

Flexible Polymer-Embedded Si Wire Arrays

By Katherine E. Plass, Michael A. Filler, Joshua M. Spurgeon, Brendan M. Kayes, Stephen Maldonado, Bruce S. Brunschwig, Harry A. Atwater,* and Nathan S. Lewis*

Wafer-based single-crystalline inorganic semiconductors such as Si and GaAs currently enable the most efficient solar cells. However, their rigidity precludes the use of inexpensive processing schemes such as roll-to-roll manufacturing and/or their installation in flexible forms. While amorphous and polycrystalline films of inorganic semiconductors can be grown on flexible substrates such as stainless steel or polymeric sheets, solar cells processed from these disordered absorber materials exhibit lower solar photovoltaic conversion efficiency than single crystal Si or GaAs. Organic and hybrid organic/inorganic solar cells offer flexibility and processability, but suffer from low efficiency and instability of the organic light-absorbing and/or charge-conducting material under prolonged illumination. We describe herein the fabrication of arrays of highly oriented, single-crystalline Si wire light absorbers and charge conductors embedded in a polymeric film. This composite material combines the photostability and solar-energy conversion potential of high quality single-crystalline semiconductors with the processability and flexibility of polymers.

Device physics modeling has suggested that wire array solar cells consisting of impure, inexpensive light absorbers can exhibit energy conversion efficiencies comparable to those achieved with high quality single-crystal planar devices.^[1] The potential for high efficiency stems from the short radial distances over which photogenerated charge carriers can be extracted. On this premise, preliminary energy conversion devices using disordered arrays of Si wires have been developed.^[2,3] Concurrently, highly ordered, vertically oriented Si wire arrays have been grown over large areas^[4] and used to fabricate photovoltaic^[5] and photoelectrochemical devices.^[6] These oriented wire arrays are grown from a templated single crystalline Si wafer that is amenable to high-temperature processing steps such as solid state diffusion to form p–n junctions for solar cells. In a secondary treatment described herein, these Si wires are embedded in a transparent

polymer matrix and removed from the rigid Si wafer substrate, yielding a composite material that combines the benefits of single-crystalline, inorganic light absorbers with the flexibility and processability of polymers. Although 1D nanostructures such as carbon nanotubes,^[7–11] CdS nanoparticles,^[12] Mo nanowires,^[13] and ZnO nanorods^[14] have been embedded in polymers, the process described herein uniquely combines flexibility, atomic-scale crystallinity, and long-range order in a single material. The process also offers an approach towards formation of nanotechnology-based 3D circuits and optoelectronic systems, allowing the user to impose, create, and maintain ordered, oriented arrays of inorganic nanoscale or microscale wires in macroscale devices.^[15]

To demonstrate the process, large area Si wire arrays were grown by the vapor-liquid-solid (VLS) growth process on a Si(111) substrate (Fig. 1a).^[4,16–19] Either Au, Cu, or Ni was used as the VLS catalyst. As previously reported,^[4] a lithographically patterned oxide buffer layer was introduced on the substrate to isolate the regions of metal catalyst and prevent ripening during the early stages of the growth process. The Si precursor was SiCl₄ and wire growth was performed at 1000 °C in an atmosphere of H₂. This process resulted in arrays of well-ordered, vertically oriented, crystalline Si wires that were 1.5–2.0 μm in diameter, approaching 100 μm long, and spaced on the substrate in a cubic pattern with a 7 μm center-to-center pitch.

To form free-standing arrays, the wires were embedded into a polydimethylsiloxane (PDMS) polymer matrix (Fig. 1b). A PDMS solution was cast onto the Si wire array and subsequently cured. The polymer and the embedded Si wires were then mechanically removed from the Si(111) wafer. This process yielded flexible, polymer-supported arrays of crystalline Si wires embedded within a transparent, mechanically and chemically robust, PDMS sheet (Fig. 1c).^[20,21] Si wire arrays with areas greater than 1 cm² were embedded and removed in a single polymer film (Fig. 1d). The area of the wire-embedded sheet was limited only by the size of the initial array, which in turn was limited by the size of the reactor used to grow the wire arrays. Cross-sectional scanning electron microscopy (SEM) images of the PDMS/Si wire array composite films revealed intimate contact between the wires and the PDMS film (Fig. 2a). The as-removed films could be bent or rolled into cylinders having diameters as small as several millimeters (see Supporting Information, Fig. S1) without significantly damaging or dislodging the embedded Si wires (Fig. 2d). The polymer/wire composite also maintained the spacing, cubic unit cell, and orientation of the arrays prior to casting. Diffraction of visible light was used to determine the embedded wire spacing and periodicity. A 670 nm diode laser incident perpendicular to a flat sample surface produced a cubic

