# Additive, nanoscale patterning of metal films with a stamp and a surface chemistry mediated transfer process: Applications in plastic electronics

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We describe a method for contact printing metal patterns with nanometer features over large areas. This nanotransfer printing (nTP) technique relies on tailored surface chemistries to transfer metal films from the raised regions of a stamp to a substrate when these two elements are brought into intimate physical contact. The printing is purely additive, fast ($<15$ s contact time), and it occurs in a single processing step at ambient conditions. Features of varying dimensions, including sizes down to $\sim 100$ nm, can be printed with edge resolution better than 15 nm. Electrical contacts and interconnects for high-performance organic transistors and complementary inverter circuits have been successfully fabricated using nTP. © *2002 American Institute of Physics.*
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Advanced techniques for nanofabrication are in widespread use for research in biology, physics, chemistry and materials science. They are also essential manufacturing tools for electronics, photonics and many other existing and emerging areas of technology. Established nanolithographic methods (e.g., electron-beam lithography, deep ultraviolet photolithography, etc.) require elaborate, expensive systems that are capable of only patterning a narrow range of specialized materials over small areas on ultraflat surfaces of rigid inorganic substrates. These limitations have created substantial interest in alternative techniques, such as those based on forms of contact printing, molding, embossing, and writing.[1,2] Although the basic operating principles of these techniques are conceptually old, recent research has demonstrated that their resolution can be extended into the micron and nanometer regimes by combining them with advanced materials and processing approaches. For example, elastomeric stamps and self-assembled monolayer inks[3] form the basis of a relatively new high-resolution printing technique.[4,5] This method, known as microcontact printing ($\mu$CP), is rapidly becoming important for a range of applications in biotechnology,[6] plastic electronics,[7,8] and fiber optics[9] where the relevant patterning requirements cannot be satisfied easily with conventional methods. Although the resolution of $\mu$CP is only $\sim 0.25$ $\mu$m, this method and other emerging printing techniques, such as those that rely on imprinted polymer resists[10] and cold-welded metals,[11] offer fast and low-cost approaches for patterning flat or curved surfaces over large areas in a single processing step. While these methods appear to be useful for many patterning tasks, they are all generally subtractive in operation, i.e., they typically require the use of sacrificial resists, etching procedures or postpatterning deposition steps.

In this letter we describe a purely additive printing technique that has nanometer resolution. The method, which we refer to as nanotransfer printing (nTP), allows us to transfer metal films from the raised regions of a stamp onto various oxide surfaces. Using nTP, we have been able to transfer metal patterns from elastomeric [e.g., poly(dimethylsiloxane) (PDMS)] as well as hard (e.g., GaAs) stamps onto both conformal (thin PDMS films supported on plastic) and rigid (e.g., Si wafer) substrates.[12] Here, we focus on systems with at least one conformal surface to ensure intimate physical contact between the stamp and the substrate (two nonconformal surfaces). It is possible to print from a rigid stamp onto a rigid substrate. In this case, however, external pressure is required to bring the stamp into contact with the substrate; the use of external pressure to provide intimate contact at the interface was previously reported in cold welding of metal films.[11] Pattern transfer relies on a common condensation reaction, similar to that used in sol–gel processing, between the hydroxyl (–OH) groups on the surfaces of the stamp and the substrate when the two are brought into contact. This printing technique can thus be used directly on materials that spontaneously form surface oxides (which can be subsequently hydroxylated). However, as we illustrate in this letter, nTP can also be used to pattern noble metal films, provided that they are bonded to surface oxide-forming metals. We demonstrate that a wide range of patterns can be printed in parallel with nanometer length scale resolution over large areas using nTP. Finally, we illustrate its versatility by fabricating the electrical components of functional plastic transistors and complementary inverter circuits.

Figure 1 presents the procedures for patterning thin metal layers with nTP. The process begins with fabrication of a suitable stamp. For elastomeric stamps, we cast and cured a prepolymer of PDMS against a pattern of photoresist on a silicon wafer according to established procedures.[4,5] For rigid stamps, we (i) patterned resist (e.g., electron beam resist or photoresist) onto a substrate (e.g., glass or GaAs), (ii) etched the exposed regions of the substrate with an anisotropic reactive ion etch and (iii) removed the resist with ac-

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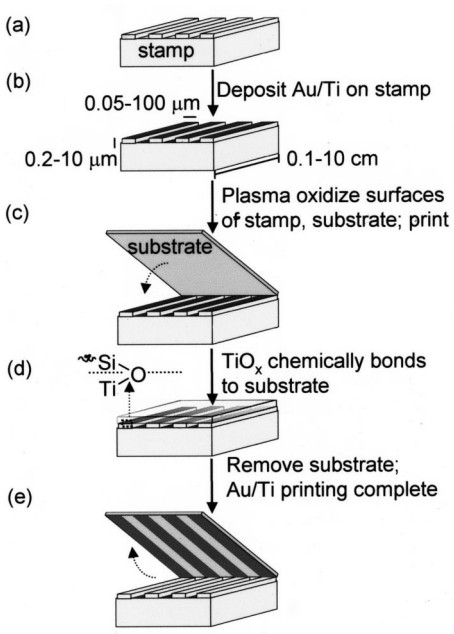


