Room-temperature metal stamping by microfluidics

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ARTICLE INFO

Article history:

Received 22 September 2009

Accepted 30 September 2009

Available online 8 October 2009

Keywords:

Patterning

Metals

Microscale

Microfluidics

ABSTRACT

We show the possibility to fabricate highly controlled metal micropatterns on a variety of substrates, such as semiconducting or metallic materials, exploiting a combination of spontaneous galvanic displacement reactions with microfluidics. The process is reliable and quite versatile and allows the fabrication of complex patterns of different metals on a number of substrates in few minutes on a conventional laboratory bench.

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Micro- and nanofabrication of metal patterned substrates is of high relevance for electronic industry as well as for recent developments in photonics, tissue engineering and material science [1–7]. Several efficient methods, such as electron beam, ion beam, X-ray and photolithography [8] pulsed laser lithography [9] and scanning probe lithography [10–12], enable controlled micro- and nanofabrication of patterned substrates. However, though these techniques can potentially deliver high-resolution features with good reliability, they are expensive and time consuming, typically requiring complex equipment and specialized personnel, with relatively low throughput. Metal patterning has also been demonstrated using self-assembly, microcontact printing [13–15], micromolding in capillary (MIMIC) [16,17], reaction diffusion etching [18], dewetting [19], and other innovative approaches [20–22], although these techniques often rely on a series of fabrication steps that are highly time consuming and cumbersome. In this frame, there is, hence, the necessity to develop alternative strategies that enable easy bench-top fabrication of metal micropatterns with high reproducibility and quick processes. In this work, we demonstrate the possibility to fabricate highly controlled metal patterns on a variety of substrates, such as silicon wafers or other metal-coated planar substrates, by combining spontaneous galvanic displacement reactions (SGDR) with MIMIC. We show that microchanneled plastic stamps can reliably guide the precise localization of the metallization processes on the substrates. Also, the plastic stamps can be used repeatedly, thus obtaining a rapid stamping of the same metallic pattern on several substrates or even

superimposed patterns of one or different metals onto a single substrate easily and in few minutes.

The basic principle underlying the proposed technique is to spatially confine the metallization process with microscale resolution, by limiting the contact area of a reactant solution with the substrate. To achieve this, we positioned patterned PDMS stamps onto the substrates to define a net of microchannels, to be filled with a suitable reactant solution. By this procedure, metallization occurs via SGDR, only within the boundaries of the microchannels. Besides the ease of execution (e.g., no surface modifications are required), the process ensures that the unmetallized part of the substrate remains pristine, avoiding the presence of any residual resist material, unlike other lithographic techniques. Compared to other approaches aimed at the fabrication of metallized patterns through SGDR [23], our method has broader applicability, since it can be applied to fast reacting systems and, in particular, to the realization of superimposed metal patterns on a single substrate. Fig. 1 shows a scheme of the process based on suitable plastic replicas that leads to precise metal stamping onto a wide variety of substrates. First, the stamp is lightly pressed onto the substrate (Fig. 1a), then it is filled by an appropriate metal ion solution (Fig. 1b). As a consequence, metallization occurs only in the regions of the substrate that are exposed to the reaction (Fig. 1c). The only requirement here is that the reduction potential of the metal ion solution injected into the microchannels is sufficiently high to react with the substrate and get deposited in the metallic form [2]. Once the reaction of the metal ions with the substrate is over (typically after few minutes), the microchannels are injected with deionized water to quench the reaction and to wash the substrate. Finally, after suction of the water from the channels, the PDMS stamp is carefully removed, the substrate is washed again with deionized water and dried under flowing nitrogen. A wide variety of substrates can be metallized by this

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Fig. 1. Schematic showing the process of fabrication of a metalized pattern on a substrate using a combination of replica mold and galvanic reaction. a) A replica mold with open continuous channels is first pressed against the substrate; b) an appropriate solution of metal ions capable of galvanically reacting and getting deposited on the substrate is injected through the microfluidic channel and left to react for few minutes; c) after few minutes the metal ion solution is washed out and the replica gently removed to obtain the pattern.

approach with arbitrary patterns. The degree of metallization can be directly controlled by controlling the amount of metal ions in the solution and the time of reaction (typical processes usually take no longer than 2 min).

As a first example, we demonstrated the fabrication of gold and silver patterns on a p-type silicon substrate. After placing the PDMS stamp onto the silicon substrate, a solution of HAuCl_4 in HF and NH_4F mixture [2] is passed through the channels, and allowed to react for 1–2 min. Within this short reaction time, a thin layer of metallic gold is uniformly and selectively deposited in the regions delimited by the microchannels. Fig. 2a and b shows representative optical images of different patterns of gold on silicon wafer. The gold stripe patterns are

Fig. 2. Optical micrographs of a) and b) two representative gold patterns on a silicon substrate; c) bimetallic gold/silver grid pattern on a silicon substrate; d) gold grid pattern on a 50 nm thick silver film coated onto a glass slide. All the stripes in (a–d) were 80 μm wide.

80 μm wide. It can be noticed that the metalized patterns are spatially well defined without any sign of diffusion under the edges of the plastic microchannels. Once a particular metalized pattern is realized on a substrate, the process can be repeated on the same substrate, thus superimposing any other pattern of the same or different metal. This is demonstrated in Fig. 2c where we show crossed gold and silver patterns on silicon. In this case, a stripe pattern of silver was first fabricated on a silicon substrate by using a reactant solution of AgNO_3 in HF and NH_4F [2]; after washing and drying, a second similar pattern of gold was realized by placing the PDMS stamp perpendicular to the previous silver pattern and following the usual reaction conditions. Importantly, no intermediate lithographic steps or complex procedures are required to fabricate such two-metal patterns with microscale resolution. Moreover, our strategy relies on a direct reaction of the metal ions with the surface of the substrate, followed by local deposition within the microchannels. This ensures a very good contact of the overlying metal pattern with the underlying silicon, as the metal is deposited by etching out the surface oxide layer and directly displacing the elemental silicon beneath it.

