Microcontact Printing of Alkanephosphonic Acids on Aluminum: Pattern Transfer by Wet Chemical Etching

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Received August 24, 1998

Microcontact printing (μCP) has been used to pattern octadecanephosphonic acid on the native oxide surface film of aluminum supported on silicon or on silicon nitride-coated silicon wafers. The patterned alkanephosphonic acid protects the Al_2O_3/Al film from etching in a solution containing phosphoric, acetic, and nitric acids and water in a ratio of 16:1:1:2 and allows the nonpatterned film to be removed selectively. The patterned Al_2O_3/Al structures resulting from etching are continuous and electrically conductive within each pattern, and separated patterns are electrically isolated. Resistance measurements of the patterned structures are presented. Using μCP, Schottky diodes of aluminum have been prepared on p-type Si(100). The Schottky diodes exhibit rectifying behavior, and the forward-bias current–voltage ($I-V$) and reverse-bias capacitance–voltage ($C-V$) characteristics are presented.

Introduction

Microcontact printing (μCP) is a soft lithographic technique useful in patterning self-assembled monolayers (SAMs).[1–4] This report describes the μCP of alkanephosphonic acids onto Al_2O_3/Al films and the performance of these patterned films in protecting Al_2O_3/Al films during wet etching. The minimum feature size achieved in this study was 6 μm, but the stamp used set this dimension. Electrical resistance measurements of the patterned lines after etching confirmed that the lines were continuous and conductive.

Aluminum is commonly used as a metalization layer in the microelectronics industry.[5] Currently aluminum is patterned by two methods: (i) conventional photolithography, followed by metal deposition and liftoff; (ii) reactive ion etching (RIE) of a continuous film (a procedure that also involves a step of photolithography for pattern definition). In the case of metal deposition followed by liftoff, the pattern is transferred by physical removal of the aluminum in the unwanted regions by dissolution of an underlying polymer. No etching of the aluminum occurs; for larger features (on the order of millimeters), however, complete removal of the unwanted aluminum can be difficult. Conventional photolithography requires access to the appropriate facilities and is not always convenient, nor is it applicable to curved surfaces. This paper presents a non-photolithographic procedure for patterning aluminum.

Microcontact Printing (μCP). Figure 1 shows a schematic representation of the μCP process for octadecanephosphonic acid on supported Al_2O_3/Al films. Alkyltrichlorosilanes have been patterned on aluminum surfaces by μCP.[6–8] The use of patterned alkylsiloxanes for the selective RIE of aluminum resulted in shallow etch depths on the order of 5–10 nm.[6,7] In this work, using μCP of octadecanephosphonic acid ($C_{18}PO(OH)_2$) followed by wet etching, we have achieved etch depths of 300 nm without loss of electrical properties in the patterned film.

Choice of Alkanephosphonic Acids. We chose to use alkanephosphonic acids for this study because they are air stable compounds that are known to form stable, ordered monolayers on metal oxide surfaces.[9,10] The use of alkanephosphonic acids to form SAMs on metal oxide surfaces was motivated by the work of Mallouk et al. on alkanebisphosphonate multilayers.[11–13] SAMs on the native oxide of aluminum have been formed from alkanecarboxylic acids,[14–21] alkanehydroxamic acids,[9] alkanephosphonic acids,[9,22–24] and alkyltrichlorosilanes.[25]

Alkanecarboxylic acids adsorb on Al_2O_3/Al as the carboxylate anion, but this interaction results in a weakly bound, easily displaced adsorbate.[15] Two studies have shown increased stability of SAMs of alkanecarboxylic

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10.1021/la981094h CCC: $18.00 © 1999 American Chemical Society
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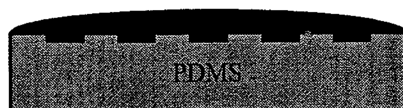
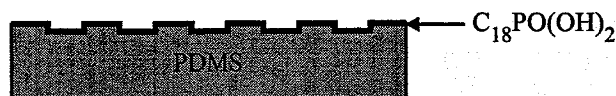
1) Ink stamp with $C_{18}PO(OH)_2$ (5 mM in 2-propanol)



2) Remove excess "ink" under a stream of N_2



3) Place stamp in conformal contact with Al

4) Stamp is removed and substrate is baked on a hotplate at 70 °C

5) Bare regions are selectively etched in Aluminum Etchant Type A

Figure 1. Schematic representation of the μCP process.

acids on Al_2O_3/Al films. Aronoff et al. developed a method to increase the binding of SAMs of alkanecarboxylic acids on a hydroxide-terminated Al_2O_3/Al surface by first priming the metal hydroxide surface with zirconium alkoxide.[26] This study was, however, performed in ultrahigh vacuum (UHV), and the reactivity of zirconium alkoxides may limit its application to monolayers formed in solution.

Wallace et al. prepared and characterized SAMs of perfluorinated alkanecarboxylic acids on Al_2O_3/Al. The results of thermal desorption studies found that the molecule was chemisorbed, with an apparent desorption activation energy of 30 ± 3 kcal/mol.[27] We attribute the increase in the binding ability of perfluorinated alkanecarboxylic acids on Al_2O_3/Al, as compared to their hydrocarbon counterparts, to the high acidity of these acids.[28]

Ramsier et al. have studied the adsorption of several phosphorus oxy-acids on alumina: phosphinic, phosphonic, methanephosphonic, hydroxymethanephosphonic, aminomethanephosphonic, and nitrilotris(methylene)-triphosphonic acids.[29] Their results indicate these acids chemisorb as the deprotonated acids on alumina. They propose a mechanism of adsorption involving a condensation reaction between the anion of the deprotonated acid and the surface oxide or hydroxide groups of the alumina. This reaction results in the formation of P–O–Al bonds.

A study of competitive binding between ferrocene-terminated alkanecarboxylic acids and alkanephosphonic acid on indium(tin) oxide (ITO) showed that the carboxylic acid derivative could not compete for the surface in a solution of the two species. The energetics of desorption of 11-ferrocenylundecanephosphonic acid on ITO were studied at various temperatures, and the activation energy for desorption was found to be 23 ± 6 kcal/mol.[30] This binding energy is indicative of chemisorption. We hoped that this interaction would not be limited to ITO but would also extend to other basic metal oxides.

A study of SAMs formed from octadecanephosphonic acid on porous ZrO_2 and TiO_2 and nonporous SiO_2 and γ-Al_2O_3 found that monolayers were formed on ZrO_2, TiO_2, and SiO_2; a bulk aluminoalkyl(phosphonate), however, was formed on Al_2O_3.[22] Elemental analysis indicated that the (aluminoalkyl)phosphonate was at least two layers thick. The authors concluded that aluminum oxide was not a suitable substrate for SAM formation due to the formation of bulk (aluminoalkyl)phosphonate. We believe that the presence of a monolayer of Al_2O_3, that is, a native oxide formed on aluminum metal, would limit bulk (aluminoalkyl)phosphonate formation. Further, if a multilayer were to form spontaneously, it might improve the etch resistance.

Choice of Octadecanephosphonic Acid. The results of our previous studies of μCP with alkanethiols on gold showed that alkyl chains containing less than 16 methylene units did not provide adequate resistance during etching.[31] The defect density in the resulting patterned structures was much higher for the shorter alkanethiols than for hexadecanethiol. Hexadecanethiol became the standard for μCP on gold and silver because it resisted etching, it is a liquid at room temperature, and it adsorbs well into the PDMS stamp. Alkanephosphonic acids are solids at room temperature, and they do not adsorb into the PDMS stamp but rather form a continuous, macroscopic film on the PDMS surface. We used octadecanephosphonic acid for this study because it contains a long alkyl chain; this chain provides a hydrophobic barrier to aqueous etching solutions. Octadecanephosphonic acid is soluble in 2-propanol, and the resulting solution can be used to ink the stamps. Shorter chain alkanephosphonic acids can be patterned on Al_2O_3/Al by μCP, and they are protective upon exposure to the etching solution. We did not, however, test the electrical performance of structures prepared from shorter chain alkanephosphonic acids.

Mask Design for the Resistance Measurements. The mask design shown in Figure 2 was used to prepare patterned films for resistance measurements. The pattern consists of a continuous line, 67.7 cm long and 6 μm wide, with 4 μm spacing between lines. There are contact pads at approximately 7.5 cm intervals along the length of the wire. This design allows us to measure resistance as a function of length along the patterned wire.