[*] Prof. N. S. Lewis, Dr. K. E. Plass, J. M. Spurgeon, Dr. S. Maldonado, Dr. B. S. Brunschwig
California Institute of Technology
Division of Chemistry and Chemical Engineering
1200 E. California Blvd. m/c 127-72
Pasadena, CA 91125 (USA)
E-mail: nslewis@caltech.edu
Prof. H. A. Atwater, Dr. M. A. Filler, B. M. Kayes
California Institute of Technology
Department of Applied Physics
1200 E. California Blvd. m/c 128-95
Pasadena CA 91125 (USA)
E-mail: haa@caltech.edu

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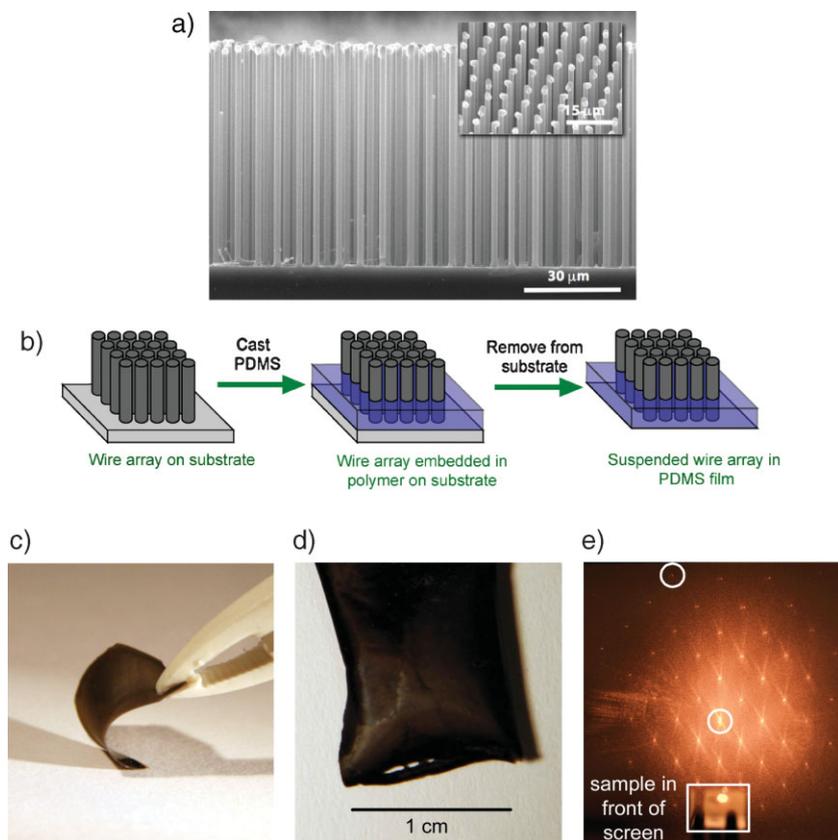


Figure 1. a) Cross-sectional SEM image of a well-ordered, vertically aligned array of uniform length and diameter Si wires grown using a Ni catalyst. A catalyst particle remained at the top of each of the wires. Inset: 45° angle SEM image. b) Schematic representation of the wire array embedding and removal process. Photographs show (c) a flexible, free-standing polymer-embedded wire array and (d) the large area as well as the near black color achievable with these films. e) Optical diffraction pattern produced by transmitted light, demonstrating the long-range order of the wires. The center (zero-order diffraction) and outer (4th-order diffraction) spots are circled.

array of diffraction spots (Fig. 1e) with a diffraction angle indicating an array spacing of $(6.9 \pm 0.2) \mu\text{m}$. Up to 4 orders of diffraction were observed even after mechanical deformation of the films. The wire array/polymer composites were highly light absorbing and/or scattering at the angle shown (Fig. 1c, d) even though PDMS is transparent to visible light and the top-down density of Si wires was less than 6.5% of the projected area of the film. This finding is in agreement with the reported enhanced light absorption in wire arrays^[22,23] and suggests that these composite films may have direct application in solar energy conversion devices.

