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# Fabrication of arrays of Schottky diodes using microtransfer molding

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### Abstract

This paper describes the application of microtransfer molding—a representative soft lithographic technique—to the fabrication of simple Schottky diodes on silicon. The fabrication of a diode involved two microtransfer molding steps. The current–voltage responses of these diodes displayed characteristic nonlinear diode behavior. The yield of pattern transfer was 95% and the yield of functional diodes was 90%. Future improvements and potential industry application is proposed. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

There is an increasing interest in low-cost, large-area pattern transfer techniques. This interest arises in part from the demand for practical pattern transfer methods for fabrication of specific devices such as flat panel displays, in part as an affection of enthusiasm for microelectronic systems containing new devices such as those in organic transistors, and in part for the general potential of new materials and processes of fabrication in developing areas such as microelectromechanical systems (MEMS) and micrototal analysis systems (µTAS). These nonphotolithographic techniques include imprint lithography [1-4], cast molding [5-7], injection molding [8-10], and soft lithography [11,12]. Soft lithography is a set of replication techniques based on contact printing and polymer molding, and is capable of transferring patterns easily with feature sizes of less than 100 nm. We have described initial research that has demonstrated the feasibility of one soft lithographic technique—micromolding in capillaries (MIMIC) -for fabrication of representative devices: simple diodes [13], high electron mobility transistors on GaAs/AlGaAs heterostructure [14], and silicon MOSFETs [15]. These examples established the compatibility of soft lithography with the processing methods used in device fabrication, and indicate that at the feature sizes explored ( $\geq 20 \ \mu m$ ), it is possible to carry out two- and three-level fabrication using this technique. The application of MIMIC is limited to transferring patterns with interconnected structures, since it requires the flow of the polymer resist through channels by capillary action [16]. This paper investigates the feasibility of a related soft lithographic technique—microtransfer molding ( $\mu$ TM) [17]—that does not have the disadvantages of MIMIC for fabrication of a simple microelectronic device—a Schottky diode. It also has a characteristic disadvantage in that it can produce a thin film of polymer on ostensibly unpatterned regions of the surface; this remaining film may require an additional step of plasma etching or reactive ion etching (RIE) for removal.

In this paper, we describe the fabrication and characterization of arrays (10 mm  $\times$  10 mm for contact size 200  $\mu$ m  $\times$  200  $\mu$ m, and 3.5 mm  $\times$  3.5 mm for contact size 80  $\mu m \times 80 \mu m$ ) of Schottky diodes using  $\mu TM$  of polymer patterns with elastomeric molds. Our objective was to demonstrate the feasibility of the µTM technique through the fabrication of this proof-of-principle device. At the end of this paper, we will propose possible ways to improve this technique and to make it suitable for manufacturing application. The Schottky diode is one of the simplest electronic devices, and requires only two patterns of resist. Each Schottky diode consists of two types of contacts: an ohmic contact and a Schottky rectifying contact. We fabricated Schottky diode arrays on p-type silicon through two registered µTM steps, each followed by deposition of metal and lift-off. These diodes displayed characteristic nonohmic current-voltage responses.

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# 2. Experimental

Microtransfer molding uses an elastomeric stamp with bas-relief structure on its surface as a mold to transfer the pattern in a polymer resist [17]. The elastomeric mold was made by casting poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow-Corning, A:B = 1:15) against masters generated by a rapid prototyping technique based on high resolution printing [18]. The resolution of the feature sizes, edge roughness and depth of the relief structure on the mold were determined by the masters. A typical  $\mu$ TM procedure had four steps: (i) a liquid prepolymer, polyurethane (PU) NOA 73 (Norland Products), was applied to the recessed regions on the mold; (ii) the mold was put in conformal contact with the substrate; (iii) the prepolymer was cured

> (g) Apply PU and align filled Quartz mold with ohmic contacts slide on Si/SiO2 PDMS -10 µm (h) Cure PU and remove mold (a) Apply PU PU PDMS (i) Remove underlayer (b) Place filled PDMS by O<sub>2</sub> RIE mold on Si/SiO PDMS Si/SiO2 (j) Cr/Au deposition (c) Cure PU and remove PDMS mold PU Underlayer (k) Lift off PU (d) Remove underlayer ♦ by O<sub>2</sub> RIE Schottky contact (I) top view of (e) Cr/Au deposition diode array 777777 11111111 (f) Lift off PU and anneal Ohmic contact

