

Letters

Selective Placement of Carbon Nanotubes on Metal-Oxide Surfaces

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We describe a method to selectively position carbon nanotubes on Al_2O_3 and HfO_2 surfaces. The method exploits the selective binding of alkylphosphonic acids to oxide surfaces with large isoelectric points (i.e. basic rather than acidic surfaces). We have patterned oxide surfaces with acids using both microcontact printing and conventional lithography. With proper choice of the functional end group (e.g., $-\text{CH}_3$ or $-\text{NH}_2$), nanotube adhesion to the surface can be either prevented or enhanced.

Carbon nanotubes (CNTs) are playing an increasingly important role in the development of nanotechnology. The electronic properties of CNTs make them particularly well-suited for nanoelectronics. For example, field-effect transistors incorporating CNT channels have been demonstrated with device performance superior to that of conventional Si devices.^{1,2} However, a major barrier to the large-scale integration of CNT devices in circuits is the lack of control over the placement and orientation of nanotubes on substrates. One promising approach to this problem is to use surface chemistry, specifically self-assembled monolayers (SAMs), to prevent or enhance nanotube adhesion at selected areas of an oxide surface. For example, in one of the first studies of selective placement, Liu et al. showed that hydrophobic SAMs prevent nanotube adhesion on SiO_2 , whereas hydrophilic SAMs enhance it.³

Here we describe a simple, robust approach to patterning Al_2O_3 and HfO_2 surfaces with nanotubes. We exploit the acid–base reaction that binds phosphonic acid to certain

metal oxides, making formation of a dense monolayer relatively easy. Phosphonic acid SAMs terminated with amine or methyl groups are used to control the surface selectivity. In addition to the simplicity of the surface chemistry, a key advantage of using phosphonic acids is that they can be transferred to the surface via microcontact printing.⁴ This offers a fast, inexpensive method to pattern oxide surfaces with CNTs for large-scale integration. Phosphonic acids have a strong affinity for metal oxide surfaces such as ZrO_2 , TiO_2 , HfO_2 , and Al_2O_3 . Many of these oxides are of interest in microelectronics because they have dielectric constants that are larger than that of SiO_2 , making them potential replacements for SiO_2 in gate dielectrics. Self-assembly of alkylphosphonic acids on metal oxides has been demonstrated by several groups.^{5–8} Monolayer formation of alkylphosphonic acids

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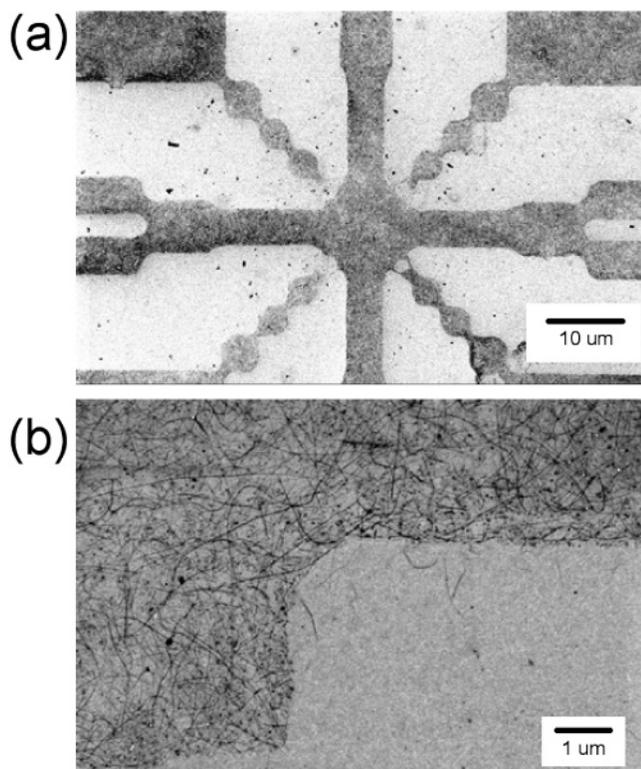


Figure 1. SEM images of nanotubes deposited on a HfO_2 surface patterned with HDPA via microcontact printing. Nanotubes adhere only the unstamped areas of the surface. (a) Large-area image illustrating uniform stamping and high-selectivity over a $\sim 2500 \mu\text{m}^2$ area. (b) High-resolution image of the corner of a stamped region.

on metal oxide substrates is achieved by a condensation reaction of the acid functionality with metal hydroxyl species to form bound phosphonates.⁹ In contrast, phosphonic acids do not react with SiO_2 at room temperature and only under high temperatures will react with hydroxyl species of SiO_2 to form phosphonates.¹⁰