Design of the Schottky Diodes. Schottky diodes are rectifying devices, which allow current flow under a

(26) Aronoff, Y. G.; Chen, B.; Lu, G.; Seto, C.; Schwartz, J.; Bernasek, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 259.
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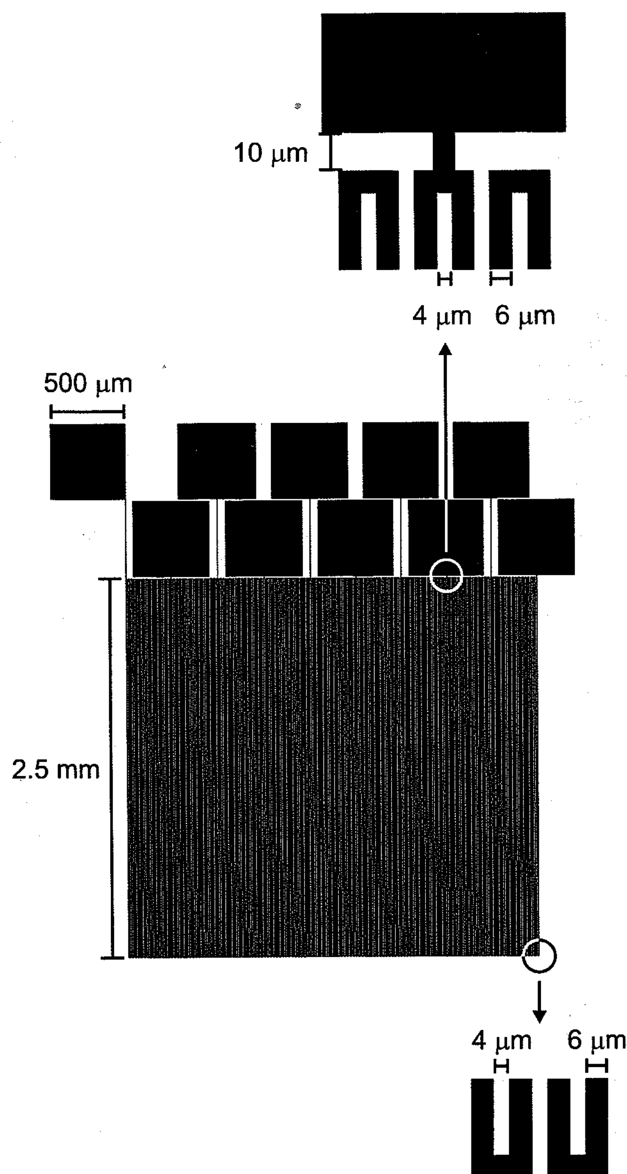


Figure 2. Mask design used for the resistance measurements. The wires were equally spaced in the mask used; the different contrast that appears in the figure is a printer artifact.

forward bias and retard current flow under a reverse bias. Schottky diodes are well suited for use in integrated circuits because they require fewer processing steps than the p–n junction diode and because they are capable of high-speed rectification.[5] A Schottky barrier is formed when a metal is deposited on a semiconductor and the work function of the metal Φ_M is greater than the work function of the semiconductor Φ_S.[32]

A Schottky diode consists of two metal–semiconductor contacts: an ohmic contact and a Schottky barrier contact. Schottky diodes are most commonly prepared on n-type silicon because of the greater energy difference between Φ_S and Φ_M (Φ_S p-type Si > Φ_S n-type Si). We chose to use p-type silicon in this instance because of the ease of preparing an ohmic contact on p-type silicon with aluminum. Any metal will form an ohmic contact with a highly doped semiconductor. Aluminum is a p-type dopant in silicon, and the diffusion of aluminum into p-type silicon during an annealing step creates the highly p-doped region necessary to form an ohmic contact.[5]

(32) Rhoderick, E. H.; Williams, R. H. *Metal-Semiconductor Contacts*, 2nd ed.; Clarendon Press: Oxford, 1988; Vol. 19.

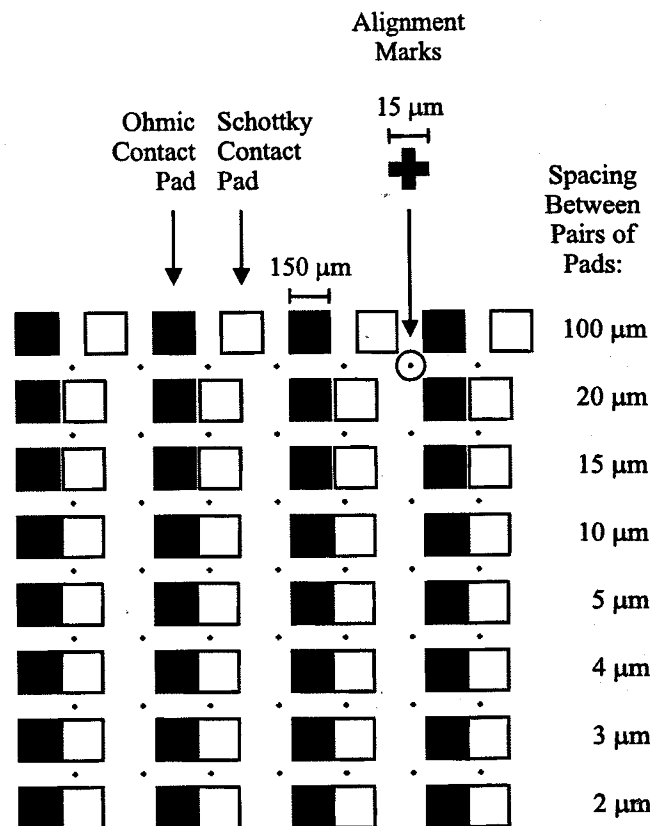


Figure 3. Mask design used to prepare Schottky diodes. The solid black features correspond to the mask used for the ohmic contacts, and the white features outlined in black correspond to the mask used for the Schottky contacts.

Mask Design for the Schottky Diodes. The Schottky diodes were prepared using the mask design shown in Figure 3. The solid black features in Figure 3 correspond to the mask used to define the ohmic contacts, and the white features outlined in black correspond to the mask used to define the Schottky contacts. The fabrication of the diodes is a multistep process that involves two metal deposition steps, two masks, and registration of the second layer with respect to the first layer. Figure 4 shows a schematic representation of the process used to fabricate the Schottky diodes.

The ohmic contacts consist of a two-dimensional array of square pads, 150 μm on a side, separated by 350 μm in each direction. The ohmic contacts were defined in photoresist, followed by metal deposition and liftoff. We used conventional photolithography in this step, rather than soft lithography, because of limitations placed on us by the clean room facilities where we carried out the initial fabrication steps.[33] Soft lithography is a viable method to prepare devices such as Schottky diodes, and the use of photolithographic techniques in this instance should not be regarded as a limitation of soft lithography.[34]

The ohmic contact consisted of three metal layers: Al (100 nm), Ti (10 nm), and Pt (200 nm). The ohmic contact was formed at the aluminum/silicon interface, and the titanium layer was used as an adhesion promoter between the aluminum and platinum layers. The platinum layer

(33) The e-beam we used to achieve uniform aluminum film thickness (see substrate preparation section) was located in the Technology Research Laboratory at MIT, and this is a regulated cleanroom. The use of PDMS was not permitted in this facility, and additionally, we were not permitted to bring in samples that had been processed with PDMS outside of the clean room.

(34) Hu, J.; Beck, R. G.; Westervelt, R. M.; Whitesides, G. M. *Adv. Mater. (Weinheim, Ger.)* **1998**, *10*, 574.