Fig. 1. Schematic illustration of the procedure for fabrication of Schottky diodes using  $\mu$ TM. (a) Polyurethane (PU) was applied to the recessed regions on the PDMS mold with a piece of PDMS with a small tip. (b) The filled PDMS mold was placed in contact with the silicon wafer. (c) The PU was cured by exposure to UV light (Canrad-Hanovia Immersion Lamp, Model 7825-34) and the PDMS mold was removed. (d) A PU underlayer was removed using O<sub>2</sub> reactive ion etch (RIE). (e) Cr/Au was deposited by thermal evaporation. (f) PU was lifted off in methylene chloride solution and the sample was annealed thermally ( $T = 300^{\circ}$ C, 5 min) to form ohmic contacts. (g) The PU was applied to the recessed regions on the PDMS mold for the Schottky contact patterns, and this filled PDMS mold was appropriately aligned with the ohmic contacts on the Si sample. (h) The PU was lifted off to form Schottky contacts.

by exposure to ultraviolet (UV) light; (iv) the mold was peeled off and an  $O_2$  RIE step was followed to remove any excess polymer.

Fig. 1 describes how  $\mu$ TM was used to fabricate arrays of Schottky diodes. The substrate was boron-doped p-type silicon having room-temperature resistivity between 1.0–4.0  $\Omega$  cm. The diode array consisted of alternating rows of ohmic contacts and Schottky rectifying contacts. In the first step,  $\mu$ TM was used to transfer PU patterns of ohmic contacts to the silicon surface. The bas-relief structure on the PDMS mold had a depth of 10  $\mu$ m and feature sizes on the order of 100  $\mu$ m. In Fig. 1a, PU was first applied to the recessed regions on the PDMS mold with a piece of PDMS with a small tip. The tip acted as an ink-jet print head: each time the tip was first dipped into a droplet of

PU, leaving a small amount of PU on the tip, and this PU was then transferred to the recessed regions of the PDMS mold by gently applying the tip to the PDMS mold. The same PDMS piece was also used to remove any excess polymer from the mold: each time the tip was first gently touched to the regions of the mold, where there was excess PU, to absorb the PU, then the tip was pressed against a dust-free, absorbent cloth, such as a cleanroom wipe, so the PU was absorbed by the cloth. Because the PDMS piece was soft, it minimized any possible damage to the elastomeric mold during both application and removal of the polymer resist. We then placed the filled PDMS mold on the substrate and annealed at 40°C for 20 min to reduce air pockets trapped in PU (Fig. 1b). Exposure to UV light cured PU (Fig. 1c). Often a thin layer of PU, the underlayer, existed in regions contacted by the raised regions on the PDMS mold. By carefully removing excess PU from the PDMS mold and annealing the sample before exposure to UV light, we could minimize the underlayer. It was, however, difficult to eliminate the underlayer completely during application and curing. The thickness of the PU underlayer ranged from 100 nm to 500 nm, varying from sample to sample as well as over a particular sample. This underlayer could be removed subsequently with a brief  $O_2$ RIE treatment (Fig. 1d). Before metal deposition, the sample was dipped in buffered HF to remove the native oxide layer. We then deposited 200 Å of Cr and 1250 Å of Au by thermal evaporation and lifted off PU in methylene chloride solution. Ohmic contacts were formed by thermal annealing (Fig. 1e–f).

In the second step,  $\mu$ TM was used to transfer PU patterns of Schottky rectifying contacts to the silicon surface. The pattern on the PDMS mold for Schottky contacts were the same as that for ohmic contacts. Alignment was done using an optical mask aligner [14]: as shown in Fig. 1g, each row of the Schottky contacts was positioned at the center between two neighboring rows of the ohmic contacts on the sample. Schottky contacts were also made of 200 Å of Cr and 1250 Å of Au by  $\mu$ TM, similar to the fabrication of ohmic contacts (Fig. 1g–k). Thermal annealing was not necessary for formation of Schottky contacts. The final sample consisted of alternating rows of ohmic and Schottky contacts.

