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Abstract. Using laser direct writing in combination with chemical vapor deposition to produce nanometer scale electronics holds several advantages over current large scale photolithography methods. These include single step electrical interconnect deposition, mask-less patterning, and parallel processing. When taken together they make quick production of individualized electronic circuits possible. This work demonstrates the ability of combining laser direct write and chemical vapor deposition to produce silicon wires a few hundred nanometers wide. Optimized parameters will be discussed, with a particular emphasis paid to the laser-material interactions. The feasibility for electronic applications will be shown by examining the deposition formation on a silicon dioxide surface without degrading the surface's integrity, and by evaluating the resistivity of the deposited silicon wires. © 2011 Society of Photo-Optical Instrumentation Engineers (SPIE). [DOI: 10.1117/1.3630225]

Subject terms: laser applications; deposition; femtosecond phenomena; focal plane arrays.

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1 Introduction

For decades, photolithography has been the predominant method of silicon circuit fabrication due to its high throughput and ability to produce feature sizes on the order of tens of nanometers. However, its drawbacks include expensive masks, multiple coating, etching, and developing steps, and photoresist restrictions. Laser-based manufacturing technology, on the other hand, can circumvent some of these limiting obstacles. Laser direct write has been demonstrated for various microfabrication and nanoscale patterning applications. Examples include the use of near-field scanning optical microscopy to achieve line sizes on the order of tens of nanometers,¹ near-field parallel lithography which

can produce tens of nanometer features in parallel,² three-dimensional polymerization of sub-micron features using femtosecond laser pulses,³⁻⁵ and forward transfer of materials from a sacrificial mask to a substrate surface to form dots hundreds of nanometers in width.^{6,7} The feasibility of laser deposition for repairing a lithographic mask,⁸ bridging broken circuits,^{9,10} and making transistors, capacitors, resistors, photonic bandgap structures and other electrical components,^{11,12} has also been demonstrated.

In this work, we combine laser direct write and chemical vapor deposition (CVD) methods, with an intention to produce feature sizes of hundreds of nanometers. We will describe the laser direct write CVD experimental methodology used to produce semiconductor nanowires, the parameter optimization for controlling the heat distribution, and an evaluation on the feasibility for electronic applications.

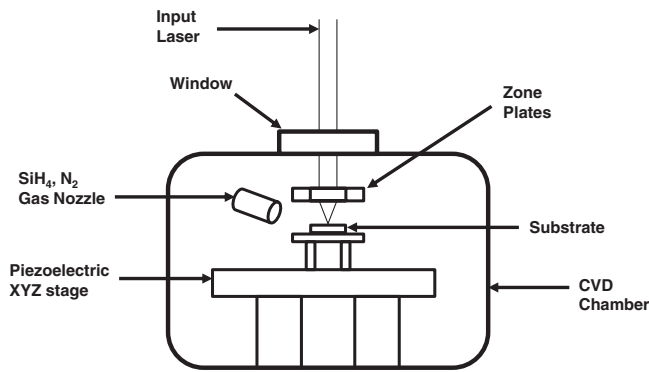


Fig. 1 Schematic diagram of the system for laser direct writing of silicon nanowires.

2 Experimental Details

In the laser direct write CVD system, the laser energy is applied to the surface of a substrate material in a vacuum chamber and creates a localized heating area. Reactive gas (silane for silicon growth) is delivered to this locally heated area and therefore decomposes, leaving behind a small amount of material deposited on the surface. While the material is being deposited, the piezoelectric stage holding the substrate moves relative to the focused laser spot, making the conductive lines into the desired pattern. A schematic illustrating the experimental setup is shown in Fig. 1.