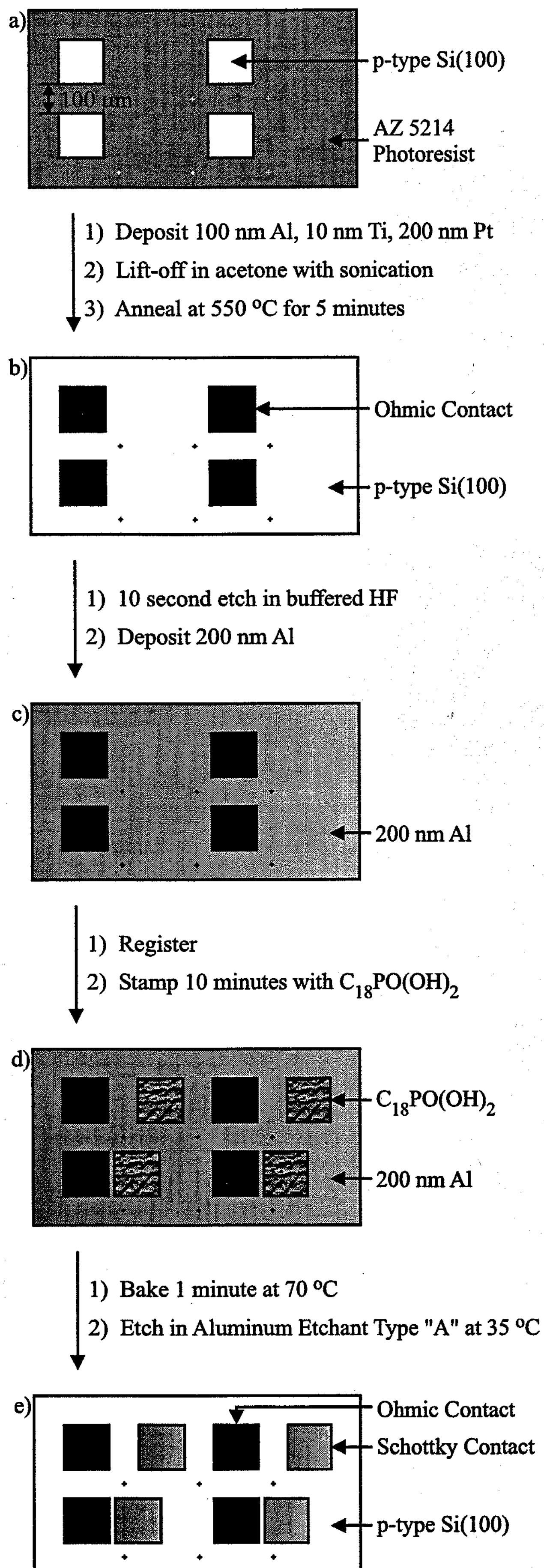


Figure 4. Schematic representation of the process used to fabricate the Schottky diodes.

was used to protect the aluminum contact during a hydrofluoric acid etching step.

The Schottky contacts consist of a two-dimensional array of square pads, 157 μm on a side, defined by μCP. The Schottky contacts were designed to be square pads, 150 μm on a side. The features in the photoresist master used to make the PDMS stamp for the Schottky contacts were 7 μm larger than designed.[35] In the horizontal direction of the array, there are rows of Schottky contacts, equally spaced with respect to the ohmic contact pads. In the vertical direction, there are columns of Schottky contacts, with a range of gaps between the ohmic and Schottky contact pads. The gap between the ohmic and Schottky contact pads was designed to vary from 100 to 2 μm (Figure 3). To aid in the registration, alignment marks were placed at regular intervals on the masks used to prepare the ohmic and Schottky contacts.

Results and Discussion

Fabrication of the Stamp. The elastomeric stamp was prepared by casting poly(dimethylsiloxane) (PDMS) against a relief pattern of interest (in this case, a photoresist pattern on a silicon wafer, prepared by photolithography).[36] The PDMS was cured at 60 °C for a minimum of 2 h and then carefully peeled away from the master. The stamp used to prepare the structures for the resistance measurements was a free-standing, unsupported PDMS stamp with a total thickness of approximately 4 mm; the thickness of the relief structure was 1 μm. The stamp used to prepare the Schottky contact pads was a thin PDMS film (~40 μm thick) supported on a glass substrate; the thickness of the relief structure was 10 μm. A glass support was used to decrease the lateral distortions previously observed for PDMS stamps.[37]

Treatment and Inking of the Stamp. The surface of the PDMS stamp was untreated and hydrophobic. A solution of octadecanephosphonic acid (5 mM in 2-propanol) was filtered through a 0.2 μm filter onto the stamp. The solution remained in contact with the stamp for at least 30 s. The excess solution was removed under a stream of filtered N_2 gas. The octadecanephosphonic acid does not absorb into the stamp but rather forms a visible film on the surface of the stamp.

Oxidation of the PDMS stamp results in a hydrophilic surface. Octadecanephosphonic acid also formed uniform films on the oxidized PDMS. Uniform pattern transfer, however, did not occur after stamping with the oxidized PDMS stamp.[38]

Preparation of the Substrates. Aluminum was deposited onto either silicon or silicon nitride-coated silicon wafers by electron beam (e-beam) evaporation. The highest degree of reproducibility was obtained from substrates that had uniform aluminum thickness across the entire wafer. This uniformity was achieved on 4 in. wafers by deposition of aluminum in an e-beam evaporation chamber equipped with planetary sample holders. The samples were rotated in three dimensions during the evaporation process; this rotation substantially improved uniformity. If the depositions were performed in chambers equipped with a sample holder that rotated by 360° in only one

(35) This error in dimensions could have been due to inadequate exposure times or inherent limitations of the thick resist used in this step.

(36) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.

(37) Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *J. Vac. Sci. Technol., B* **1998**, *16*, 88.

(38) This result might be due to a stronger interaction of the phosphonic acid headgroup with the oxidized stamp, as compared to the hydrophobic, untreated stamp.

dimension, the resulting coated 3 or 4 in. wafers exhibited a gradient in thickness across the wafer; upon etching, this gradient resulted in overetching in some regions and incomplete etching in other regions. The formation of the native oxide of aluminum occurred by air oxidation of the wafers after removal from the evaporation chamber. To limit contamination of the aluminum by airborne contaminants, the wafers were used after exposure to air for a minimum of 2 h but not more than 72 h.

Stamping and Baking. The inked stamp was placed in contact with the aluminum surface, and in cases where it did not make complete conformal contact with the surface, the top of the stamp was touched lightly with tweezers to initiate the wetting of the stamp with the surface. The stamp was left in contact with the substrate for 10 min. A pattern is visible on the aluminum surface after stamping, indicative of a multilayer film on the surface. The multilayer film of octadecanephosphonic acid on the surface is removed by rinsing with 2-propanol, leaving a patterned surface.[39] The process used in μCP here is thus qualitatively different than that for alkanethiols on gold, in which a monolayer forms rapidly and cleanly.

Figure 5 shows scanning electron microscopy (SEM) images of octadecanephosphonic acid stamped on aluminum before and after rinsing with 2-propanol. The stamp used to prepare these patterns consisted of 6 μm wide lines, separated by 4 μm. This difference in line widths between the stamped and unstamped regions allowed us to assign the appropriate regions in the SEM micrographs. Figure 5a shows a SEM image of the surface after stamping without rinsing. We attribute the dark, irregular lines in the center of the stamped region to a thick film of octadecanephosphonic acid. Figure 5b shows the same sample after rinsing with 2-propanol. The dark lines no longer appear in the stamped region, and the width of the bare aluminum region is the same in both images.

After stamping, the patterned substrate was baked at 70 °C for 10 min.[40] The baking step was required for the stamped monolayers to act as resists during etching in Aluminum Etchant Type "A". We believe the baking step is a dehydration step that forms alkyl(aluminophosphate) by reaction of the phosphonic acid headgroup with terminal hydroxide groups and waters of hydration on the aluminum oxide surface.

