Electric-Field-Mediated Assembly of Silicon Islands Coated with Charged Molecules

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The self-assembly and integration of heterogeneous materials and devices at the nano- and microscale is of paramount interest from a scientific and practical point of view. For example, integration of silicon devices on glass or plastic substrates can result in high performance and flexible displays, while selective placement of silicon nanowires can result in future ultrascaled integrated circuits. Since Mirkin et al.[1] and Alivisatos et al.[2] demonstrated DNA-mediated self-assembly of gold nanoparticle, there has been tremendous interest in this area. Self-assembly can have a significant impact in surmounting some of the manufacturing challenges faced by the microelectronics industry,[3] but many challenges lie in making it practical, such as obtaining a high yield, retention of material quality, achieving a high throughput, etc. Some of these issues can be circumvented by the use of fluidic self-assembly (FSA) and shape-mediated assembly for device sizes about 50 μm or larger.[4,5] As the device size is scaled down, however, the effectiveness of fluidic assembly reduces, since the mass of the device islands becomes negligible. One technique that holds a lot of promise is that of electrostatic field induced self-assembly of devices. Tein et al.[6] have demonstrated the assembly of 10 μm diameter Au disks, which were positively charged with organic molecules, on 100 μm wide regions that were negatively charged. Without any applied electric fields, the Au disks were shown to assemble due to attractive forces from electrostatic charges. The devices used were not active devices but rather passive Au pads that were not suitable for any electronic applications. Edman et al.[7] fabricated 20 μm diameter InGaAs light-emitting diodes and demonstrated an electrophoretic process for assembling them on silicon substrates. No details were given on the charging of devices or the mechanisms behind the device transport. Most likely the mechanism consisted of some variant of electroosmotic transport, where movement of ions in the fluid medium would force the movement of objects along the flow contours. The process will require a higher current density as compared to a purely electrophoretic transport.

The use of DNA as the linking material for site selective assembly has also been proposed in the past[8−10] but, in this Note, we extend the prior art by actually demonstrating a process for the fabrication, release, and electrophoretic assembly of silicon-based islands which can be used to make active (MOSFETs, BJTs, etc.) and passive devices (resistors, diodes, etc.). The material used for the proof of concept was device-sized silicon islands which had a gold layer on one side, as also described earlier,[11,12] on which a negatively charged self-assembled monolayer was attached, which was derived from 2-mercaptoethanesufonate or deoxyribonucleic acid (DNA). The process can be applied to silicon devices, quantum wires, and carbon nanotubes and can also result in three-dimensional circuits, reconfigurable electronic circuits, and heterogeneous integration of materials such as silicon on glass, polymer, or GaAs. After the devices were released, they were subsequently transported and manipulated on an array of electrodes to prove the presence of charges on them. The devices not treated with the charged molecule did not show any movement, even at a much higher applied voltage.

The fabrication of the silicon device islands is shown in Figure 1a−f and began on commercially available bonded and etched-back silicon-on-insulator (BESOI) wafers, which had a 2.5 μm ($\pm$0.5 μm) thick top silicon layer and a 1 μm thick buried oxide layer. Photolithography techniques were used to define 4 μm $\times$ 4 μm windows in a photoresist mask for subsequent lift-off of metal. The native oxide on the surface was etched in BHF solution for 5 s, and a 300 Å thick chromium layer and a 500 Å thick gold layer were deposited sequentially in an electron beam evaporator. The photoresist was lifted off in acetone, and the resulting pattern, as shown in Figure 1b, was used as a mask for the etch of silicon to the buried oxide, as shown in Figure 1c. The silicon layer was etched at a temperature of 55 °C for 20 min in a solution, consisting of 30 g of KOH, 250 mL of deionized water, and 80 mL of 2-propanol. The wafers were then placed in an HF solution to partially etch the buried oxide while leaving a 1 μm wide pedestal holding the silicon islands on the substrate as shown in Figure 1d. Then, two different molecules were used to provide charge to the islands. A self-assembled monolayer (SAM) of a 2-mercaptoethanesulfonic acid (sodium salt), as shown in Figure 2a, was formed on the gold layer on top of the silicon islands by treatment with a 1 mM

