Reliable fabrication method of transferable micron scale metal pattern for poly(dimethylsiloxane) metallization

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We have developed a reliable fabrication method of forming micron scale metal patterns on poly(dimethylsiloxane) (PDMS) using a pattern transfer process. A metal stack layer consisting of Au–Ti–Au layers, providing a weak but reliable adhesion, was deposited on a silicon wafer. The metal stack layer was then transferred to a PDMS substrate using serial and selective etching. We demonstrate that features as small as 2 μm were reliably transferred on to the PDMS substrate for use as interconnects and electrodes for biosensors and flexible electronics application.

Introduction

PDMS is a very attractive material for MEMS and BioMEMS applications as it is cheap, optically transparent, elastic, biocompatible, and easy-to-use. Because of its elastic and flexible properties, it can be also used as a material for flexible electronics or displays.[1] Because of the porosity and low surface energy of PDMS, there are also some limitations associated with this material. Solvent absorption of fluids such as pentane, hexane and water serves to limit its microfluidic applications.[2] The low surface energy of PDMS makes it difficult to be metallized for electrical or electrochemical applications. A metal pattern fabricated directly on the PDMS can also be easily damaged or de-bonded.[3,4] Instead of direct metal patterning on the PDMS, pattern transfer techniques have been reported where metal patterns are fabricated on a solid substrate and then transferred to the PDMS substrate. Park *et al.* fabricated metal patterns on glass slides and transferred them to the PDMS.[5] Because a metal like gold has weak adhesion to the oxide surface, metal patterns fabricated on this substrate can be transferred to the activated PDMS surface.[5] Lee *et al.* reported a technique of PDMS metallization where metal patterns were fabricated on a slide glass or a Si wafer, treated chemically, and then transferred to the PDMS during its curing process.[6] The metal pattern generated by this technique is embedded in the PDMS substrate, and hence it is easy to cover and seal the substrate without any step heights and mechanical hindrances. In these techniques, mercaptosilane is used as a chemical glue to generate the chemical bond between the metal pattern and PDMS.

Because of the weak adhesion between gold and substrates like silicon or glass, gold patterns on these substrates cannot be reliably fabricated. The use of an adhesion layer like Ti or Cr, generally used for gold patterning on a solid substrate, makes it difficult to transfer patterns to PDMS. For these reasons, a reliable fabrication method of transferable metal patterns on solid substrate is required for PDMS metallization.

In this paper, we use a metal stack layer for pattern transfer and demonstrate a method of fabrication of micron-scale metal feature on PDMS substrates. Features as small as 2 μm were formed as a demonstration and the adhesion was verfied using a Scotch tape test.

Experimental

Materials and equipment

3-Mercaptopropyltrimethoxysilane was obtained from Aldrich (St. Louis, MO) AZ1518 photoresist and AZ351 developer was obtained from Clariant Corp. (Somerville, NJ), and TFA (gold etchant) obtained from Transene (Danvers, MA). Sylgard 184 (PDMS) was purchased from Dow Corning (Midland, MI). All other chemicals used were obtained from J. T. Baker (Phillipsburg, NJ). A Suss MJB3 mask aligner from Suss Microtech (Waterbury, VT) was used for the photolithography processes. Metal layers were deposited with an e-beam evaporator from CHA Industries (Fremont, CA)

Fabrications

Silicon wafers were cleaned with piranha solution (H_2SO_4:H_2O_2 = 7:3) for 20 min and rinsed with deionized water, blow-dried with N_2 gas, and dried at 120 °C for 20 min (Fig. 1(a)). 1500 Å of first Au layer (deposition rate ~ 2.5 Å s^{-1}), a 500 Å Ti layer (deposition rate ~ 0.5 Å s^{-1}) and 50 Å of second Au layer (deposition rate ~0.5 Å s^{-1}) were deposited step by step to form a metal stack layer (Fig. 1(b)). The pattern was formed on the silicon substrate with a conventional photolithographic method and then 3000 Å of gold was deposited on this patterned substrate at a rate of 2.5 Å s^{-1}. After deposition, the wafer was dipped into acetone for 10 min to remove the photoresist on the substrate (Fig. 1(c)).

