Ultrafast and direct imprint of nanostructures in silicon

Stephen Y. Chou*, Chris Keimel & Jian Gu

NanoStructure Laboratory, Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544, USA

The fabrication of micrometre- and nanometre-scale devices in silicon typically involves lithography and etching. These processes are costly and tend to be either limited in their resolution or slow in their throughput[1]. Recent work has demonstrated the possibility of patterning substrates on the nanometre scale by 'imprinting'[2,3] or directed self-assembly[4], although an etching step is still required to generate the final structures. We have devised and here demonstrate a rapid technique for patterning nanostructures in silicon that does not require etching. In our technique—which we call 'laser-assisted direct imprint' (LADI)—a single excimer laser pulse melts a thin surface layer of silicon, and a mould is embossed into the resulting liquid layer. A variety of structures with resolution better than 10 nm have been imprinted into silicon using LADI, and the embossing time is less than 250 ns. The high resolution and speed of LADI, which we attribute to molten silicon's low viscosity (one-third that of water), could open up a variety of applications and be extended to other materials and processing techniques.

In LADI, a single XeCl excimer laser pulse (308 nm wavelength and 20 ns pulse duration) passes through a quartz mould (which does not absorb the laser energy because it has a bandgap larger than the photon energy) and melts a thin surface layer of the silicon substrate within picoseconds[5]. The molten silicon layer (which can be about 300 nm deep and remain molten for hundreds of nanoseconds) is then embossed by the quartz mould (Fig. 1). After the liquid silicon solidifies, the mould is separated from the imprinted silicon for the next imprint.

The experimental details are follows. First, the moulds, made of fused quartz 1 mm thick, have patterns on the quartz surface ranging from 10 nm to tens of micrometres in size that were fabricated by nanoimprint lithography and reactive ion etching. The moulds were diced into 1.5 mm × 1.5 mm pieces to fit within the excimer laser beam area of 2.5 mm × 2.5 mm, ensuring that all the silicon beneath the mould melts during LADI. The patterns on a LADI mould are of three types: (1) the 300 nm period grating of 140 nm linewidth and 110 nm depth; (2) the 10 nm wide and 15 nm deep lines, which were created as a result of the trenching effect in reactive ion etching during the mould fabrication; and (3) the rectangles of length and width in tens of micrometres and a depth of 110 nm.

Second, the pressure between the mould and silicon wafer was applied by sandwiching them between two large press plates. The silicon wafer was placed on the lower plate with the mould on top of the silicon wafer. The top plate, also made of fused quartz and hence transparent to the laser beam, was placed on top of the mould. Pressure was provided by screws between the two large plates. The exact pressure between the mould and the silicon wafer is unknown, but can be estimated from imprint time, imprint depth, and the mass of the mould, as discussed later. In this set-up the pressure is applied before the silicon is melted.

Third, the measured transmittance of the mould for the laser radiation is 93%, which indicates that the mould indeed does not absorb the laser energy, because the total reflection due to the
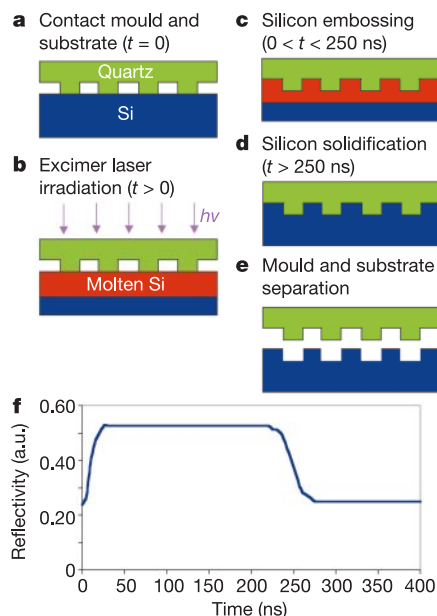

