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Both TiO2 and HfO2 are common materials for semiconductor fabrication that have shown memristive properties. Nanoparticles of these metal oxides have great prospect to provide nanoscale materials with tunable electronic properties for integration in advanced circuits such as neuromorphic networks based on memristive crossbar elements. We seek to take advantage of the unique interaction between the phosphate end-group of DNA and TiO2/HfO2 nanoparticles to enable a guided assembly of circuit elements via specific nucleotide sequences in a bottom-up fashion.

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Biologically self-assembled memristive circuit elements

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***Abstract*— Both TiO_2 and HfO_2 are common materials for semiconductor fabrication that have shown memristive properties. Nanoparticles of these metal oxides have great prospect to provide nanoscale materials with tunable electronic properties for integration in advanced circuits such as neuromorphic networks based on memristive crossbar elements. We seek to take advantage of the unique interaction between the phosphate end-group of DNA and TiO_2/HfO_2 nanoparticles to enable a guided assembly of circuit elements via specific nucleotide sequences in a bottom-up fashion.**

I. Introduction

Memristive circuit elements, often referred to as "memristors", are typically fabricated with bulk metal oxide materials layered between two electrodes [1]. Nanoscale materials are being considered for use in such memristive elements, where focus has been on the bulk properties of larger assemblies of nanoparticulate memristor materials rather than the probing and integration of single particles [2]. To harness and evaluate the memristive properties of individual nanoparticles, we aim to develop metal oxide nanoparticles, capable of bottom-up assembly in complex integrated circuits. Our focus has been on nanoparticle synthesis using materials commonly found in memristors, such as HfO_2 and TiO_2. We also developed immobilization strategies to attach nucleic acids to these nanoparticle surfaces, which ultimately will be used for particle self-assembly.

Controlled attachment of nucleic acids (DNA and RNA), onto surfaces is important for applications such as microarrays, gene mapping, and biosensors. Sequence-dependent recognition between nucleic acids immobilized to surfaces (such as nanoparticles) enable self-assembly of hierarchical structures and constructs. The interaction of nucleic acids with solid interfaces typically occurs either electrostatically, through negative charges present on the phosphate backbone, or covalently, relying on the introduction of functional end groups in the 3' or 5' termini, typically amines or thiols.

A more straightforward approach to covalent attachment involves the direct interaction between the naturally occurring 5'-terminal phosphate in DNA and transition metal oxides. This binding takes advantage of the strong coordination between the electron donating oxygen on the phosphate group and Lewis-acid sites on the surface. Previously, we and others have demonstrated that alkanephosphonates and terminal phosphate groups present on nucleic acids play an important role interfacing with group IV metal oxides such as hafnium, providing a stable linkage to the surface [3]. Titanium dioxide (TiO_2), which is often used in various nanoscale applications belongs to the same group as hafnium and similar interactions with phosphate is predicted. Here we will discuss our first efforts toward biologically self-assembled memristive structures composed of metal oxide-based nanomaterials. The long-term goal of this work is to develop memristive circuit elements via directed self-assembly of modified nanomaterials (as shown in Figure 1). This paper describes the synthesis and initial characterization of metal oxide nanomaterials as well as DNA-surface immobilization strategies for directed assembly.

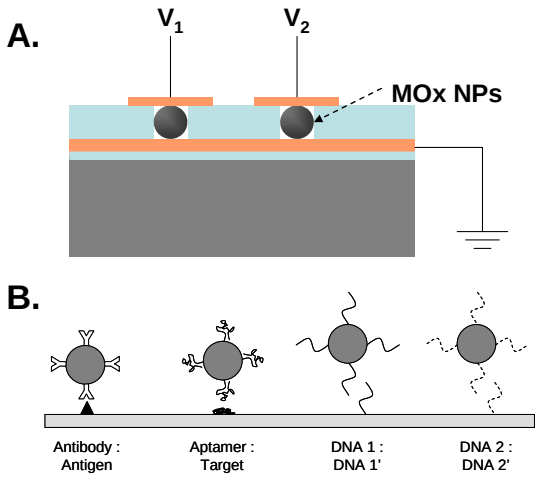

Figure 1. A schematic representation of embedded nanomaterial-based circuit elements (A) and self-assembly of nanomaterials on surfaces via biomolecular interactions (B).