In our work for producing silicon nanowires, deposition was performed at a pressure between 10 and 15 Torr with a constant flow rate of 5 sccm of 10% silane in argon. Continuous wave (cw) and femtosecond (fs) laser systems were tested to compare the results. The cw laser used was a ND:yttrium-aluminum-garnet laser with a wavelength of 532 nm and a maximum power of 10 W. The femtosecond laser used was a mode-locked Ti:sapphire laser with a wavelength of 800 nm, about 100 fs pulse duration, 14 nJ per pulse maximum, and a repetition rate of 86 MHz. The femtosecond laser output was then frequency-doubled to 400 nm using a 0.5-mm thick barium borate (BBO) crystal and then focused onto the substrate surface with high numerical aperture Fresnel phase zone plates. These phase zone plates are made from hydrogen silsesquioxane (HSQ) coated on a quartz substrate and patterned by electron beam lithography (EBL). Indium tin oxide (ITO) is coated on the quartz substrate to avoid charging during EBL, and a hexamethyldisilazane (HMDS) layer is used to improve the adhesion of the developed HSQ to the ITO. In order to produce nanoscale structures, a small laser spot is desirable. The size of the spot produced by the zone plate is calculated as¹³

$$w_o = \frac{0.61\lambda}{n \sin[\arctan(D/2f)]}, \quad (1)$$

where w_o is the spot size, λ is the wavelength, n is the index of refraction, D is the diameter of the zone plate, and f is the focal length. Using the typical zone plate diameter and focal length of 300 and 50 μm , respectively, the diffraction-limited spot sizes become 0.342 μm for 532 nm light and 0.257 μm for 400 nm light.

Since the sample substrate must be positioned at the zone plate focal point, it is important to know the depth

of focus (DOF) of the zone plate, which is computed as:¹³

$$DOF = 0.64 \frac{\pi w_o^2}{\lambda}. \quad (2)$$

For the zone plates used in this work, the depth of focus is 0.332 and 0.442 μm for 400 and 532 nm wavelength, respectively. The gap distance between the zone plate and the substrate therefore needs to be very well controlled. In this work, an interferometric spatial phase imaging (ISPI)¹⁴ technique was used to detect the gap distance between the zone plate and the substrate, and then a five-axis high precision piezoelectric nanopositioning stage was employed to adjust and maintain the desired distance. ISPI is an alignment technique with nanometer resolution developed by Moon et al.¹⁴ In our case, the sensitivity achieved is on the order of tens of nanometers, which is sufficient to give accurate readings for the gap distance between the zone plate and the substrate. The piezoelectric nanopositioning stage has a resolution of better than 1 nm and the overall noise of the system is less than 15 nm. Therefore, the combination of these components yields more than adequate control for the required precision.

Two different substrates were used in our work. The first was 1-mm thick quartz with a 200 nm polysilicon top layer. The second substrate was the same as the first substrate with an additional deposition of 50 nm of silicon dioxide on top of the quartz and polysilicon. Quartz was chosen to minimize the heat conducted away from the area directly under the incident laser while the thin polysilicon layer acted as a means for absorbing laser radiation. The topmost silicon dioxide layer in the second substrate acted to electrically insulate the deposited lines from the polysilicon for potential electronic applications.

3 Results and Discussion

Silicon wires with fully controlled lengths up to 200 μm (limited by the scan range of the piezoelectric stage) on both substrates have been fabricated using either cw or fs lasers.

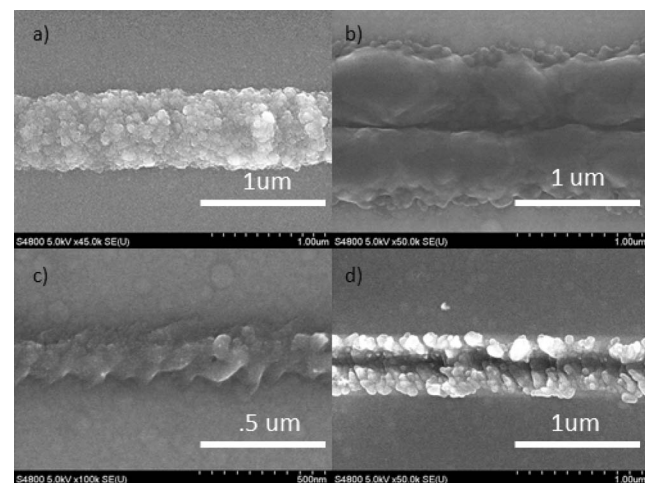


Fig. 2 SEM images of (a) cw laser deposited silicon line on polysilicon with a linewidth of around 600 nm. (b) cw laser deposited silicon line on silicon dioxide with a linewidth around 1.2 μm . (c) fs laser deposited silicon line on silicon dioxide with a linewidth of around 300 nm. (d) fs laser deposited silicon line on polysilicon with a width of around 500 nm.

