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Vertical arrays of Pd nanowire electrodes with controllable and reproducible diameters and lengths are fabricated using a porous anodic alumina (PAA) template supported on a metallized Si substrate. The process described here employs a hydrogen plasma to penetrate the alumina pore barrier oxide prior to electrodeposition, enabling direct electrical contact with the back electrode metallization, thereby eliminating the need for electrochemical processing with high current or voltage pulsing that can lead to delamination or voiding. Electrical characteristics reveal Ohmic contact between the Pd nanowires and the underlying Ti conductive layer for samples with a range of pore diameters from 30 to 130 nm. This process enables both the fabrication of vertical nanowire arrays on prefunctionalized substrates, as well as the *in situ* fabrication of contacts to semiconductor nanodevices using a thin-film nanowire array. The hydrogen plasma step is particularly well suited to the fabrication of carbon nanotube arrays in PAA by plasma-enhanced chemical vapor deposition. © 2007 American Vacuum Society. [DOI: 10.1116/1.2647379]

I. INTRODUCTION

While interest in nanowire device research continues to increase, efficient and repeatable fabrication of nanowires on prefunctionalized substrates remains a challenge. Nanowire arrays have proven useful for application in sensors,^{1–3} thermoelectrics,^{4–7} field emitters,^{8–10} transistors,^{11,12} and photonics.¹³ Porous anodic alumina (PAA), with its high density of nanoscale pores, provides a convenient template for the synthesis of nanowire arrays.^{7,14–32} However, one of the most pervasive challenges for using PAA to template devices on prefunctionalized substrates is the presence of an intrinsic alumina barrier at pore bottoms (Fig. 1). This oxide layer, typically 20–60 nm thick, hinders the creation of electrical contact to either the remaining aluminum (Al) beneath the pore bottoms or to a buried conductive layer that is designed to serve as an electrode in a subsequent electrochemical deposition process. In the present study, a hydrogen

plasma has been used to penetrate the bottom oxide layer in PAA films having pore diameters of 10–130 nm, and supported on silicon wafers. Vertical arrays of palladium (Pd) nanowires of controllable length are then deposited into the PAA templates using a chronopotentiometry technique. Uniform deposition of the Pd nanowires suggests a consistent opening of the oxide barrier in each pore. Furthermore, the Ohmic contact between the Pd nanowire array and the underlying conductive layer is verified, enabling the array structure to be directly integrated into devices.

The hydrogen plasma process is particularly convenient in the context of a process flow for fabricating vertical carbon nanotube devices by plasma-enhanced chemical vapor deposition (PECVD), as the hydrogen plasma treatment can be performed immediately prior to the carbon nanotube (CNT) growth step. Subsequent electrodeposition of Pd nanowire back contacts would allow for the formation of an Ohmic contact to the CNT in each pore.³³

Pd nanowires also show promise for use in hydrogen sensors. Pd absorbs up to 900 times its own volume in hydrogen

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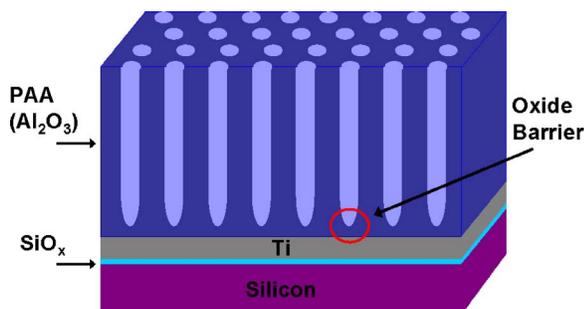


FIG. 1. Schematic of a porous anodic alumina (PAA) structure on a silicon substrate (PAA/Ti/SiO_x/Si) with the oxide (alumina) barrier emphasized.

at room temperature—a property that has been exploited in Pd nanowire hydrogen sensors.^{14,34,35} Sensors developed using Pd nanowires in a PAA template can be functionalized without having to disperse the nanowires across a patterned substrate. Furthermore, by patterning the aluminum film before anodization to define microscale nanowire arrays, complex structures such as three-dimensional interconnect patterns and embedded catalyst arrays can be fabricated.