FIG. 1. Schematic of procedures for nanotransfer printing (nTP). (a) A stamp with relief features defines the geometry of the pattern. The overall stamp dimensions are between 0.1 and 10 cm, the relief is in the range of 0.2–10 $\mu$m, and the lateral dimensions of the features are between 0.05 and 100 $\mu$m. (b) 20 nm Au and 5 nm Ti are uniformly evaporated on the stamp. (c) Both the stamp and the substrate are plasma oxidized, resulting in (–OH) groups on the surfaces; they are then brought into contact. (d) In the regions of physical contact, an interfacial reaction produces strong chemical bonds that bind the metal on the stamp to the substrate. (e) Separating the stamp and substrate results in complete transfer of the Au/Ti pattern from the raised regions of the stamp to the substrate.

etone. We selected depths of relief $>0.2$ $\mu$m for patterning metal films with thicknesses $<50$ nm.

We evaporated uniform layers of Au (20 nm; 1 nm/s) then Ti (5 nm; 0.3 nm/s) on the stamp surface [Fig. 1(b)]. We note that, in the absence of a primer layer, gold adheres extremely poorly to the stamp. The Ti layer that was subsequently deposited on top of the Au layer serves two purposes: (i) it promotes adhesion between the Au layer and the substrate after pattern transfer, and (ii) it readily forms a $\sim$3 nm oxide layer under ambient conditions[13] which provides a surface on which the condensation reaction can take place. Exposing the titanium oxide ($TiO_x$) surface to an oxygen plasma[14] and subsequently to air results in the formation of hydroxyl (–OH) groups (titanol) on the surface.[15,16] While the exact mechanism of (–OH) formation on the oxide surface is unclear, we believe that, in addition to removing adsorbed hydrocarbons, plasma oxidation breaks bridging oxygen bonds on the surface, thereby creating defect sites where water molecules can adsorb. Exposing the titanium oxide surface to ultraviolet radiation in air produces similar results.[17]

The conformal substrates, which are designed for laminated plastic circuits,[18] consisted of thin films of PDMS (10–50 $\mu$m thick) cast on sheets of poly(ethylene terephthalate) (PET) (175 $\mu$m thick). Exposing the PDMS to an oxygen plasma and subsequently to air[14,19] produces surface (–OH) groups (silanol). Placing the plasma oxidized, metal-coated stamps (either the PDMS stamps or the hard stamps) on top of these substrates (or vice versa) leads to intimate, conformal contact between the raised regions of the stamp and the substrate, without the application of any external pressure [Fig. 1(d)]. We believe a condensation reaction takes place at the (–OH)-bearing interface during contact; this reaction results in permanent Ti–O–Si bonds at the interface. Peeling the substrate and stamp apart transfers the Au/Ti bilayer from the raised regions of the stamp (to which the metal has extremely poor adhesion) to the substrate. Patterns of Al, which readily form surface oxides, were also transferred successfully under the same conditions. Complete pattern transfer occurs readily at room temperature in open air at contact times of less than 15 s. We can also transfer metal patterns from elastomeric stamps onto rigid substrates (e.g., $SiO_2$ surfaces) using similar procedures. The slight differences in printing conditions for the various stamp/substrate combinations are the subject of current study. We speculate that they reflect different efficiencies in achieving stamp/substrate contact; similar effects have been observed in cold welding of gold films.[11,20]

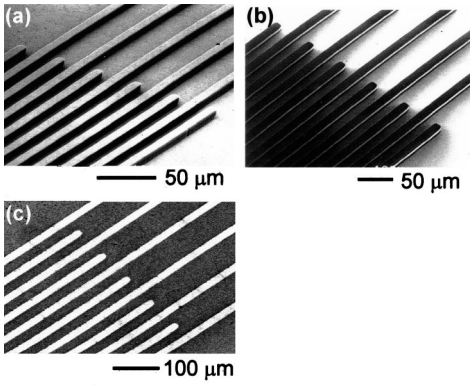


FIG. 2. Scanning electron micrographs of a region of an elastomeric PDMS stamp coated with 20 nm Au and 5 nm Ti (a) before, and (b) after nTP. (c) The printed pattern on a PDMS/PET substrate. The relief features on the stamp are 10 $\mu$m wide spaced 30 $\mu$m apart. The depth of the relief is approximately 10 $\mu$m.