Figure 1 Schematic of laser-assisted direct imprint (LADI) of nanostructures in silicon. **a**, A quartz mould is brought into contact with the silicon substrate. A force presses the mould against the substrate. **b**, A single XeCl (308 nm wavelength) excimer laser pulse (20 nm pulse width) melts a thin surface layer of Si. **c**, The molten silicon is embossed while the silicon is in the liquid phase. **d**, The silicon rapidly solidifies. **e**, The mould and silicon substrate are separated, leaving a negative profile of the mould patterned in the silicon. **f**, The reflectivity of a HeNe laser beam from the silicon surface versus the time, when the silicon surface is irradiated by a single XeCl (308 nm) laser pulse with 1.6 mJ cm^{-2} fluence and 20 ns pulse duration. Molten Si, becoming a metal, gives a higher reflectivity. The measured reflectivity shows the silicon in liquid state for about 220 ns.
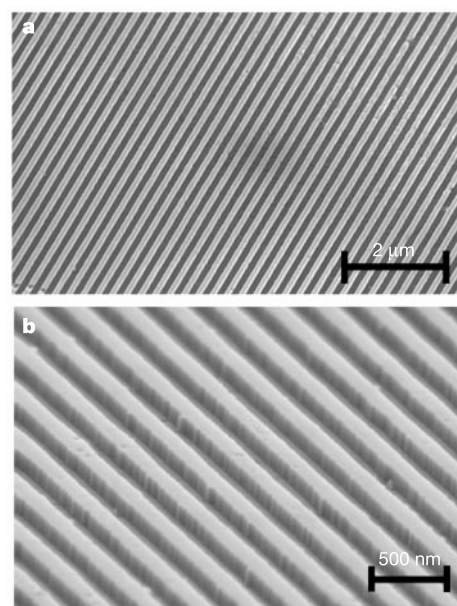

Figure 2 Scanning electron microscope (SEM) images. **a**, A uniform 300 nm period silicon grating patterned by LADI. The grating has 140 nm linewidth and is 110 nm deep. **b**, The mould after the two LADI processes showing no visible damage. During LADI the quartz mould does not melt, because quartz has a melting temperature about 300 °C higher than Si (quartz is used as the crucible material in Si-melting furnaces) and quartz conducts heat much less well—two orders of magnitude more poorly—than Si. Moreover, the quartz mould does not bind to Si during LADI.

 835

difference in refractive index at the two mould–air interfaces should be around 7%.

Fourth, the melting of silicon surface can be monitored *in situ* during the LADI process, by measuring the time-resolved reflectivity of a HeNe laser beam (wavelength $\lambda = 633$ nm) from the silicon surface. When silicon melts, it changes from a semiconductor to a metal, hence its surface reflectivity to visible light increases by about a factor of two[6]. Figure 1f shows that under the laser radiation, the reflectivity of the Si surface increases rapidly in the first 25 ns, then saturates for 200 ns, and finally returns to the original solid silicon reflectivity in 50 ns. The silicon starts to melt immediately in less than picoseconds after the laser hit the surface[7], so the reflectivity raise time should be the same as the laser pulse duration (20 ns), rather than 25 ns as measured. The discrepancy might be related to the RC (resistor–capacitor) time constant of the oscilloscope (100 MHz), which is 10 ns. The reflectivity measurements showed that the silicon surface was kept in liquid phase for about 220 ns. On the basis of theoretical calculations[7] and the melting depths experiments by other groups[8,9], the melting depth was estimated to be about 280 nm.

Using the time-resolved reflectivity measurements, we also investigated the effect of laser beam fluence on the silicon melt. We found that a fluence lower than 0.8 J cm^{-2} does not melt the silicon surface, but for a fluence higher than 2 J cm^{-2}, laser ablation of silicon will occur. We found that a laser pulse of 20 ns duration and 1.6 J cm^{-2} fluence melts a silicon surface sufficiently without ablation and has been used for all the results shown here.

The nanostructures directly imprinted in Si were characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM) and optical microscopy. We found that the entire mould (1.5 mm × 1.5 mm) was imprinted into the silicon wafer. Large-area uniform 300 nm period gratings in silicon by LADI have been achieved (Fig. 2a). The mould after two times of use does not show observable damage (Fig. 2b).

