Fig. 3. SEM images of laser machined micro channels on bare silicon wafer after chemical wet etching as a post process: 30% KOH etching for 10 min. (a), 49% HF and 69% HNO$_3$ etching for 2 min. after 30% KOH etching for 10 min. (b), and 49% HF and 69% HNO$_3$ etching for 2 min. after 30% KOH etching for 10 min. (c)](image-url)

The roughness of the non-patterned area of bare silicon wafer after the etching process as shown in figure 3 (b, c) prevents the area from adhering closely to a top sealing film. Nitride coated silicon wafers were used to protect the non-patterned polished silicon surface from chemical etching. In addition, the chemical etching is limited to the laser ablated area so that required amount of the hazardous etching solution is reduced. Figure 4 shows how the surface morphology of the microchannels on the nitride coated silicon changes with increasing the etching time. Obviously, different initial surface profiles of microchannels created by different overlaps of laser pulses result in different surface morphologies after the chemical etching. The secondary etching on the edge of microchannels happens since the accumulation of hot molten material on the edge of channel destroys the nitride coating in the area resulting selective etching for this area. This secondary etching makes the resolution of microchannel structures worse. Figure 5 shows the dependence of channel depth and width on the etching time. The etching rate of the width of channels is about twice of that of the depth as etching happens in the two opposite wall directions of a channel. In the graphs of the figure 5,
initial width and depth is not measured because it is difficult to define the boundary of channels.

**Fig. 4.** SEM images of laser machined micro channels on nitride coated silicon wafer after chemical wet etching as a post process: 30% KOH etching for 10 min. (a-1, b-1, c-1), 49% HF and 69% HNO₃ etching for 10 sec. after 30% KOH etching for 10 min. (a-2, b-2, c-2), and 49% HF and 69% HNO₃ etching for 30 sec. after 30% KOH etching for 10 min. (a-3, b-3, c-3)

**Fig. 5.** The depth (left) and the width (right) of a microchannel on nitride coated silicon wafer vs. etching time

### 3. 3D microchannel network on a silicon wafer

Figure 6 shows an SEM image of a simple straight microchannel with a semi-circular cross-section connected to a wider and deeper reservoir, which is for a tube fitting. This microstructure shows the benefit of laser direct writing over the photolithography based technique to fabricate microfluidic channels:
- A photo-mask is not required.
- A multi-level structure is easily acquired by changing the number of laser pulses.
- Redesign is easily done by changing the computer programmable motion control of stage.

As a result, laser direct writing reduces cost, time, and effort, especially in development of microfluidic devices where frequent redesign is inevitable.
As shown in figure 7, a multi-depth, multi-width four generational microchannel network with a tapered inlet connection is successfully fabricated with laser direct write using nanosecond fundamental Nd:YAG laser. Remarkable thing in this microfluidic structure is the exact realization of the 3D tapered inlet connection which is impossible to fabricate with conventional photolithography techniques. In addition, the depth of the multi-depth structure ranges from a few tens of microns to above one millimeter. This wide range of the structural dimension is also hard to achieve with conventional photolithography. This kind of 3D microfluidic structures can benefit the design of the microfluidic devices. For example, one of the major challenges in development of tissue-engineered organs such as the heart, liver, and kidneys is how to transport oxygen and nutrients and remove waste to sustain the function of cells in the organs. Most studies on developing artificial vasculature use the photolithography based technique so that their designs of microchannel networks were limited to single-depth planar geometries [13-14]. However, uniform depth of microchannel results in non-physiological flow patterns and high flow resistance. Murray’s law ($d_0^3 = d_1^3 + d_2^3$, where $d_0$ is the diameter of the parent vessel, and $d_1$, $d_2$ are the diameters of daughter vessels) gives an optimal solution for designing bifurcation of branching artificial vasculatures. The laser direct writing can meet this demand on flexibility of the 3D microstructures with a single step process just by simply controlling the computer programmable motion stage and laser parameters such as the number of beam passes, and average power.

4. PDMS replica and flow visualization
Polydimethylsiloxane (PDMS) is one of the most commonly used materials in the fabrication of microfluidic devices. PDMS is optically transparent, non-toxic, gas-permeable, and electrically and thermally insulating [15]. A PDMS replica is generated from the laser machined silicon structure for microfluidic tests such as flow visualizations, cell cultivations and monitoring of cell behaviors. Figure 8 shows the molding process of the PDMS replica. The whole process from the laser machining of silicon structures to the final PDMS replica takes less than 8 hours. This short processing time is very attractive in device development where incremental improvement is achieved by frequent redesign.

**Fig. 8.** (a) Schematic representation of molding process: in order to prevent PDMS from sticking to the laser machined silicon mold, the surface of the silicon should be silanized in a vacuum. Next, the mixture of the liquid PDMS pre-polymer base and its curing agent in the ratio of 10:1 is poured over the laser machined silicon structure and then cured for 3 hours at 60°C. The cured PDMS replica mold is peeled off from the silicon mast mold. To get the same positive pattern on PDMS as the silicon mast mold, the negative patterned PDMS replica is used as a mold. In making a positive PDMS replica from the negative PDMS mold, the procedure to make the PDMS replica from a silicon structure is repeated. The microchannel network on the PDMS is sealed with a cover glass to enclose the channel. Then the reservoirs are connected to the inlet and outlet of the network. The complete microchannel network is plasma oxidized to make the PDMS channel surface hydrophilic. (b) A laser machined silicon structure after chemical wet etching and (c) its PDMS replica.

Figure 9 shows a microchannel system on a fluorescence microscope. Fluorescent dye solution flowing through the microchannel absorbs incident blue light and emits green light, thus visualizes the flow. Figure 10 shows empty microchannel images (top) and flow images in the channel (bottom).
Conclusions
Laser micromachining of microfluidic channels on silicon wafers was studied with nanosecond fundamental Nd:YAG laser. With help of Argon gas injection, molten material is ejected out of the ablated channel, and thus laser energy transfer to the target surface is improved. Debris buildup composed of solidified molten material was removed effectively after the wet chemical etching in the mixture of HF and HNO₃ solution. A Multi-depth and multi-width microchannel structure with 3D tapered inlet connection was successfully fabricated in a one step process. Once the program of the motion stage was prepared, then the overall process to make microfluidic structures on PDMS from laser machining of a silicon master mold took less than 8 hours.

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References