Wet Etching. Aluminum can be etched by both acidic and basic etching solutions, by oxidizing solutions, and by electrochemical dissolution.[41] The aluminum etch rate is highly dependent on the choice of etching solutions and the temperature. We tested several solutions for their selectivity in etching Al_2O_3/Al films patterned with octadecanephosphonic acid: oxidizing solutions of ferricyanide (pH 13.6), sodium hydroxide solutions, hydrochloric acid solutions, and various ratios of combinations of phosphoric, acetic, and nitric acids in water. The highest selectivity between the patterned octadecanephosphonic acid and bare aluminum was obtained from Aluminum Etchant Type "A", which is a combination of phosphoric, acetic, and nitric acids and water in a ratio of 16:1:1:2.[42]

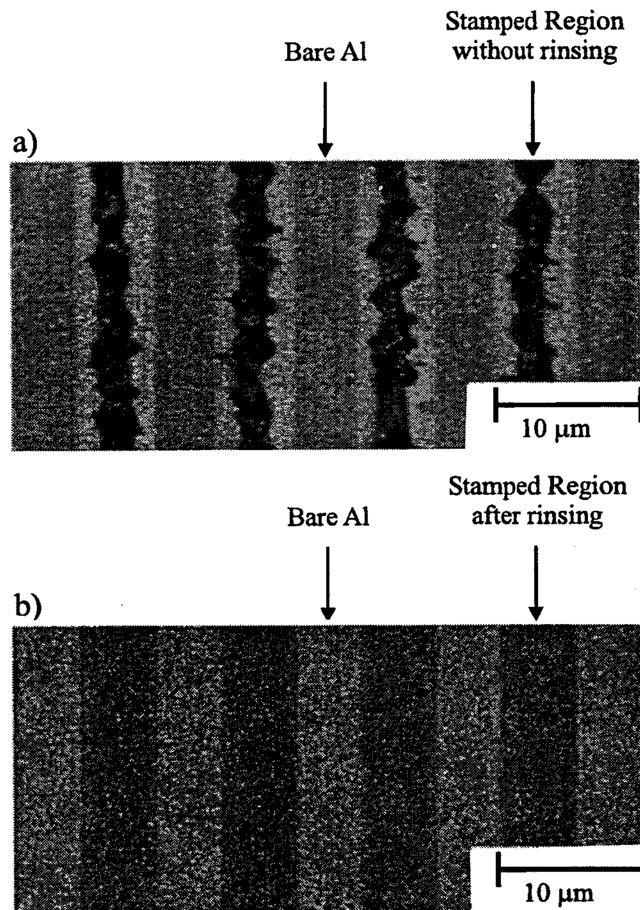


Figure 5. SEM images of octadecanephosphonic acid patterned by μCP on aluminum: (a) as stamped; (b) after rinsing the surface with 2-propanol to remove the excess octadecanephosphonic acid.

Figure 6a shows a three-dimensional atomic force microscopy (AFM) image depicting the relief structure of the stamp used to prepare the structures for resistance measurements, and Figure 6b shows an AFM image of 300 nm thick aluminum patterned by μCP without rinsing, followed by baking at 70 °C for 10 min and wet etching in Aluminum Etchant Type "A" at 35 °C. We measured the line width as the width of the features at half the thickness of the relief structure. The line width of the stamped pattern, as compared to that of the PDMS stamp, is unchanged as a result of stamping and baking; that is, no reactive spreading was observed upon pattern transfer by stamping or baking. The original film thickness was 300 nm, and after etching, the thickness of the patterned aluminum was 295 $\pm$ 5 nm. The decrease in thickness corresponds to a loss of less than 5%, without loss of lateral resolution.

Edge Resolution and Nature of Defects. Figure 7a shows the edge resolution of the patterns prepared by liftoff, and Figure 7b shows the edge resolution of the patterns prepared by μCP and wet etching. The edge resolution of the patterns prepared by liftoff was 50 nm, and the edge resolution of the patterns prepared by μCP and etching was 150 nm. We attribute 100 nm of the edge roughness in the etched patterns to the stamping and etching process.

(39) The rinsing step was employed in order to obtain SEM images of the patterned surface. The etched films after rinsing, followed by baking, contained many defects and exhibited a decrease in aluminum thickness. There appeared to be a correlation between the rinsing time and the quality of the etched samples: samples that were rinsed for 10 s contained fewer defects than those rinsed for 30 s. We did not investigate this behavior further because, in all cases, the rinsed samples contained too many defects to be useful.

(40) The initial baking time chosen was 10 min. Subsequent studies varied the baking time; there was no observable change in pattern definition, line width, or aluminum thickness after etching for samples which had been baked a minimum of 1 min.

(41) Vossen, J. L.; Kern, W. *Thin Film Processes*; Academic Press: Orlando, FL, 1978; p 564.

(42) Materials Safety Data Sheet for Aluminum Etchant Type "A", Transene Co. Inc., Danvers Industrial Park, 10 Electronics Avenue, Danvers, MA 01923.

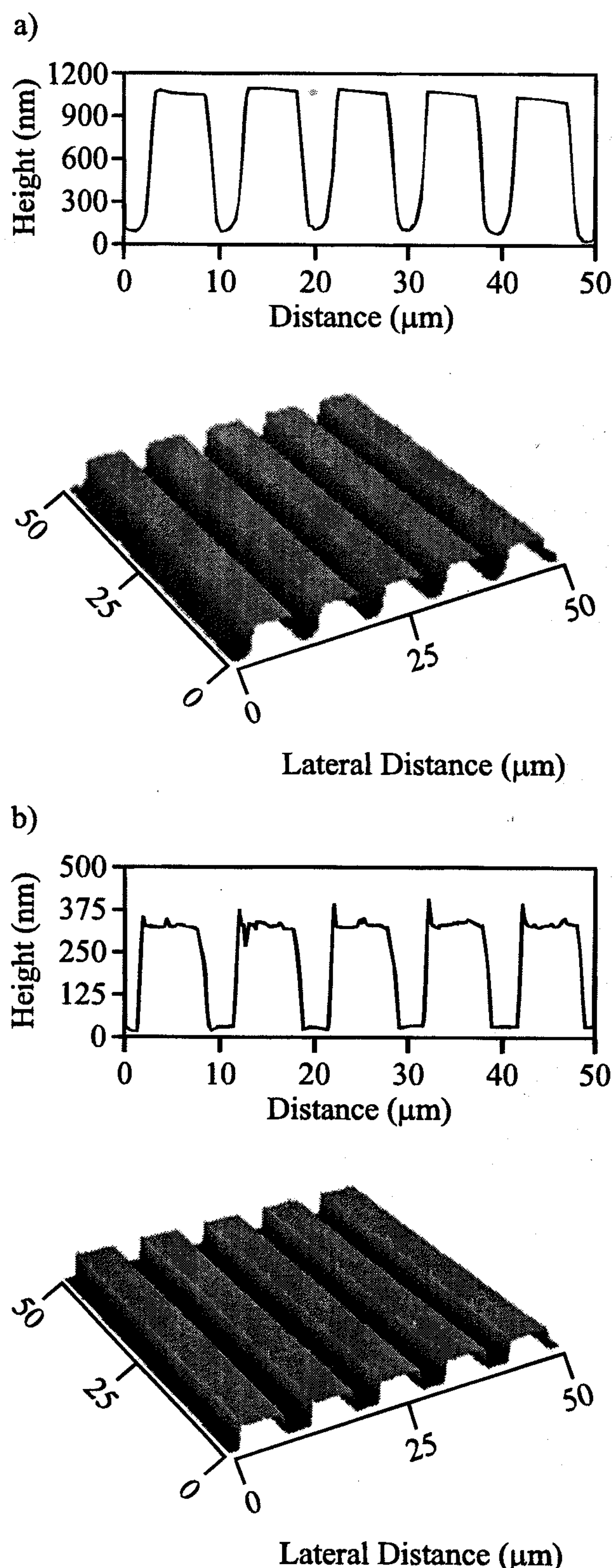


Figure 6. (a) AFM image of the stamp used to prepare structures for the resistance measurements. (b) AFM image of 300 nm thick aluminum, patterned by μCP of octadecanephosphonic acid, followed by baking for 10 min at 70 °C and wet etching in Aluminum Etchant Type "A" at 35 °C.

Pattern transfer occurs as a result of differing etch rates between the stamped and unstamped regions. Prolonged exposure of a stamped pattern to the etching solution ultimately results in overetching and a decrease in aluminum thickness in the patterned areas. We observed two types of defects in the etched patterns. The first type of defect we observed was large (>3 μm) circular holes in the etched pattern. We speculate that these defects are due to inadequate pattern transfer in stamping, possibly due to air bubbles or particles trapped between the surface and the stamp. If these defects are due to trapped particles, stamping in a clean room should decrease the occurrence of these defects. Figure 7b shows the second type of defect we observed. These defects appear as dark, circular "pinholes" (~40 nm diameter) in high-resolution SEM images of the etched pattern. We were unable to determine if these "pinhole" defects result in holes extending through the entire thickness of the patterned aluminum.[43] SEM does not provide information on the thickness of the films, and the AFM images did not show these defects extending through the entire thickness of the patterned aluminum. We note, however, that the defects are on the order of the radius of curvature of the pyramidal AFM tip, and the geometry and aspect ratio of the AFM tip prevent us from determining their depth.

