

Self-assembled single-crystal silicon circuits on plastic

Sean A. Stauth and Babak A. Parviz*

Department of Electrical Engineering, The Paul G. Allen Center for Computer Science and Engineering, University of Washington, Room AE100R, Campus Box 352500, Seattle, WA 98195-2500

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We demonstrate the use of self-assembly for the integration of freestanding micrometer-scale components, including single-crystal, silicon field-effect transistors (FETs) and diffusion resistors, onto flexible plastic substrates. Preferential self-assembly of multiple microcomponent types onto a common platform is achieved through complementary shape recognition and aided by capillary, fluidic, and gravitational forces. We outline a microfabrication process that yields single-crystal, silicon FETs in a freestanding, powder-like collection for use with self-assembly. Demonstrations of self-assembled FETs on plastic include logic inverters and measured electron mobility of 592 cm²/V-s. Finally, we extend the self-assembly process to substrates each containing 10,000 binding sites and realize 97% self-assembly yield within 25 min for 100- μ m-sized elements. High-yield self-assembly of micrometer-scale functional devices as outlined here provides a powerful approach for production of macroelectronic systems.

macroelectronics | plastic electronics | self-assembly

Macroelectronics is an emerging area of interest in the semiconductor industry. Unlike the traditional pursuit in microelectronics to build smaller devices and achieve higher degrees of integration over small areas, macroelectronics aims to construct distributed active systems that cover large areas. Often, these systems are constructed on flexible substrates with multiple types of components and allow for distributed sensing and control. A number of applications are already under consideration for macroelectronics, including smart artificial skins (1), large-area phased-array radars (2), solar sails (3), flexible displays (4, 5), electronic paper (4), and distributed x-ray imagers (6). A candidate macrofabrication technology must be able to integrate a large number of various functional components over areas exceeding the size of a typical semiconductor wafer in a cost-effective and time-efficient fashion.

The substrate of choice for many macroelectronic applications is plastic. Flexible plastic substrates are thermally and chemically incompatible with conventional semiconductor fabrication processes. To incorporate electronic devices, a number of venues have been explored for low-temperature integration of semiconductors on plastics. The integration of semiconductor is followed by steps to build and interconnect functional devices. These material integration methods have demonstrated functional devices on plastic built from amorphous silicon (7), low-temperature polysilicon (8), and organic semiconductors (9, 10). Although in some applications low-performance devices are acceptable, in many applications, such as phased-array radar antennas or radio frequency tags, the integrated devices are required to perform at high frequencies with low power consumption. Devices built with the material integration methods outlined above suffer from low charge carrier mobility. Typical amorphous silicon transistors have electron mobility of 1 cm²/V-s (11), low-temperature polysilicon transistors on plastic have electron mobility of ≈ 65 cm²/V-s (8), and organic semiconductor transistors demonstrate charge carrier mobility of ≈ 1 cm²/V-s or much lower (12, 13). Poor charge carrier mobility in these devices [in comparison, the electron mobility in single-crystal silicon transistors exceeds 1,000 cm²/V-s (14)] translates to poor frequency response and high power consumption. Some of the best devices demonstrated to date were made by means of a

creative approach that uses silicon ribbons released from a wafer and reassembled on a polymer substrate to yield stretchable circuits (15, 16). This method has produced circuits with form factors replicating the original silicon wafer (the area and coverage attained are similar to a wafer originally used for processing) and with performance parameters that are affected by strain applied to the substrate. The approach has demonstrated electron mobility as high as 100 cm²/V-s, which remains short of the performance offered by transistors fabricated in single-crystal silicon.

