ADVANCED MATERIALS

Reprint

data revealed surface enrichment of Br to be around 8.9 %. We attribute the remaining bromine to surface carbon–Br₂ complexes, which are formed by the charge transfer to the bromine molecule acting as an electron acceptor.[12] Again, no evidence of Br-intercalation compound was found; however, we cannot discount the possibility that the intercalated compounds may have been de-intercalated before the characterizations were made.

In conclusion, we have demonstrated a small scale method for the purification of nanotubes from other nanoparticles by a combined process of bromination followed by selective combustion with oxygen. It appears that the bromination causes a lesser degree of damage and fragmentation of the nanotubes, so they are slower to combust.

Experimental

Cathodic soot-containing nanotubes (denoted CS) were synthesized using the dc arc evaporation method as reported previously [13]. Two electrolytic-grade graphite electrodes with 10 and 12 mm inside diameters were employed and the arc was struck at a voltage and current of 30 V and 160 A, respectively. The electric arc was maintained in a reduced atmosphere of helium (500 torr). A freshly prepared CS sample (1.0 g) was mixed with pure bromine liquid (20.0 g). The mixture was then heated at 55 °C for 10 days. The resulting brominated sample was then heated at 100 °C under vacuum (1×10^{-4} torr) for at least 5 h to remove excess bromine. The product is denoted as BS.

Temperature programmed oxidation of the BS sample was conducted by placing 200 mg sandwiched between two silica wool plugs in a quartz tube (4 × 300 mm). The sample was heated under a stream of oxygen (4 % O_2 in 96 % helium, flow rate 20 mL/min) from room temperature to 700 °C at 5 K/min. The formation of carbon oxide (CO and CO_2) products was monitored at 5 min intervals by gas chromatography fitted with a methanator and a FID detector.

Oxidation of the BS sample was conducted by heating 0.1 g of the BS sample in a 300 mm-long silica test tube of inside diameter 8 mm at 530 °C for about 3 days. A stream of 30 mL/min of diluted oxygen (4 % O_2 in helium) was delivered to the sample *via* a small silica dip tube of (4 mm inside diameter). The optimum duration for the oxidation was mainly determined by monitoring the samples using TEM. The oxidation was halted when complete purification was achieved. The product is denoted as PT.

The nanotube samples (CS, BS, PT) were characterized by powder X-ray diffraction, TEM, XPS, elemental analysis, and BET surface area measurements.

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Microcontact Printing with a Cylindrical Rolling Stamp: A Practical Step Toward Automatic Manufacturing of Patterns with Submicrometer-Sized Features**

By *Younan Xia, Dong Qin,* and *George M. Whitesides**

This paper describes microcontact printing (µCP)[1] using a rolling elastomeric stamp to generate patterned self-assembled monolayers (SAMs)[2] with a minimum feature size of ~300 nm over areas of ~50 cm². This procedure is remarkable for its simplicity and speed.

Microcontact printing uses an elastomeric stamp (usually made from polydimethylsiloxane (PDMS)) having relief structures on its surface to transfer molecules of the "ink" (for example, an alkanethiol or alkylsiloxane precursor) to selected regions of the surface of a substrate. It is a very convenient technique for generating patterned SAMs of alkanethiolates on evaporated films of Au,[1] Ag,[3] and Cu;[4] it has been extended to form patterned SAMs of alkylsiloxanes[5–7] and of colloidal particles of Pd and other metals[8] on Si/SiO_2. When combined with selective wet etching, this technique is routinely capable of generating the features of coinage metals with dimensions down to ~500 nm; and, with greater difficulty, down to ~100 nm.[9,10] The technique has found a number of applications in microfabrication,[11] materials science,[12] and cell biology.[13]

Microcontact printing using self-assembled monolayers is a new strategy for forming small, high-quality structures that requires remarkably little capital investment. It is immediately applicable to simple and larger structures (that is, structures that do not require multiple superimposed patterns with accurate registration between them); sensors,[14] microelectrode arrays,[15] consumer electronic systems, and supports for cell cultures[13] are examples. For these types of systems, it is important to be able to form large areas of micropatterns rapidly.

