Crystalline silicon core fibres from aluminium core preforms

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Traditional fibre-optic drawing involves a thermally mediated geometric scaling where both the fibre materials and their relative positions are identical to those found in the fibre preform. To date, all thermally drawn fibres are limited to the preform composition and geometry. Here, we fabricate a metre-long crystalline silicon-core, silica-cladded fibre from a preform that does not contain any elemental silicon. An aluminium rod is inserted into a macroscopic silica tube and then thermally drawn. The aluminium atoms initially in the core reduce the silica, to produce silicon atoms and aluminium oxide molecules. The silicon atoms diffuse into the core, forming a large phase-separated molten silicon domain that is drawn into the crystalline silicon core fibre. The ability to produce crystalline silicon core fibre out of inexpensive aluminium and silica could pave the way for a simple and scalable method of incorporating silicon-based electronics and photonics into fibres.
Silicon (Si) and its oxide silica (SiO₂) have both played an important role in modern day electronics and communications. In recent years the opportunities for tighter integration between electronics and photonics have led to the emergence of the field of Si photonics where wafer processes are used to combine the best features of both materials. In a mirror effort the advanced demonstrations of incorporating Si into fibres have been explored in electronics and photonics, such as photodetection, fibre battery, fibre solar cell, electro-optical modulation, material engineering, non-linear optics, pressurized Si sphere fabrication and so on. Two disparate methods of producing Si-core silica-cladded fibres have been reported, the first relies on the physical flow process and the second on a chemical reaction internal to a pre-fabricated fibre. In the first method, high-purity Si is placed inside a silica preform and drawn down into a silica fibre with a molten Si core. The second involves the use of high-pressure Si precursor gas (SiH₄) to deposit Si inside a pre-fabricated hollow channel fibre via a chemical vapour deposition (CVD) process. The CVD method is more versatile while the thermal drawing approach is more scalable.

The placement of disparate materials thermally drawn into close proximity at elevated temperatures presents compelling opportunities for inducing chemical reactions between the constituent materials that could in principle provide the versatility of chemical reactions with the scalability of fibre drawing. Results of this approach that we call fibre-draw synthesis to date have been confined to reactions in only very small domains at an interface between materials.

In this work, we utilize the redox reaction between aluminium (Al) and silica (SiO₂) during fibre drawing to produce a fibre with a different core composition than that of the preform. This occurs through the following reaction:

\[ 4\text{Al} + 3\text{SiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Si} \]

At high drawing temperature, the metallic Al reacts with the cladding material SiO₂ and reduces the Si. The products (Al₂O₃ and Si) then get phase separated, thus forming a pure Si-core in silica fibre. The reaction, diffusion and the phase separation all take place at an elevated temperature close to the fibre draw temperature.

**Results**

**Fibre fabrication and characterization.** The proposed method centres on a technique so-called preform-to-fibre fabrication by thermally drawing a macroscopic solid-state preform into extended lengths of uniform fibres, as shown in Fig. 1a. The preform consists of one piece of Al wire (3 cm long, 250 μm diameter) placed inside a silica tube (inner diameter 300 μm, outer diameter 600 μm). This assembly is further cladded with two concentric silica tubes (one with 1 mm inner diameter, 6 mm outer diameter, and the other one with 6 mm inner diameter and 12 mm outer diameter), as shown in Fig. 1b. The chamber where the Al wire resides is then pumped to 10⁻³ mbar and sealed with silica rods on both ends to prevent Al in contact with air. The preform with the Al core is then heated up to 2,200 °C in Argon atmosphere and pulled into metre-long fibres with the diameters of ~500 μm. During the fibre draw, Al melts and reacts with the surrounding silica cladding, and reduce Si atoms out of silica. Si atoms accumulate during this process and finally occupy the entire core, resulting in a Si-core fibre with silica cladding, as shown in Fig. 1c.

