structures, the shrinkage was anisotropic and changed the shapes of the features. By contrast, free structures were annealed with an isotropic shrinkage that did not perturb even very small features of the pattern.

In summary, this method seems promising as a complement to conventional combinations of photolithographic and reactive ion etching (RIE) methods for production of glass micro- and nanostructures. It is, however, limited to structures with an aspect ratio between ca. 0.5 and 2, because of the compliance of the mold. Furthermore, the deformability of the elastomeric mold may make it difficult to control the long-range order of the structures. The real limits to registration and achievable pattern resolution have, however, not been quantified yet.

Experimental

Materials: Silicon wafers (Silicon Sense, MA) were cleaned briefly in a O_2/plasma cleaner before use. Aluminum (99.99 %, Alfa) coated wafers were prepared by electron-beam evaporation. Tetramethylorthosilicate and di-*sec*-butoxyaluminoxytriethoxysilane (United Chemicals), titanium isopropoxide and boron triethoxide (Aldrich), oxalic acid and acetonitrile (Fisher) were used as received. The elastomeric molds were prepared by casting the silicone precursor (Sylgard 184, Corning, NY) on masters prepared by regular photolithography [18].

Patterned Solid: A 50 nm thick gold film was prepared on a ⟨100⟩ silicon wafer primed with 2 nm of titanium by electron-beam evaporation. A monolayer of hexadecanethiolate was patterned on the wafer using microcontact printing so that the resulting pattern presented uncovered 2 μm squares [18]. The unprotected gold was removed with a cyanide etch [18]. The native silica oxide layer was then removed by etching in 2 % HF for 30 s. The silicon was etched in a 40 wt.-% solution of KOH in water and isopropanol; this anisotropic etch generated pyramidal pits. The remaining gold was removed with aqua regia. The surface of the resulting textured solid was treated by putting the wafer under static vacuum with a drop of (tridecafluoro-1,1,2,2-tetrahydro-octyl)-1-trichlorosilane for 30 min. This compound polymerized on the surface and made a layer that reduced adhesion to the surface.

A mixture of 6.5 g TMOS and 1.5 g of water acidified to pH 1 by adding oxalic acid was stirred for 1 min and left at room temperature for 1 h. (We will refer to this solution as sol A throughout the paper. This solution can remain fluid and clear for days.) The mold was prepared by putting a 1 cm² piece of the textured wafer in a plastic petri dish. Just before casting in the mold, 5 drops of aqueous ammonia (pH 11) were added to 3 g of sol A. The wafer was covered with 0.5 mL of this solution. The preparation was then placed in a closed 100 cm³ container for 24 h. The solid structure was not adhering to the mold at this point and was carefully removed. It was then dried slowly at room temperature for a week, then at 60 °C for 2 days. It was finally annealed at 1100 °C for 10 h.

Membrane: We allowed 3 g of sol A to react at room temperature for 12 h. A solution of 0.34 g of titanium isopropoxide in 0.5 g of acetylacetone and 3 g of acetonitrile was added. One drop of this solution was placed on a freshly cleaned, aluminum-coated silicon wafer and the 1 cm² elastomeric mold was immediately pressed against the surface. The whole structure was placed in a closed 100 cm³ container with one drop of aqueous ammonia (30 %). The ammonia vapors diffused slowly through the elastomer into the sol and induced gelation. The mold was removed after 12 h. The glass film remained on the wafer and was annealed at 400 °C for 10 min. The aluminum support was then removed by etching in a 8:1 mixture of phosphoric acid and nitric acid to release the membrane.

Optical Waveguides: We added 0.5 g of di-*sec*-butoxyaluminoxytriethoxysilane to 3 g of sol A. After stirring for 6 h, 3 g of acetonitrile was added to the clear solution (sol B). A solution of 0.8 g of trimethylborate in 3 g of acetonitrile was added to 3 g of sol A and left at room temperature for 1 h (sol C).

One drop of the solution (sol B or C) was placed on a freshly cleaned silicon wafer bearing a 2 μm thick thermal oxide layer. The 1 cm² elastomeric mold was immediately pressed against the surface. The whole structure was placed in a closed 100 cm³ container with one drop of aqueous ammonia

(30 %). After 18 h, the mold was removed and the structure was consolidated by annealing for 3 h at 1100 °C (for sol B) and 15 min at 800 °C or 900 °C (for sol C).

