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

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(Received 14 February 2002; accepted for publication 16 May 2002)

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 ~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.

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. 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 form the basis of a relatively new high-resolution printing technique. This method, known as microcontact printing (µCP), is rapidly becoming important for a range of applications in biotechnology, plastic electronics, and fiber optics where the relevant patterning requirements cannot be satisfied easily with conventional methods. Although the resolution of µCP is only ~0.25 µm, this method and other emerging printing techniques, such as those that rely on imprinted polymer resists and cold-welded metals, 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. 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. 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. 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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metal films with thicknesses ~100 μm, the exact mechanism of this 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 the substrate. 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., SiO₂ 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

Figure 2 presents 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. The printed pattern on a PDMS/PET substrate. The relief features on the stamp are 10 μm wide spaced 30 μm apart. The depth of the relief is approximately 10 μm.
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 transistors and complementary inverter circuits on PDMS/PET electronics, we patterned Au/Ti features for functional organic metal in the recessed regions.

Figure 4(a) shows the current–voltage characteristics of a pentacene $p$-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 ($0.1 \text{ cm}^2/\text{V s}$) and on/off ratio ($\sim 10^5$) 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 ($\text{CuPC}$) 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.

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.

The authors gratefully acknowledge useful discussions with E. A. Chandross, Z. Bao, P. Ho, and T. Someya. They also thank Kenneth S. Feder for the quartz hard stamp and Luis F. Garfias for assistance with scanning electron microscopy.

14 A PlasmaTherm reactive ion etcher was used with an oxygen flow rate of 30 cm$^3$/min and pressure of 30 mTorr at 100 V. The stamp was first exposed to the oxygen plasma for 4 min. The substrate was then placed in the chamber, and both the stamp and substrate were oxidized for an additional 5 s.