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Electrochemical Protection of Thin Film Electrodes in Solid State Nanopores

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Abstract

We have eliminated electrochemical surface oxidation and reduction as well as water decomposition inside sub-5-nm wide nanopores in conducting TiN membranes using a surface passivation technique. Nanopore ionic conductances, and therefore pore diameters, were unchanged in passivated pores after applying potentials of ± 4.5 V for as long as 24 h. Water decomposition was eliminated by using aqueous 90% glycerol solvent. The use of a protective self-assembled monolayer of hexadecylphosphonic acid was also investigated.

Keywords

solid state nanopore; TiN electrode; ionic conductance; oxidation; water decomposition; electrochemical passivation

Solid State nanopores ^{1, 2} as well as protein nanopores ³⁻⁷ constitute a core element of next-generation single molecule tools in the field of nano-biotechnology. Thin film electrodes integrated into a nanopore can be used to detect or manipulate charges and fields within the nanopore. Embedding thin film electrodes into a nanopore environment is a known design concept in the field of electrofluidic applications ⁸, most importantly in the area of DNA-sequencing applications ⁹. Electrode materials typically include but are not limited to graphene sheets ^{10, 11}, carbon nanotube or STM probes ^{12, 13}, and thin metal films containing doped silicon ¹⁴, TiN ¹⁵ or gold ¹⁶. We have recently introduced a nanopore-based DNA-sequencing platform which we call a DNA-transistor ¹⁷. Functionality of this device is enabled by three TiN thin film electrodes exposed to a DNA-containing electrolyte/solvent solution inside a nanopore and the application of an electric field between the electrodes to trap the DNA molecule. In order to keep the nanopore open and thus maintain functionality of the device electrochemically induced surface alteration of electrode surfaces and bubble formation inside the pore through water decomposition have to be eliminated. The primary goal of the work presented in this paper was to prove that our recently presented processes used to eliminate TiN surface reactivity in a planar thin film geometry ¹⁸ can be applied to and performed in a nanopore geometry.

This paper provides electrochemical analyses of nanopores drilled into TiN membranes which in turn were employed as thin film electrodes. We studied physical pore integrity and the occurrence of water decomposition yielding bubble formation inside pores by applying voltages between -4.5 V and $+4.5$ V to membranes in various protection stages continuously for up to 24 h. During potential application pores were exposed to selected

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electrolyte-solvent systems which are known to suppress surface reactivity in planar environments¹⁸.

We have investigated and successfully eliminated electrochemical pore oxidation and reduction as well as water decomposition inside nanopores of various diameters ranging from 3.5 nm to 25 nm in 50-nm-thick TiN membranes by passivating the nanopores with a thin plasma-oxidized layer and using a 90% solution of glycerol in water as KCl solvent. Nanopore ionic conductances were measured before and after voltage application in order to test for changes in pore diameter due to electrochemical oxidation or reduction. TEM imaging was used to confirm these observations. While non-passivated pores were electrochemically oxidized in both solutions, electrochemical oxidation and reduction were not observed for passivated pores. Bubble formation through water decomposition could be detected in non-passivated pores in KCl/water solutions but was not observed in 90% glycerol solutions. The use of a protective self-assembled monolayer of hexadecylphosphonic acid (HDPa) was also investigated. The presented work constitutes an essential study of the core element of a DNA-transistor device proving that it will be electrochemically robust under working conditions.

Supported TiN membranes were fabricated on silicon wafers using standard DUV photolithography; a schematic of the device is shown in Fig. 1. The TiN film was deposited by reactive sputtering of Ti in the presence of nitrogen. Because sputtered TiN films typically have very large compressive stresses, the TiN was deposited at 425°C and sandwiched between layers of 400-nm-thick SiO₂ and 50-nm-thick Si₃N₄ on each side in order to avoid mechanical failure of the membranes. 6-μm-wide vias were patterned through each pair of dielectrics to expose the TiN layer for TEM drilling using reactive ion etching and a buffered hydrofluoric acid dip. To form freestanding membranes, a backside Si₃N₄ hardmask was used to pattern an anisotropic Si etch in 23% tetramethylammonium hydroxide heated to 80°C.

Following membrane fabrication, wafers of devices were broken into individual chips and nanopores were drilled through the supported TiN membranes using a 300 kV JEOL 3000F field emission transmission electron microscope (TEM). After focusing on the TiN film exposed at the bottom of the 6-μm-wide vias, the electron beam was focused as tightly as possible in order to drill a nanopore through the film, typically done at 600 kx magnification. Nanopores ranging from approximately 3 to 20 nm were used in this study. After drilling, the beam was expanded again to image the pore and measure its initial size.

Some TiN nanopores were passivated with a nanometer-scale oxide layer, as we had shown previously that this process can be used to passivate thin planar TiN films from electrochemical reactions¹⁸. The passivation process consisted of an oxygen plasma treatment step ($P = 150$ mT, $flow = 100$ sccm, $power = 200$ W, $time = 8-30$ s) using an Unaxis 950 Series Etch Chamber. In order to calibrate the TiN oxidation rate within nanopores, TEM imaging before and after oxidation was used to measure the change in pore radius and therefore the thickness of added oxide. The areas of five to ten pores were measured for each oxidation time and used to define an effective circular radius in order to account for slightly elliptical pores. Images taken before and after the oxidation of a nanopore for 20 s are shown in Fig. 2.

The surrounding TiN regions definitely show signs of oxidation, as a significant amount of amorphous material is now visible on the TiN in Fig 2(b). Pore oxidation was typically uniform around the pore circumference for the oxidation times studied. The amount of oxide grown depended linearly on oxidation time, as shown in Fig 3, where error bars signify the standard error. The oxidation rate observed at this time range is about 3 Å/s.