Although methods have been developed for electrochemically depositing material into PAA films without removing the oxide barrier, these methods usually involve either ac or pulsed electrodeposition with large peak-to-peak voltage swings or the use of a metal layer that forces ion migration through the oxide to create a channel.^{15–17} Such methods either hinder uniform deposition of metal nanowires or increase the resistance between a deposited nanowire or nanotube and the conductive layer, thereby degrading the performance of prospective integrated devices. The present work uses a current density that is more than an order of magnitude lower than that used by most of these processes,^{15–17} made possible by the penetration of the oxide barrier using a hydrogen plasma prior to electrodeposition.

In the present study, a microwave-generated hydrogen plasma is used to penetrate the bottom oxide barrier in PAA films supported on silicon substrates. A titanium layer between the alumina film and the silicon substrate is incorporated to promote adhesion and to provide a conductive layer for subsequent electrodeposition of Pd. Following the hydrogen plasma treatment, Pd nanowire arrays of controllable length and diameter are synthesized in templates of various pore diameters by utilizing the exposed Ti layer as the working electrode for electrodeposition. Of the reported techniques for penetrating the oxide barrier, the hydrogen plasma treatment process is advantageous because it does not significantly widen the pores,²¹ does not form voids in the PAA,¹⁸ and provides consistent penetration of the oxide barrier across the template that yields nanowires with a high uniformity in length.^{18,20} Additionally, this process is shown to provide nanowires with Ohmic contact to the underlying substrate—this characteristic is very convenient for use in conjunction with further fabrication steps for nanoscale devices, such as PECVD synthesis of CNTs.³³

II. EXPERIMENTAL PROCEDURE

Electron-beam evaporation at a base pressure of 5×10^{-7} torr was used to deposit 50 nm SiO_x, 150 nm Ti, and 1500 nm Al, on a thermally oxidized silicon substrate. Anodization of the Al to form PAA was performed using three electrolytes: 0.3M H₂SO₄ (sulfuric acid), 0.3M H₂C₂O₄ (oxalic acid), and 0.3M H₃PO₄ (phosphoric acid). Anodization employing sulfuric acid yielded the smallest pores (5–10 nm), while oxalic acid and phosphoric acid anodization yielded pore diameters of 20–30 nm and 100–130 nm, respectively. Anodization voltages were 18 V for sulfuric acid, 40 V for oxalic acid, and 100 V for phosphoric acid. All acid electrolytes were maintained at a temperature of 5 °C during anodization. Some of the structures anodized in sulfuric and oxalic acids were immersed in 0.1M H₃PO₄ solution following anodization to widen the pores slightly. By choosing the correct acid and voltage for anodization, a structure with the desired pore diameter and pitch may be obtained. The ability to control the PAA structure allows for variations in nanowire diameter and density.

To obtain highly ordered pores with thin Al films, multiple anodization steps were employed.³² Following the initial anodization steps, the PAA was removed by immersion in a mixture of diluted chromic and phosphoric acids, leaving the remaining Al imprinted with the pore structure of the removed PAA to serve as initiation sites for subsequent anodization steps. The samples examined in this study were anodized in two- or three-step processes.

Hydrogen plasma treatments were performed in a microwave PECVD chamber. The plasma power was maintained at 300 W at a pressure of 10 torr and a hydrogen flow rate of 50 SCCM (SCCM denotes cubic centimeter per minute at STP). Plasma treatments were performed for 10 min with the substrate maintained at a constant temperature of 900 °C using inductive heating. Treatments were also performed at room temperature to study the effect of a lower temperature environment on the penetration of the oxide barrier. Samples were cooled to room temperature in a 3 torr hydrogen ambient prior to removal from the chamber.

Electrodeposition of Pd into the PAA structures was accomplished using a three-electrode system comprised of a platinum gauze auxiliary electrode, a silver/silver chloride reference electrode, and a Ti layer beneath the PAA as the working electrode. Pd nanowires were deposited using a solution of PdCl₂ (0.0067 g PdCl₂, 0.2 ml HCl, and 20 ml deionized H₂O) in a cyclical chronopotentiometry process using a BAS Epsilon system. A constant current was established between the auxiliary and working electrodes, while the potential of the working electrode was monitored with respect to the reference electrode. For all experiments, a constant current density of 1.5 mA/cm² was applied in cycles of 500 ms duration, during which the monitored voltage ranged from 0.0887 to 0.2081 V. To control the length of Pd nanowires, the number of cycles was varied. Following the electrodeposition of Pd, samples were characterized using a Hitachi S-4800 field emission scanning electron microscope (FESEM). Pd nanowires created in a template anod-