Figure 2a shows an optical image of the fibre and indicates a change in core material as the fibre is drawn. From top to bottom, the colour of the fibre core is seen to transit from light yellow to black. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) analyses are taken at four locations along the length of the fibre. Figure 2b–e is SEM images of the cross-sections at locations 1–4 marked in Fig. 2a, respectively. Comparing these four figures, one notice there are light-grey dots within the core region in Fig. 2c–e. The grey dot in Fig. 2c is so small that is hardly noticed, but can be seen more clearly from EDX mapping on a zoomed-in area as shown in Fig. 2o. The dots in Fig. 2d,e are much larger. It is worth mentioning though that these dots in Fig. 2c–e, however, are quite different in forming mechanism and in 3D shape. In Fig. 2c the dot is actually a precipitated spherical drop composed of a majority of Si. But in Fig. 2e the dot is actually cross-section of the long crystalline Si wire (Supplementary Note 1). The EDX analyses around these areas are shown to the right of the four SEM images and confirm that the dots in locations #3 and #4 are composed of high-purity Si. In Fig. 2f–q, green, red and yellow colours denote element Al, oxygen (O) and Si, respectively. In Fig. 2f, n (location #1), the core is composed mainly of Al and O. In Fig. 2g, k, o (location #2), a small agglomeration of Si appears while Al and O still dominate the core area. In Fig. 2h, p (location #3), a large Si core is formed in the centre of the core area, surrounded by a thick layer composed of Al and O. Finally, in Fig. 2m, q (location #4 which is in the black core section), Si occupies the entire core region, leaving Al to only a thin layer between the core and the cladding.

To further explore the differences between the light-yellow and black core regions, transmission electron microscopy (TEM)-based analyses are performed at two different cross-sections (see Supplementary Fig. 1 for preparation of TEM samples), corresponding approximately to locations 2 and 4, respectively. In the core of a yellow-core region, we find that spherical drops form scattered along the axial direction (Supplementary Fig. 2). If we focus on one of these spherical drops, we obtain the results shown in the top panel of Fig. 3. Figure 3a shows that the sphere is about 100 nm in diameter and is surrounded by a circle of different materials. The diffraction pattern in Fig. 3b,c shows that the materials are mostly amorphous, and the EDX maps in Fig. 3c–e reveal that the sphere is Si rich while the surrounding...
Figure 2 | Transition of fibre core. (a) The optical image of a piece of fibre where a light-yellow core transits to a black core. The white dashed arrow illustrates the fibre drawing direction. (b–e) The SEM images of the cross-sections at the four labelled locations in a. (f–q) The EDX mappings of the marked area in b–e correspondingly. Green, red and yellow denote element aluminium (Al), oxygen (O) and silicon (Si), respectively.

Figure 3 | Nano-scale analyses on fibre core. On the top panel, a–f data are measured inside the core region of the fibre with a yellow core (near location #2 in Fig. 2a). (a) TEM image, the dot is one of the many dots seen on the sample. (b) The diffraction pattern indicates that the sample is mostly amorphous. (c–e) EDX mappings on a, red, green and yellow denote O, Al and Si, respectively. (f) EDX line scan result. The white arrow in e shows the line scanning path corresponding to f. On the bottom panel, g–l data are measured at the core-cladding interface of the fibre with a black core (near location #4 in Fig. 2a). In g, the yellow dashed line indicates the interface between the crystalline part (core) and the amorphous part (clad). The parallel orange lines are (110) faces, and the distance between them is measured 0.192 nm. (h) Taken from crystalline side of the yellow line, and the zone axis has been tilted to \textless 111\textrangle. (i–k) EDX mappings on g, red, green and yellow denote O, Al and Si, respectively. (l) EDX line scan result. The white arrow in k shows the line scanning path corresponding to l.
melts when fed into the heating zone and keeps its molten state.

Silica cladding. Al has a melting temperature of 660.32°C, and the reaction rate is orders of magnitude higher. Chemical reaction progress, more and more Al in the Al-Si melt gets consumed hence much less Al2O3 remains in the melt, while more Al2O3 is produced, the excessive Al2O3 precipitates out of molten Al. Meanwhile, Si stays with molten Al because of their miscibility. As the density of molten Al and Si are about 2.4 g cm−3 and are smaller than that of molten alumina that is about 2.8 g cm−3 (refs 34–36), molten Al-Si floats up and molten alumina sinks to the bottom as shown in Fig. 5b. As the draw and chemical reaction progress, more and more Al in the Al-Si melt gets consumed hence much less Al2O3 remains in the melt, while Si keeps accumulating in the Al-Si melt on top of alumina melt. Finally, when Al is completely consumed in the reaction, a highly pure Si melt is obtained on the top of the core. Further drawing results in a highly pure Si-core fibre. Figure 5c–e depicts the above-mentioned core composition change during the draw.