The capability for large-area patterning by µCP is just beginning to be explored. In the past, microcontact printing has been carried out with a flat PDMS stamp with a surface patterned with relief structures. During printing, air bubbles trapped between the stamp and the substrate limited its use in forming patterns over areas larger than several square centimeters. This paper reports on a new procedure—rolling a cylindrical PDMS stamp across the surface—that has allowed us to rapidly form patterned SAMs over the entire surface of a 3 in wafer (that is, an area of

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~50 cm^2). The surface area that we have explored has been limited simply by the availability of appropriate elastomeric stamps. and we believe that this procedure will be applicable to much larger areas. This work establishes that μCP with a rolling PDMS stamp can form submicrometer-sized features over large areas, and suggests that it will be possible to carry out continuous printing at this feature size over very large areas on appropriate substrates (for example, continuous foils. plastic films, sheet glass and related wafers).

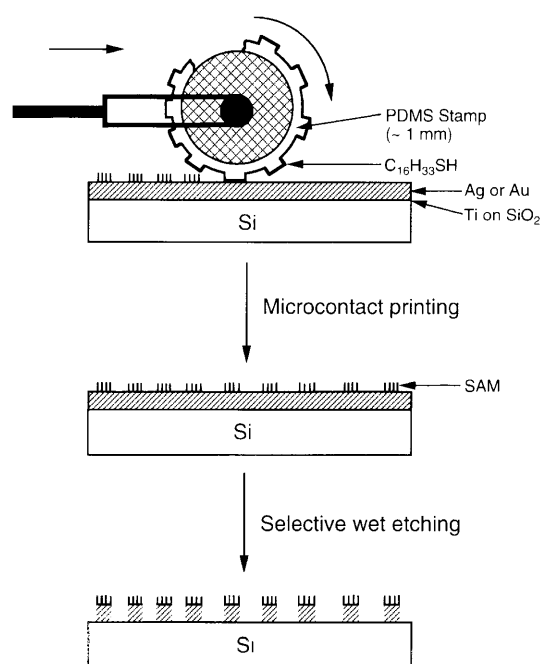Figure 1 schematically shows the procedure. A thin (~1 mm) PDMS stamp (prepared as described pre-

Fig. 1. Schematic procedure for conducting μCP with a rolling PDMS stamp (not to scale).

viously)[3 5] was applied with the ink solution, dried under a stream of nitrogen for ~15 s, wrapped around a cylindrical rod (~4 cm in diameter, see Fig. 2a) with a thin layer of solid adhesive on its surface (Magic Lint Remover, Emson, NY), and then rolled across the surface of a substrate to generate patterned SAMs. The rolling speed was ~2 cm/s. Submicrometer-sized features can be produced over the entire surface of a 3 in wafer (an area of ~50 cm^2, see Fig. 2b) in a single printing. The whole printing process was completed in ~20 s. With a single inking, the stamp could be used to make 4–5 printings (without any measurable reduction in quality) before requiring more ink. In principle, a conventional rotary printing apparatus would apply ink to one region of the surface of the stamp while printing occurs on another. At present, we have only demonstrated a single impression from the patterned stamp, rather than continuous rotary printing.
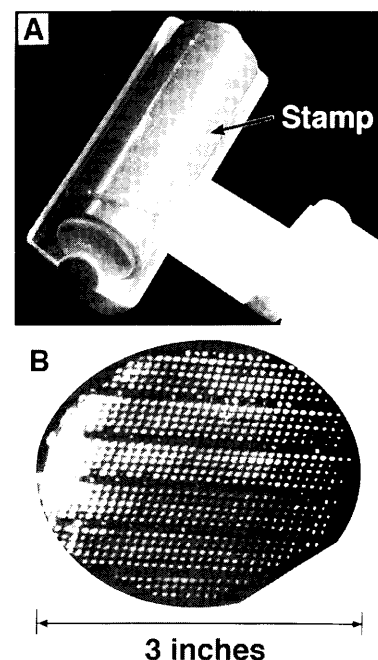

Fig. 2. Photographs of a) the rolling PDMS stamp wrapped around a cylindrical rod and b) the largest type of wafer (3 in diameter) that we have patterned with submicrometer-sized features (see Fig. 3) using this procedure.

Figure 3 shows SEM images of test patterns of Ag (50 nm thick) that were fabricated by μCP of hexadecanethiol with a rolling stamp, followed by selective wet etching in an aqueous ferricyanide solution[3,16] The smallest feature size is ~300 nm. This PDMS stamp was cast from a wafer whose surface has been patterned with numerous electronic devices; the complexity of these patterns represents those that are usually encountered in real circuit patterns.