The thickness of the PDMS film determined both the structural integrity of the composite and the extent to which the wires were exposed. PDMS/Si wire sheets were prepared in which one (Method 1, Fig. 2a) or both (Method 2, Fig. 2b, c) ends of the Si wires were exposed, allowing for subsequent formation of electrical contacts to the Si wires. To produce thinner polymer films, a low-boiling point siloxane was added to the PDMS solution that was used to embed the wires. The low-boiling point siloxane evaporated significantly during the curing step, resulting in 20 μm thick polymer films having greater than 50% of the length of the wires exposed (Fig. 2b–d). The wire arrays in such films were electrically conductive from top to bottom, but

exhibited immeasurably high resistances laterally. This finding indicated that the embedded Si wires extended through the polymer film and were also electrically isolated from each other by the polymer matrix.

Wires in the polymer sheet were highly crystalline and the polymer embedding process retained the wire orientation and symmetry produced by the VLS growth step. Figure 3a presents 2θ X-ray diffraction data comparing a Czochralski (CZ)-grown Si(111) wafer to that of PDMS composite films produced from Si wire arrays that were grown using either Au, Cu, or Ni as the VLS catalyst. All of the PDMS/Si wire films, as well as the Si(111) wafer, exhibited a single (111) diffraction peak located near 28.4° . The intensity and sharpness of this reflection demonstrated the crystal quality of the composite material. The (111) rocking curves (Fig. 3b) of the PDMS/Si wire films were centered near that of the CZ Si(111) wafer, attesting to the highly oriented nature of the wires. The deviations of the rocking curve center relative to that of the CZ wafer indicated that the PDMS/Si wire films did not lie completely flat on the substrate holder. The structure and large full-width at half-maximum of each curve indicated that the PDMS films contained multiple wire populations with small deviations from the vertical. A phi scan (Fig. 3c) showed six degenerate {220} reflections of the Si lattice, indicating a high degree of inter-wire rotational symmetry in the PDMS film. The difference in peak heights as a function of rotation angle resulted from the X-ray beam passing through different

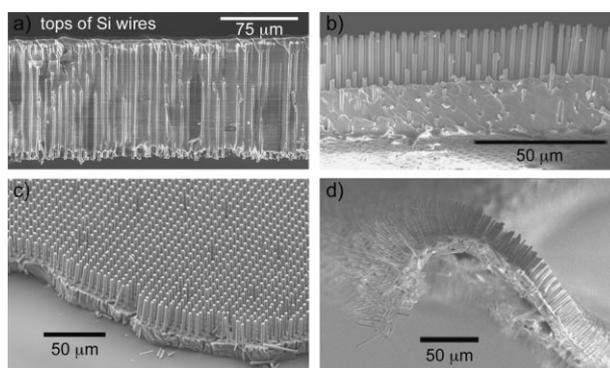


Figure 2. Cross-sections of embedded Si wire arrays of two different polymer thicknesses. a) Cross-section of a composite film fabricated with Method 1. Upon removal from the growth substrate, wires were exposed only at the bottom of the film. Note the conformal filling of the gaps between wires. b–d) The thinner composite film fabricated with Method 2 had a significant fraction of the wire length emerging from the polymer while the array pattern was maintained. b) The bottom of the film can be seen, demonstrating that the rods passed through the polymer. c) The array order from the top of the film is visible. d) The films remained flexible even while containing ordered arrays of single-crystalline wires.