II. Methods

Surface Immobilization of DNA on HfO_2

DNA attachment to planar HfO_2 surfaces was investigated by printing single-stranded DNA oligonucleotides with or without 5' terminal phosphate groups onto piranha cleaned HfO_2. A BioForce Nanosciences (Ames, IA) Nano eNabler instrument was used to print 5 μM ssDNA in tris-EDTA (TE) buffer, pH 8.0 with 5% v/v glycerol onto the surface. The HfO_2 films, approximately 2 nm thick, were prepared by atomic layer deposition (ALD) onto silicon wafers using tetrakis(ethylmethylamido)hafnium (TEMAH) and ozone at 290°C wafer temperature as previously described [4]. Samples with printed DNA were incubated overnight at room temperature, rinsed three times with TE, blocked with 0.1 μg/μl bovine serum albumin (BSA) for 20 min, rinsed three additional times with TE, then hybridized with 0.1 μM complementary DNA at 60°C for 5 min in 5X SSC buffer. Following hybridization, the samples were rinsed three times in TE buffer, incubated for 20 min in 1:400 PicoGreen double-stranded DNA stain (Invitrogen, Carlsbad, CA), and finally rinsed two times in TE prior to imaging via epifluorescence microscopy. The printing pattern for these experiments is shown in Figure 2, below. DNA containing 5' phosphate groups was printed in the green spots, while DNA without 5' phosphate groups were printed in the red spots.

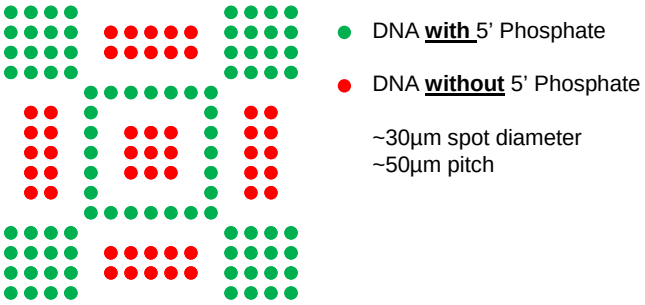

Figure 2. Pattern used for printing DNA onto HfO_2 surfaces.

TiO_2 Nanoparticle Synthesis

TiO_2 nanoparticles were synthesized using two methods. The first was based on a sol-gel synthesis [5] while the second used a hydrolytic approach [6]. The resulting particles from each method were characterized by several methods as follows. Hydrodynamic radii were determined via dynamic light scattering (DLS) using a Zetasizer Nano (Malvern Instruments, Worcestershire, UK), Transmission electron microscopy (TEM, JEOL 2010), scanning electron microscopy (SEM, Zeiss LEO 1550), and atomic force microscopy (AFM, Veeco DI3100,) for determination of particle size and morphology. Crystallinity of the particles were determined using X-Ray Diffraction (XRD, Scintag). In the hydrothermal approach, TiO_2 nanoparticles were synthesized by slowly stirring a 1:3 volumetric ratio mixture of titanium isopropoxide (TTIP) and isopropyl alcohol (IPA). The resulting mixture was then added dropwise to 0.3M HNO_3 (pH 2.0) to obtain a 1:12.5 volumetric ratio. The Ti/IPA/HNO_3 mixture was stirred for 30 min after which tetrabutyl ammonium hydroxide (TBAH) was added to double the total volume. This solution was left overnight to stir, then transferred to a Parr (Moline, IL) 5525 Reactor and heated for 6 hr at 240°C. In the sol-gel synthesis approach, a mixture of TTIP/TBAH/ethanol was prepared with a 1/0.092/170 molar ratio. This mixture was left to stir at room temperature for 30 min. For both methods, synthesized metal oxide particles were washed three times using a cycle of centrifugation (5 min at 16,000 x G), resuspension of particles in 18.2MOhm·cm H_2O (diH2O), and sonication for 5 min (Branson 1510).

