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Micro/nano-patterned metal transfer using UV-curable polymers

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Abstract

This study was aimed at developing a metal-transfer technique to fabricate micro/nano metal patterns by using the adhesion force between metal layers and polymer surfaces. The force was generated by partial curing on a UV-curable polymer surface. This polymer contained glycido methacrylate, polyurethane diacrylate (PU-2) and O₂-sensitive initiators, and was polymerized by covering it with an O₂-permeable film under UV irradiation. Another UV-curable polymer, containing isobonyl acrylate, hexa-acrylated PU (PU-6) and O₂-insensitive initiators, was utilized as the master mold. A layer of gold, pre-coated on the mold, was adhered to the partially cured intermediate layer, transferring gold patterns onto the intermediate layer. A scanning electron microscope, an optical microscope and atomic force microscopy were used to inspect the transferred yield and morphology of the gold patterns. A force–distance evaluation was also carried out to explore the adhesion force of the surfaces. The results show that the partially cured polymer can maintain the morphology of the pattern after a short period of irradiation and still displays its adhesive property on its surfaces. Instead of using the traditional photolithography and the lift-off process, the technique was performed to fabricate some complex patterns having micro and nano features, and interdigital electrodes, giving the potential for direct printing of microelectrodes and flexible circuits.

1. Introduction

Commonly used imprinting techniques were investigated to replace photolithographic processes in metal pattern transfer. The requirements of the photolithographic process, including UV irradiation, development, metal deposition and lift-off procedures, restrict the applications of nano/micro patterning on a flexible substrate. The direct metal-transfer method, possessing some advantages for nanoimprint and microcontact printing methods, can produce nanosized metal patterns or electrodes on a flexible or rigid substrate with low equipment cost, fast duplication and good fidelity.

Recently, some investigations have provided high-quality pattern transfer results by adhering a gold pattern onto an adhesion layer [1–12]. Typically, thin gold or copper film is deposited on polymeric elastic or rigiflex mold, formed by polydimethyl siloxane (PDMS) or poly(urethane acrylate) (PUA). Only the metal layer deposited on the protruded mold surface can be transferred to the substrates, such as silicon wafer, GaAs, glass and plastic substrate [6]. The achievement of transferring metal from mold to substrates is based on the difference of adhesion work between the metal–mold interface and the metal–substrate interface. The adhesion work of the metal–mold interface is minimized by choosing a mold having relatively low surface energy and carefully depositing the gold on the pattern surfaces, avoiding excessive deposition on lateral walls. Typically, the adhesion work of the metal–substrate interface is promoted by plasma or UV/ozone activation on both surfaces [7], or by adding a thin layer of self-assembled monolayer [8], a softening polymer [9, 10],
or a photo-adhesive [11]. For instance, nanotransfer printing (NTP) developed by Rogers et al was employed to transfer a deposited metal pattern from the protrusion of a mold to a substrate by the chemical bonding between Au and thiolated surface. The adhesion layer requires the addition of thiol groups on the surface of the substrate in order to form chemical bonding with gold. However, such a chemical reaction limits the variety of substrates [12]. Han and his coworkers provided another way to transfer a metal pattern with polymer adhesives instead of using chemical reactions. Plastic polymers, such as PMMA, PS, and so on, were used as the adhesive layer once the operation temperature was increased to reach the glassy temperature of the polymer ($T_g$). The plastic polymer starts to soften and deform when the temperature arrives $T_g$. Successful metal pattern transfer occurs when the polymer only adheres the metal pattern on the protrusions without contacting the concave area [9]. However, both adhesion and large-area deformation of polymers occurred during the heating process, and then the deformed and extruded polymer was filled into the concave area of a patterned stamp, leading to the transfer technique only working in the case of transferred patterns with a feature size greater than several micrometers. Suh’s group found that a commercialized optical adhesive NOA71 could also successfully transfer gold from a relatively rigid PUA mold. NOA71 was formulated to provide a strong bond to glass surfaces [11]. In order to use the pattern transfer method in the application of flexible electronics, the large-scaled fidelity of gold electrodes on a polymer substrate was required.

Accordingly, we developed a convenient roller-printing process by which a partially cured adhesive layer is used to facilitate transfer of gold from a patterned elastomer stamp to a substrate. In order to apply the process to practical fabrication of metal microelectrodes instead of a trivial incremental advance over the above methods, we also investigated the microelectrodes by circuit testing and employed the roller-printing process to fabricate a nanowire transistor (data are not shown here and will be included in another article). The current work represents a significant improvement in the process can be applied to flexible substrates at relatively low processing temperatures.