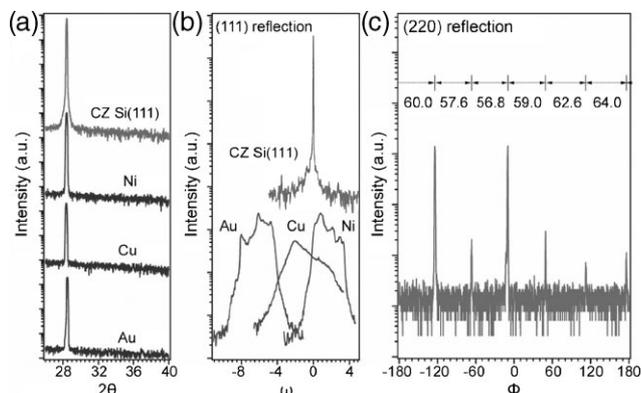


Figure 3. X-ray diffraction data for free-standing, polymer-embedded Au, Cu, and Ni-catalyzed wire arrays compared to that of an n-Si(111) Czochralski-grown wafer (a,b). a) The 2θ diffraction pattern indicated that the wires grew in the (111) direction and were highly crystalline. b) Rocking curves of the (111) reflection illustrated that the wire arrays were largely oriented perpendicular to the plane of the film, but exhibited a greater population spread than was observed for the single-crystalline wafer. c) A (220) ϕ scan of a PDMS/Ni-catalyzed wire film showed six degenerate {220} reflections, indicating a high degree of rotational lattice symmetry among the wires in the array.

percentages of Si wires and PDMS at each {220} reflection. Hence, this material behaved similarly to single-crystalline silicon as probed with X-ray diffraction (XRD), even though a flexible, pliable PDMS matrix separates each wire.

To demonstrate potential utility in solar cells, wire array-based Schottky diodes were prepared from the polymer-embedded Si wire array films. Of the VLS catalyst metals used to date, Au is expected to yield the highest barrier height with n-type Si. When Au was used as the VLS catalyst, a hemisphere of the metal remained on the top of each Si wire. Electrical contact was made to the metal hemispheres using a conducting polymer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), that formed a film on the tops of the wires while not penetrating into the array. Contact to the bottoms of the wires was made with Ga:In eutectic on the side of the film that originally faced the Si substrate. This device exhibited rectifying behavior, as expected for a contact between n-type Si and Au, albeit with a low barrier height when compared to that expected for a well-controlled junction (see Supporting Information, Fig. S2).^[24] This prototype device represents a worst-case scenario because mid-gap Au impurities exist near equilibrium concentrations in the bulk of the wires,^[5,25] junctions were formed only on the ends of the wire (i.e., not radially), and the wire surfaces were not explicitly chemically passivated. In addition, the Au–Si junction was formed during wire growth at temperatures near 1000 °C, which is expected to lead to non-ideal diode characteristics. Nevertheless, current was passed through the embedded Si wires, demonstrating that electrical contact to either end of the polymer-suspended wires is feasible. Ongoing studies will include careful comparisons between diodes constructed on and off of the substrate, and with various types of contacts.

The method described herein offers an approach to the transfer of single-crystalline inorganic nanowires onto a variety of substrates. This approach is complementary to recent work in which a thin bubble film was used to transfer and disperse

Si nanowires in an orientation parallel to the plane of the substrate.^[26] With our technique, solar cell absorber materials with the potential to achieve high efficiency can now be prepared by high-temperature processing and then transformed into a flexible, processable form. Removal of rods from the growth substrate allows reuse of the single-crystalline base, improving the economic feasibility of this process.^[27] New avenues of research into the optical, chemical, and mechanical properties of these composites are now available. For example, chemically or thermally shrinking the polymer matrix can increase the wire density without requiring short nearest-neighbor distances during the initial growth step and represents a means of further improving the light absorption/trapping of such films. The availability of large area, free-standing Si wire array films enables the optoelectronic and electrochemical properties of VLS-grown wire arrays and the substrate to be deconvoluted. Ultimately, we envision the inclusion of such wire-array structures in a variety of electronic and photonic applications, in which ordered, extended, 3D structures of nanoscale devices are desired on the macroscale.