An alternative approach for the construction of macroelectronic systems is to perform the integration at the device instead of the material level (17). Significant infrastructure is available to cost-effectively fabricate high-performance devices on single-crystal semiconductor substrates. These devices can be released and reassembled on a large-area plastic substrate. Recent advances in robotic assembly (18) allow for positioning of up to 26,000 components per hour on plastic substrates; however, the relatively moderate speed, high cost, and limited positional accuracy of these systems make them unsuitable candidates for cost-effective mass production of macroelectronics. For component sizes of <200 – 300 μ m, robotic assembly techniques become exceedingly slow because of the delay in the control mechanisms necessary to position parts with high accuracy and the need to overcome parasitic stiction forces (18). A conservative estimate puts the assembly cost with a state-of-the-art robotic pick-and-place system at ≈ 0.7 cents per component (19). At this rate, assembly of large-area systems with thousands to millions of components becomes too costly for most applications.

A powerful technology that can meet all of the criteria for an effective macrofabrication technology is self-assembly. In a device-level integration approach based on self-assembly, functional devices are batch-microfabricated and released to yield a freestanding collection. These components are then allowed to self-assemble onto a template, for example on a plastic substrate, to yield a functional macroelectronic system. Used in this fashion, self-assembly is an inherently parallel construction method that allows for cost-effective and fast integration of a large number of functional components onto unconventional substrates (19). The key components of a self-assembly-based macroelectronic fabrication technology are (i) development of fabrication processes that generate freestanding micrometer-scale functional components, (ii) implementation of recognition/binding capabilities that guide the self-assembly of components in the correct location, and (iii) determination of self-assembly procedures that construct the final system with a high yield.

Self-assembly of micrometer- and millimeter-scale components has been studied previously both for 2D (20–24) and 3D integration (25, 26). In 2D integration via self-assembly, a

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Abbreviations: FET, field-effect transistor; SOI, silicon-on-insulator.

*To whom correspondence should be addressed. E-mail: parviz@u.washington.edu.

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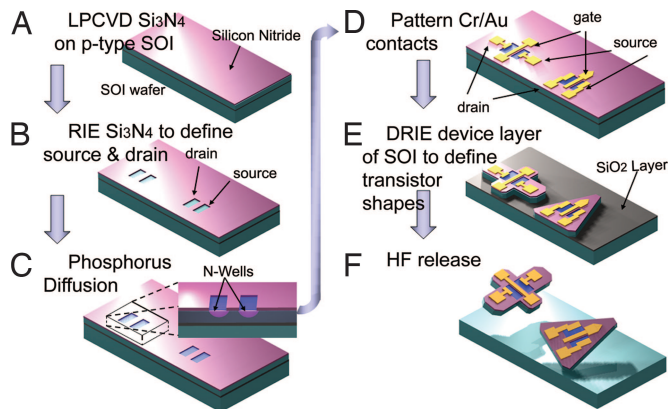


Fig. 3. Transistor microfabrication process flow. Completion of the last step yields a collection of micrometer-scale, released components.

microcomponent types were constructed in a similar fabrication process that is based on (i) metallization to create Cr/Au contact pads, (ii) geometric shape definition through deep reactive ion etching, and (iii) microcomponent release from the SOI wafer by wet etching the buried silicon dioxide layer. The fabrication of the FETs contains additional steps as delineated in *Materials and Methods* and shown in Fig. 3. Fabrication of the transistors was unusual, however, because we used Si_3N_4 both as a diffusion mask and as the gate dielectric layer. Silicon dioxide is the standard gate dielectric in most FETs, but the hydrofluoric acid used to release the components in our process would readily etch a silicon dioxide dielectric layer. Therefore, we used a low-pressure, chemical-vapor-deposited, low-stress Si_3N_4 to serve as the gate dielectric layer and the mask during phosphorus diffusions (Fig. 3A).