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The Use of Soft Lithography to Fabricate Arrays of Schottky Diodes**

607

By *Junmin Hu, Rex G. Beck, Robert M. Westervelt*, and *George M. Whitesides**

Soft lithography is developing rapidly as a new approach to microfabrication.[1–8] Although it has been applied most actively to optical[9,10] and microanalytical systems,[11] it also has potential for application in microelectronic devices.[12] While it is improbable that it will compete with photolithography-based techniques for conventional, planar silicon devices having feature sizes >100 nm, it is attractive for less familiar device structures: non-planar and

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3D structures, organic devices, large-area systems, and systems with integrated electronic, optical sensor, and microelectromechanical system (MEMS) functions.[13] Among the issues in applying soft lithography in the fabrication of microelectronic devices are: registration of multiple layers, damage or contamination of interfaces, the size of the areas that can be patterned in a single impression, and the reproducibility of the performance of the devices. The primary objective of the work described here was to begin to address these issues through the fabrication of arrays of simple, electrically functional devices.

In this communication we describe the fabrication and characterization of arrays of Schottky diodes on silicon using a representative soft lithographic technique: micromolding in capillaries (MIMIC). The diode array covered an area of ~1 cm². Each diode had overall dimensions of 300 μm × 660 μm. The fabrication process required the registration of two micromolding steps. Over 90 % of the Schottky diodes displayed the expected characteristics.

Instead of conventional photolithography, micromolding in capillaries is used for each layer of the diode fabrication. A Schottky diode consists of two metal–semiconductor contacts: an ohmic contact and a Schottky rectifying contact. MIMIC begins with an elastomeric mold containing the contact pattern made by casting poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow-Corning, A:B = 1:15) against masters generated by a rapid prototyping technique based on commercially available high-resolution printers.[14] This mold is put in conformal contact with the substrate. Interconnected, recessed regions on the elastomeric mold form a continuous network of channels between the mold and the substrate. A liquid prepolymer is then applied to the open ends of the channels and fills the channels automatically by capillarity. The prepolymer is cured thermally or by exposure to long wavelength ultraviolet (UV) light. The elastomeric mold is then removed, leaving a polymeric pattern on the substrate.

Figure 1 illustrates the procedure for fabrication of arrays of Schottky diodes using MIMIC. The Schottky diodes were fabricated on p-type silicon doped with boron. At room temperature the resistivity of the wafer was 1.0–4.0 Ω cm and the corresponding doping concentration was 2×10^{16}–3×10^{15} cm^{-3}. The first step in fabrication generated an array of ohmic contacts. The relief structure on the elastomeric mold used in this step was an array of 300 μm × 300 μm raised squares separated by perpendicular recessed channels with widths 30 μm and 360 μm. The depth of the relief structure was 10 μm. Both ends of the PDMS mold were opened with a razor blade for filling of the prepolymer. As shown in Figure 1a, the PDMS was put in conformal contact with Si wafer and a liquid prepolymer, polyurethane (PU) NOA 73 (Norland Products), was applied to the open ends of the PDMS mold. The filling of an 8 mm channel took about 30 min. Once filled, the sample was exposed to a 450 W UV lamp (Canrad-Hanovia Immersion Lamp, Model 7825-34) for an hour to cure the PU. The