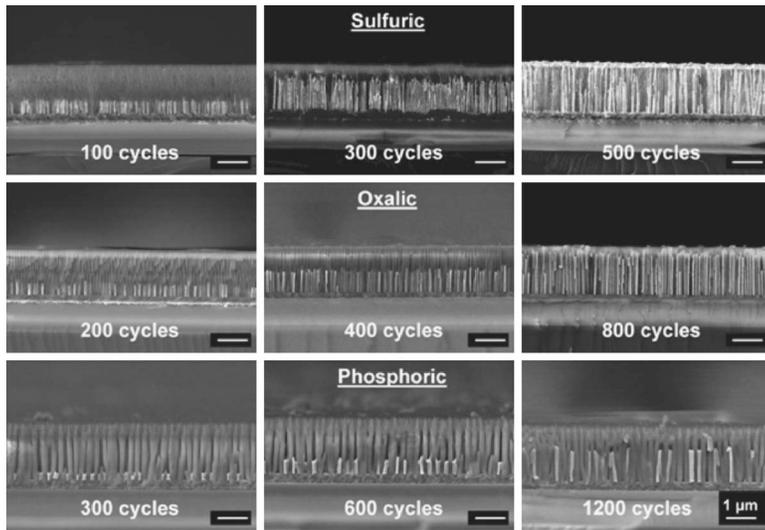


FIG. 2. FESEM cross-sectional images of PAA structures demonstrating control of Pd nanowire array length by varying the number of electrodeposition cycles. The average diameter of nanowires is 30 nm for sulfuric, 50 nm for oxalic, and 130 nm for phosphoric anodized PAA (all scale bars are 1 μm). Note that the FESEM specimens were prepared by fracture, leaving some of the fractured pores without a nanowire on either the imaged or discarded side of the specimen.

ized in oxalic acid at 40 V (without subsequent pore widening) were released by removing the PAA using a NaOH mixture. These nanowires were subsequently imaged using the scanning transmission electron microscope mode of the aforementioned FESEM.

III. RESULTS AND DISCUSSION

The incorporation of pore widening by many reported methods for penetrating the oxide barrier limits the minimum nanowire diameter and porosity. This excessive pore widening also places the nanowires in very close proximity to each other, thereby greatly limiting the ability to integrate the array into a device structure. Treating the PAA film in a hydrogen plasma did not significantly affect pore diameters. This anisotropic result allows for the fabrication of nanowire arrays in PAA templates of a wide range of diameters. From our results, templates were created with pores of diameters as small as 10 nm and as large as 130 nm. Within each template, nanowires were successfully synthesized.

As shown in the FESEM images of Fig. 2, the length of the Pd nanowires in various templates was uniformly controlled by varying the number of 0.5 s electrodeposition cycles. In order to maintain the applied current during electrodeposition, a reduction reaction of the positive Pd ions occurs at the Ti working electrode at the bottom of the pores. If the oxide barrier was not penetrated, then the reduction of the Pd ions could not occur at the pore bottom. Therefore, uniform deposition of Pd into the PAA structures confirms a consistent penetration of the oxide barrier layer. As expected, the Pd conforms to the shape of the pores, thus replicating the pore diameter. The length of the nanowire arrays was more uniform in the larger (phosphoric acid anodized) pores, and this observation is attributed to the slower linear growth rate of the larger diameter Pd nanowires. The standard deviation of nanowire lengths was calculated by sampling various cross-sectional FESEM images of each structure. Table I summarizes deviations of nanowire lengths associated with different anodization voltages and average pore diameters.

As mentioned previously, a hydrogen plasma treatment was performed with the substrate at two different temperatures (32 and 900 $^{\circ}\text{C}$), as recorded from an embedded thermocouple beneath the substrate.³⁶ For both temperatures used, the oxide barrier was sufficiently penetrated to allow for electrodeposition of Pd; however, samples treated at the higher temperature (900 $^{\circ}\text{C}$) produced a more uniform penetration of the barrier. The length of the nanowires in 130 nm diameter pores of a sample treated at 32 $^{\circ}\text{C}$ had a standard deviation of 32%, compared to a similar sample treated at 900 $^{\circ}\text{C}$ with only a 2% standard deviation. Though this result is not conclusive regarding the need for higher temperature treatment, we do attribute the higher temperature to a more uniform reduction reaction rate with the alumina bottom oxide barrier. Experiments are underway to study the effect of lower temperature plasma treatment on the subsequent nanowire density further.