We chose four mutually exclusive (one shape cannot assemble in another shape's binding site) element geometries (circles, rectangles, squares, and triangles), because they present different levels of symmetry. Symmetric elements assemble faster and with a higher yield; however, elements with asymmetric structure offer a higher degree of control over the final configuration of the self-assembled structure. We used circular elements for high-yield self-assembly experiments and triangular components for self-assembly of FETs to ensure the proper electrical contact with the three terminals of the transistors. The dimensions of the microcomponents varied depending on the particular shape, ranging from 100 μm (circle diameter) to 300 μm (rectangle length). For all shapes, the microcomponent thickness ranged from 10 to 20 μm , according to the device layer thickness of the SOI wafer used for fabrication. The metal contact pad dimensions were 50 \times 50 μm for the elements and 40 \times 40 μm for the FETs and diffusion resistors. Fig. 4 shows the FETs after release from the SOI wafer. The measured transistor performance of the triangular FETs is shown in Fig. 4D. The fabrication process of the plastic templates is illustrated in Fig. 5 and described in detail in *Materials and Methods*.

The Self-Assembly Procedure. To prepare the components for self-assembly, we cleaned them with a short piranha etch [3:1 (vol/vol) $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$] to ensure that the metal contacts were contaminant-free. To make certain the solder pads on the substrate were clean, we performed the alloy dip-coat immediately before use for self-assembly. After the dip-coat process, we positioned the substrate on an angled glass slide (20–60°) and immersed it into neat ethylene glycol serving as the self-assembly medium.

To perform the self-assembly, we first heated the ethylene glycol solution to 70°C to melt the alloy within the binding sites

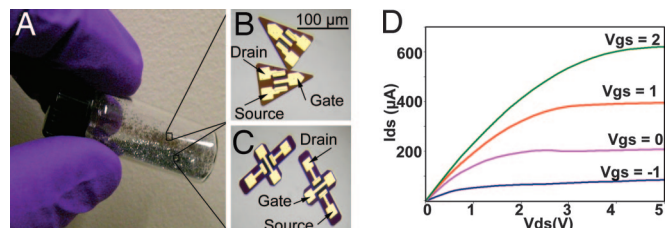


Fig. 4. Released silicon FETs. (A) A collection of freestanding single-crystal silicon FETs. (B and C) Optical microscope images of and triangle-shaped (B) cross-shaped (C). (D) Measured performance of a typical triangular transistor before release from SOI wafer.

and to decrease the viscosity of the ethylene glycol to allow for better motion of the microcomponents through the fluid. Next, we lowered the solution pH to 3.0 with the addition of HCl to clean surface oxides forming on the molten alloy. We manually introduced a collection of microcomponents (using only one microcomponent shape at a time) directly above the substrate binding sites. Typically, we introduced 10–100 times more microcomponents than the number of available binding sites to increase the likelihood of self-assembly. The microcomponents were allowed to flow over the template and self-assemble upon an encounter with a complementarily shaped binding site (refer to Fig. 1). Once all available microcomponents had passed over the substrate (one microcomponent pass), we initiated the process again by collecting and manually reintroducing microcomponents over the substrate. We repeated this process until all available binding sites contained a self-assembled microcomponent, which typically occurred after five microcomponent passes (refer to *High-Yield Self-Assembly in Results and Discussion*).

We provided a constant fluid motion with a pipette and positioned the self-assembly medium over a shaker table (set to provide gentle vibrations at 20 Hz) to provide extra external agitation. Ideally, the agitation should induce microcomponent movement across the substrate, break-up microcomponent aggregations, and disassemble incorrectly assembled microcomponents while allowing the correctly assembled microcomponents to remain in place. We found that a laminar fluid flow 5–10 cm/s across the substrate was sufficient to break up aggregations or wash them off of the substrate but gentle enough not to disturb correctly self-assembled microcomponents. After the completion of the self-assembly process, we lowered the temperature of the ethylene glycol solution to room temperature to solidify the alloy and make the connections permanent. We then removed the template from the solution for further testing and measure-

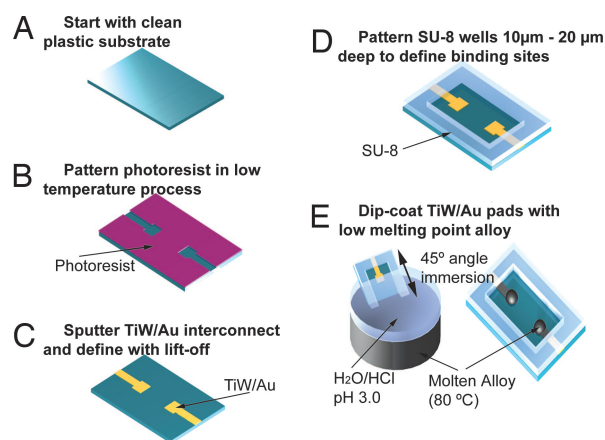


Fig. 5. Plastic template fabrication flow.