### 3. Results and discussion

Fig. 2 shows pictures of arrays of Schottky diodes with two contact sizes fabricated by  $\mu$ TM. In Fig. 2a, the contact size was 200  $\mu$ m × 200  $\mu$ m with a separation of 50  $\mu$ m. In Fig. 2b, the contact size was 80  $\mu$ m × 80  $\mu$ m with a separation of 30  $\mu$ m. The insets show single Schottky diodes with the above two contact sizes. The edge roughness was ~ 2  $\mu$ m and the variation of the feature sizes was within 10  $\mu$ m, both determined by the rapid prototyping technique that generated the masters,



Fig. 2. SEM micrographs of arrays of Schottky diodes with contact areas of (a) 200  $\mu$ m × 200  $\mu$ m and (b) 80  $\mu$ m × 80  $\mu$ m. Both arrays were fabricated using  $\mu$ TM. The insets in (a) and (b) are magnified views of single Schottky diodes corresponding to the two contact sizes.

rather than by  $\mu$ TM procedure or depth of relief (~10  $\mu$ m). The registration was ~ 10  $\mu$ m over 1 cm<sup>2</sup>, arising mainly from the distortion of the elastomeric molds. The pattern transfer yield for the final diode array after two  $\mu$ TM steps was 95%.

Fig. 3 shows the room-temperature performance of a representative diode with contact area 200  $\mu$ m × 200  $\mu$ m made by  $\mu$ TM. The forward break voltage of this diode was  $V_F \approx 0.27$  V, and the reverse leakage current density was on the order of 10 mA/cm<sup>2</sup>. The inset shows the breakdown characteristics of the diode. The peak inverse voltage (PIV) was  $V \approx -16$  V and the maximum reverse current density at PIV was  $J_o \approx 1.7$  A/cm<sup>2</sup>. These characteristics were similar to those of diodes made by photolithography [19,20], and were also similar to those of diodes made by MIMIC [13]. These observations suggest that the removal of PU underlayer by RIE is complete and that contact of the PDMS mold and PU with the substrate does not cause contamination or damage of the metal–



Fig. 3. Current density vs. applied voltage of a representative Schottky diode with contact area 200  $\mu$ m×200  $\mu$ m fabricated using  $\mu$ TM. The inset is the reverse breakdown characteristics of the Schottky diode.

semiconductor interface. 90% of the diodes measured displayed characteristic nonlinear current-voltage behaviors.

#### 4. Conclusions

The Schottky diode was the first proof-of-principle microelectronic device fabricated by µTM and it establishes µTM as a soft lithographic technique that can be used for microelectronic device fabrication. The diode array had a registration level of 10  $\mu$ m over a 1 cm<sup>2</sup> area. Poor registration was mainly due to the elastic distortion of the PDMS mold. Rogers et al. [21] demonstrated that it was possible to minimize distortion to less than 500 nm over  $\sim 1 \text{ cm}^2$  area in microcontact printing—a representative soft lithographic technique. The polymer underlayer in µTM was 100 nm to 500 nm thick. Both the thickness and the uniformity of polymer underlayer can be drastically improved by using machine-controlled application of the liquid polymer instead of by application by hand with a PDMS piece. Machine controlled application, perhaps employing a device similar to an ink-jet print head controlled by a computer, is also suitable for industrial application.

Both  $\mu$ TM and MIMIC (demonstrated in previous work [13–15]) share characteristics that may provide advantages over photolithography in some circumstances. They can transfer patterns over nonplanar surfaces; they allow the use of nonphotosensitive resists and functional materials; they are low-cost processes. There are some differences between the two techniques. Microtransfer molding is suitable for transferring structures with any type of connectivity, while MIMIC is limited to transferring interconnected structures because the filling capillaries by liquid prepolymer by capillarity requires that they be continuous. Microtransfer molding can be used for large-area pattern transfer without much modification, while MIMIC is limited.

ited to small areas due to the time required to fill the capillaries. <sup>1</sup> At the present time, MIMIC provides better control of the polymer underlayer than does  $\mu$ TM. These characteristics make  $\mu$ TM and MIMIC a complimentary set of soft lithographic techniques for fabrication of micro-electronic devices [22], especially for applications such as flat panel display systems and organic devices [22].

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<sup>&</sup>lt;sup>1</sup> The filling rate is inversely proportional to the length of the capillary. Typically, it takes about an hour to fill a capillary having dimensions 10  $\mu$ m (*d*)×200  $\mu$ m (*w*)×10 cm (*l*) with liquid prepolymer NOA 73. By multiport filling of liquid prepolymer, MIMIC can be extended to transfer patterns over large areas.

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