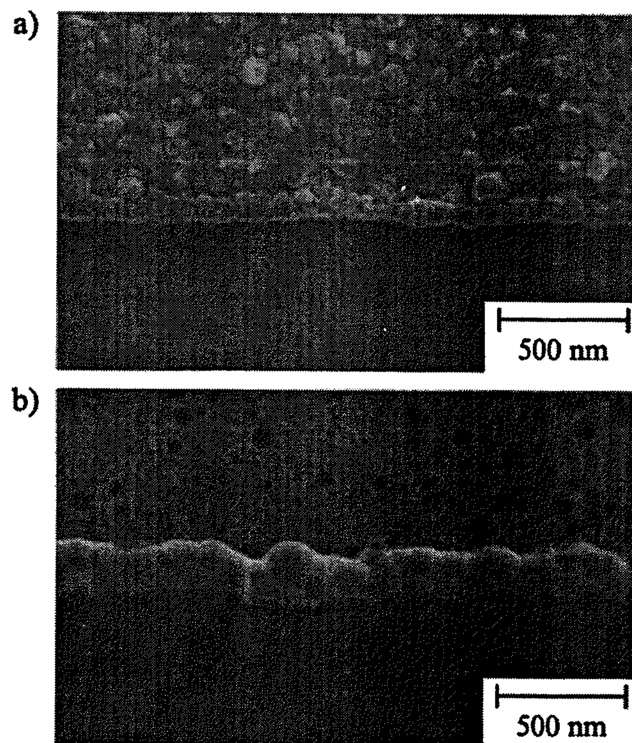


Figure 7. (a) SEM image of the edge resolution of patterned aluminum wires prepared by photolithography and liftoff. (b) SEM image of the edge resolution of patterned aluminum wires prepared by μCP and wet etching. We attribute the bright edge of the wet-etched sample to charging (the substrate in both cases was a silicon nitride-coated silicon wafer, yet we observed more charging in the wet-etched sample). We have defined the dark circular features in the wet-etched image as "pinhole" defects (see text).

Characterization of the Electrical Properties of the Etched Structures. We measured the resistance as a function of length for structures prepared using the mask design in Figure 2. The structures were patterned, by two different methods, on 300 nm thick aluminum films supported on silicon nitride-coated silicon wafers: (i) deposition of evaporated aluminum onto a photoresist replica of the mask pattern, followed by liftoff in acetone, and (ii) stamping octadecanephosphonic acid onto Al_2O_3/Al with a PDMS stamp that was cast against a photoresist

(43) We were unable to use the amplification procedure of Zhao, et al.[31] to quantify the size and number of our defects because the etch solution used in that study is also an etchant for aluminum.

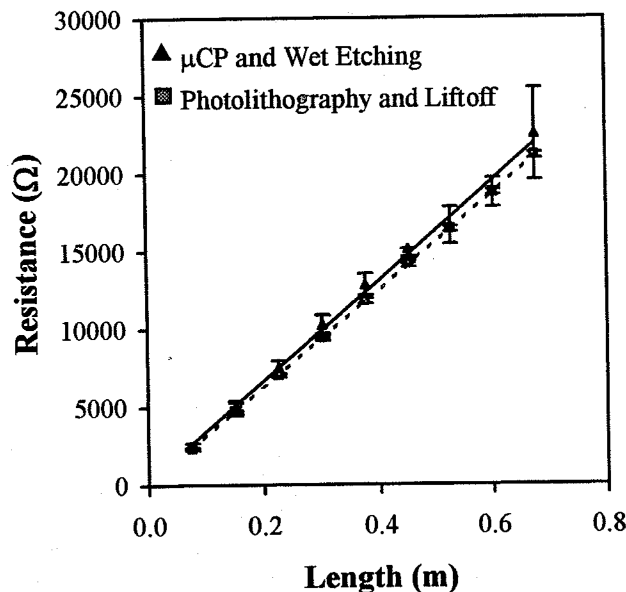


Figure 8. Plot of resistance versus length for 6 μm wide aluminum wires, patterned by stamping, followed by baking and wet etching, compared to the same wire patterned by photolithography.

replica of the mask, followed by baking and wet etching. The silicon nitride provides an insulating layer between the metal and the silicon substrate and isolates the patterned aluminum wires electrically.

Figure 8 shows a plot of resistance versus length for the structures prepared by the two methods described above. Three different samples, each containing at least 12 of the resistance patterns shown in Figure 2, were measured for the plot in Figure 8. Each data point represents the average of all the samples measured, and the error bars represent the standard deviation associated with the average. The data points for the shorter distances in the plot (<22.6 cm) were the average of 13−71 measurements, and the longer distances (30.1−67.7 cm) were the average of 2−6 measurements. There were fewer measurements for the longer distances because of defects in the stamped pattern, which resulted in breaks along the patterned wire. On average, we observed approximately 10−15 breaks per pattern. The position of the break determined the maximum length of the wire that we could assay. The plots of the stamped pattern and the liftoff pattern are linear, indicating that the resulting films are homogeneous over the length assayed.

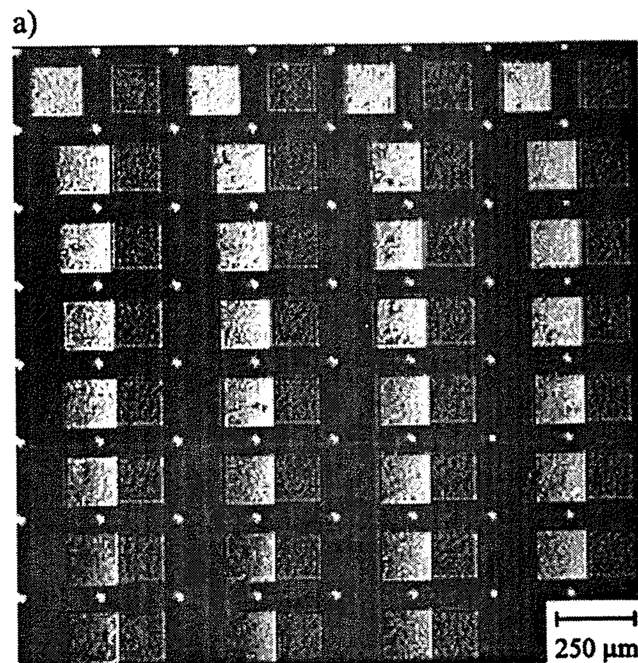
Equation 1 relates resistance (R, Ω), resistivity (ρ, Ω m), length (l, m), and cross-sectional area (A, m^2). The

$$R = \frac{\rho l}{A} \qquad (1)$$

slope for the patterned wires prepared by μCP and wet etching is 32 100 ± 700 Ω m^{-1}, and the slope for those prepared by photolithography and liftoff is 31 300 ± 100 Ω m^{-1}. The thickness of the structures prepared by liftoff is 300 ± 3 nm, and the average thickness of the samples prepared by μCP and wet etching is 295 ± 5 nm. Using eq 1, the resistivity of the samples prepared by μCP and wet etching is $(5.6 \pm 0.2) \times 10^{-8}$ Ω m and the resistivity of the samples prepared by photolithography and liftoff is $(5.6 \pm 0.1) \times 10^{-8}$ Ω m.