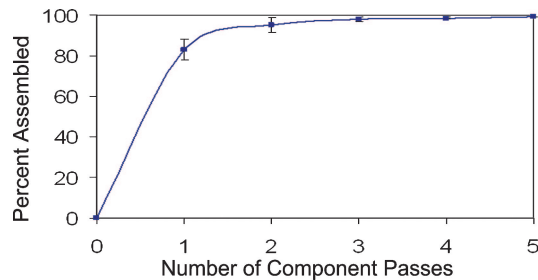


Fig. 9. Measured self-assembly rate. The percentage of correctly self-assembled elements after each element pass step is shown, indicating a 99% average self-assembly yield after five element passes. Error bars indicate the standard deviation.

fashion; however, it should be noted that the assembly of a large collection of similar elements is of use in applications such as the construction of flexible displays.

Surface Energy Modeling. At the heart of the self-assembly process is the reliance on energy minimization to guide the microcomponents; therefore, we developed finite element models to examine the role of both capillary and fluidic forces on a microcomponent as it self-assembles into a binding site. To model the fluidic forces, we developed a finite element simulation model by using FEMLAB to solve the incompressible Navier–Stokes equation for a constant fluid flow of ethylene glycol across the template in presence of microcomponents. Details of this model are provided elsewhere (29). For this model we assumed a steady-state, laminar flow of 5–10 cm/s across the substrate and a dynamic viscosity of 0.005 Pa·s for ethylene glycol at 70°C. To determine the capillary force acting on the microcomponents as they minimize their free surface energy and become bound in the well, we used the modeling program Surface Evolver (30). The model consisted of two fixed elements: the microcomponent and the template, both containing metallic pads wettable by the molten alloy. The extent of wettability between the alloy and the metal pads is determined by the contact angle, which we experimentally measured to be 30° (low-melting-point alloy on Au while immersed under ethylene glycol at 70°C; refer to Fig. 10*B Inset*).

Fig. 10 shows the calculated energy landscape (as determined by Surface Evolver) for different spatial configurations as a microcomponent self-assembles. With our particular configuration, the capillary forces were calculated to be in the range of a few hundred micronewtons, whereas the fluidic forces were much smaller, at 2.0–2.5 nN (30). These results indicate that once the microcomponent has self-assembled and established a firm bond to the substrate via the molten alloy, the fluid force alone cannot cause disassembly.

Conclusions

Self-assembly provides a powerful tool for the production of macroelectronic systems. We have demonstrated that microfabrication processes can be developed to make functional microcomponents, such as single-crystal silicon FETs in a powder-like collection and that this collection of microcomponents can be self-assembled onto a flexible plastic template in a single step to yield functional circuitry. The method allows for the integration of microcomponents that are made independently in potentially incompatible microfabrication processes. We have demonstrated functional devices and circuits on plastic substrates with measured electron mobility exceeding 590 cm²/V·s, constituting almost an order of magnitude improvement over the prior state of the art in measured charge carrier mobility of semiconductor devices operating on plastic. Furthermore, there is significant