After plasma treatment, the oxide barrier is still visible in most PAA structures with larger diameter pores (and thus thicker oxide barriers) when the samples are fractured for FESEM imaging, as in Fig. 3. However, as shown at the interface of some nanowires with the Ti layer, the plasma treatment creates small openings in the oxide, sufficiently exposing the Ti layer. The exposure of the Ti layer beneath each pore is evident from the demonstration of uniform electrodeposition of Pd at a low potential. Occasionally, such openings can be observed, as shown in Fig. 3, but in most cases they are likely too small to detect. The thinner oxide

TABLE I. Anodization voltages, average pore diameter after hydrogen plasma treatment (and thus the average diameter of Pd nanowires), and standard deviation of Pd nanowire length.

Acid	Anodization voltage (V)	Average pore diameter (nm)	Length standard deviation (%)
Sulfuric	18	30	6
Oxalic	40	50	4
Phosphoric	100	130	2

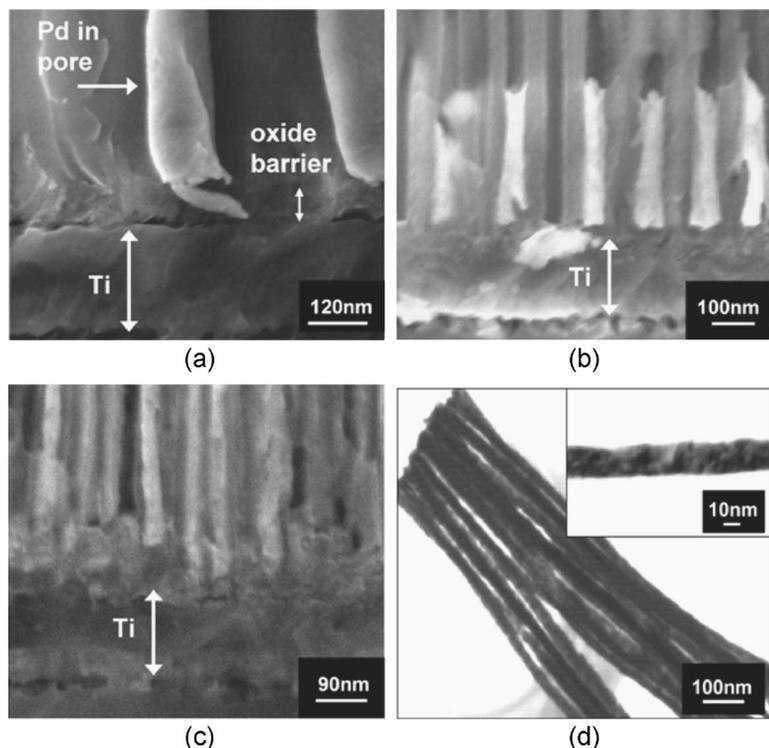


FIG. 3. FESEM images of Pd contacting the Ti layer in templates anodized in (a) phosphoric acid (~ 130 nm pores), (b) oxalic acid (~ 50 nm pores), and (c) sulfuric acid (~ 30 nm pores). (d) STEM images of Pd nanowires released by etching the PAA template (which was anodized in oxalic acid at 40 V with no subsequent pore widening) showing uniformity of diameter along the length of nanowires.

barriers in structures with smaller-diameter pores [Fig. 3(c)] appear to be completely removed, thus fully exposing the Ti layer. This exposure of the Ti layer in the plasma seems to affect the planarity of the Ti surface. Because the oxide barrier is only approximately 10 nm thick for these structures, we hypothesize that during the anodization process, a thin titanium oxide layer is formed on the top surface of the Ti layer.²¹ With this titanium oxide/Ti layer more fully exposed to the plasma, this topology is thought to be a result of the titanium oxide being reduced and roughened by the plasma.