PDMS mold was then removed to reveal the PU pattern (Fig. 1b). Often a small amount of PU penetrated into the regions contacted by PDMS during capillary filling, leaving a thin layer of PU with thickness <0.1 μm. This thin PU underlayer could be removed by using an O$_2$ reactive ion etch (RIE). A dip in buffered hydrogen fluoride was used in the fabrication of both ohmic contacts and Schottky rectifying contacts before metal evaporation to remove native SiO$_2$. We deposited 200 Å of Cr and 1250 Å of Au by thermal evaporation and lifted off the PU in a solution of methylene chloride, ammonium hydroxide, and methanol (100:25:3 v/v). The sample was annealed thermally at 300 °C for 5 min to form ohmic contacts (Fig. 1c).
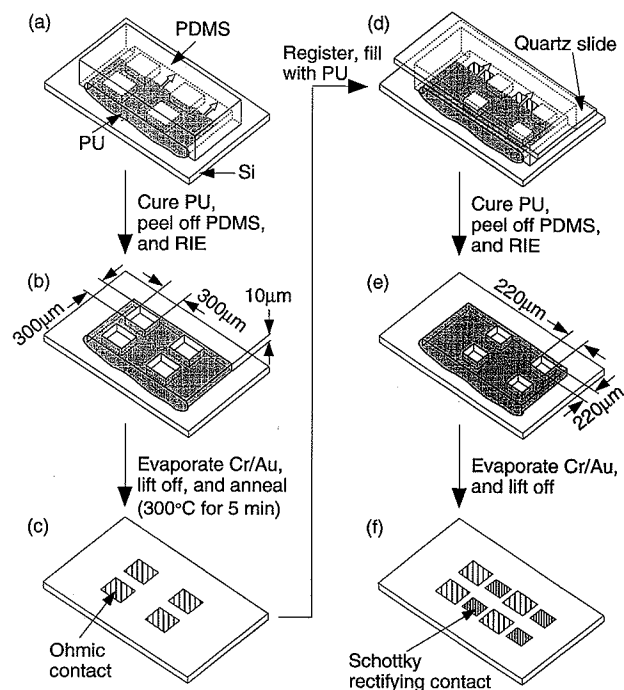

Fig. 1. Schematic illustration of the procedure for fabrication of an array of Schottky diodes using MIMIC. a) The PDMS mold is placed on the Si wafer and a few drops of polyurethane (PU) are applied to the open ends to define ohmic contacts. b) Exposure to UV light cures the PU. The PDMS mold is peeled off and PU underlayer is removed using O$_2$ reactive ion etching (RIE). c) Cr/Au is deposited on the wafer; the PU layer is lifted off; the sample is annealed thermally to form ohmic contacts. d) The PDMS mold is registered with the Si wafer and PU is applied to the open ends to define Schottky rectifying contacts. e) Exposure to UV light cures the PU. The PDMS mold is peeled off and the PU underlayer is removed using O$_2$ RIE. f) Cr/Au is deposited on the wafer and PU is lifted off to form the Schottky rectifying contacts.

The second step in the fabrication generated an array of Schottky rectifying contacts. The relief structure on the mold used was an array of 220 μm × 220 μm raised squares separated by perpendicular recessed channels with widths 110 μm and 440 μm. The registration was done using a Karl Suss mask aligner. A similar alignment scheme to that of photolithography was used. The PDMS mold was placed on a quartz slide to minimize elastic distortion and then mounted on the mask holder. We put the sample on the sample holder and slowly brought the mold and the sample

into focus. The position and the orientation of the sample were adjusted to align the sample and the mold. The sample was then carefully brought into contact with the PDMS mold (Fig. 1d). The PDMS mold remained in contact with the sample due to van der Waals interactions. The same MIMIC procedure as that used for the fabrication of ohmic contacts was carried out to make an array of rectifying contact patterns (Figs. 1d,e). Schottky rectifying contacts were formed by thermal evaporation of 200 Å of Cr and 1250 Å of Au and lifting off PU (Fig. 1f).