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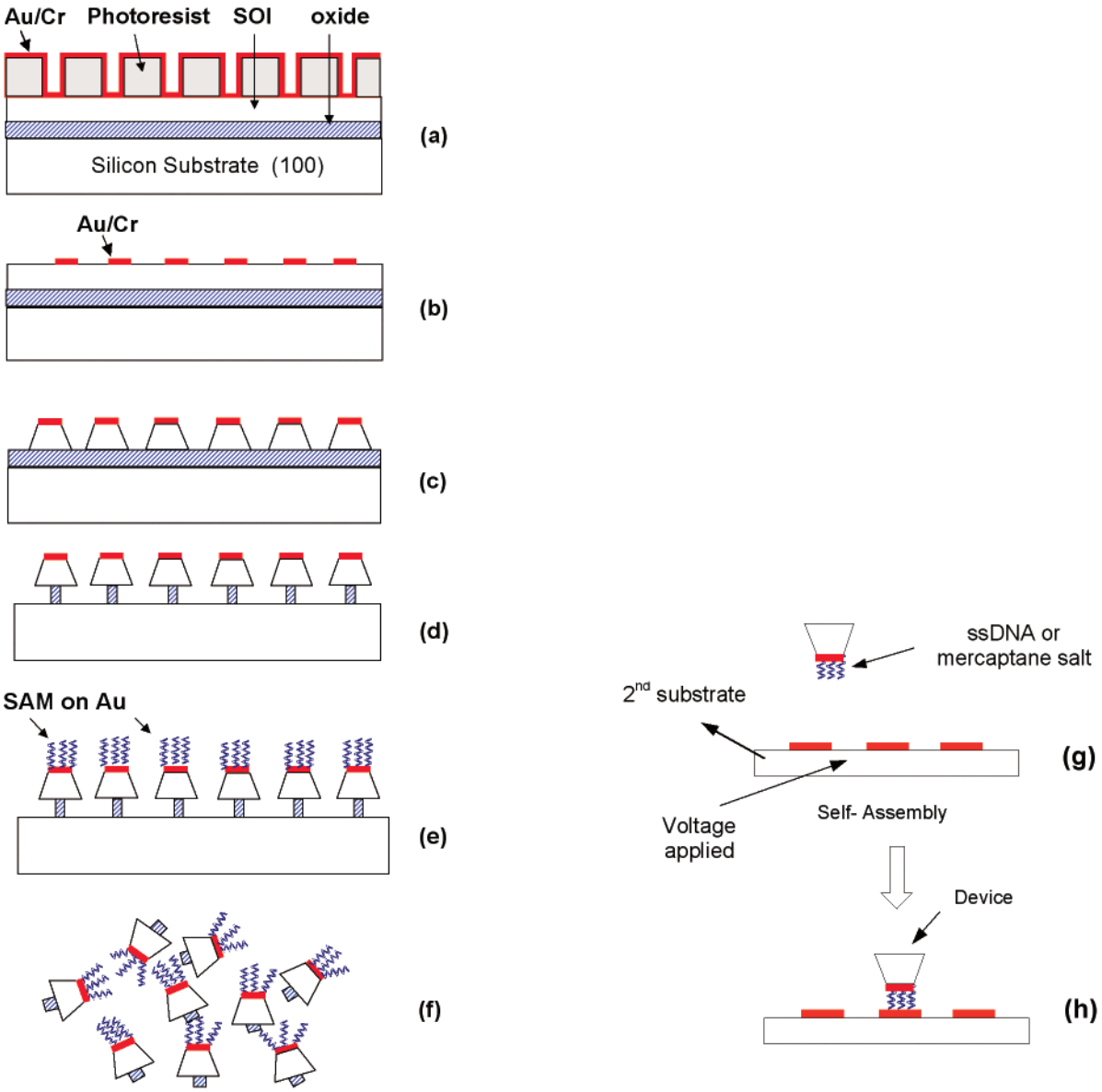

Figure 1. The process for fabrication, charging, release, and assembly of the Au/Cr/Si islands.

solution of the mercaptane in deionized water for 12 h. After a thorough rinsing step to remove the nonspecifically adsorbed molecules, the substrate was transferred to a low conductivity Tris-Glycine buffer solution (47 mM glycine, 3.6 mM Tris, $3.33 \times 10^{-8}/\Omega$ cm, pH = 8.3).