In order to use the Pd nanowires as electrodes in nanoscale devices, or for any other *in situ* device functionalization, electrical contact between the nanowires and the underlying substrate must be confirmed. Verification of electrical contact between the Pd nanowires and the Ti layer was obtained from three samples (anodized in oxalic acid at 40 V, sulfuric acid at 18 V, and phosphoric acid at 100 V) that were intentionally overfilled with Pd, thereby electroplating the top PAA surface. *I-V* characteristics were obtained between the Pd plated on the PAA top surface and the bottom Ti layer that was exposed approximately 3 mm away. Measurements were also obtained from a PAA template that was not completely overfilled by nanowires, and this sample exhibited no measurable conduction. For all three overfilled samples, Ohmic contact between the Pd nanowires and the Ti layer was observed (Fig. 4). Because of the low resistance of the nanowire arrays compared to the probes, as well as the uncertainty in the precise number of filled pores, such measurements do not provide an accurate measurement of

conductivity for individual nanowires. Nevertheless, the establishment of Ohmic electrical contact between the Pd nanowires and the Ti is an important accomplishment for integration of the nanowire arrays into device structures. For example, Pd is known to create Ohmic contacts to single-walled CNTs and is therefore very convenient to use in addressing template-grown CNTs.³³

IV. SUMMARY AND CONCLUSIONS

The use of PAA thin films as templates for controlled fabrication of Pd nanowires on conductive substrates has been accomplished by uniformly penetrating the intrinsic oxide barrier using a hydrogen plasma. Uniform and controllable electrodeposition of Pd nanowires suggests a consistent penetration of the oxide barrier in each pore. This process allows for the synthesis of nanowires in PAA templates ranging in diameter from 10 to 130 nm without the diameter limitations of chemical pore widening. The length of the vertical Pd nanowire arrays exhibited a standard deviation of 6% for 30 nm diameter pores and only 2% for 130 nm diameter pores. The Ohmic contact between the Pd nanowire array and the underlying Ti layer was verified, demonstrating the sustainability of the as-synthesized array for device integration. The efficient removal of the bottom oxide layer in a PAA template can be employed in many applications requiring different nanowire materials, device integration, and utilization of vertical nanowire arrays. This process can also be integrated with the PECVD synthesis of CNTs to create Ohmic nanowire contacts *in situ*.³³

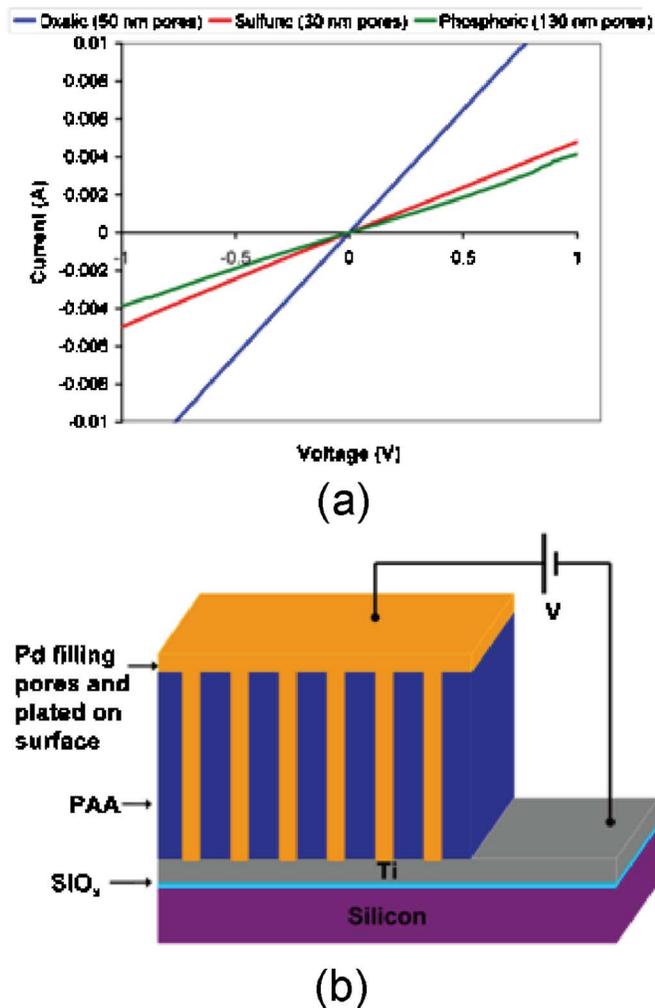


Fig. 4. (a) *I-V* characteristic showing Ohmic contact between the Pd nanowires and the Ti layer from samples anodized in oxalic acid at 40 V with 50 nm pores (blue), in sulfuric acid at 18 V with 30 nm pores (red), and in phosphoric acid at 100 V with 130 nm pores (green). (b) Schematic of a Pd-filled PAA structure detailing the electrical measurement arrangement.

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