2. Experimental details

2.1. Materials

Diacrylated urethane oligomer (PU-2), hexa-acrylated urethane oligomer (PU-6), isobornyl acrylate (IBOA), and dipentaerythritol hexa-acrylate (DPHA) were kindly given by Eternal Chemical Corporation, Ltd. Glycidyl methacrylate (GMA, purchased from TCI Corporation) was used as received. Initiators including benzophenone (BP, from Sigma Corporation), Irgacure 184 and 369 (kindly given by Ciba Corporation), and tertiary amine acrylate (TAA, given by Eternal Chemical Corporation, Ltd.) were used as is. All the involved solvents like chlorobenzene (from TEDIA) and toluene (from ECHO) were used as obtained. Octadecyltrichlorosilane (OTS, purity 95%, from ACROS Corporation) is a surface modifier that prevents polymer residue on the mold from imprinting. PDMS precursors containing siloxane prepolymer, crosslinkers and a platinum catalyst were purchased from Dow Corning Corporation.

2.2. Preparation of gold-patterned stamp (IBOA/PU-6)

The elastomer mold was a replica from a silicon template having relief structures on its surface and some anti-adhesion pretreatment to prevent polymer adhesion. The PDMS mold was fabricated by the casting method as mentioned in publications elsewhere [14]. Briefly, a two-part kit with a weight ratio of 1:10 (curing agent: PDMS base) was mixed thoroughly and dropped on the silicon mold, then was degassed in vacuum for 2 h and heated at 70 °C for 2 h for complete curing before it was peeled off from the silicone template. The UV-curable monomer contained 20 wt% of photoinitiator (BP/TAA = 1/3 (v/v)), 40 wt% of IBOA and 40 wt% of PU-6. The prepolymer solution was dropped on a PET film and imprinted by a patterned PDMS stamp under UV exposure for 25 s. After peeling off the PDMS stamp, a 10 nm-thick gold layer was deposited on the UV-cured patterned mold for transfer use.

2.3. Preparation of a UV-curable intermediate layer

The UV-curable monomer solution contained 5 wt% of photoinitiator (Irgacure184/369 = 1), 45 wt% of GMA and 50 wt% of PU-2. The prepolymer recipe was spin coated onto a fresh-cleaned glass slide at the first spin speed of 500 rpm for 20 s, and then the second spin speed of 2000 rpm for 30 s. Then, the prepolymer was covered by a flat PDMS membrane and cured by UV exposure for a certain period.

2.4. Gold-pattern transfer

The IBOA/PU-6 mold with the deposited gold layer was put in conformal contact with the adhesive intermediate layer (GMA/PU-2) using a home-made roller machine. During the transfer process, they needed to be heated to 50 °C under 50 g of load for 10 min. After the pressure was removed, the sample was peeled off. Two separated complementary patterns were obtained: one was a positive pattern having a gold pattern transferred onto the adhesive layer, and the other was a negative pattern having gold left in the depressions of the mold.

2.5. Characterization of patterns

All the transferred gold layers were observed by a high-resolution scanning electron microscope (SEM) (HR- FESEM, JSM-6700F, Joel Corporation, Ltd.) to evaluate the
achievement of transfer and their transfer efficiency. An optical microscope (Optem, Navitar Corporation) was employed to check the microscaled patterns and microelectrodes. An angiometer (Future Digital Scientific, Asia Inc.) was used to measure surface energy of a material to calculate the adhesion work between each two contact layers. The gold layer was deposited using a custom-made sputtering system (Kao Duen Tech. Corporation) with a thickness monitor attached to control the thickness of gold to be 10 nm at a deposition rate of 0.1 or 2 nm s\(^{-1}\). Adhesion force measurement: an atomic force microscope (AFM, model: NTEGRA, NT-MDT Corporation) with a heating stage attachment (SU045NTF) was used to explore the thermal effects and adhesion forces on polymer surfaces. The temperature was controlled between room temperature and 110 °C to within ±0.5 °C stability. Commercial V-shaped SiN integrated tip/cantilevers with a force constant of 0.03 N m\(^{-1}\) and a tip curvature radius of 6 nm were used. The whole setup was kept in an atmosphere where the humidity was controlled to 70% to imitate the real transfer process.