DNA Binding to TiO_2 Nanoparticles

DNA binding to TiO_2 particles was determined by varying the concentration of TiO_2 particles while keeping the amount of DNA constant. A stock solution of 0.79% w/v TiO_2 particles (made via the hydrothermal route) was used to prepare serial diluted samples in 10mM HEPES pH 7 buffer. Single stranded DNA (ssDNA) was added to each concentration of TiO_2 to obtain a 10 ng/μl final concentration. Samples were incubated on ice for 1 hr and then centrifuged for 15 min at 16,000 x G leaving only unbound DNA in the supernatant. Two 50 μl samples were withdrawn from each sample supernatant and their absorbance was measured at 260 nm to determine the concentration of unbound DNA. We used two 24 base ssDNA oligonucleotides with the same sequence but with different end-group modification (IDT DNA Technologies, Coralville, IA). One ssDNA had a 5'-hydroxyl and the other a 5'-phosphate group to determine phosphate dependence on TiO_2 particle binding. Negative (10 mM HEPES buffer) and positive control samples (10 ng/ul DNA without particles) were prepared in a similar manner as above.

Electrical Characterization

Electrical measurements were performed on TiO_2 particles synthesized via the sol-gel approach using a FEI Dualbeam 600 with an Omniprobe attachment (Hillsboro, OR). Carbon nanotubes (CNT) were attached to electrochemically etched tungsten wires [7] using dielectrophoresis [8]. The resulting tungsten-CNT (W-CNT) tips were secured to the Omniprobe using silver epoxy and inserted into the Dualbeam 600 instrument. Titania particles dispersed in ethanol were deposited onto a TiN-coated wafer and the solvent was allowed to evaporate. The wafer was then attached to a standard SEM mounting stub where silver epoxy ensured good electrical contact between the stub and TiN layer. A Keithly (Cleveland, OH) 4200 SCS Parameter Analyzer was connected to the Omniprobe and used to collect current-voltage (IV) curves. Alignment and contact of the W-CNT tip to a TiO_2 particle could be monitored in real-time by observing current flowing between the Omniprobe and stage while imaging. Once contact was established between W-CNT probe and the particle, I-V curves were collected by sweeping the voltage between +/-10V and +/-20V.

III. Results

DNA Immobilization on HfO_2

DNA attachment to HfO_2 surfaces was shown to be dependent on the phosphorylation state of the 5' terminus of DNA molecules. Single-stranded DNA containing a 5' phosphate group could be specifically immobilized on HfO_2

and remain available for hybridization with target DNA strands. Hybridized DNA is clearly visualized with PicoGreen stain as shown in Figure 3. Non-phosphorylated, single-stranded DNA did not bind efficiently to the HfO_2 surface and no complement hybridization was seen. Closer inspection of the non-phosphorylated printing sites revealed spots that had slight fluorescence, which indicates a certain degree of surface attachment (data not shown). DNA without 5'-phosphate groups can most likely adsorb to the surface through electrostatic interactions between the surface and charges present in the DNA backbone, but the amount is insignificant compared to the level of attachment observed for phosphorylated DNA (Figure 3).

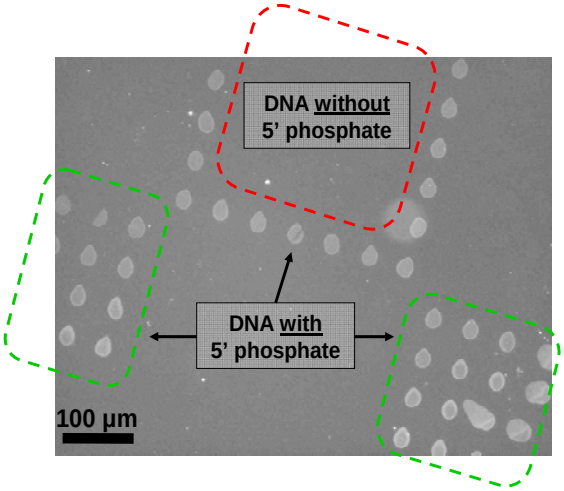

Figure 3. Single-stranded DNA printed onto a HfO_2-coated silicon surface and hybridized with target DNA. DNA containing terminal 5' phosphate groups was printed in the locations outlined in green, while non-phosphorylated DNA was printed into locations outlined in red.