We have used two different approaches to pattern surfaces with nanotubes. In the first, microcontact printing was used to transfer the templating acids. Specifically, a poly(dimethylsiloxane) (PDMS) stamp was inked with a 2 mM solution of hexadecylphosphonic acid (HDPA) in isopropyl alcohol. In all of our experiments the oxide surfaces were cleaned using an oxygen plasma prior to processing. We find that plasma cleaning promotes the adhesion of the templating acids to the oxide. The oxide surface (either HfO_2 or Al_2O_3) was then stamped to transfer the pattern to the surface. HDPA is strongly hydrophobic and excess solvent was removed by heating the surface at 110 °C for 15 min. A suspension of nanotubes in an organic solvent was then applied to the surface. Typically, the suspension consisted of single-walled nanotubes¹¹

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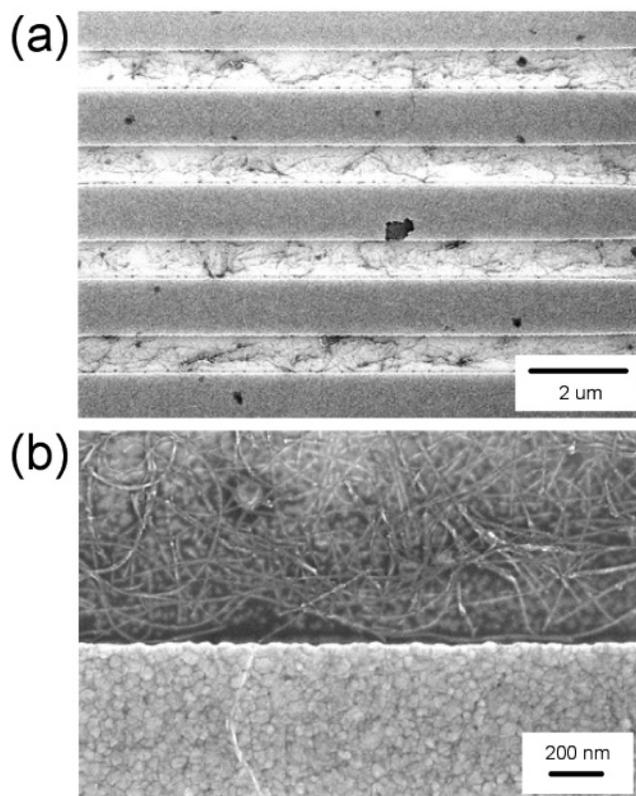


Figure 2. SEM images of nanotubes deposited on a 100 nm thick SiO_2 substrate patterned with Al_2O_3 lines (horizontal). The Al_2O_3 lines are treated with HDPA which prevents nanotube adhesion. Tubes only adhere to the (clean) SiO_2 regions. (a) Large-scale image demonstrating good selectivity over a large area, (b) high-resolution image showing very good local selectivity.

densely dispersed in either 1,2-dichloroethane (DCE) or 1-methyl-2-pyrrolidone (NMP) with a density of roughly 0.01 mg/L. Because our suspensions were made using unpurified tubes, they contained some amorphous carbon. The suspensions were sonicated briefly just prior to deposition.

Scanning electron microscope (SEM) images of a 5.3 nm thick HfO_2 oxide layer patterned with HDPA are shown in Figure 1. The selectivity is very good: the density of tubes in the unstamped area is nearly 10 tubes/ μm^2 , whereas in the stamped area, it is virtually zero. As the sharp boundary in Figure 1b shows, the fidelity of the stamping is also quite good. Finally, relatively large areas of the surface can be stamped reliably, as shown in Figure 1a.

In the second approach, we exploited the selective binding of phosphonic acid to basic oxides to achieve patterning. Using standard electron-beam lithography, we patterned a 100 nm thick SiO_2 substrate with 25 nm thick Al lines of various widths. The Al was then oxidized in an oxygen plasma. (Ellipsometry measurements on similar samples suggest that an ~ 4 nm Al_2O_3 layer forms on the evaporated Al.¹²) The patterned sample was then immersed in a 2 mM solution of HDPA in 2-propanol for 24 h. The treated sample was removed and sonicated for 30 s in ethanol and finally dried in N_2 . Single-wall nanotubes were deposited from a dense CNT suspension in DCE, as described above.