3. Results and discussion

The procedure can be seen in scheme 1. The partially cured polymer, an intermediate layer between substrate/gold, was prepared using a rapid UV-curing lamp (1000 W, medium-pressure mercury lamp, with 3.2 mW cm\(^{-2}\) at 300 nm of wavelength) and O\(_2\)-permeable PDMS coverage. This curable polymer for adhesion was composed of an oligomer of polyurethane diacrylate, which provides the polymer with toughness and suitable viscosity for imprinting, and monoacrylate monomer-GMA, which provides an epoxide group to enhance the bonding to the gold layer. To achieve a controllable partial curing situation, three factors should be addressed: initiator, covering membrane, and irradiation time. The PDMS membrane was used instead of quartz plates to cover the adhesive layer and have it cured. Since the oxygen permeability of PDMS is as high as 600 barrer [12, 13], it leads to an O\(_2\) inhibition reaction, adversely affecting the free radical polymerization. It was found that an adhesion layer containing phenone-type initiators, such as Irgacure 184 and 369, could provide a partially cured layer on the top of the polymer under a suitable period of irradiation. Only the top surface of the polymer was in contact with oxygen through the PDMS membrane, whereas the polymer in bulk was cured completely. The partially cured adhesive layer felt sticky and served to adhere gold layers to the surface. Jeong et al also demonstrated that an oxygen inhibition effect was utilized in the course of UV irradiation curing and a two-step molding process, to form multiscale hierarchical structures [13]. In order to enhance the reproducibility of metal transfer and increase the fidelity of large-area patterns, the softened layer of polymer surfaces should be controlled well. We first tried the UV-curable polymer containing oxirane groups that bind with metal surfaces and also took advantage of the nature of photoinitiators to produce a thin softened layer on UV-curable polymer surfaces. After a period of curing, the protruding gold layers could easily adhere to the polymer, leaving the gold in the depressions of the PDMS mold.

On the other hand, a completely cured UV-curable polymer was used as the patterning mold to transfer gold layers. Young’s modulus of gold is 78 GPa, whereas that of PDMS is less than 2 MPa. Therefore, the gold layer fractured easily on the PDMS due to low Young’s modulus of PDMS. Instead, a cured and rigiflex polymer was utilized as the master mold for gold layer deposition to tolerate strain and avoid any deformation when the gold layer was peeled from the master mold. The curable polymer for gold deposition was composed of an oligomer of polyurethane hexa-acrylate, which provides the polymer with network strength and
Figure 1. AFM measurement on 2 μm × 2 μm UV-curable sample surfaces at room temperature (the tapping mode is used). (a) The morphology image and (b) phase image for partially cured GMA/PU-2 after 30 s of curing while covered with a PDMS membrane. (c) The morphology image and (d) phase image for completely cured GMA/PU-2 while covered with a Si wafer. (e) The morphology image and (f) phase image for completely cured IBOA/PU-6. Dragging between polymer surface and tip obviously exists when the surface is partially cured (from (a) and (b)). However, Dragging phenomena are absent when the surface has been completely cured (compare (c) with (d) and (e) with (f)).

Figure 2. Typical force–distance curve obtained from AFM measurement and the schematic of tip approaching to and retraction from a polymer surface, in which the adhesion force $F_{\text{pull-off}}$ is indicated.
suitable viscosity for imprinting, and monoacrylate monomer-IBOA, which provides a soft cyclic structure to enhance the conformal contact with the adhesion layer. A photoinitiator, benzophenone (BP)/tertiary amine acrylate (TAA) complex, was chosen to reduce the O₂ inhibition effect due to its hydrogen abstracting function. The free radical on the amine group will transfer to BP and become a complex compound during UV irradiation, preventing reaction with oxygen [15]. Although the UV-curable mold came into contact with O₂ during photopolymerization, it was still cured completely.

A pattern with a 2 μm × 2 μm adhesive layer surface (GMA/PU-2) was scanned by the AFM in the tapping mode to investigate the dependence of its morphology on temperature (shown in figure 1). In phase images, the phase lag of the cantilever oscillation, relative to the signal sent to the cantilever’s piezo driver, is monitored by the controller. The phase lag is very sensitive to variations in adhesion and viscoelasticity on the surfaces. The heterogeneous phase lag in the phase image of the GMA/PU-2 layer (figure 1(b)) illustrates the soft and hard segmental domains coexisting on the surfaces, evidencing that the top surface of the layer had been partially cured due to the oxygen contact, as compared to the polymer surface being completely cured by covering a Si wafer to prevent the O₂ contact; therefore, the top surface exhibited a similar phase image to its morphology image (figures 1(c) and (d)). Conversely, the IBOA/PU-6 polymer could be fully cured on the surface whenever using PDMS or Si wafer as the supporting substrate, showing no apparent phase lag in its phase image, and could therefore provide a rigid pattern for gold coating. Dragging between polymer surface and tip obviously exists when the surface is partially cured (from figures 1(a) and (b)). However, the dragging phenomena are absent when the surface has been completely cured (compare figure 1(c) with figure 1(d), and figure 1(e) with figure 1(f)).