The other molecule used was a four nucleotide long single-stranded DNA oligonucleotide (5′-CGTA-spacer-$SH_{[3]}$) with three thiols (SH) at the 5′ end. The oligonucleotide was synthesized using standard automated synthetic procedures (Purdue University Laboratory for Macromolecular Structures). Trebler phosphoramidite and C6 thiol modified S−S phosphoramidite (Glen Research) were incorporated in the oligonucleotide to provide the three thiol groups at the 5′ end as shown in Figure 2b. This approach could result in a more robust and reliable bond between the Au and the DNA molecule. The DNA SAM formation procedures were similar to that reported for Au nanoparticles.[1,2,13] The oligonucleotide was purified, desalted, and used in aqueous solutions at a concentration of 12 μM. The sample with the unreleased islands was incubated in this solution for 12 h. The sample was then rinsed in a 10 mM phosphate buffer solution containing 0.3 M sodium chloride The phosphodiester monoanion linking each nucleoside is typically neutralized by counterions present in the vicinity. However, under conditions where not enough counterions are available or an electric field is applied, the phosphodiester group can develop a net charge. Thus, each DNA molecule with the linker can provide up to seven negative charges to the device.

The substrate with the silicon islands, with either molecule, was then immersed in the buffer and placed in an ultrasonic agitator at a frequency of 40 kHz for 20 min. The oxide pedestal holding the islands to the substrates

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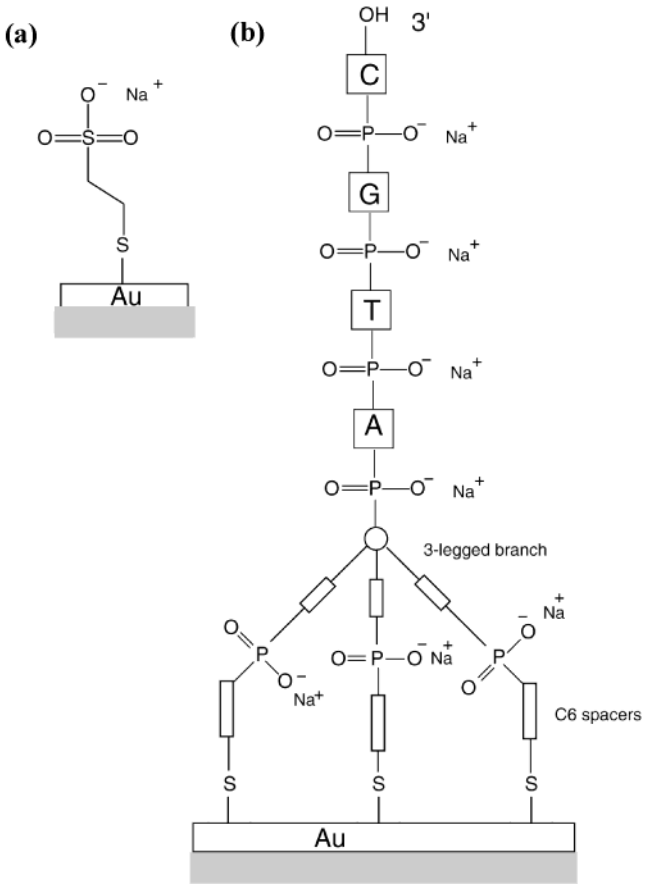

Figure 2. (a) Monoanion-derived surfaces using 2-mercaptoethansulfonate. (b) Hepta-anion-derived surfaces using DNA. The charged sulfonate and phosphodiester molecules are covalently fixed to the surface while the positively charged counterions are free to migrate in solution.