The cross-sectional views of the mould and the imprinted silicon features show that the imprinted Si structures are consistent with the mould (Fig. 3). One interesting feature in Fig. 3b is the ridge formed along the top corners on the imprinted grating lines. These ridges are about 10 nm wide and 15 nm high. The comparison with the mould indicates that these ridges come from the notches formed in the mould, which were caused by the trenching effect during reactive ion etching of the mould. The complete transfer of these 10-nm ridges in a LADI process suggests that the resolution of LADI is better than 10 nm.

Besides nanoscale features, LADI also demonstrated that isolated mesas and trenches of size of over tens of micrometres can be patterned, such as an isolated square mesa of 8 μm side and 110 nm height (Fig. 4). Successful imprinting of these large patterns indicates that the molten silicon can easily flow over tens of micrometres within nanoseconds.

The three intriguing characteristics of LADI—sub-10-nm resolution, sub-250-ns processing time, and excellent imprint of large
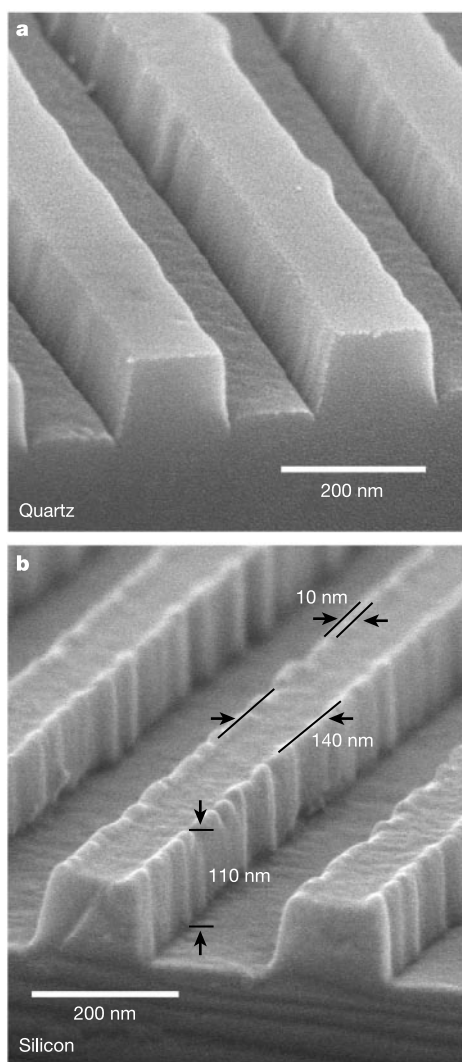

Figure 3 SEM image of the cross-section of samples patterned using LADI. **a**, A quartz mould. **b**, Imprinted patterns in silicon. The imprinted silicon grating is 140 nm wide, 110 nm deep and has a 300 nm period, an inverse of the mould. We note that the 10 nm wide and 15 nm tall silicon lines at each top corner of the silicon grating are the inverted replicas of the small notches on the mould (the notches were caused by the reactive ion etching trenching during mould fabrication). This indicates the sub-10-nm resolution of the LADI process. (These images are representative only. In fact, the Si structure in the image was probably not imprinted by the structure shown in the mould image.)
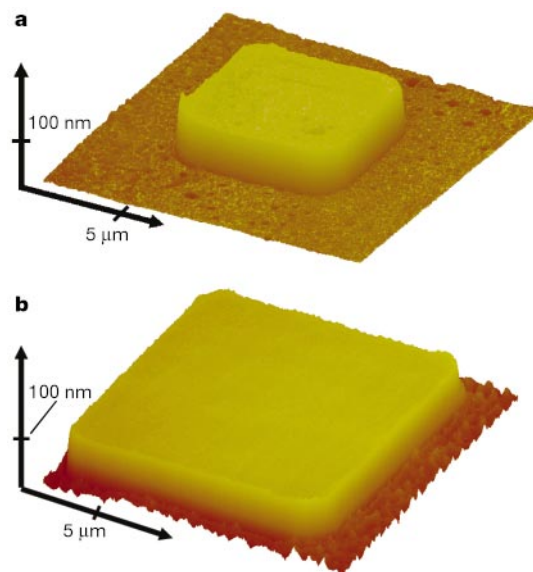