In addition, although the reduced Si atoms are mixed with the other product Al2O3 and not-yet-reacted Al atoms in the beginning, their solubility properties play an important role in separating them and finally forming a Si core. Most importantly, Si is completely miscible with Al in the liquid state, but their solubility with Al2O3 is comparatively low32,34. As more and more Al2O3 is produced, the excessive Al2O3 precipitates out of molten Al. Meanwhile, Si stays with molten Al because of their miscibility. As the density of molten Al and Si are about 2.4 g cm−3 and are smaller than that of molten alumina that is about 2.8 g cm−3 (refs 34–36), molten Al-Si floats up and molten alumina sinks to the bottom as shown in Fig. 5b. As the draw and chemical reaction progress, more and more Al in the Al-Si melt gets consumed hence much less Al2O3 remains in the melt, while Si keeps accumulating in the Al-Si melt on top of alumina melt. Finally, when Al is completely consumed in the reaction, a highly pure Si melt is obtained on the top of the core. Further drawing results in a highly pure Si-core fibre. Figure 5c–e depicts the above-mentioned core composition change during the draw.
Solubility not only plays an important role in obtaining a Si-core fibre, but also explains the embedded spheres seen in Fig. 3a as well. Those Si-rich spheres in alumina are from the small amount of Si that dissolves in molten alumina in the heating zone. As the fibre is pulled out of the furnace and the temperature drops, the solubility of Si in Al\(_2\)O\(_3\) decreases. The excess Si then precipitates out and forms spheres in alumina.

Besides accumulating with the help of miscibility properties, the Si core is also purified by going through the furnace. Because the preform is fed into the furnace from the top side and the fibre is pulled out of the furnace from the bottom, the difference between the hot furnace temperature and room temperature constructs a temperature profile in which Si melts when entering the hot zone and solidifies when leaving the hot zone. This temperature profile provides the zone melting condition to further purify the Si core\(^3^7\). In addition, Si is crystallized when it cools down from liquid state after pulling out of furnace\(^3^7\).

### Discussion

Our method remains further optimization for future applications. For example, the size of Si-core could be significantly reduced by redesigning the core-clad ratio and adjusting the fibre draw parameters. The redraw technique could also be applied to achieve nanometer-scale Si wires\(^2^3\). Also the thin interface layer that lies between the core and the cladding as seen in Figs 2i and 3j could be of interest for the potential advantage on oxygen gettering and surface modification for the post-drawing process\(^8,^3^9\). The smoothness of the Si is verified in the atomic force scan (AFM) image (Supplementary Fig. 8, Supplementary Note 3). Last but not least, the mechanism of producing Si during fibre drawing is also applicable to other reductive metals, for example, Titanium (Ti) or Calcium (Ca), which could reduce Si because of their more negative reduction potentials\(^4^0\).

To conclude, we demonstrate a new way to fabricate a high-quality crystalline Si-core fibre by thermally drawing a preform consisting of low-cost metal. The methods described herein set the stage for extending the materials and architecture selections with fibre drawing, thus paving the way towards more sophisticated fibre-based devices.

### Methods

**Preform fabrication and fibre drawing.** For the preform preparation we use the fused-quartz tubes and rods supplied by Technical Glass Products and the Al wire from Alfa Aesar. The fused-quartz capillary fibre (300 \(\mu\)m inner diameter and 660 \(\mu\)m outer diameter) is from Molex Incorporated (product # TSP300794). The coating material on the capillary fibre is burned with flame and cleaned up with isopropanol.

The 0.25-mm-diameter Al wire is first inserted into the capillary fibre and then put into a fused-quartz tube with an inner diameter of 1 mm and outer diameter of 6 mm (1 \(\times\) 6 tube). Two 1-mm-diameter fused-quartz rod are also inserted into the 1 \(\times\) 6 tube, one on top of the capillary fibre and the other in the bottom of the capillary fibre. The whole assembly is put into a fused-quartz tube with an inner diameter of 6 mm and outer diameter of 12 mm. With the help of propane flame, one end of the structure is fused and the whole assembly is pumped to vacuum and the other end is fused under vacuum.