TiO_2 Nanoparticle Characterization

TiO_2 particles synthesized via the sol-gel and hydrothermal methods were analyzed with DLS, SEM, AFM and XRD. The sol-gel synthesis resulted in particles with a range of diameters from ~500-3000 nm as imaged in SEM (Fig 4a). These particles appeared non-crystalline in XRD (Fig 4b), which was expected considering the relatively mild synthesis conditions. The hydrothermal method, which is performed under higher pressure and temperature, resulted in approximately 20 nm diameter nanoparticles with a brookite crystalline phase as determined through DLS, AFM and XRD (Fig 4c-d).

DNA Attachment to TiO_2 Nanoparticles

Surface attachment of DNA to metal oxide nanoparticles is important for biological-based bottom-up fabrication and directed self-assembly. Common surface-linking strategies rely on organic spacers and reagents. To reduce the amount of potentially insulating organic material at the metal oxide-nanoparticle interface, we opted to investigate approaches that rely on DNA immobilization directly to "unmodified" nanoparticle surfaces. As shown, DNA 5'-phosphates have preferential and specific attachment to hafnia surfaces, and we decided to investigate this immobilization strategy on our titania surfaces. The loading of ssDNA onto various

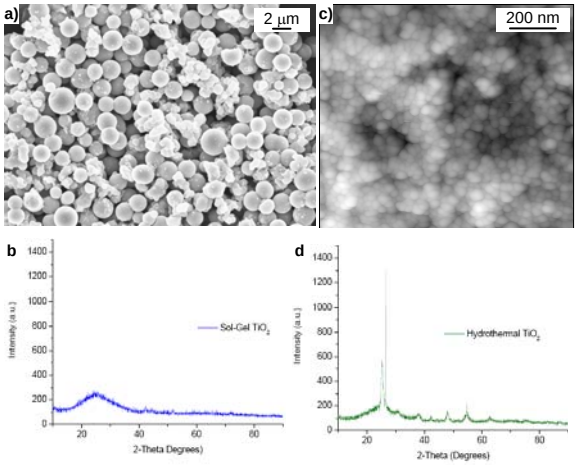

Figure 4. SEM of TiO_2 particles made via the sol-gel approach (a) where the lack of peaks in the XRD data indicate amorphous TiO_2 (b). AFM of TiO_2 nanoparticles made with the hydrothermal method (c) showing the brookite crystalline phase in XRD (d).

concentrations of TiO_2 nanoparticles are shown in the adsorption curves in Figure 5. The amount of DNA adsorbed to the particles was the same regardless whether a terminal 5' phosphate was present or not. Results indicate that the DNA binding to TiO_2 surfaces, although efficient, is not phosphate specific. In this case, adsorption of DNA to the nanoparticle surface most likely occur through a charge-based interaction where DNA is physically adsorbed via the negatively charged backbone.

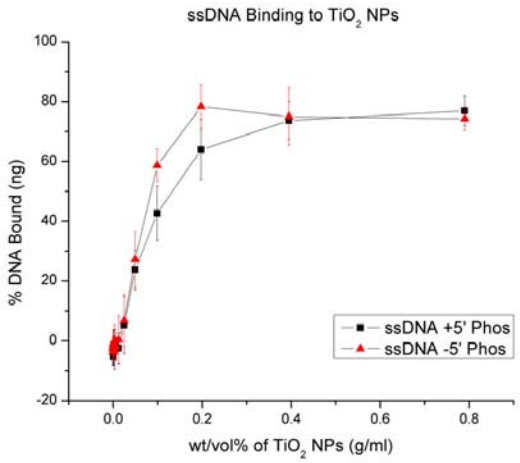

Figure 5. DNA adsorption to TiO_2 nanoparticles. Percentage of total DNA added is shown for increasing percentages (w/v) of TiO_2 nanoparticles. ssDNA with 5' phosphate (black squares) is compared to ssDNA w/o 5' phosphate (red triangles).