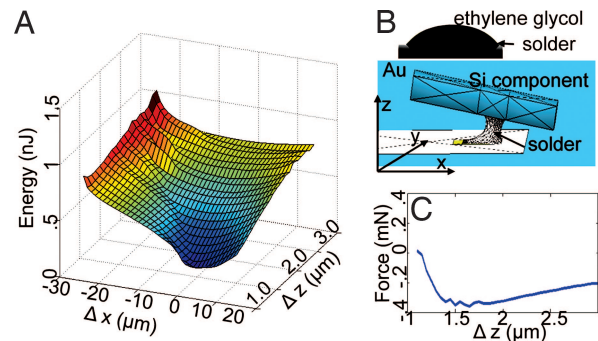


Fig. 10. Modeling results. (A) Calculated energy landscape of component as it joins with solder. (B) Surface Evolver model of capillary forces of molten solder. (*Inset*) An optical microscope image used to determine the contact angle of molten alloy on gold under ethylene glycol. (C) Capillary forces in the z direction.

room for improvement in electrical performance of the self-assembled systems. For example, the microcomponent-to-substrate contact resistance of 40 Ω can be decreased by using bismuth-free alloys that are less prone to oxidation. The fairly large FET source resistance, due to a lightly doped region under the gate nitride not covered by the gate metal, can be reduced by using an aligner tool with higher accuracy.

More importantly, we show that self-assembly can provide very high yields of >97%. Although the self-assembly experiments demonstrated here were performed in a laboratory with minimal equipment and manual introduction of parts, the self-assembly rate of 10,000 per 25 min for 100-μm microcomponents rivals the assembly rate of the fastest multimillion dollar robotic assemblers (18). The self-assembly rate can be improved by orders of magnitude via automation of the set-up.

We relied on a shape-matching effect to control the binding locations of multiple microcomponent types on the template and used capillary forces to make connections between the microcomponents and the templates. Both of these effects are scaleable down to the nanoscale should the need arise. Examples of shape recognition for self-assembly (such as in antigen–antibody binding) and capillary-force-driven self-assembly (such as in cell membrane formation) are abundant in nature. Energy minimization driven by gravity is not expected to scale well to the submicrometer region, however, and other binding mechanisms based on charge or hydrogen binding are more appropriate in this regime.

In our demonstrations, we incorporated single FETs or single diffusion resistors in the microcomponents to construct circuits on plastic. In many macroelectronic applications, more complex microcomponents, each perhaps carrying tens of interconnected transistors, may be needed. The microfabrication processes outlined here can be easily modified to accommodate this need. The appropriate level of complexity for each microcomponent for a given application is yet to be determined. Although we made the templates with standard microfabrication techniques, it should be noted that all of the critical dimensions are in the microcomponent structures and not in the template. Once the microcomponents are made and released to form a powder-like collection, the templates can be produced with a variety of techniques that are suitable for large-area patterning. We believe, as verified by the demonstrations provided here, that self-assembly offers an extremely promising venue for construction of the large-area, high-performance macroelectronic systems of the future.

Materials and Methods

Fabrication of Microcomponents. To fabricate the FETs, we first cleaned the 10- to 20-μm-thick SOI wafers (<100>p-type, 1–10 Ω-cm