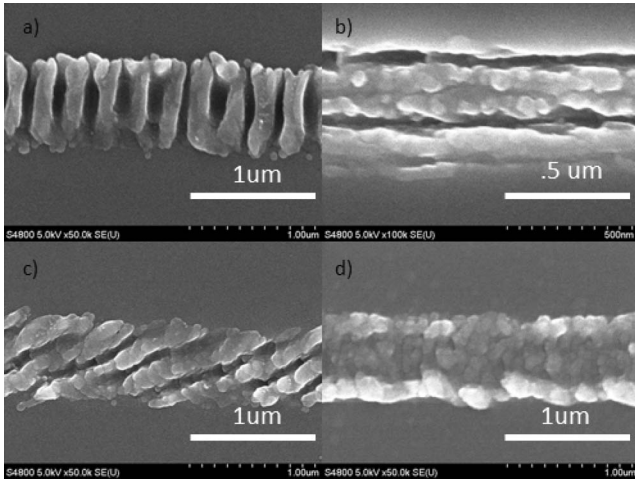


Fig. 3 SEM image of femtosecond laser deposited silicon line with (a) horizontally polarized light, (b) vertically polarized light, (c) 45 deg polarized light, and (d) circularly polarized light. For all images the substrate is 200 nm of polysilicon on 1 mm of quartz.

For nanowires deposited using the cw laser on the substrate of polysilicon on quartz, the minimum linewidth is around 600 nm [Fig. 2(a)]. This linewidth is slightly larger than the diffraction-limited spot size of 0.442 μm due to heat diffusion. When tested on the substrate with a silicon dioxide top layer, the minimum linewidth was in excess of 1 μm [Fig. 2(b)]. This larger linewidth is also due to heat diffusion since the heat absorbed by the polysilicon diffuses more in the lateral direction before it reaches the surface. Conversely, for the fs laser deposition, the narrowest lines were around 300 nm as seen in Fig. 2(c), on the substrate with the

silicon dioxide top layer. When the fs laser was tested on polysilicon on quartz, the minimum line width was around 500 nm as shown in Fig. 2(d). The surface of the nanowires produced is generally rough, which may be beneficial for applications such as chemical sensing where a large surface area is desirable.

The substrate characteristics play a key role in understanding and optimizing the deposition formation. The most important substrate qualities are the absorptivity and thermal diffusivity. For the substrate of polysilicon on quartz, the thickness of the polysilicon layer is adequate for absorbing both the 532 nm cw laser and the 400 nm fs laser. The linewidth produced by the cw laser is larger than that produced by the fs laser due to the longer heat diffusion lengths produced by a cw laser. For the substrate with a silicon dioxide top layer, there is a difference between the absorption of the two types of lasers. For the fs laser, the top silicon dioxide layer absorbs laser energy,³ whereas the silicon dioxide does not absorb energy from the cw laser. Ultrafast laser pulses incident on wide bandgap materials can create a multiphoton absorption effect, causing absorption in materials that would otherwise be transparent. This multiphoton absorption decreases the laser absorption area and can reduce the fabricated feature size,^{3,15} which explains why the deposited silicon on silicon dioxide is narrower compared with that on polysilicon.

Various experimental parameters were tested to explore the minimum linewidth, the measure for the resolution of the laser writing method. Minimizing the laser intensity was proven to be critical for minimizing the linewidth. The Gaussian shape of the laser beam allows only the most intense portions at the center of the profile to be absorbed, which reduces the size of the heated area and the linewidth produced. This further explains why for the case using a fs laser, the