Before pattern transfer, the metal surface was treated with 20 mM of 3-mercaptopropyltrimethoxysilane in isopropyl alcohol for about 2 hours (Fig. 1(d)). The purpose of this step was to get a strong bond between the metal pattern and

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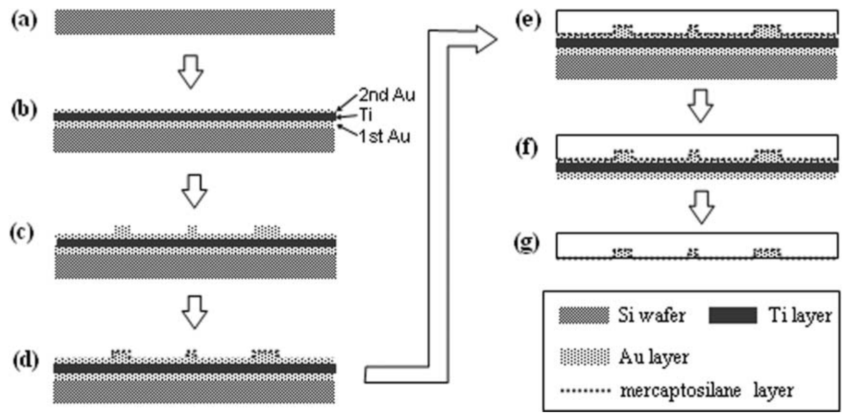

Fig. 1 Process flow of metal micro-patterning on PDMS: (a) substrate cleaning, (b) serial metal deposition (1500 Å of 1st Au, 500 Å of Ti, and 50 Å of 2nd Au) on Si wafer, (c) metal patterning with conventional photolithography, metal deposition (3000 Å or 3rd Au), and lift off, (d) mercaptosilane treatment, (e) pouring and curing PDMS, (f) peeling off PDMS from Si wafer, and (g) removal of 1st Au, Ti, followed by a short 2nd Au etch.

the PDMS. PDMS pre-polymer mixture (1:10) was poured on this patterned substrate and then cured at room temperature to prevent distortion or buckling of the metal layer caused by temperature differences (Fig. 1(e)). Because PDMS is flexible, it is not easy to detach it from the substrate without damaging the pattern. Cracks can be generated and extended when PDMS is bent. Hence we used another Si wafer as a hard support to prevent the PDMS from bending. Exposing the interface between the metal layer and the Si wafer to water also makes it easy for the PDMS to come apart from its substrate. After detaching the PDMS from the substrate (Fig. 1(f)), the metal stack layer (1500 Å 1st Au layer, 500 Å Ti layer, and 50 Å 2nd Au layer), which is now transferred to PDMS, is removed step by step by selective etching (Fig. 1(g)) with gold etchant (TFA) and titanium etchant (BHF–H_2O_2–H_2O), respectively. Since the metal pattern is gold and is the same as the second gold layer of the stack, controlled timed etching is required to remove the second Au layer without overetching of the metal patterns. This etch also serves as a short etch to clean the Au metal patterns.

Results and discussion

One of the most important issues in the fabrication of a transferable metal pattern is to get moderate adhesion to the substrate. The adhesion has to be strong enough to withstand the fabrication process. It should also be weak enough to be transferred to the PDMS substrate. To get moderate and reliable adhesion of metal pattern on a substrate, we used a metal stack layer consisting of a first Au, a Ti layer, and a second Au layer on a solid substrate (Fig. 1(b)). During the metal fabrication process, the first gold layer works as a substrate layer instead of Si surface and as a separator between metal pattern and Si wafer in the pattern transfer process. The Ti layer deposited on the first Au layer provides good adhesion between micropattern and substrate to prevent metal pattern from being damaged during the fabrication process. We have also found that the deposition rate of Ti has to be less than 1 Å s^{-1} to prevent cracking of the first Au layer during the