Experimental

Si Wire Array Growth: Wire arrays were grown by photolithographically patterning S1813 photoresist (Microchem) on an oxide covered Si(111) wafer, then exposing the wafer for 4 min to buffered HF (aqueous) (Transene, Inc., 9% HF, 32% NH₄F), followed by thermal evaporation of 300 nm of Au, Cu, or Ni (ESPI, 99.995%) and lift-off of the resist [1]. During Ni evaporation, a low-temperature sample stage was used to prevent film strain from damaging the photoresist film. This procedure produced a square array of 3 μ m diameter catalyst islands with a center-to-center distance of 7 μ m. Samples were annealed in a tube furnace at 900–1000 °C for 20 min under 1 atm of H₂ at a flow rate of 1000 sccm, followed by wire growth at the same temperature under 1 atm of H₂ and SiCl₄, at flow rates of 1000 and 20 sccm, respectively. Upon removal from the growth reactor, the wire surfaces become oxidized and were not further treated.

Polymer Application and Film Removal: The PDMS base and curing agent were mixed in a 10:1 w/w ratio and stirred (Sylgard 184, Dow Corning).

Application Method 1: Uncured polymer was diluted with methylene chloride (0.5 g mL⁻¹) and drop-cast on the wire arrays. Dilution of the uncured polymers with methylene chloride decreased the viscosity of the polymer solution to enable casting of thinner films. After drop-casting of the polymers, overnight curing allowed slow evaporation of the methylene chloride, avoiding bubble formation. After 13–16 h the PDMS was still tacky, and was further cured by heating to 120 °C for 1.5–2.0 h.

Application Method 2: The uncured polymer was diluted (4:1 w/w) with a solution of hexamethylcyclotrisiloxane (Alfa Aesar, 97%, nearly saturated in methylene chloride) and spin-cast on the wire arrays at 1000 rpm for 2 min. After spin-coating, the methylene chloride rapidly evaporated, and the samples were cured at 150 °C for 0.5 h.

Film Removal and Growth Substrate Cleaning: After cooling, the PDMS overlayer and wires were mechanically removed by scraping the substrate with a razor blade. Residual PDMS was removed with sulfuric acid.

Characterization: SEM was performed using either a Hitachi S-4100 or a LEO 1550VP instrument after amorphous C- or Pt-coating the polymer-embedded wire arrays. A 10 or 15 kV beam voltage was used to minimize charging effects. XRD measurements were performed with a Panalytical MRD PRO high-resolution X-ray diffractometer equipped with a monochromated CuK α excitation source. Each diffraction spectrum was recorded at room temperature with the sample placed on a stainless steel plate. Fe diffraction peaks were visible only at 44.4° and 64.6° and did not interfere with reflections from the wire array.

Diode formation was achieved by affixing the wire array film to a piece of electrically insulating tape that had been pierced to produce a 0.40 cm diameter circular hole. PEDOT:PSS (Baytron P, 1:1 v/v solution with ethanol, 20 μ L) was drop-cast onto the exposed area of the film, on the metal catalyst side (top). The sample was heated to 150 °C to form a thin film, which did not fill the area between wires, but instead was suspended, touching only the tops of the wires. The back of the film was etched in buffered HF (Transene) for 30 s, Ga:In eutectic was then applied and sandwiched between the film and a stainless steel substrate. Electrical contact was made between the stainless steel and silver epoxy in contact with the PEDOT:PSS layer. Current–Voltage data were obtained using a Solartron SI 1287 electrochemical interface.