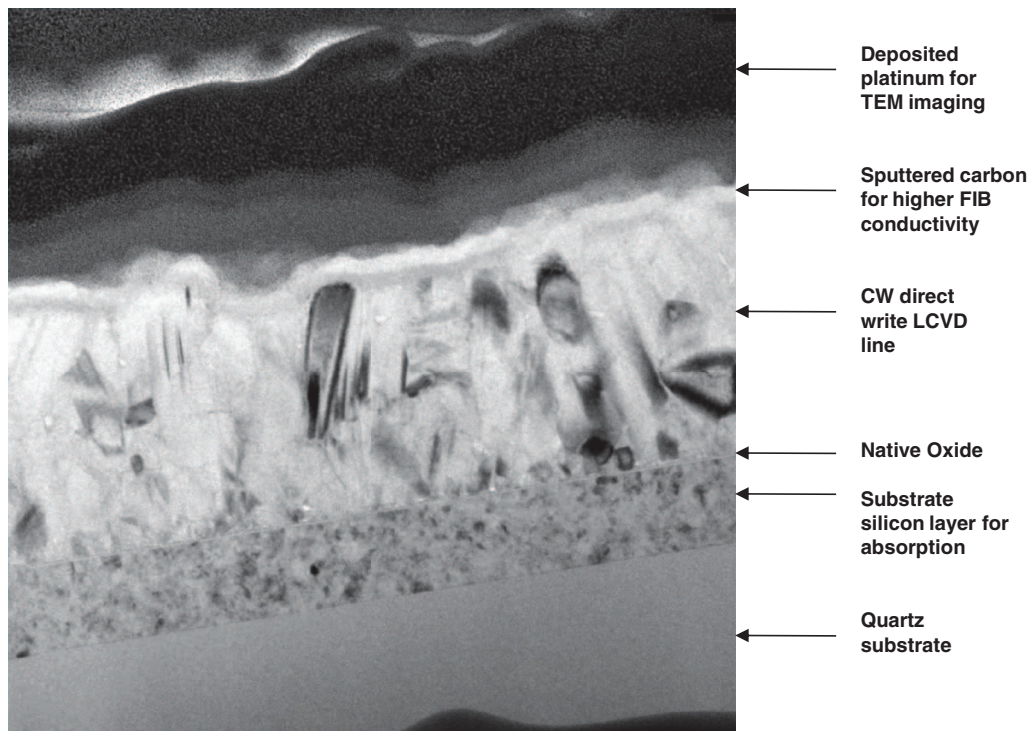


Fig. 4 Cross sectional TEM image of cw laser deposited silicon showing the substrate surface.

minimum linewidth can be even smaller than the laser spot size. In contrast, the linewidth was relatively insensitive to pressure, silane flow rate, and scan speed of the piezoelectric stage. Pressures ranging from 1 to 25 Torr, silane flow rates of between 1 and 20 sccm, and laser scan speeds from 0.1 to 5.0 $\mu\text{m/s}$ were tested. Although they had some effect on the width, these parameters were by no means heavily influential in the linewidth. An alteration to flow rate, pressure, or scan speed will cause changes in the amount of deposited material (thickness of the nanowire), but the linewidth is less affected.

The polarization of the laser beam also affects the morphology of the deposited lines, similar to the formation of laser induced polarization surface structures (LIPSS) reported in the literature.¹⁶ These LIPSS form perpendicular to the incident electric field, and for our laser direct write CVD process they make undesirable ridges which can degrade the line continuity. Figures 3(a)–3(c) show the relationship between the polarization direction and the deposition continuity. The ridges are all formed perpendicular to the laser polarization direction. To circumvent this drawback the laser was circularly polarized using a quarter wave plate, and subsequently the ridges were almost completely removed as shown in Fig. 3(d).

For this laser direct write CVD technique to be considered a legitimate method for creating a device, the fabrication process must not degrade the surface integrity and the lines that are created must have a functional resistivity. The transmission electron microscopy (TEM) image in Fig. 4 shows that the silicon dioxide surface directly under the deposition remains completely intact after deposition, demonstrating that this can be done without destroying the top layer or ablating the substrate surface. The electrical conductivities of these laser direct written wires were obtained by first fabricating metal contacts directly on as-written wires on silicon dioxide substrates, followed by current–voltage (I – V) measurements. The I – V measurements were carried out for various wire lengths deposited on silicon dioxide. A linear curve fit was then used to find the resistivity of the polysilicon wires, which was estimated to be $2 \times 10^5 \Omega \cdot \text{cm}$. This value is consistent with the value of undoped polysilicon ($4.5 \times 10^5 \Omega \cdot \text{cm}$),¹⁷ indicating that it is foreseeable to use these lines for device fabrication. Controlled *in situ* doping is currently being carried out to fabricate functional devices such as chemical sensors.