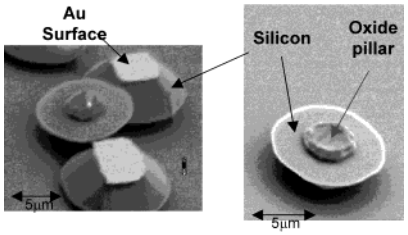

Figure 3. Scanning electron micrograph of the released silicon islands.

broke off, thus releasing the islands in the buffer. This release process is very advantageous since the islands can be released in any buffer desired and since the formation of the SAM is performed prior to the island release. Doing so also eliminates any extra handling of the islands during a postreleased SAM formation step. Figure 3 shows scanning electron micrographs of the released islands showing their trapezoidal shape, smooth side walls, and the gold top layer. The release process currently provides a yield of about 10^6 islands/mL of the buffer solution, which can be further improved through use of filters and other concentration techniques. The concentration was determined by taking small, known volumes from the solution with the released islands. The volumes were dropped on clean, flat surfaces, and the number of islands was visually counted. These numbers were then scaled to obtain the approximate concentration.

To demonstrate the electric field mediated assembly of the devices, an interdigitated electrode array with a 5 μm line and space was used. A 100 μL solution of the buffer was applied on a test chip with the interdigitated electrodes placed under a microscope. A digital camera was used to capture the images. Micromanipulator probes were used to make contact to the electrodes while a silicone rubber ring isolated the probes from the solution at the test sites. After 10 min and prior to applying any voltages, it was observed that more than 95% of the islands have the gold/charged surface facing down as they settle on the surface of the chip. It can be postulated that this happened due to the trapezoidal shape of the islands and that the devices would orient themselves such that the gold layer is at the bottom and the wider base of the trapezoid is on top. The controlled experiment consisted of using islands without chemical treatment for the formation of the SAM layer. Results showed that even voltages as high as 9 V ($E \sim 1.8 \times 10^6$ V/m between the electrodes) did not result in movement of the islands. On the other hand, when the gold/chromium/silicon islands charged with the SAM layers (sodium salt or DNA) were used, the islands demonstrated electrophoretic movement toward the positively charged electrodes with as low as 1 V applied between the electrodes. Visual results are the best confirmation of the concept, and Figure 4 shows a closeup of a sequence of pictures of one of the device islands on the microelectrodes. As clearly shown, the device has moved from the negative electrode, where it initially happened to locate, to the positively charged electrode that was 5 μm away. The same phenomenon was observed for other islands. The movement can be rather precise, as shown, and can be controlled in both dimensions on the surface, given the proper electrode geometry. The islands that landed on electrodes, on which a positive voltage was applied initially, did not show the movement. On the other hand, the islands that landed on the electrodes on which a negative voltage was applied exhibited the electrophoretic movement. The movement was also repeated by changing the applied bias every 5 min, and the islands moves back and forth between the electrodes that are positively biased.

In summary, the electric-field-mediated (electrophoretic) assembly of devices charged with organic or biomolecules is very promising for many applications. We have demonstrated a process that can be used to form, charge, release, and assemble silicon-based devices on other substrates. 2-Mercaptoethanesulfonic acid sodium salt or deoxyribonucleic acid (DNA) was used to provide a charge to the device islands. As long as any device can be charged and released from a substrate, it can be reassembled on a different substrate to form silicon circuits in plastic or glass substrates, three-dimensional integrated circuits, or other electronic components and devices. Once the devices are placed at the desired site of location, a low-temperature film deposition process can hold the devices in place for subsequent processing. Our work continues to use DNA (deoxyribonucleic acid) as the molecule providing the charge and as the linking molecule at the device and at the substrate to provide site selective assembly.[11,12]