Preparation and Characterization of Schottky Diodes. The Schottky diodes were prepared according to the fabrication scheme shown in Figure 4. The ohmic contacts were defined in 1 cm^2 arrays, consisting of 19

a)



b)

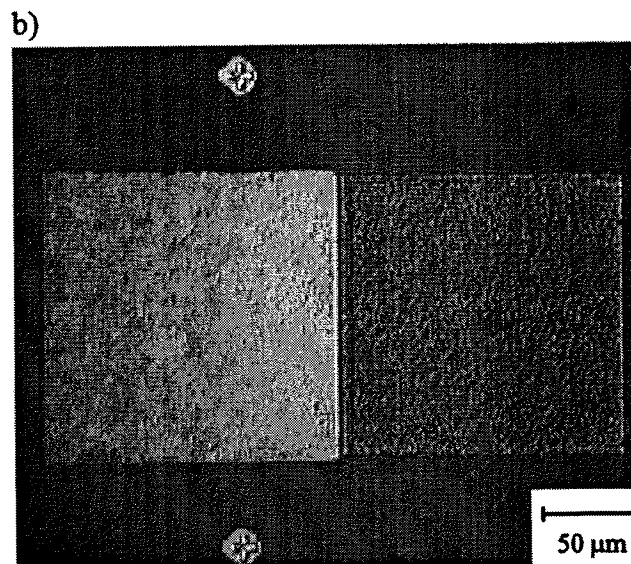


Figure 9. Optical micrographs of the fabricated diodes: (a) optical micrograph of an array of 32 diodes; (b) optical micrograph of a single diode with a 3 μm gap between the ohmic and Schottky contacts.

columns and 39 rows of contacts, across a 4 in. wafer. The wafer was cleaved into 1 cm^2 pieces for stamping the Schottky contacts, resulting in an array of 741 diodes. We defined the registration after stamping as the average of the difference in the placement of the center of the stamped alignment mark relative to the center of the alignment mark prepared by photolithography. This average difference was 1 μm across the 1 cm^2 array. The main factors contributing to the misalignment were larger than the designed features in the photoresist pattern used to prepare the stamp plus the human error in judging the centers of the two alignment marks. The alignment marks were designed as crosses, 4 μm wide and 14 μm long; the fabricated registration marks were distorted crosses, with rounded edges, approximately 6 μm wide and 18 μm long. The fabricated diodes contained gaps which varied from 97 μm to 260 nm. Figure 9a shows an optical micrograph

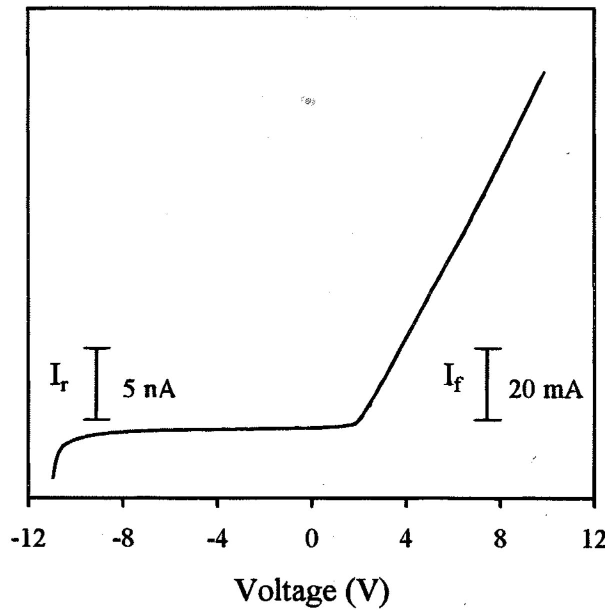


Figure 10. Current–voltage ($I-V$) characteristics of a fabricated Schottky diode. The forward and reverse $I-V$ scans were collected separately, with different current scales.

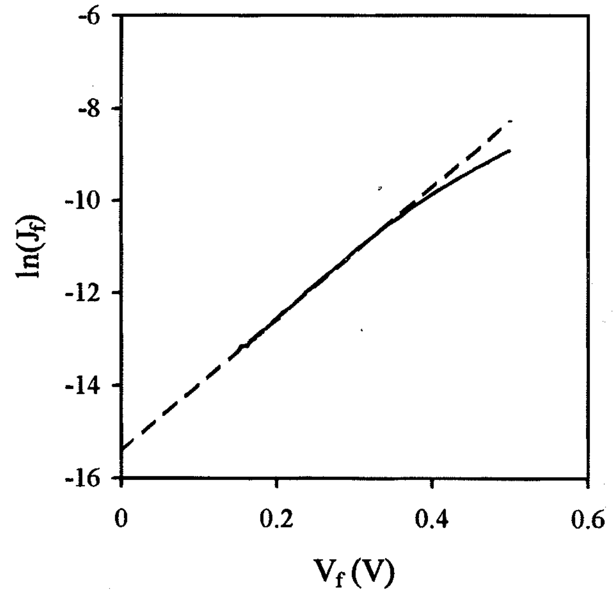


Figure 11. Plot of the natural log of current density $\ln(J_f)$ versus the forward bias voltage V_f, from 150 to 500 mV, for a fabricated Schottky diode (solid line) and the associated linear fit over the range 150–350 mV, extrapolated to $V_f = 0$ (dashed line).

of part of a 1 cm^2 array of Schottky diodes (32 diodes), and Figure 9b shows a single diode with a gap of 3 μm.

Forward Current–Voltage ($I-V$) Characteristics. Figure 10 shows the current–voltage characteristics of a representative Schottky diode. The upper line corresponds to the forward voltage bias, and the lower curve corresponds to the reverse bias. The forward $I-V$ characteristics of a Schottky diode display an exponential relationship between current density J_f and forward voltage V_f at low forward biases. The J_f-V_f relationship of an ideal Schottky diode can be modeled by the thermionic-emission theory for current transport.[32,44] This relationship, shown in eq 2, relates the forward current density J_f (A/cm^2), the

$$J = J_0 e(qV/nkT) \qquad (2)$$

saturation current density J_0 (A/cm^2), the magnitude of electronic charge q (1.602×10^{-19} C), the forward voltage V_f (V), the Boltzmann constant k (1.381×10^{-23} J/K), the temperature T (K), and the ideality factor n. The ideality factor takes into account the bias dependence of the barrier height, and the thermionic-emission theory model is valid for $n < 1.1$.[32] The ideality factor is determined from the slope of a linear plot of the natural log of current density versus forward bias voltage. If the diode can be modeled by the thermionic-emission theory, the effective barrier height Φ_e is calculated from the saturation current density J_0 according to the relationship shown in eq 3, where A^{**} is the modified Richardson constant ($A^{**} = 32$ A cm^{-2} K^{-2} for p-type Si) and all other parameters are as defined above.

$$\ln(J_0) = \ln(A^{**}T^2) - q\Phi_e/kT \qquad (3)$$

For $n > 1.1$, the current–voltage characteristics cannot be modeled by the thermionic-emission theory and a more complex model must be invoked. An ideality factor greater than 1.1 is usually attributed to current arising from the recombination of electrons and holes in the depletion region.[32] The current–voltage characteristics of 24 arbitrarily chosen diodes with differing gaps between the ohmic and Schottky contacts were measured. Figure 11 shows a typical plot of the $\ln(J_f)-V_f$ characteristics from 150 to 500 mV and the linear fit for the voltage region 150–350 mV. The deviation from linearity above 350 mV is attributed to the series resistance of the silicon.[32] The ideality factor ranged from 1.3 to 3.3, with the average equal to 2.4 ± 0.6. There was no correlation between the ideality factor and the gap between the contact pads, nor is such a correlation expected from theory. The average value we obtained for the ideality factor is in agreement with that of Adegboyega et al. for aluminum Schottky contacts prepared on p-type silicon.[45] The value of our measured ideality factor precludes us from determining the barrier height using eq 3.

Capacitance–Voltage ($C-V$) Measurements. The barrier height can be determined from dark capacitance–voltage ($C-V$) measurements. The relationship between capacitance and reverse bias is shown in eq 4, where C

$$\frac{1}{C^2} = \frac{2}{q\epsilon_s N_a}\left(V_{bi} - V - \frac{kT}{q}\right) \qquad (4)$$

is the capacitance per unit area (F cm^{-2}), ϵ_S is the permittivity of the semiconductor ($\epsilon_S = 1.04 \times 10^{-14}$ F cm^{-1} for Si), N_a is the acceptor concentration for p-type semiconductors (cm^{-3}), V_{bi} is the built-in potential at zero bias (eV), V is the applied voltage (V), and all other terms are as defined previously. A plot of C^{-2} versus reverse bias should be a straight line with a slope equal to $2/q\epsilon_S N_a$ and the intercept on the voltage axis V_I equal to $V_{bi} + kT/q$. The barrier height Φ_B is given by eq 5, where ξ,

$$\Phi_B = V_{bi} + \xi \qquad (5)$$

equal to $(kT/q)\ln(N_v/N_a)$, is the distance of the Fermi energy below the valence band and N_v is the effective density of states in the valence band ($N_v = 1.01 \times 10^{19}$ cm^{-3} for Si).[32]

(44) Rhoderick, E. H. *IEE Proc., Part I: Solid-State Electron Devices* **1982**, *129*, 1.