Figure 2a shows a scanning electron microscopy (SEM) micrograph of a part of an array of Schottky diodes fabricated using soft lithography. The whole array comprised about 500 diodes and covered an area of ~1 cm². The large square pads are ohmic contacts and the small square pads are Schottky rectifying contacts. The registration was within 30 μm over the whole sample.[15] Figure 2b is a magnified view of a single Schottky diode in the array. The rapid prototyping technique used to produce the masters reproduced feature sizes to within 10 μm with an edge roughness of ~2 μm. These dimensions are not lower limits of soft lithography; smaller features and better defined edges have
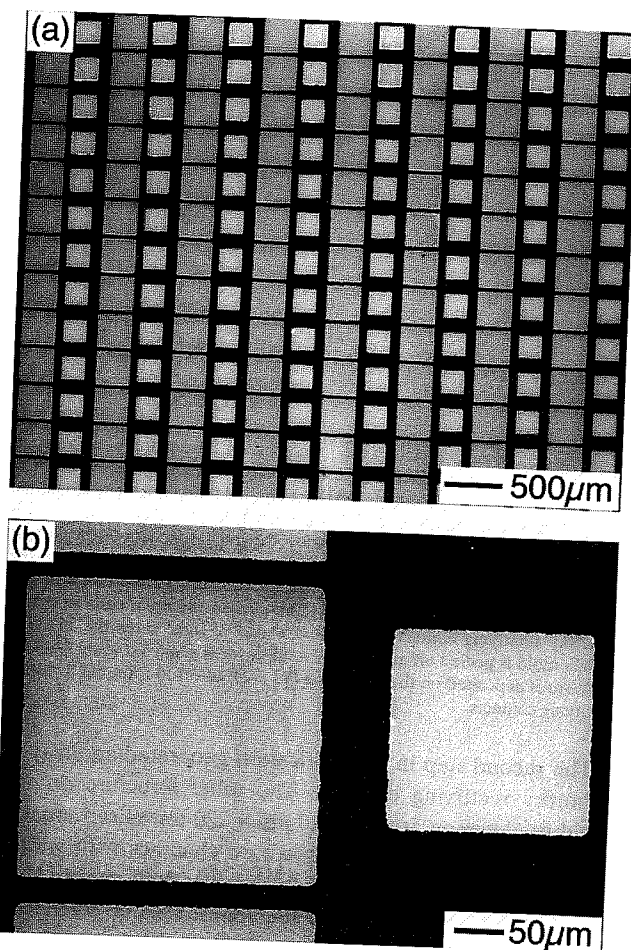

Fig. 2. SEM micrographs of a) an array of Schottky diodes and b) a magnified view of a Schottky diode in the array fabricated by soft lithography. The large squares (300 mm × 300 mm) are ohmic contacts, and the small squares (220 mm × 220 mm) are Schottky rectifying contacts.

been achieved.[16,17] Each MIMIC step had a pattern transfer yield >98 %.

Figure 3 shows the performance of a representative Schottky diode fabricated using this soft lithographic process. Contact of the PDMS mold with the Si sample does not seem to interfere with the formation of either ohmic or rectifying contacts. The current–voltage (I–V) characteristics of the diode (see Fig. 3a) resemble the I–V characteris-
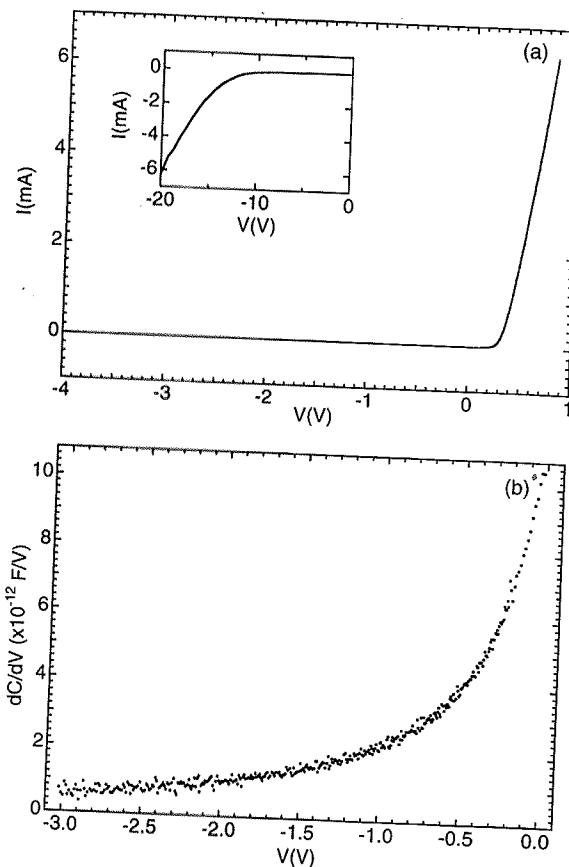

Fig. 3. Performance of a representative Schottky diode fabricated by MIMIC. a) Current–voltage characteristics. The inset shows the reverse breakdown of a Schottky diode. b) dC/dV vs. applied voltage V.