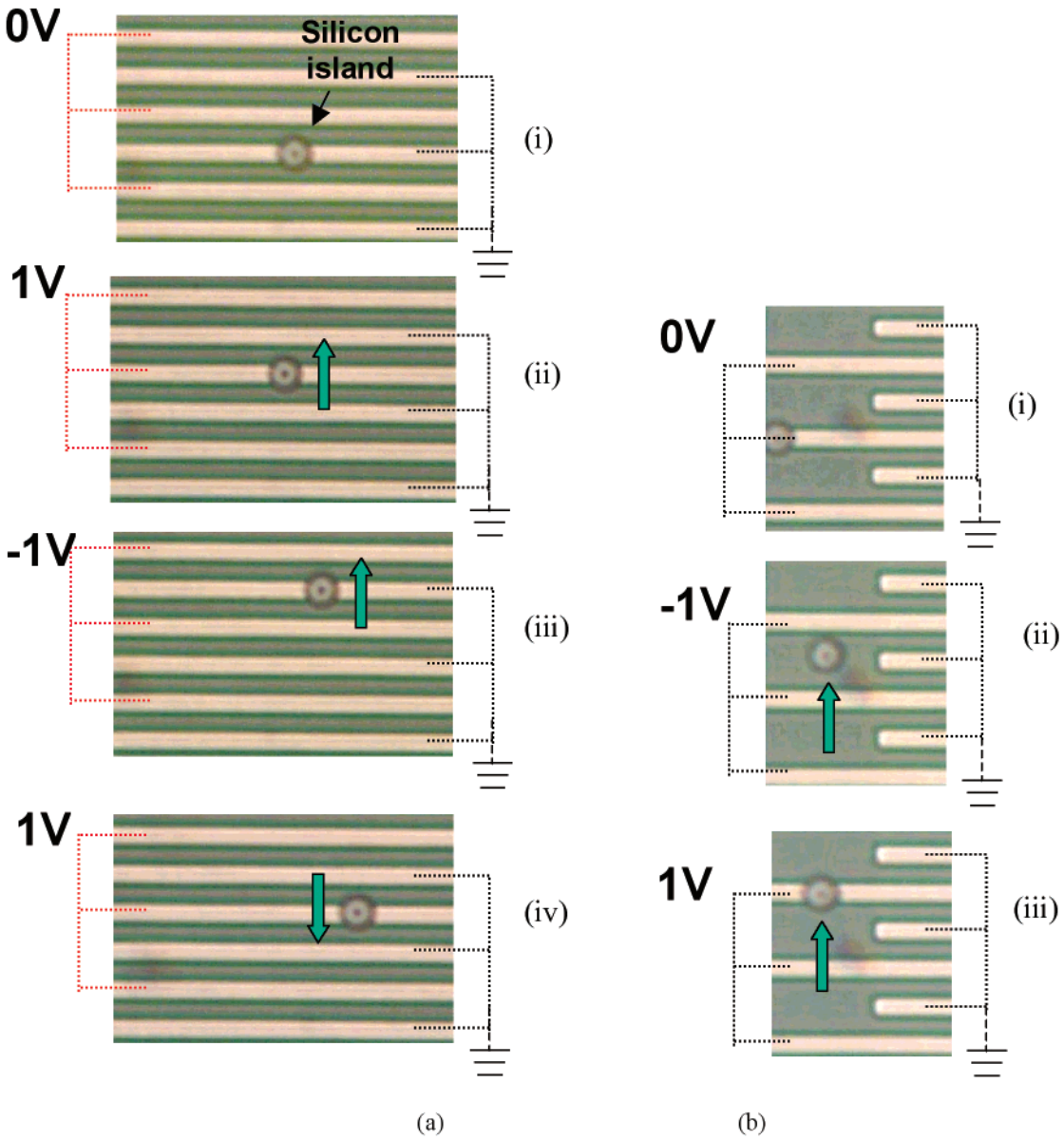

Figure 4. Optical micrographs showing the movement of one of the charged islands in electrostatic fields. The line width and spacing of the electrode are 5 μm.

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