(45) Adegboyega, G. A.; Poggi, A.; Susi, E.; Castaldini, A.; Cavallini, A. *Appl. Phys.* **1989**, *A48*, 391.

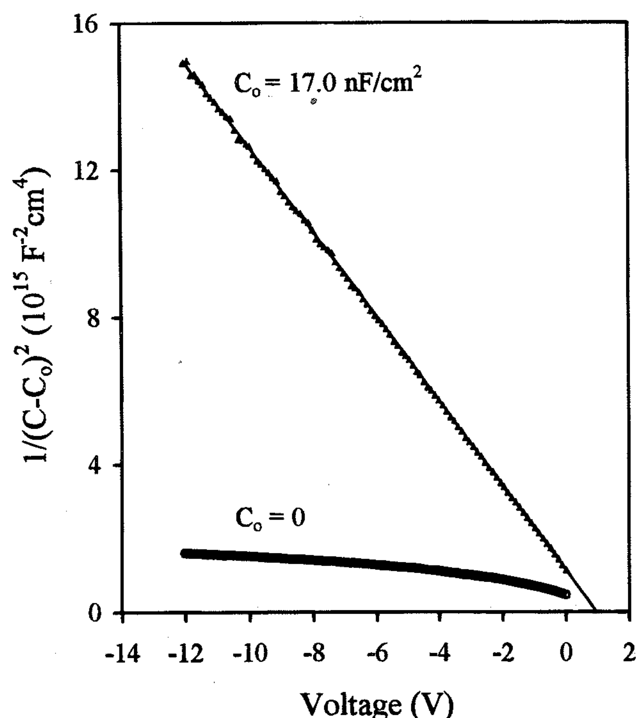


Figure 12. Capacitance–voltage (C–V) characteristics of a fabricated Schottky diode. The upper trace corresponds to a plot of $1/(C - C_0)^2$ versus the reverse bias voltage V_r and the associated linear fit (solid line) extrapolated to the x-axis intercept, where $C_o = 17.0$ nF/cm^2. The lower trace corresponds to a plot of $1/C^2$ versus the reverse bias voltage V_r.

Nonideal diodes with a thin interfacial oxide layer may contain an "excess capacitance" C_0 that results in a nonlinear C–V plot. This excess capacitance is an empirical constant which accounts for the bias dependent charge on surface states and/or deep bulk states. Vasudev et al. have shown that C_0 can be determined from the y-intercept of a plot of capacitance versus $(V_{bi} + V)^{-0.5}$.[46] Figure 12 shows the plot of $1/C^2$ and $1/(C - C_0)^2$ as a function of reverse bias and the associated linear fit of the $1/(C - C_0)^2$ data extrapolated to the x-axis intercept.

Using the linear fit from the plot of $1/(C - C_0)^2$ versus V_r, we calculated a barrier height Φ_B of 1.17 eV and a majority carrier density of 1.04×10^{16} cm^{-3}. The majority carrier density corresponds to a resistivity value of 1.25 Ω cm, which is within the specification range of the wafers we used (0.5–2 Ω cm). Adegboyega et al. attribute the high-barrier-height values for aluminum p-type silicon Schottky contacts and the nonideal behavior of the current–voltage characteristics to the presence of a thin interfacial oxide layer.[45] Our results are consistent with this hypothesis. Silicon forms a native oxide in air, and it is likely that this oxide formed on our samples during the time period between the silicon dioxide etching step and the evaporation chamber achieving high vacuum.

Conclusions

We have shown that octadecanephosphonic acid can be patterned on Al_2O_3/Al by μCP and that the patterned structures are electrically similar to samples prepared by conventional photolithography and liftoff. We have not established the lower limit of the features that can be produced, but we note that the edge roughness of the features we have produced was 150 nm: a feature size of 600 nm might therefore be possible. We have demonstrated that μCP of octadecanephosphonic acid is compatible with semiconductor device fabrication and that the Schottky diodes we prepared behave similarly to those fabricated by conventional fabrication techniques.

Experimental Section

Materials. 2-Propanol (HPLC grade, B&J Brand, Burdick & Jackson, 99.9%), ethanol (Pharmco, 200 proof), water (HPLC grade, Omnisolve, EM Science), Aluminum Etchant Type "A" (Transene Co.), (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane (United Chemical Technologies, Inc.) and poly(dimethylsiloxane) SYLGARD 184 (Dow Corning) were used as received. Octadecanephosphonic acid was available from a previous study: It was prepared using the Michaelis–Arbuzov reaction according to published procedures.[47–49] Aluminum, titanium, and platinum (Pure Tech) used for the e-beam evaporations were of 99.999% purity. Wafers used for the resistance measurements (Wafernet, Inc.) were test grade, 4 in. diameter, p-type Si(100) wafers that were modified first with 500 nm of thermally grown SiO_2 followed by 150 nm of LPCVD Si_3N_4. Wafers used for the Schottky diodes (Wafernet, Inc.) were prime grade p-type Si-(100): boron doped; 4 in. diameter; thickness, 500–550 μm; resistivity, 0.500–2.000 Ω cm. The following chemicals were provided in the clean room facilities and were used as supplied: Buffered Oxide Etch (7:1 HF/NH_4F with surfactant), methanol, acetone, 2-propanol, sulfuric acid (concentrated), hydrogen peroxide (30%) (Baker Analyzed Low Sodium CMOS Electronic Grade, J. T. Baker), Nanostrip (Cyantek Corp.), hexadimethyldisilazane (Ultrapure Grade, MicroSi, Inc.), AZ 5214-E IR Photoresist, AZ P 4260 Photoresist, AZ 422 MIF Developer, and AZ 440 MIF Developer (Hoechst Celanese).

Substrate Preparation for Resistance Measurements. The substrates for the resistance measurements were prepared at the Technology Research Laboratory, a class 100 clean room facility at MIT. The silicon nitride-coated silicon wafers were cleaned for 10 min in Piranha solution (a 7:3 (v/v) mixture of 98% H_2SO_4 and 30% H_2O_2)[50] followed by rinsing with deionized water and spin drying at 2000 rpm. The wafers were divided into two batches at this point: the substrates for the liftoff samples were processed further, and the substrates for the stamping studies were stored in the clean room facility during the preparation of the photoresist pattern on the liftoff samples. The liftoff samples were first coated with hexamethyldisilazane vapor in a YES Vapor Prime Oven followed by spin coating of AZ 5214-E IR photoresist at 4000 rpm for 30 s with a Solitec 5110 Coater. The wafers were baked for 30 min in a 90 °C oven. The photoresist-coated wafers were exposed through a chrome-on-glass mask with a Karl Suss Model MA4 contact aligner for 2 s (10 mW/(cm^2 s) @ 365 nm), followed by baking at 120 °C for 90 s and a second exposure through a clear glass mask for 70 s. The photoresist was developed for 75 s in AZ 422 MIF developer, followed by rinsing with deionized water and spin drying at 2000 rpm. The two sets of substrates were combined and transferred to a Temescal Semiconductor Products Model VES 2550 e-beam evaporator equipped with a cryopump. The system was evacuated to a pressure less than 9×10^{-7} Torr prior to deposition, and the aluminum was deposited at a rate of 5 Å/s. The samples were cooled under vacuum for 20 min after the deposition, followed by venting with N_2 gas. The substrates for the stamping studies were immediately placed in individual 4 in. Fluoroware wafer holders. The liftoff samples were sonicated in acetone, followed by rinsing with acetone, methanol, 2-propanol, and water. The liftoff samples were then dried individually under a stream of filtered N_2 gas and placed into wafer holders. The two sets of samples were sealed in a plastic bag and transferred from the clean room to our laboratories at Harvard.