tics of a Schottky diode fabricated by photolithography.[18,19] The forward break voltage of the diode was $V_F \simeq$ 0.35 V, as expected for a silicon Schottky diode.[18] The inset of Figure 3a shows the reverse breakdown characteristics of the diode. The reverse current before diode breakdown was in the microamp range. The peak inverse voltage (PIV) of the diode was $V \simeq -14$ V and the maximum reverse current at PIV was $I_0 \simeq 0.8$ mA. The low PIV value for the diode is a result of the simple geometry of the Schottky rectifying contact; improved reverse characteristics can be achieved by the use of diffused guard rings or field plates where three or more fabrication steps are required.[19] Figure 3b is the capacitance–voltage response of the diode plotted as dC/dV vs. V to exclude stray source-drain capacitance.[20] The measured doping concentration of the diode is ~3.3×10^{15} cm⁻³. The capacitance at $V = 0$ V is $C \simeq 13$ pF.

We measured 25 diodes chosen randomly from three diode arrays. Over 90 % of the diodes fabricated displayed similar I–V characteristics.

Fabrication of functional Schottky diodes using MIMIC demonstrates that soft lithography is compatible with multilayer fabrication of electronically functional structures; this conclusion has also been confirmed by fabrication of high electron mobility transistors (HEMTs) using related processes.[12] Soft lithography has characteristics that make it superior to photolithography in certain aspects for application to device fabrication.[1] Soft lithography can transfer patterns onto non-planar surfaces; it allows the use of non-photosensitive polymers and materials as resists or functional materials; it offers low-cost processes; it can make 3D and quasi 3D structures; it can easily fabricate structures with dimensions <100 nm. One key issue to be defined is the registration that it can achieve. There is the obvious concern that the elastomeric nature of the PDMS mold will lead to distortions and inaccurate registration. In a study of distortion, Rogers et al.[21] demonstrated that it was possible to achieve pattern transfer in microcontact printing—a representative soft lithographic technique—with distortion of less than 500 nm over a ~1 cm² area in a single impression. Errors in registration should be the same as for photolithography and other related pattern-transfer techniques. MIMIC currently has its limitations: it cannot transfer patterns with isolated structures since it requires continuous channels for capillary filling; it is slow when channels with length >4 cm must be filled. These issues can be addressed by modifications of MIMIC, and by using other soft lithographic techniques.[1,2]

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Sol-Gel-Derived Carbon Ceramic Electrodes: A New Lithium Intercalation Anode**

By *Leonid Rabinovich, Jenny Gun, Ovadia Lev,** Doron Aurbach, Boris Markovsky,* and *Michael D. Levi*

Lithium-ion cells are composed of a cathode made of lithiated transition-metal oxide and a carbonaceous material anode. The anode is made of graphite powders or fibers held together by binding polymer. Carbonaceous materials are useful anodes because lithium also intercalates into graphite at potentials close to the Li/Li$^+$ standard potential, and these electrodes are safer and more reversible compared to lithium metal anodes. There is a technological interest in binding materials that provide high accessibility of the organic solvent and lithium ions to the graphitic material. Such a binder should also be electrochemically stable at least up to 4–5 V, to be compatible with commonly employed transition-metal oxides, such as LiMn$_2$O$_4$, LiNiO$_2$, and LiCoO$_2$. The binder should be sufficiently elastic to withstand volume changes during lithium intercalation and deintercalation, but still the composite material should have sufficient mechanical strength to withstand electrode stack pressure. Additionally, the carbonaceous material should be easily processed and deposited as thick or thin films and should adhere well to metallic current collectors. Poly(tetrafluoroethylene) (PTFE), ethylene propylene diene elastomer (EPDM), and poly(vinylidene difluoride) (PVDF) are commonly used binders and the latter is used here as a basis for performance comparison.

In this communication we demonstrate a new type of reversible lithium anode, namely sol-gel-derived carbon ceramic electrodes (CCEs). These electrodes were first introduced by our group[1] as a general purpose, versatile class of electrodes, suitable for a wide range of electroanalytic and electrocatalytic applications.[2–4] The electrodes comprise graphite powder dispersed in sol-gel-derived

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