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- [1] B. M. Kayes, H. A. Atwater, N. S. Lewis, *J. Appl. Phys.* **2005**, *97*, 114302.
- [2] L. Tsakalakos, J. Balch, J. Fronheiser, B. A. Korevaar, O. Sulima, J. Rand, *Appl. Phys. Lett.* **2007**, *91*, 233117.
- [3] A. P. Goodey, S. M. Eichfeld, K. K. Lew, J. M. Redwing, T. E. Mallouk, *J. Am. Chem. Soc.* **2007**, *129*, 12344.
- [4] B. M. Kayes, M. A. Filler, M. C. Putnam, M. D. Kelzenberg, N. S. Lewis, H. A. Atwater, *Appl. Phys. Lett.* **2007**, *91*, 103110.
- [5] M. D. Kelzenberg, D. B. Turner-Evans, B. M. Kayes, M. A. Filler, M. C. Putnam, N. S. Lewis, H. A. Atwater, *Nano. Lett.* **2008**, *8*, 710.
- [6] J. R. Maiolo, B. M. Kayes, M. A. Filler, M. C. Putnam, M. D. Kelzenberg, H. A. Atwater, N. S. Lewis, *J. Am. Chem. Soc.* **2007**, *129*, 12346.
- [7] V. L. Pushparaj, M. M. Shaijumon, A. Kumar, S. Murugesan, L. Ci, R. Vajtai, R. J. Linhardt, O. Nalamasu, P. M. Ajayan, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 13574.
- [8] E. Sunden, J. K. Moon, C. P. Wong, W. P. King, S. Graham, *J. Vac. Sci. Technol. B* **2006**, *24*, 1947.
- [9] Y. J. Jung, S. Kar, S. Talapatra, C. Soldano, G. Viswanathan, X. S. Li, Z. L. Yao, F. S. Ou, A. Avadhanula, R. Vajtai, S. Curran, O. Nalamasu, P. M. Ajayan, *Nano Lett.* **2006**, *6*, 413.
- [10] N. R. Ravavikar, A. S. Vijayaraghavan, P. Koblinski, L. S. Schadler, P. M. Ajayan, *Small* **2005**, *1*, 317.
- [11] E. B. Sansom, D. Rinderknecht, M. Gharib, *Nanotechnology* **2008**, *19*, 035302.
- [12] D. Meissner, R. Memming, B. Kastening, *Chem. Phys. Lett.* **1983**, *96*, 34.
- [13] M. P. Zach, K. Inazu, K. H. Ng, J. C. Hemminger, R. M. Penner, *Chem. Mater.* **2002**, *14*, 3206.
- [14] S. A. Morin, F. F. Amos, S. Jin, *J. Am. Chem. Soc.* **2007**, *129*, 13776.
- [15] D. H. Kim, J. H. Ahn, W. M. Choi, H. S. Kim, T. H. Kim, J. Z. Song, Y. G. Y. Huang, Z. J. Liu, C. Lu, J. A. Rogers, *Science* **2008**, *320*, 507.
- [16] H. J. Fan, P. Werner, M. Zacharias, *Small* **2006**, *2*, 700.
- [17] Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim, Y. Q. Yan, *Adv. Mater.* **2003**, *15*, 353.
- [18] R. S. Wagner, W. C. Ellis, *Trans. Metall. Soc. AIME* **1965**, *233*, 1053.
- [19] I. Lombardi, A. I. Hochbaum, P. D. Yang, C. Carraro, R. Maboudian, *Chem. Mater.* **2006**, *18*, 988.
- [20] J. N. Lee, C. Park, G. M. Whitesides, *Anal. Chem.* **2003**, *75*, 6544.
- [21] J. C. McDonald, G. M. Whitesides, *Acc. Chem. Res.* **2002**, *35*, 491.
- [22] Z. P. Yang, L. J. Ci, J. A. Bur, S. Y. Lin, P. M. Ajayan, *Nano Lett.* **2008**, *8*, 446.
- [23] L. Tsakalakos, J. Balch, J. Fronheiser, M. Y. Shih, S. F. LeBoeuf, M. Pietrzykowski, P. J. Codella, B. A. Korevaar, O. Sulima, J. Rand, A. Davuluru, U. Rapolc, *J. Nanophotonics* **2007**, *1*, 013552.
- [24] E. H. Rhoderick, R. H. Williams, *Metal-Semiconductor Contacts*, Clarendon Press, Oxford **1988**.
- [25] M. C. Putnam, M. A. Filler, B. M. Kayes, M. D. Kelzenberg, Y. Guan, N. S. Lewis, J. M. Eiler, H. A. Atwater, *Nano Lett.* **2008**, submitted.
- [26] G. H. Yu, A. Y. Cao, C. M. Lieber, *Nat. Nanotechnol.* **2007**, *2*, 372.
- [27] J. M. Spurgeon, K. E. Plass, B. M. Kayes, B. S. Brunschwig, H. A. Atwater, N. S. Lewis, *Appl. Phys. Lett.* **2008**, *93*, 032112.