SEM images of the surface after CNT deposition are shown in Figure 2. Nanotubes were found on the SiO_2

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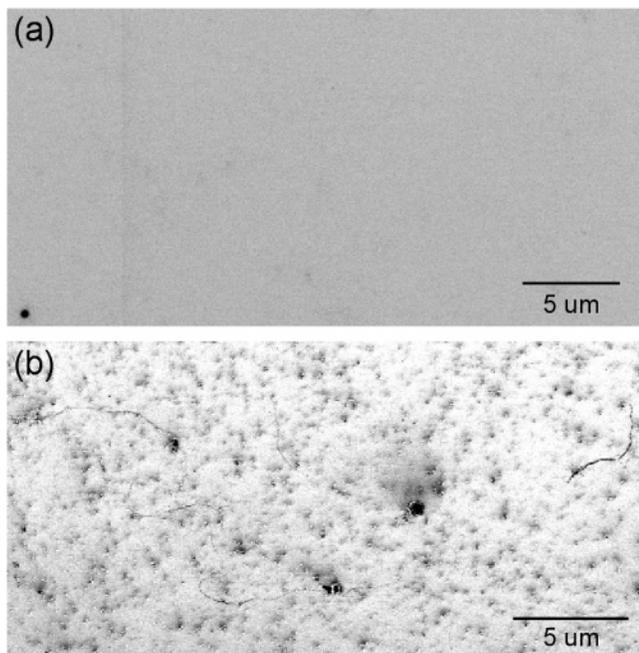


Figure 3. SEM images of a 3.2 nm film of HfO_2 . (a) After deposition of CNTs from an NMP solution. No CNTs or amorphous carbon are seen. (b) After an identical deposition on an identical film pretreated with an amine-terminated phosphonic acid. A high density of amorphous carbon, and a low density of CNTs, is observed.

regions but not on the Al_2O_3 lines, which are treated with HDPA (Figure 2a). High-resolution images at the interface between the SiO_2 and Al_2O_3 show excellent selectivity as well as high density of nanotubes (Figure 2b).

The two approaches described above are negative tone patterning. That is, nanotubes do not bind to the patterned areas of the surface. This approach has advantages for nanoelectronics. For example, the CNTs will not be in contact with the passivating acids, reducing the potential for adverse electronic effects (e.g., unintentional doping of the nanotube by the acid or chemical modification of the gate dielectric). However, for some applications, positive tone patterning might be desired. For basic oxides, positive tone patterning can be accomplished by patterning with amine-terminated alkylphosphonic acids. The equivalent approach for SiO_2 was demonstrated by Liu et al.³ The key challenge in positive-tone patterning is how to prevent nanotube adhesion to the untreated areas of the surface. One approach is to use photoresist to block off areas of the substrate.¹³ Another is to coat the nanotubes with surfactants, which prevent adsorption on SiO_2 (as well as on HfO_2 and Al_2O_3). The interaction of the surfactant-covered

tube with the amine-terminated SAMs is strong enough to induce some adsorption on the patterned areas, as shown by Choi et al.¹⁴ One disadvantage of using surfactants is that the adhesion is relatively poor. Consequently, it is difficult to achieve a high density of tubes on the surface.¹⁵

One alternative to the use of photoresists or surfactants was demonstrated by Valentin et al.¹⁵ They found that CNTs dispersed in NMP do not adhere well to SiO_2 but will bind to an amine-terminated SAM on SiO_2 . They were able to show good density and alignment for CNTs deposited on SiO_2 patterned with (aminopropyl)triethoxysilane (APTS). We investigated positive tone patterning on Al_2O_3 and HfO_2 using an amine-terminated SAM, specifically aminobutylphosphonic acid (ABPA). Single-wall nanotubes dispersed in NMP were deposited on a plasma-cleaned HfO_2 surface using the methods described above. An SEM image of the surface following deposition is shown in Figure 3a. The sample remained perfectly clean; no nanotubes or amorphous carbon were detected. A second sample was treated with a 5 mM solution of APBA in methanol. The ABPA was applied to a second HfO_2 sample, and the methanol was allowed to evaporate. This presumably leaves a thick (i.e., thicker than one monolayer) film of ABPA on the oxide. An identical deposition of nanotubes from the same suspension was performed. An SEM image from the resulting surface is shown in Figure 3b. Amorphous carbon is found over the entire sample, as well as a low density of nanotubes (we find that NMP solubilizes more amorphous carbon than DCE). These results show that the approach used by Valentin et al.¹⁵ for positive-tone patterning on SiO_2 can be extended to Al_2O_3 and HfO_2 .

In summary, we have shown that highly selective nanotube deposition on “high k ” HfO_2 and Al_2O_3 substrates can be achieved using alkylphosphonic acids. The surface chemistry is robust and easy to implement, and the formation of acid monolayers on HfO_2 and Al_2O_3 is relatively simple. Schemes for both positive- and negative-tone patterning have been demonstrated. These results are a step toward the ultimate goal of reliably positioning nanotubes on surfaces with 1–10 nm accuracy. The selectivity demonstrated here suggests that this goal is attainable. The challenge is to increase the density of nanotubes on the surface (i.e., the sticking probability) so that small features (e.g., lines) can be populated with high probability.

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