Electrical Characterization of TiO_2 Nanoparticles

One of the unique properties of memristive materials is the functional relationship between current and voltage. A memristor typically has a turn-on/turn-off voltage and once current flows through the system, a pinched hysteresis loop should be evident in the measured I-V curve. To initially test the electronic properties of our synthesized particles we measured current–voltage characteristics of three individual TiO_2 particles with different size (1, 2, and 3 µm in diameter). As seen in Figure 6, a size-dependent I-V response is

obtained, where smaller particles shows lower resistance. This is to be expected since there is less material to impede the current flow. No memristive behavior is evident for any of the micron-sized particles that were tested. The relatively large size of these particles could yield a "turn on" voltage greater than 20V, which was the upper voltage limit in our experimental setup. Measurements on the smaller (20 nm) TiO_2 are in progress and are expected to provide valuable data on the electric properties of single nanoparticles. One

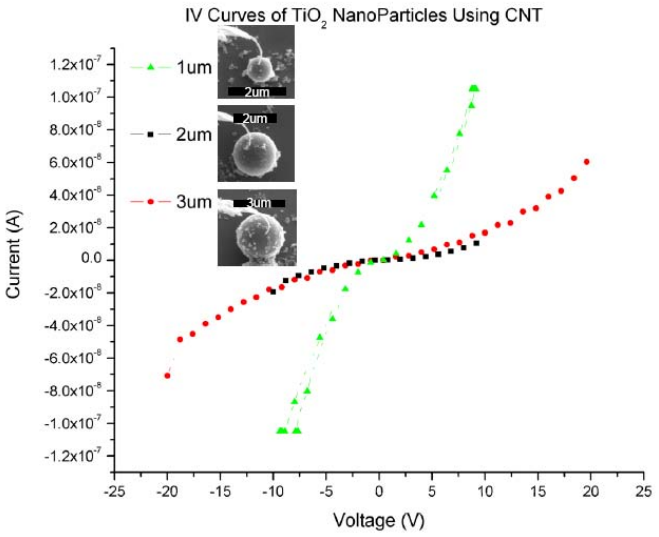

Figure 6. Current-Voltage (I-V) measurements for various size TiO_2 nanoparticles are shown (green triangle, 1μm; black square, 2μm; red circle, 3μm).

challenge in measuring smaller particles is the positioning of the probe, which is on the same size scale as the particle to be measured.

IV. Discussion

Biologically-assisted assembly allows directed, bottom-up fabrication of nanoscale memristive elements. To realize such systems, several components need to be designed and tested. This includes efficient fabrication of nanoparticles/structures with memristive properties, as well as efficient surface anchoring of biomacromoleucles to such structures. Here we demonstrate two different approaches for TiO_2 particle synthesis that lead to either amorphous or crystalline materials. The sol-gel and hydrothermal methods described are based on similar chemistry and would, in principle, allow us to vary precursor concentration, composition, temperature, pressure, and solvent conditions to adjust particle size, crystallinity, and vacancies/defects of the end-product. Reliable methods to investigate memristive properties in synthesized nanoscale materials are also vital for our approach. Our initial I-V measurements on individual, micron-sized particles demonstrate that carbon-nanotube modified probes enable analysis of single particles in an efficient manner. Surface attachment of ssDNA was shown to be efficient on both TiO_2 and HfO_2 surfaces although the interaction mechanism appeared different. In the case of TiO_2 the interactions are likely electrostatic while on HfO_2, interactions occur specifically through terminal phosphate groups. The specific immobilization of DNA to HfO_2 is ideal, as it orients the DNA in such a way to enable directed assembly via complement binding. Continued efforts include the synthesis and assembly of HfO_2 nanoparticles based on procedures developed for TiO_2. Also, electrical probing to evaluate the memristive properties of individual nanoparticles of both TiO_2 and HfO_2 are underway.

V. Conclusion

Here we demonstrate two synthesis methods for TiO_2 particles, enabling fabrication of materials with varying crystallinity. Electrical testing with a novel carbon nanotube probe on individual TiO_2 particles was realized. Oriented immobilization of self-assembling biomolecules on metal oxide interfaces for future bottom-up assembly was shown.

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