Post-exposure baking was found to be crucial for gold transfer. We carried out the scanning force microscopy (SFM) based on the AFM to evaluate the adhesion force on the polymer surfaces and its dependence on the baking temperature. Figure 2 shows a representative set of retraction force–distance curves obtained from various samples. In the figure, the vertical axis is the normal force experienced by the cantilever due to interactions between the tip and the sample (F). The horizontal axis is the displacement of the cantilever produced by the piezoelectric actuator to which the cantilever is attached (δpiezo). The tip usually rebounds once it snaps back; then, the pull-off force causing detachment between the sample and the tip is measured as the adhesion force. However, when the polymer was heated to be soft, the pull-off point at the curves displayed a prominent curvature (higher temperature curves in figure 3(a)), showing no abrupt, distinctive interfacial breakage of the sample tip adhesive bond. Adhesion was then determined as the maximum pull-off force noted in the force–distance curve [16]. According to the force balance between the tip and the sample

\[ F = k_c \delta_s = -k_c \delta_{tip} \]  \tag{1}

where \( k_c \) and \( k_c \) represent the force constants of the sample and the cantilever, respectively, \( \delta_s \) and \( \delta_{tip} \) are the depth of indentation on sample surface and the amount of bending in the cantilever, respectively [16, 17], and there we have

\[ \delta_{piezo} = \delta_s + \delta_{tip} \]  \tag{2}

The sample surface was deformed comparable to the deformation undertaken by the cantilever, leading to the prominent curvature. Combining with equations (1) and (2), we know that if \( k_c \ll k_s \), then \( \delta_{piezo} \sim \delta_{tip} \) and near zero indentation occurs. Here, we employed a softer (low \( k_c \)) probe to amplify the snap-back behavior and distinguish the tail in detail (large \( \delta_{tip} \)). The existence of an extended deformation tail (up to 200 nm) evidences plastic deformation in the sample. Meanwhile, the slope of the force–distance curve corresponds with the elasticity of the surfaces. The GMA/PU-2 surfaces demonstrate a decreasing slope corresponding to the increase in the measuring temperature, showing the loss of elasticity. Therefore, as measuring temperature is increased, the adhesion force also increases, owing to enhanced plasticity. To estimate the adhesion work between interfaces, the Johnson–Kendall–Roberts (JKR) model for describing the contact between two surfaces.
Figure 4. SEM microphotographs for gold transfer in a ruled pattern, complex microcircuit and nan pattern. (a), (c) and (e) Gold patterns transferred on an adhesive layer. (b), (d) and (f) Gold patterns left on a recessed area of mold.

materials was applied [18]. The adhesion work $\gamma$ is defined as the energy per unit of area required to separate two flat surfaces in vacuum from contact to infinity. It assumes that the adhesive forces are confined to the inside of the contact area. Therefore, we correlated the force with adhesion work, showing $F_{\text{pull-off}} = -1.5\pi RW_{12}$, and also the adhesion work $\gamma = W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}$. With a tip radius of about 10 nm, the adhesion work between the tip/adhesive layer for the sample after 30 s of irradiation was $0.17 \text{ N m}^{-1}$ at $26^\circ \text{C}$ and increased to $2.26 \text{ N m}^{-1}$ at $80^\circ \text{C}$.

Originally, the adhesion force of sample surfaces used to be estimated by surface tension measurements and calculation of adhesion work, which is not available for the partially cured surface owing to elution of some residual monomers when an organic liquid is dropped in. We therefore employed the adhesion force estimation of the surfaces by the AFM instead of surface tension measurements. The pull-off force was collected as the index of adhesion force for GMA/PU-2 prepolymers under different irradiation periods, as shown in figure 3(b). Each datum of the pull-off force was determined by averaging from eight independent measurements. 30 s of UV irradiation for the polymer displayed a higher adhesion force than others after longer irradiation time, probably due to continuing crosslink reactions on the surface and softening of short chains. The evidence supports that the baking process is required to contribute to the adhesion of the intermediate layer and conformal contact with gold layers. As the polymer softens, the effective yield strength lowers naturally with the elastic modulus, while the interfacial adhesive bond strength increases. Meanwhile, the more crosslinks the network forms as temperature increases, the more rigid the molecular chains become. Here, the completely cured polymer was prepared using the same recipe as before, but cured by covering with a silicon wafer to resist O$_2$ transport. The completely cured sample shows its surface $T_g$ at about $70^\circ \text{C}$ owing to appearance of a turning point [19]. 30 s of irradiation and post-exposure baking at $70^\circ \text{C}$ were suitable to supply a high adhesion force toward gold layers.