Apart from the fabrication of patterns on silicon substrates, metal patterns can also be realized directly onto metal surfaces. Fig. 2d shows a representative image of a pattern of gold over a silver thin film. In this case, a 50 nm thick film of silver was first thermally vacuum deposited over a glass (or silica) substrate and then covered with the PDMS stamp. The microchannels were subsequently filled with aqueous HAuCl_4 solution and allowed to react for 2 min before washing with water. The grid pattern in Fig. 2d was obtained by repeating the patterning process with the stamp put perpendicular to the first pattern and following the reaction with the same HAuCl_4 aqueous solution. Such bimetallic pattern is similar to those recently achieved by our group for different applications, although this latter was fabricated using a more complex procedure based on photoresists and electron beam or optical lithographies [24,25].

To better assess the morphology of the fabricated patterns, we performed scanning electron microscope (SEM) analyses. Fig. 3a and b shows representative SEM images of a large gold pattern on a silicon wafer, showing the features at one end of the pattern. It can be observed that even the corners of the microchannel in the stamp are

Fig. 3. Scanning electron microscope (SEM) images of various metal pattern substrates. a, b) Representative SEM images of a gold pattern on silicon substrate at different magnifications. c) SEM image of a grid pattern consisting of perpendicular gold (vertical) and silver (horizontal) stripes on silicon. d) SEM image of gold stripe pattern on a nickel coated silica substrate. All the stripes in (a–d) were 80 μm wide.

precisely reproduced on the substrate. Fig. 3c is a SEM image of the Au–Ag grid pattern on a silicon substrate, corresponding to the sample shown in the optical image of Fig. 2c. The metallic stripes show a not perfectly flat and smooth surface. It is known, in fact, that in SGDR the deposition of the metal on the silicon substrate in the presence of HF is governed by the following reaction [2]:

From the above equation, it can be readily inferred that the amount and rate of metal deposited are dependent on the oxidation state of its corresponding metal ion solution used for the galvanic displacement reaction. This can lead to minor differences in the surface structure within the two-metal stripe regions. However, by properly tailoring the SGDR reaction parameters (concentration of the species, incubation time, etc.), it is possible, if required, to precisely control the surface morphology of the different metal regions, obtaining, for instance, flat or uniform and controlled nanostructured surfaces [24,25].

After getting encouraging results from gold and silver patterns on silicon substrates, and of one noble metal over another noble metal surface, we also demonstrated the possibility to fabricate metal patterns that could act as potential candidates for patterned magnetic materials. To this purpose, we used a silica substrate, covered by a 50 nm thick layer of nickel, and HAuCl_4 as the reactant solution. The rest of the process was similar to that described above. Galvanic displacement of nickel substrate by copper has been earlier demonstrated, emphasizing their catalytic properties [26]. However, patterned deposition over such substrates has not yet been demonstrated, thus paving the way for new potential applications. In Fig. 3d, a SEM image of such a substrate with a gold stripes pattern on a nickel coated substrate can be observed. Clearly, the stripes are well defined as observed in the previous cases. This example proves that the technique described here is equally efficient for a wide variety of systems and, thus, is quite versatile.

Finally, we investigated in more detail the spatial control of the reaction by an elemental mapping of the different species on the patterned substrates, using energy dispersive X-ray microanalysis

Fig. 4. EDAX elemental distributions analysis of the gold–silver patterned silicon substrate. a) SEM image of the area used for the elemental analysis. b) Silicon distribution on the surface of the substrate, imaged from the K line of the silicon species. c) Gold distribution on the surface imaged from the M line of the gold species. d) Silver distribution imaged from the L line of the silver species.

(EDAX). The area of the Au/Ag grid pattern, studied for mapping the elemental distribution on the patterned substrate, is shown in Fig. 4a (SEM image). Fig. 4b–d reports, in false colors, the spatial distributions of Si, Au and Ag, respectively, on the sample surface. In Fig. 4b, it can be noticed that a strong reduction of the Si K line signal is obtained in correspondence of the patterned region. This indicates that, after the Galvanic displacement reaction ends, the substrate under the microchannel region is covered by a thick layer of metal concealing well the underlying silicon part. Similarly, from Fig. 4c and d, it can be confirmed that the two metals, gold and silver, have been selectively deposited in the predetermined regions only. In particular, gold stripes preserve a uniform width also in the presence of raised regions, as in the case of crossings with Ag stripes. This proves that the sealing effect of PDMS on the substrate is verified also on rough or terraced substrates, giving further generalizability to our approach.

In conclusion, we have demonstrated that the use of capillary microchanneled PDMS stamps is a feasible way to readily fabricate micropatterns of single or multiple metals on a single galvanically reactive substrate. The process is quite versatile and can be applied on a wide range of semiconducting, metallic or even magnetic substrates without resorting to high end instruments. Each fabrication process can be realized in few minutes time conveniently on a conventional laboratory bench, and can be reliably replicated on a number of substrates using a single polymeric stamp of desired microchanneled patterns. As a way ahead, we would like to use this technique to fabricate patterned substrates for tissue engineering, cell patterning and for the patterned assembly of magnetic materials (or magnetic NPs-labeled biomolecules) under the influence of magnetic field, exploiting the underlying magnetic metal pattern.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matlet.2009.09.066.

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