The fibre drawing process starts at the temperature of 2,150 °C and the drawing process continues at 2,200 °C. The preform is fed into the furnace from top with a speed of 1 mm min\(^{-1}\), and the fibre is pulled out from the bottom end of the furnace with a speed of 660 mm min\(^{-1}\). The fibre is further coated with coating material, which is called ‘DSM Desotech 3471-3-14(941-314) Desolite single coat coating’, and cured by an in-line ultraviolet coating system.

**Characterization instruments and methods.** The SEM images and related EDX mappings on cross-sections of the fibres are taken with the JEOL 6010LA SEM. The TEM images and related EDX scans are taken using the JEOL 1010 FEG Analytical Electron Microscope. The Raman spectrum is taken in the Horiba Jobin Yvon LabRAM Model HR800. The XRD spectrum is taken in Rigaku SmartLab with a parallel-beam optics and capillary-sample set-up. The electrical characterization of the Si wire is on a 4-point stage using the Hewlett-Packard (HP) 4155A Semiconductor Parameter Analyser. The surface smoothness of the Si wire is characterized with Digital Instruments Vecco Dimension 3100 AFM, and the data are processed in the Nanoscope Analysis software (v1.40) from Bruker Corporation.

### References

1. Dresselhaus, G., Kip, A. & Kittel, C. Cyclotron resonance of electrons and holes in silicon and germanium crystals. *Phys. Rev.* 98, 368–384 (1955).
2. Klement, W., Willens, R. H. & Duwez, P. Non-crystalline structure in solidified gold-silicon alloys. *Nature* 187, 869–870 (1960).
3. Seto, J. V. W. The electrical properties of polycrystalline silicon films. *J. Appl. Phys.* 46, 5247–5254 (1975).
4. Lin, V. S.-Y., Motesharei, K., Dancil, K.-P. S., Sailor, M. J. & Ghadiri, M. R. A porous silicon-based optical interferometric biosensor. *Science* 278, 840–843 (1997).
5. Pavesi, L., Dal Negro, L., Mazzoleni, C., Franzò, G. & Priolo, F. Optical gain in silicon nanocrystals. Nature 408, 440–444 (2000).
6. Vlasov, Y. A., Bo, X. Z., Sturm, J. C. & Norris, D. J. On-chip natural assembly of silicon photonic bandgap crystals. Nature 414, 289–293 (2001).
7. Cui, Y. & Lieber, C. M. Functional nanoscale electronic devices assembled using silicon nanowire building blocks. Science 291, 851–853 (2001).
8. Xiang, J. et al. Ge/Si nanowire heterostructures as high-performance field-effect transistors. Nature 441, 489–493 (2006).
9. Tian, B. et al. Coaxial silicon nanowires as solar cells and nanoelectronic power sources. Nature 449, 885–889 (2007).
10. Atwater, H. A. & Polman, A. Plasmonics for improved photovoltaic devices. Nat. Mater. 9, 205–213 (2010).
11. Foster, M. A. et al. Silicon-chip-based ultrafast optical oscilloscope. Nature 456, 81–84 (2008).
12. Leuthold, J., Koos, C. & Freude, W. Nonlinear silicon photonics. Nat. Photon. 4, 535–544 (2010).
13. Reed, G. T., Mashanovich, G., Gardes, F. Y. & Thomson, D. J. Silicon optical modulators. Nat. Photon. 4, 518–526 (2010).
14. Liu, A. et al. A high-speed silicon optical modulator based on a metal-oxide-semiconductor capacitor. Nature 427, 615–618 (2004).
15. He, R. et al. Integration of giga赫ertz-bandwidth semiconductor devices inside microstructured optical fibres. Nat. Photon. 6, 174–179 (2012).
16. Lin, H. et al. Twisted aligned carbon nanotube/silicon composite fiber anode for flexible wire-shaped lithium-ion battery. Adv. Mater. 26, 1217–1222 (2014).
17. He, R. et al. Silicon p-i-n junction fibres. Adv. Mater. 25, 1461–1467 (2013).
18. Martensson, F. et al. Silicon-core glass fibres as microwire radial-junction solar cells. Sci. Rep. 2, 591 (2014).