Figure 4 Atomic force micrographs (AFM) of isolated mesas patterned by LADI. **a**, Crystalline silicon. **b**, Polysilicon. We note that the results of crystalline silicon and polysilicon are the same, except that the polysilicon has a slightly lower melting energy than crystalline silicon. The crystalline silicon mesa is 8 μm in length on each side and 110 nm tall. The large isolated pattern indicates that in LADI the liquid Si can flow over a large distance on the nanosecond scale. The polysilicon mesa is 17 μm in length on each side and 110 nm tall.

isolated patterns—are related to the fact that molten silicon has a viscosity of $0.003\ cm^2\ s^{-1}$, which is one-third that of water ($0.01\ cm^2\ s^{-1}$; ref. 10). This low viscosity enables the molten silicon to flow rapidly into all crevasses, filling them completely and conforming to the mould. Furthermore, silicon, like water, has a liquid phase density ($2.52\ g\ cm^{-3}$) greater than its solid phase ($2.32\ g\ cm^{-3}$; ref. 11). The transformation from liquid to solid causes the silicon volume to expand about 3% in each direction. However, during LADI the mould was at a lower temperature than that of molten silicon, so the shrinking of silicon caused by the temperature drop can offset the expansion of silicon from liquid phase to the solid.

LADI can be applied to other materials. We have deposited, by chemical vapour deposition (CVD), a 230 nm polysilicon layer on top of a 200 nm thick silicon dioxide layer grown on a silicon substrate. Nanostructures have been patterned in the polysilicon layer by LADI (for example, Fig. 4b). The results are the same as that of crystalline silicon, except that the polysilicon has a slightly lower melting energy than crystalline silicon[7]. This indicates that LADI may become a good tool to directly pattern nanoscale gates for metal-oxide-semiconductor field-effect transistors (MOSFETs).

The velocity, acceleration, force, pressure, and Reynolds number involved in LADI of silicon can be estimated to provide further information about the process. In our experiments the imprint depth was 110 nm and the imprint time was around 250 ns. For simplicity, we assume that the mould travelled a distance of 100 nm in 200 ns; however, this distance may be slightly overestimated owing to elastic distortion of the mould under pressure and the upward flow of liquid silicon. This leads to an average imprint velocity of about $0.5\ m\ s^{-1}$ and an average acceleration of $5 \times 10^6\ m\ s^{-2}$—nearly a million times the gravitational acceleration. Because the mould has a weight of about 5.6 mg, the total force needed for the acceleration is about 28 N. For the given mould area ($2.25\ mm^2$), the total pressure on the mould needed for the imprint is $1.7 \times 10^6\ Pa$ or about 17 atm. If we assume the liquid Si flow during LADI is one-dimensional and into a 140 nm opening at a speed of $0.5\ m\ s^{-1}$, then the Reynolds number is 0.23, which is quite small, indicating a laminar flow.

Finally, LADI can be extended to large areas, other materials, and other processes. The LADI area could be as large as a whole wafer (4 inch or 8 inch diameter), or a one-inch-square die (that die can be used to cover an entire wafer by step and repeat), provided that a uniform laser beam over a large area is available. Conventional nanoimprint has demonstrated excellent uniformity over a 4-inch wafer in a single step[2,3]. LADI also could be used for other materials beyond crystalline silicon and polysilicon, such as Ge, III–V compound semiconductors and dielectrics (a different laser wavelength would be needed). LADI could help to crystallize polysilicon further. LADI might be well suited for three-dimensional patterning (for example, forming a lens on a Si or glass surface), which is challenging to achieve by conventional lithography and etching. LADI could offer a unique method to fill tiny holes in a dielectric (for example, silicon dioxide) with silicon, and a unique means of flattening the surface of a semiconductor deposited on a dielectric. Both are difficult issues in integrated circuit fabrication. Many applications of LADI are yet to be explored. □