Preparation of Stamps for the Resistivity Measurements. The photoresist pattern used to prepare stamps for the resistivity measurements was prepared in the same manner, at

(46) Vasudev, P. K.; Mattes, B. L.; Pietras, E.; Bube, R. H. *Solid-State Electron.* **1976**, *19*, 557.
(47) Kosolapoff, G. M. *J. Am. Chem. Soc.* **1945**, *67*, 1180.
(48) Bhattacharya, A. K.; Thyagarajan, G. *Chem. Rev.* **1981**, *81*, 415.
(49) Woodward, J. T.; Ulman, A.; Schwartz, D. K. *Langmuir* **1996**, *12*, 3626.
(50) **Caution:** Piranha solution is an extremely strong oxidant and should be handled with care.

the same time as the pattern for the liftoff samples described in the substrate preparation section, with the following exception. The substrate for the stamping pattern was test grade Si(100) used as received. The silicon wafer patterned with photoresist was placed in a wafer holder and transferred to our laboratories at Harvard. The wafer was placed under vacuum in a desiccator with a vial containing (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane for 30 min. After silanization, the wafer was placed in a 15 cm Petri dish and a degassed mixture of PDMS prepolymer and curing agent (10:1 w/w) was poured over the wafer. The PDMS was cured in a 60 °C oven for 2 h. After curing, the PDMS stamp was peeled away from the photoresist-coated silicon master and cut into approximately 6 cm^2 pieces with a razor blade.

Inking, Stamping and Etching. A solution of octadecanephosphonic acid (5 mM in 2-propanol) was filtered through a 0.2 μm Acrodisc LC PVDF syringe filter onto the precut PDMS stamp on a glass microscope slide. The solution remained in contact with the stamp for 30 s, and then the excess solution was removed under a stream of filtered N_2 gas. The stamp was placed onto the Al-coated substrate with tweezers. After stamping for 10 min, the stamp was removed from the substrate with tweezers and the substrate was baked on a stainless steel plate in a 70 °C oven for 10 min. After baking, the samples were etched, with agitation, in Aluminum Etchant Type "A" at 35 °C. The entire sample area was larger than the area stamped, and the end point was judged by the complete dissolution of the aluminum in the unstamped regions. Once the end point had been reached, the samples were immediately transferred to a beaker of deionized water and then rinsed for 1 min under a stream of water, followed by drying with filtered N_2 gas.

Resistance Measurements. We used a Keithley 197 Autoranging Microvolt DMM to measure the resistance of the patterned samples. The samples were secured on a stainless steel plate with Scotch Double Stick Tape, and contact was made to the various contact pads with two sharpened tungsten wires mounted on Rucker and Kolls Model 448 micropositioners with magnetic bases.

Preparation of Stamps for the Schottky Diode Contact Pads. The photoresist pattern used to prepare stamps for the Schottky contact pads was prepared using a thick resist that gave a relief structure of 10 μm at a spin speed of 1500 rpm. The substrate used to prepare the stamps for the Schottky diode contact pads was a test grade Si(100) wafer, used as received. The procedure for patterning the photoresist was similar to that described previously with the following differences: The photoresist (AZ P 4260) was spin-coated at 1500 rpm, the exposure time was 5 s, and the developing time was 180 s in AZ 440 MIF developer. The preparation of the PDMS stamp from the silicon wafer patterned with photoresist was performed in the same manner as described previously with the following exception: After silanization, the wafer was coated with a thin layer of degassed PDMS (~0.5 mm). A 36 cm^2 square window was defined on a 58 cm^2 clean glass plate with two layers of masking tape. The glass plate was placed onto the PDMS-coated wafer, and four binder clips were used to hold the assembly together. The entire assembly was placed in a 60 °C oven for 12 h to cure the PDMS. After curing, the glass-supported PDMS stamp was separated from the silicon wafer under deionized water. The tape was removed from the glass plate, resulting in a thin (~40 μm) PDMS stamp supported on a glass plate.

Diode Preparation. *1. Ohmic Contacts.* The ohmic contacts for the Schottky diodes were prepared at the Technology Research Laboratory, a class 100 clean room facility at MIT. The prime, p-type Si wafers (Wafernet, Inc.) were used as received. The first step in the fabrication of the ohmic contacts involved defining the pattern in photoresist. This pattern transfer was accomplished with AZ 5214-E IR photoresist in the same manner described above for the liftoff samples prepared for the resistance measurements. The samples were cleaned in an oxygen plasma cleaner for 3 min to remove any residual undeveloped photoresist. The wafers were transferred from the plasma cleaner to a Temescal Semiconductor Products Model VES 2550 e-beam evaporator equipped with a cryopump. The system was evacuated to a pressure less than 9×10^{-7} Torr prior to deposition. Aluminum (100 nm) was deposited at a rate of 5 Å/s, followed by titanium (10 nm, 2 Å/s) and platinum (200 nm, 5 Å/s). The samples were cooled under vacuum for 20 min after the final deposition, followed by venting with N_2 gas. The samples were sonicated in acetone, followed by rinsing with acetone, methanol, 2-propanol, and water. The samples were then dried individually under a stream of filtered N_2 gas. The samples were cleaned in Nanostrip for 3 min to remove any residual photoresist or carbonaceous contaminants prior to the annealing step. After cleaning in Nanostrip, the samples were rinsed with deionized water, followed by spin drying at 2000 rpm. The wafers with the defined ohmic contacts were then annealed for 3 min at 550 °C in an AG Associates Heatpulse 410 rapid thermal annealer. The ohmic contacts were tested to confirm that they exhibited nonrectifying behavior prior to the formation of the Schottky contacts.

2. Schottky Contacts. The wafers with the defined ohmic contacts were cleaned for 30 s in Buffered Oxide Etch (7:1 HF/NH_4F with surfactant) to remove any silicon oxide on the silicon surface, followed by rinsing with deionized water and spin drying at 2000 rpm. The samples were immediately transferred to the Temescal Semiconductor Products Model VES 2550 e-beam evaporator. Aluminum (200 nm) was deposited at 5 Å/s over the entire wafer containing the Ohmic contacts. The samples were cooled under vacuum for 20 min after the aluminum deposition, followed by venting with N_2 gas. The samples were placed into wafer holders and sealed in a plastic bag for transfer to the clean room facilities at Harvard. The definition of the Schottky contacts involved one registration step, and this was carried out in a class 100 clean room at Harvard. The glass-supported PDMS stamp was inked with octadecanephosphonic acid (5 mM in 2-propanol) in the same manner as the unsupported PDMS stamp. The glass plate supporting the PDMS stamp was mounted on the mask holder of a Karl Suss Model MJB3 contact aligner. The aluminum-coated wafers with the defined ohmic contacts were cut into 1 cm^2 square pieces. A 1 cm^2 sample was placed on the sample holder of the Karl Suss aligner, and the sample was raised to within 0.5 mm of the PDMS stamp for alignment. The registration marks on the sample and the PDMS stamp were used for alignment. Once the alignment was completed, the sample was brought into contact with the stamp and the sample was left in contact with the stamp for 10 min. After stamping, the sample was removed from the stamps with tweezers and the sample was baked for 1 min on a stainless steel plate in a 70 °C oven. After baking, the sample was etched in a solution of Aluminum Etchant Type "A" at 35 °C. After etching, the sample was rinsed with deionized water and dried under a stream of filtered N_2 gas.

Current–Voltage Measurements. The dark current–voltage characteristics (I–V) were measured with a Pine AFCBP1 computer-controlled potentiostat. The data were collected at a scan rate of 200 mV/s. The samples were secured on a stainless steel plate with Scotch Double Stick Tape, and contact was made to the various contact pads with two sharpened tungsten wires mounted on Rucker and Kolls Model 448 micropositioners with magnetic bases. The reverse bias data in Figure 10 were collected with a Keithley Yieldmax 450 process monitor system.

Capacitance–Voltage Measurements. The dark capacitance–voltage characteristics (C–V) were measured with a Keithley Yieldmax 450 process monitor system. The data were collected at a frequency of 1 MHz.

AFM. The AFM measurements were performed with a Topometrix TMX 2010 scanning probe microscope, equipped with a linearized tripod scanner. The PDMS stamp was imaged in noncontact mode using a high-resonant-frequency silicon cantilever and a scan rate of 100 μm/s. The aluminum patterns were imaged in contact mode using a silicon nitride cantilever and a scan rate of 100 μm/s.

SEM. The SEM images were obtained with a LEO Digital Scanning Microscope, Model 982.

Acknowledgment. This work was supported in part by the Office of Naval Research and DARPA and by ARO Grant DAAH 04-95-1-0102. We thank Junmin Hu and Noo-Li Jeon for helpful comments and discussions. L.B.G. thanks the Department of Chemistry at MIT for support and Mark S. Wrighton for helpful discussions.

LA981094H