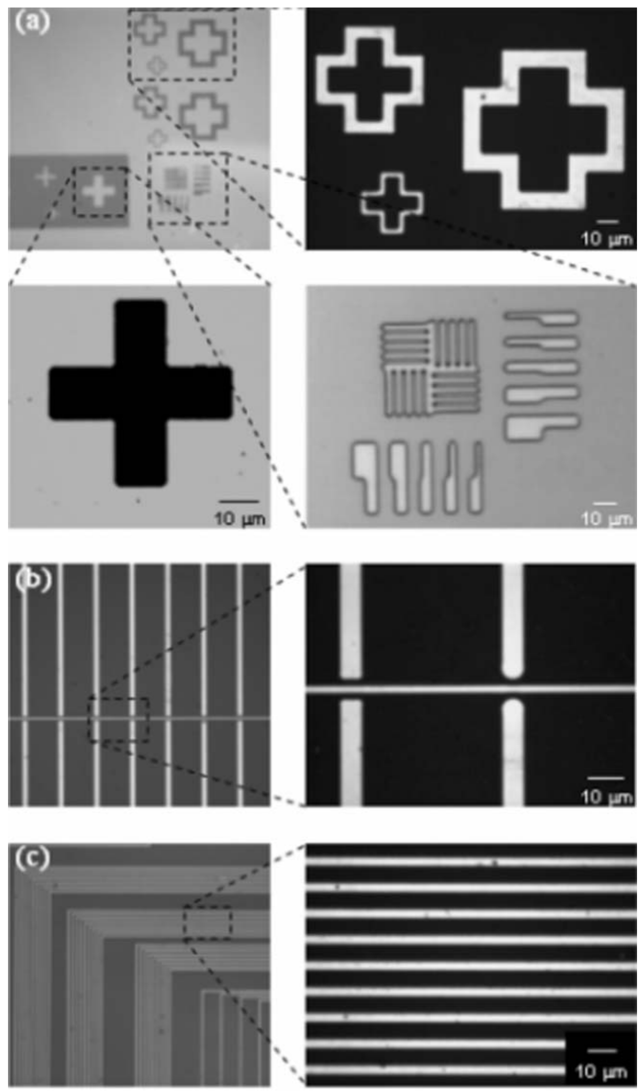

Fig. 2 Various gold micropatterns embedded into the PDMS fabricated with our method.

Fig. 3 Results of the Scotch tape test of gold patterns embedded in PDMS: (a) no treatment, (b) treatment with 3-mercaptopropyltrimethoxysilane vapor, and (c) treatment with 20 mM 3-mercaptopropyltriethoxysilane in isopropyl alcohol.

Ti deposition. The second Au layer minimizes oxidation of the Ti layer, which would reduce adhesion between the Ti layer and the metal micropatterns.

Because solvent can go through the Au–Si interface, gold layer is lifted off from Si wafer when it is dipped in the developing solution or solvent for washing. In our method, the first gold layer can withstand the conventional photolithographic process even though adhesion of gold to the Si substrate is poor. We think that is due to the discontinuity of the first gold layer at the edge area. A small number of Ti atoms diffuse through the gold layer and are deposited onto the Si surface in the region close to the edges. This increases the bonding strength between the first gold layer and the Si surface slightly, hence the gold layer is not lifted off from the Si wafer in wet processes like solvent washing or developing. Great care is required to protect the metal stack layer from mechanical damage in the process. Any damaged layers can be lifted off from the substrate when they are dipped in the developer after photo-exposure or acetone for photoresist lift-off.

Because of the strong adhesion between the substrate (2nd Au layer) and the metal patterns, they were not lifted off from the substrate during the fabrication and patterning, even when they were less than 2 μm wide. Fig. 2 shows various metal micropatterns embedded into the PDMS fabricated with this method. The minimum feature size we fabricated is 2 μm line width. We think that the minimum feature size generated by this method is limited only by the photolithography and patterning of the metal lift-off pattern itself.

A strong bond between the metal pattern and the PDMS substrate is also very important for reliable metallization on PDMS. If the metal pattern does not bind to the PDMS surface strongly, it could be damaged or lifted off easily by applied voltage or fluidic pressure. To generate a strong bond between the metal pattern and PDMS, the surface of the metal pattern is treated with 20 mM 3-mercaptopropyltrimethoxysilane before being transferred to PDMS. In our experiments we found that actually the metal patterns can be transferred to PDMS without any treatment, due to the surface properties of native PDMS. To examine the adhesion between the metal pattern and the PDMS substrate, we used the Scotch tape test after pattern transfer. As expected, non-treated metal pattern was lifted off from PDMS after the Scotch tape test (Fig. 3(a)). We found that metal patterns treated with 3-mercaptopropyltrimethoxysilane vapor were partially lifted-off with scotch tape frequently (Fig. 3(b)). However, the metal pattern treated in 20 mM 3-mercaptopropyltrimethoxysilane solution was more reliable, those patterns remaining after removal of the Scotch tape (Fig. 3(c)).

Conclusions

We have developed a new reliable fabrication method of transferring metal patterns on a solid substrate for PDMS metallization with a metal stack layer between metal pattern and a substrate. With this method, we can fabricate gold patterns with 2 μm wide lines and spaces. The process developed here can be used to form interconnect and metallization layers for flexible circuits or displays. Even though we have demonstrated gold patterns in this paper, this method will be also very useful to fabricate metal patterns like Cr or Ti, which are difficult to transfer because of their strong adhesion to oxide surface.

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