device layers and 0.5- to 1- μm -thick buried silicon dioxide layers) with a 5-min piranha etch [3:1 (vol/vol) $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$] followed by a 1-min buffered oxide etch (BOE) to strip the native oxide. Next, the wafers were cleaned for 5 min in 1:1:5 ammonium hydroxide/ $\text{H}_2\text{O}_2/\text{H}_2\text{O}$, followed by 5 min in 1:1:5 $\text{HCl}/949\text{H}_2\text{O}_2/\text{H}_2\text{O}$, at 70°C . Next, we deposited 200 nm of Si_3N_4 using low-pressure, chemical vapor deposition. The next step was to pattern the nitride to define the n-well areas of the transistor. After patterning the photoresist AZ1512 (Microchem, Newton, MA) and baking the resist for 5 min at 110°C , we etched the nitride using reactive ion etching (50 standard cm^3/min of SF_6 at 250 mTorr and 100 W for 100 s) to expose the underlying p-type silicon (Fig. 3B). We removed the photoresist with acetone and repeated the cleaning procedure described above to prepare the wafers for doping. We used spin-on phosphorus dopant glass (catalog no. P-8545; Honeywell, Tempe, AZ) and a drive-in at 950°C for 30 min to achieve a junction depth of 0.9 μm (Fig. 3C). After diffusion, we removed the dopant glass with a 1:10 BOE. Next, we performed a low-temperature (850°C) dry oxidation and anneal for 30 min on the wafers and stripped all of the remaining silicon dioxide with BOE. To create the source, drain, and gate contacts, we first patterned a photoresist AZ4620 (target, 6 μm) and performed an oxygen plasma clean at 300 W for 1 min. By using an electron-beam evaporator, we deposited 10 nm of Cr followed by 400 nm of Au. After evaporation, the metal pads were defined by sonication and lift-off in acetone (Fig. 3D). With an additional photoresist-patterning step using AZ4620 coating, we defined the transistor microcomponent shapes first by using reactive ion etching through the nitride layer and second by using a deep reactive ion etch through the device layer of the SOI wafer down to the buried oxide (Fig. 3E). We then removed the photoresist with acetone and released the transistors by immersing the wafer in a 49% hydrofluoric acid bath for 20 min. Exposure to hydrofluoric acid removed the buried silicon dioxide layer and released the microcomponents into the solution. We isolated, rinsed, and stored the powder-like collection of released microcomponents in deionized water (Fig. 3F). We used a similar fabrication process to make the diffusion resistor by taking advantage of the phosphorous diffusion region to form the resistive path. We fabricated the freestanding silicon elements in a similar but much simplified process, because they required only metallization, geometric shape definition, and hydrofluoric acid release.

Fabrication of the Plastic Templates. To prepare the templates, we used 8.5- \times 11-inch (1 inch = 2.54 cm) sheets of thermally stable, 100- μm -thick polyester (part no. LT04_08_5_11L100S; Polycrom, DriveBensalem, PA) cut into the shape of a 4-inch wafer. We chose this plastic because it is clear, flexible, can withstand temperatures of up to 80°C without significantly warping, and is compatible with the developer used for photolithography (AZ400K; Microchem). We thoroughly rinsed the substrate with acetone and isopropyl alcohol to remove any contaminants and patterned it by using photolithography (AZ460, target thickness, 6 μm) as shown in Fig. 5B. We followed the photoresist patterning by sputtering TiW/Au (10 nm/200 nm) on the substrate performed at low power (50 W; deposition rate, 10 nm/min) to prevent heat-induced warping of the plastic wafer. After the sputter deposition, we performed a lift-off process by stripping the remaining photoresistant coating with acetone and a brief sonication to define the metal interconnects on the wafer (Fig. 5C). To shape the binding sites with the desired geometry and depth (10–20 μm), we used a clear, cross-linkable negative photoresist, SU-8. The binding-site wells were designed to accommodate a microcomponent with a complementary shape and express a flat surface after the completion of the self-assembly process. To prepare the wafer for SU-8 deposition, we thoroughly rinsed the wafer with isopropyl alcohol and baked it at 60°C for 5 min. The SU-8 layer was formed by spinning SU-8 2015 (Microchem) at 3,000 rpm (Photoresist spin coater 100 from CEE) for 30 s to give an average thickness of 15 μm followed by exposure and development. To prevent heat-induced warping of the wafer, we modified the hard bake and postexposure bake from the Microchem specifications to be 60°C for 10 min each. After SU-8 patterning, the only metal areas exposed were contact pads (30 \times 30 μm) centered at the bottom of the SU-8 wells (Fig. 5D). We used dip-coating in a low-melting-point alloy, 44.7% Bi/22.6% Pb/19.1% In/8.3% Sn/5.3% Cd (melting point, 47°C ; part no. LMA-117 from Small Parts, Inc., Miami Lakes, FL), which was pooled to dewet the alloy on the exposed metal pads (Fig. 5E) and complete the template fabrication process.

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