Figure 4 compares test patterns of Ag that were fabricated by μCP with a flat PDMS stamp and with a rolling stamp moving along different directions. The flat and curved stamps were cast from the same master. The dimensional change caused by curving the elastomeric stamp was less than 100 nm (a more exact value cannot be obtained due to the edge roughness of the silver lines). Any dimensional change caused by distorting the pattern on the stamp by wrapping it around a cylindrical rod can be reduced by increasing the diameter of the rod.

In conclusion. we have demonstrated a new procedure for large area fabrication using microcontact printing. The smallest features that we have fabricated so far were silver structures with dimensions of ~300 nm. The largest area (as limited by the availability of stamps) that we have printed in a single impression (in less than 20 s) was ~50 cm^2. We believe that this new procedure indicates a potential route to automated printing machines that can be used for large area patterning of submicrometer features.

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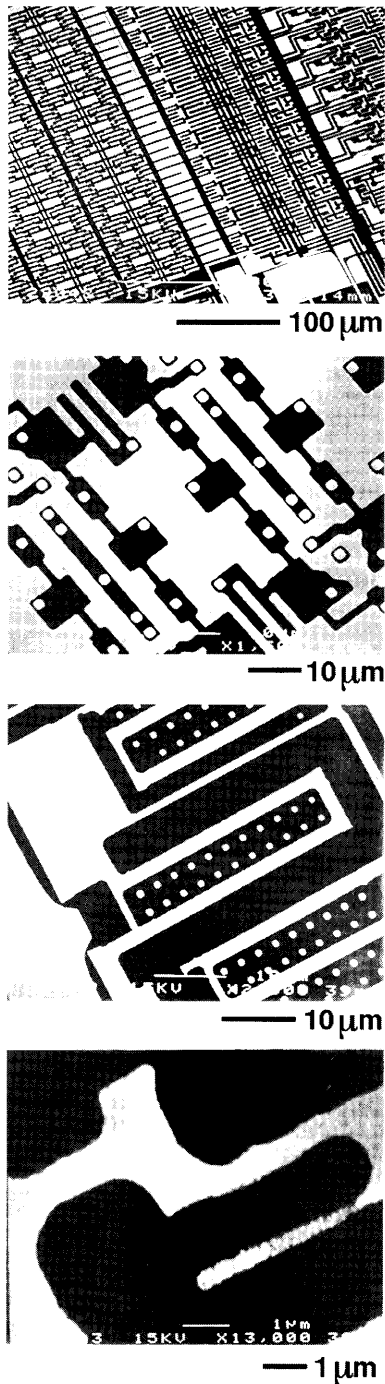[2] L. H. Dubois, R. G. Nuzzo, Annu. Rev. Phys. Chem. 1992, 43, 437.

Fig. 3. SEM images of test patterns (in four different magnifications) generated in Ag films using µCP with a rolling stamp, followed by selective wet etching in an aqueous ferricyanide solution for ~18 s. The bright regions are Ag; the dark regions are Si/SiO₂, where the unprotected Ag has dissolved.
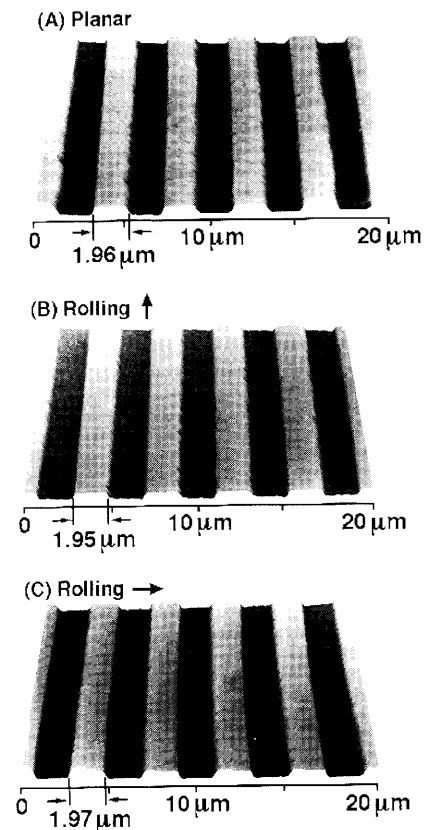

Fig. 4. AFM images of Ag lines (50 nm thick) generated with the PDMS stamp a) in the planar configuration; and generated by rolling the PDMS stamp b) along or c) perpendicular to the direction of the lines. The dimensional change caused by curving the PDMS stamp was less than 100 nm.

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