1. Ito, T. & Okazaki, S. Pushing the limits of lithography. *Nature* **406**, 1027–1031 (2000).
2. Rogers, J. A. & Mirkin, C. Emerging methods for micro- and nanofabrication. *Mater. Res. Bull.* **26**, (2001).
3. Chou, S. Y., Krauss, P. R. & Renstrom, P. J. Imprint lithography with 25-nanometer resolution. *Science* **272**, 85–87 (1996).
4. Chou, S. Y. & Zhuang, L. Lithographically induced self-assembly of periodic polymer micropillar arrays. *J. Vac. Sci. Technol. B* **17**, 3197–3202 (1999).
5. Silvestrelli, P. L., Alavi, A., Parrinello, M. & Frenkel, D. Ab initio molecular dynamics simulation of laser melting of silicon. *Phys. Rev. Lett.* **77**, 3149–3152 (1996).
6. Ivlev, G. D. & Gatskevich, E. I. Liquid phase reflectivity under conditions of laser induced melting. *Semiconductors* **34**, 759–762 (2000).
7. Poute, J. M. & Mayer, J. *Laser Annealing of Semiconductors* (Academic, New York, 1982).
8. Carey, P. G. & Sigmon, T. W. In-situ doping of silicon using gas immersion laser doping (GILD). *Appl. Surf. Sci.* **43**, 325–332 (1989).
9. Weiner, K. H. & Sigmon, T. W. Thin-base bipolar transistor fabrication using gas immersion laser doping. *IEEE Electr. Device Lett.* **10**, 260–263 (1989).
10. Glazov, V. M., Chizhevskaya, S. N. & Glagoleva, N. N. *Liquid Semiconductors* (Plenum, New York, 1969).
11. Langen, M., Hibiya, T., Eguchi, M. & Egry, I. Measurement of the density and the thermal expansion coefficient of molten silicon using electromagnetic levitation. *J. Cryst. Growth* **186**, 550–556 (1998).

Correspondence and requests for materials should be addressed to S.Y.C.
(e-mail: chou@ee.princeton.edu).

··

Growth of early continental crust controlled by melting of amphibolite in subduction zones

Stephen Foley*, Massimo Tiepolo† & Riccardo Vannucci†

* *Institut für Geologische Wissenschaften, Universität Greifswald, F.L. Jahnstrasse 17a, D-17487 Greifswald, Germany*
† *Dipartimento di Scienze della Terra, Università di Pavia and CNR- Istituto di Geoscienze e Georisorse (IGG) - Sezione di Pavia, Via Ferrata 1, I-27100 Pavia, Italy*

It is thought that the first continental crust formed by melting of either eclogite or amphibolite, either at subduction zones[1] or on the underside of thick oceanic crust[2]. However, the observed compositions of early crustal rocks and experimental studies have been unable to distinguish between these possibilities[3–5]. Here we show a clear contrast in trace-element ratios of melts derived from amphibolites and those from eclogites. Partial melting of low-magnesium amphibolite can explain the low niobium/tantalum and high zirconium/samarium ratios in melts, as required for the early continental crust, whereas the melting of eclogite cannot. This indicates that the earliest continental crust formed by melting of amphibolites in subduction-zone environments and not by the melting of eclogite or magnesium-rich amphibolites in the lower part of thick oceanic crust. Moreover, the low niobium/tantalum ratio seen in subduction-zone igneous rocks of all ages is evidence that the melting of rutile-eclogite has never been a volumetrically important process.

The early continental crust is characterized by the tonalite–trondhjemite–granodiorite gneisses (TTG) of Archaean terrains[3]. Their compositions have been explained as the products of magmatic processes, namely melting of basaltic source rocks in the form of either eclogite or amphibolite[1,4–5]. However, it is debated whether the melting process occurred principally in subduction zones[1] or on the underside of oceanic crust[2] that may have been much thicker in the Archaean owing to higher geothermal gradients.

TTG gneisses have low Nb/Ta and high Zr/Sm ratios relative to modern oceanic basalts and mantle rocks. They share these charac-