Figure 2 presents scanning electron micrographs of a PDMS stamp before and after printing [Figs. 2(a) and 2(b), respectively] and the resulting pattern of Au/Ti transferred to the substrate [Fig. 2(c)]. Figure 3 illustrates various Au/Ti patterns with submicron features formed by nTP with rigid stamps. The line pattern in Fig. 3(a) was printed with a fused silica stamp that was produced by holographic lithography and etching. The structures in Figs. 3(b) and 3(c) were transferred from different parts of a GaAs stamp, whose features were defined by electron-beam lithography. The printed patterns are uniform across large areas and the edges are sharp. Figures 3(b) and 3(c) show that the edge roughness is less than 15 nm. The edge resolution of the printed patterns is limited by the grain size of the evaporated metals. We note that the transferred patterns easily pass Scotch™ tape adhesion tests, confirming that they are strongly bonded to the substrate. Although we have not yet quantified the accuracy in multilevel registration that is possible with nTP, we expect the dimensional fidelity and registration of transfer to be similar to those of embossing techniques, especially when rigid stamps are used.[21] Aside from its purely additive nature, nTP has another advantage over conventional nanolithographic techniques: the stamps employed in nTP are re-

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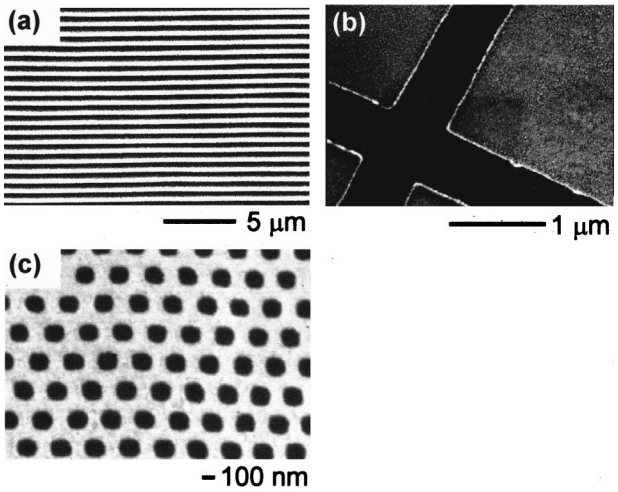


FIG. 3. Scanning electron micrographs of Au/Ti patterns generated by nTP printing. (a) 500 nm Au/Ti lines and spaces were printed with a fused silica stamp onto a PDMS/PET substrate. The relief depth in the stamp is 0.2 $\mu$m. The patterns in (b) and (c) were printed with a GaAs stamp that consists of (b) intersecting trenches that are 500 nm wide and (b) arrays of 130 nm holes, all with a relief depth of $\sim$0.5 $\mu$m. The bright and dark regions in the micrographs represent transferred Au/Ti and exposed PDMS, respectively.

usable, which makes this method an inherently low cost technique for nanofabrication. The stamps do, however, require occasional cleaning to prevent excessive buildup of metal in the recessed regions.

To demonstrate its potential application in plastic electronics, we patterned Au/Ti features for functional organic transistors and complementary inverter circuits on PDMS/PET using nTP. Laminating these patterned sheets against substrates that contain active organic semiconductor, dielectric and gate levels produces embedded plastic circuits.[18] Figure 4(a) shows the current–voltage characteristics of a pentacene[22] (*p*-type) transistor whose drain and source electrodes are patterned with nTP. The saturation drain–source current as a function of the driving gate voltage is plotted in the inset. The effective mobility ($0.1\,\mathrm{cm^2/V\,s}$) and on/off ratio ($\sim 10^4$) are comparable to top-contact transistors fabricated with conventional shadow-mask gold electrodes. Figure 4(b) shows the transfer characteristics of a complementary organic inverter circuit whose electrodes and connecting lines are defined by nTP. Pentacene and hexadecafluorophthalocyanine[23] (FCuPC) serve as the *p*- and *n*-type semiconductors, respectively. The performance of this circuit is comparable to larger-scale top-contact devices fabricated by shadow masking.

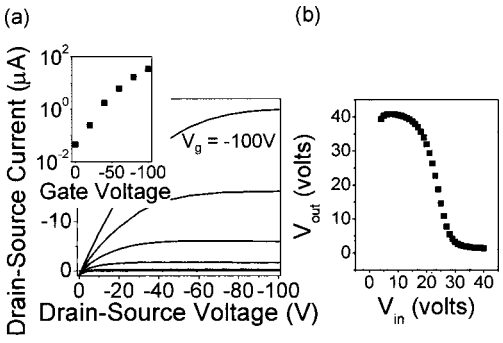


FIG. 4. (a) $I-V$ characteristics of pentacene thin film organic transistors whose gold electrodes were fabricated by nTP. The inset shows the saturated drain–source current as a function of the gate voltage ($W/L=8$). (b) Transfer characteristics of a complementary inverter circuit whose gold electrodes are fabricated by nTP.

In summary, in this letter we introduced an operationally simple transfer printing technique that is capable of nanometer resolution. The method is fast, purely additive, can pattern large areas, and can be carried out at room temperature in open air. We can effectively transfer a variety of materials, both surface oxide-forming (e.g., Al) as well as nonsurface oxide-forming metals (e.g., Au) using nTP. By exploiting other interfacial chemistries, we believe that this approach will be suitable for patterning a wide range of single- and multilayer conducting, dielectric and semiconducting films.

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