We carried out the noncontact scanning on the partially cured GMA/PU-2 surfaces. When elevating the measuring
Figure 5. SEM microphotographs for gold transfer in microcircuit and nanodot patterns on adhesive layer. (a) The lines are 250 nm wide and (b) the nanodots derived from a polycarbonate filter are 200 nm diameter.

Figure 6. Metal transfer to fabricate an interdigital microelectrode on a flexible PET film. (a) Photograph of flexible circuit and (b) its magnification of brush microelectrodes. (c) The contact points of the in-circuit test for the interdigital microelectrode. (d) The $I$–$V$ performance change of the microelectrode with different contact points.

temperature, the surface of the intermediate layer did not show any apparent change, suggesting that the surface morphology of the polymer had been fixed after 30 s of irradiation and would not have changed at any temperature, as shown in figure S1 available at stacks.iop.org/JMM/22/035008/mmedia. This phenomenon occurring on a crosslinked polymer surface can help the surface as a superior stamp to stick a gold layer on at an elevated operation temperature because the patterned morphology on the polymer surface would not change any longer, even under the baking process of imprinting. Heating on the partially cured polymer surface enhances its crosslinking density and also increases the adhesion force. We therefore assume that the baking process is required to soften segmental polymer chains but their movement is
restricted in crosslinked nanodomains. Another study showed that using a softened linear polymeric layer, such as PMMA, as the adhesive layer resulted in non-uniform transfer owing to heterogeneous softened polymer chains.

The operation conditions of UV-irradiation for 30 s and post-exposure baking at 70 °C were applied to fabricate the gold pattern when we employed variety patterns, including ruled pattern, complex microcircuit, nanodot pattern and interdigital microelectrodes (figures 4–6). The technique was proved to fabricate gold pattern features at both the microscales and nanoscales. Figure 4 shows the SEM photographs of dual transferred gold patterns on PET substrates and on recessed areas of molds. All the ruled patterns, complex microcircuits and nanodot patterns were employed to successfully transfer gold patterns with submicro features. The IBOA/PU-6 polymer replica, having the shape of the microelectrode on the protruding area, was coated with a 10 nm-thick gold layer and then pressed onto a PET substrate coated with the GMA/PU-2 polymer as an adhesive layer. The adhesive layer was able to transfer gold patterns from a microcircuit mold with 250 nm linewidth, and a nanohole mold, derived from track-etched polycarbonate filter (Millipore, Isopore™ Membrane) with 200 nm diameter, as shown in figure 5. The metal transfer was also used to fabricate a gold microelectrode on a flexible PET film. Figure 6 shows photographs of the transferred IDE circuit. It is apparent that the gold pattern transfer could be performed on a large-area PET film, leaving a gold micro/nano-featured pattern and its complementary one. We also measured the I–V performance of IDE using a probe station (model: Agilent 4156b). The left pad of one electrode was grounded and the resistances of Con 1 and Con 2 were measured as 1.8 and 5 kΩ, respectively. The connection test showed the gold micropattern could be transferred completely, as can be seen in figure 6. However, an overly thin gold layer (about 10 nm thick) caused some resistance loss. A thicker gold layer can be achieved using a high-aspect-ratio mold.

4. Conclusions

In summary, a partially cured UV-curable polymer was employed to provide a suitable network structure and adhesion property to adhere the protruding gold layer without deforming and transferring the recessed gold. A completely cured UV-curable polymer was used as the patterning mold to help gold layer transfer. Detailed AFM measurement for evaluating the adhesion force on the surface of the intermediate layer showed that partially cured polymers can display their softened chains in crosslinked nanodomains to transfer gold patterns. A post-exposure baking process is required to enhance the adhesion force of softened surfaces, resulting from increasing the initiated crosslink and polymerization reactions so as to enhance the adhesion force to gold patterns. 30 s of curing time for the GMA/PU-2 layer was the preferential choice because the morphology of the gel network was defined but the surface could still adhere to metal patterns strongly. Partially cured UV-curable polymers can provide a suitable network structure and adhesion property to adhere the protruding gold layer but not deform and transfer the recessed gold. Large-area transfer can be achievable using the technique combined with a roller imprint method, indicating promising applications to microelectronics, microsensors and optoelectronics.

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atomic force microscopic adhesion measurements

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