4 Conclusions

Laser direct write CVD is shown to be capable of producing feature sizes on the scale of a few hundred nanometers. It was found that the narrowest linewidth was produced using an fs pulsed laser on a silicon dioxide surface, due to multiphoton absorption in silicon dioxide and confined heating by fs pulses. There is minimal damage to the substrate surface after deposition, and the deposited lines have the necessary electronic properties for successful integration into an electronic device.

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References

1. D. Hwang, S. G. Ryu, N. Misra, H. Jeon, and C. P. Grigoropoulos, "Nanoscale laser processing and diagnostics," *Appl. Phys. A* **96**, 289–306 (2009).
2. S. M. V. Uppuluri, E. Kinzel, Y. Li, and X. Xu, "Parallel optical nanolithography using nanoscale bowtie aperture array," *Opt. Express* **18**(7), 7369–7375 (2010).
3. J. Koch, F. Korte, C. Fallnich, A. Ostendorf, and B. N. Chichkov, "Direct-write subwavelength structuring with femtosecond laser pulses," *Opt. Eng.* **44**(5), 051103 (2005).
4. F. Korte, J. Serbin, J. Koch, A. Egbert, C. Fallnich, A. Ostendorf, and B. N. Chichkov, "Towards nanostructuring with femtosecond laser pulses," *Appl. Phys. A* **77**, 229–235 (2003).
5. H. Schuck, D. Sauer, T. Anhut, I. Reimann, and K. König, "Sub-100 nm nanostructuring of silicon by ultrashort laser pulses," *Opt. Express* **13**(17), 6651–6656 (2005).
6. D. P. Banks, C. Grivas, J. D. Mills, R. W. Eason, and I. Zergioti, "Nanodroplets deposited in microarrays by femtosecond Ti:sapphire laser-induced forward transfer," *Appl. Phys. Lett.* **89**, 193107 (2007).
7. C. B. Arnold, P. Serra, and A. Pique, "Laser direct-write techniques for printing of complex materials," *Mater. Res. Soc. Symp. Proc.* **32**, 23–31 (2007).
8. D. Bauerle, *Laser Processing and Chemistry*, Springer-Verlag, Berlin Heidelberg (1996).
9. T. H. Baum and P. B. Comita, "Laser-induced chemical vapor deposition of metals for microelectronics technology," *Thin Solid Films* **218**, 80–94 (1992).
10. J. B. Park, C. J. Kim, P. E. Shin, S. H. Park, H. S. Kang, and S. H. Jeong, "Hybrid LCDV of micro-metallic lines for TFT-LCD circuit repair," *Appl. Surf. Sci.* **253**, 1029–1035 (2006).
11. E. C. Kinzel, H. H. Sigmarsson, X. Xu, and W. J. Chappell, "Laser sintering of thick-film conductors for microelectronic applications," *J. Appl. Phys.* **101**, 063106 (2007).
12. M. C. Wanke, O. Lehmann, K. Müller, Q. Wen, and M. Stuke, "Laser rapid prototyping of photonic band gap microstructures," *Science* **275**(5304), 1284–1286 (1997).
13. F. L. Pedrotti, L. S. Pedrotti, and M. L. Pedrotti, *Introduction to Optics*, pp. 316, Pearson Education Inc., San Francisco, California (2007).
14. E. E. Moon, L. Chen, P. N. Everett, M. K. Mondol, and H. I. Smith, "Interferometric-spatial-phase imaging for six-axis mask control," *J. Vac. Sci. Technol. B* **21**(6), 3112–3115 (2003).
15. W. H. Teh, U. Durig, U. Drechsler, C. G. Smith, and H.-J. Guntherodt, "Effect of low numerical-aperture femtosecond two-photon absorption on (SU-8) resist for ultrahigh-aspect-ratio microstereolithography," *J. Appl. Phys.* **97**(5), 054907 (2005).
16. A. Borowiec and H. K. Haugen, "Subwavelength ripple formation on the surfaces of compound semiconductors irradiated with femtosecond laser pulses," *Appl. Phys. Lett.* **82**(25), 4462–4464 (2003).
17. T. I. Kamins, "Resistivity of chemically deposited polycrystalline-silicon films," *Solid-State Electron.* **15**, 355–358 (1972).



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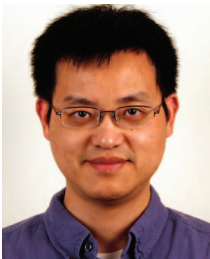
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