19. Won, D.-J. et al. All-optical modulation of laser light in amorphous silicon-filled microstructured optical fibers. Appl. Phys. Lett. 91, 161112 (2007).
20. Healy, N. et al. Extreme bandwidth modification in laser-crystallized silicon optical fibres. Nat. Mater. 13, 1122–1127 (2014).
21. Mehta, P., Healy, N., Day, T. D., Badding, J. V. & Peacock, A. C. Ultrafast wavelength conversion via cross-phase modulation in hydrogenated amorphous silicon optical fibres. Opt. Express 20, 26110–26116 (2012).
22. Peacock, A. C., Mehta, P., Horak, P. & Healy, N. Nonlinear pulse dynamics in multimode silicon core optical fibers. Opt. Lett. 37, 3351–3353 (2012).
23. Gunemnik, A. et al. Silicon-in-silica spheres via axial thermal gradient in-fibre capillary instabilities. Nat. Commun. 4, 2216 (2013).
24. Ballato, J. et al. Silicon optical fiber. Opt. Express 16, 18675–18683 (2008).
25. Sazio, P. J. et al. Microstructured optical fibers as high-pressure microfluidic reactors. Science 311, 1583–1586 (2006).
26. Oref, N. D. et al. Fiber draw synthesis. Proc. Natl Acad. Sci. 108, 4743–4747 (2011).
27. Morris, S. et al. Reactive molten core fabrication of silicon optical fiber. Opt. Mater. Express 1, 1141–1149 (2011).
28. Hou, C. et al. Direct atomic-level observation and chemical analysis of ZnSe synthesized by in situ high-throughput reactive fiber drawing. Nano Lett. 13, 975–979 (2013).
29. Wang, D. & Shi, Z. Aluminothermic reduction of silica for the synthesis of alumina-aluminum-silicon composite. J. Mater. Synth. Process 9, 241–246 (2001).
30. Finlayson, C. E., Ameszcu-Corra, a., Sazio, P. J. a., Baril, N. F. & Badding, J. V. Electrical and Raman characterization of silicon and germanium-filled microstructured optical fibers. Appl. Phys. Lett. 90, 132110 (2007).
31. Lagonigro, L. et al. Low loss silicon fibers for photonics applications. Appl. Phys. Lett. 96, 041105 (2010).
32. Okamoto, H. & Massalski, T. B. in Desk Handbook: Phase Diagrams for Binary Alloys (ed. Okamoto, H.) xxxix–xliii (ASM International, 2000).
33. Standage, A. E. & Gani, M. S. Reaction between vitreous silica and molten aluminum. J. Am. Ceram. Soc. 50, 101–105 (1967).
34. Hatch, J. E. Aluminum: Properties and Physical Metallurgy vol. 1 (ASM International, 1984).
35. Inatomi, Y., Onishi, F., Nagashio, K. & Kuribayashi, K. Density and thermal conductivity measurements for silicon melt by electromagnetic levitation under a static magnetic field. Int. J. Thermophys. 26, 44–59 (2007).
36. Aksay, I. A., Pask, J. A. & Davis, R. F. Densities of SiO2-Al2O3 melts. J. Am. Ceram. Soc. 62, 332–336 (1979).
37. Pfann, W. G. Zone Melting: This technique offers unique advantages in purification and in control of composition in various substances. Science 135, 1101–1109 (1962).
38. Olson, G. L. & Roth, J. A. Kinetics of solid phase crystallization in amorphous silicon. Mater. Sci. Rep. 3, 1–77 (1988).
39. Nordstrand, E. F., Dibbs, A. N., Eraker, A. J. & Gibson, U. J. Alkaline oxide interface modifiers for silicon fiber production. Opt. Mater. Express 3, 651–657 (2013).
40. Atkins, P. W. & de Paula, J. Physical Chemistry (W.H. Freeman, 2002).

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Author contributions
C.H. and L.W. fabricated fibre, S.T. prepared TEM samples, C.H., S.T. and X.J. conducted TEM analysis, C.H. and X.Z. provided electrical characterization, C.H. conducted other experiments, C.H., X.J. and Y.F. discussed the Si-core forming mechanism and C.H. and Y.F. wrote the manuscript.

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