Selected nanopores were additionally coated with a protective self-assembled monolayer of C-16 hexadecylphosphonic acid (HDPa, chain length approx. 1.9 nm) after passivation. The coating process was carried out by wetting the pores with a dilute solution of HDPa in ethanol and soaking them overnight. We introduced this coating process for planar TiN samples and described its details in reference 18. Figure 4 shows the same TiN nanopore in all three protection preparation stages: (a) no passivation and no coating, as drilled, (b) passivated but not coated, and (c) passivated and coated.

Following nanopore drilling, device chips were loaded into a flow cell, shown schematically in Fig. 1 that allows fluidic exchange between both sides of the nanopore. After wetting the pore with an electrolyte/solvent solution, baseline ion conductance measurements were performed by applying a voltage across the membrane using Ag/AgCl electrodes and reading out the ion current using a picoammeter. After establishing a baseline pore conductance, a probe was used to contact the TiN membrane layer and apply a voltage to it that was larger than the oxidation potential of TiN (1.3 V) ¹⁹ the redox potential of water (1.9 V), and the estimated trapping potential of a DNA transistor (4 V). Hence, for all presented experiments we chose to apply a voltage of +4.5 V to the TiN membrane, measured relative to the grounded electrolyte solution. Once the voltage had been applied for the desired amount of time, the probe was removed from the TiN membrane and the ionic conductance of the nanopore was measured again. Because the conductance of a pore depends on its area, electrochemical oxidation would manifest itself as a decreased ionic conductance corresponding to a decreased pore diameter. If the pore did not oxidize, then the conductance would not change from the baseline value. Additionally, bubble generation through water decomposition inside a pore would be indicated by (i) measuring no pore conductance right after applying the potential to the pore, and (ii) being able to re-establish a non-zero pore conductance simply by flushing the pore with the solution.

We studied selected combinations of nanopores in all three protection stages and highly concentrated KCl solutions in three oxidation test schemes. In test type I, non-passivated membranes were characterized in two different solutions, in test type II passivated but non-coated pores were studied, and passivated and coated pores were analyzed in test type III. Table 1 gives a detailed overview of all executed test schemes.

Figure 5 shows the results of all test schemes described in Table 1. We used the ratio of the final to initial conductance, given by $G_{\text{ratio}} = G_f / G_i$, as a measure for electrochemical pore closing for each test scheme. Here, $G_{\text{ratio}} = 1$ means no change in the conductance and hence an unchanged pore diameter, whereas $G_{\text{ratio}} = 0$ describes a completely closed pore. Detailed explanations of the test results for all three different types of pores are given below.

The pore conductances of type I(a) devices dropped by almost 50% in an hour, with $G_{\text{ratio}} = 0.52 \pm 0.12$. Additionally, all pores tested showed strong evidence of bubble generation, where the pores appeared at first to be closed with zero conductance, but recovered to a finite value after a period of flushing.

TEM images confirming that type I(a) pores were heavily oxidized and partially closed during voltage application are presented in Fig. 6. These results were strongly expected based on previous experiments testing planar TiN samples ¹⁸ and the oxidation potentials of water and TiN ¹⁹. Type I(a) tests were used as positive control to verify the functionality of our test platform and the efficacy of our passivation scheme.

Type I(b) pores resulted in $G_{\text{ratio}} = 0.85 \pm 0.09$, signifying a conductance drop of ~15%, less than the type I(a) samples tested in water. Additionally, no bubble generation was observed in any of the tested type I(b) pores. These results show that substituting a 1 M KCl water solution with a 0.1 M 90% glycerol in water solution substantially decreases but does not

eliminate electrochemical oxidation of non-passivated pores and suppresses bubble formation inside the pore.

Type II pores (passivation layer thickness 1.75 nm) were tested for 1 h and showed no conductance drop ($G_{\text{ratio}} = 1.00 \pm 0.03$). Additionally, no bubble formation could be detected during testing. One of the pores previously tested for 1 hour was re-used for an additional 24-hour run after which G_{ratio} was measured as 1.02 and again no bubbles were detected in the pore. We conclude from these results that passivated pores exposed to 0.1 M 90% glycerol in water solution are completely shielded against corrosion for operating voltages up to 4.5 V continuously applied for up to 24 h, and bubble formation is successfully suppressed in these pores within the same voltage and time windows. Confirming TEM images are provided in Fig. 7.

We have also applied a potential of -4.5V to a type II pore for 24 h to test its reduction behavior. G_{ratio} was measured as 1.01 and no bubbles were detected in the pore. Although further tests have to be performed to statistically confirm this result it still indicates that type II pores are also resistant against electrochemical reduction effects for voltages of down to -4.5 V .

As expected, type III devices (passivation layer thickness 1.75 nm, HDPA-coating monolayer thickness 1.9 nm) showed the same conductance preserving behavior as type II pores, with $G_{\text{ratio}} = 1.01 \pm 0.06$ for one hour and 1.08 for a 24 hour-long test. Again, bubble formation was not observed. These results indicate that HDPA-coating is not necessary for corrosion protection if passivated pores are employed. However, we want to emphasize that a coating process for passivated pores has successfully been established which may be interesting or useful for nanopore functionalization or sensing. Our results do, however, confirm that the self-assembled monolayer is not damaged or removed by the application of 4.5 V, otherwise a conductance ratio greater than one would have been observed.

We have developed and characterized a plasma oxidation process known to passivate TiN and have demonstrated that it translates successfully into a nanopore geometry. We have shown that this passivation process effectively protects TiN nanopores against electrochemical oxidation and thus pore closing when the TiN electrodes are used in a wet electrolyte/solvent environment at voltages of up to 4.5 V continuously for up to 24 h. Preliminary results also indicated that passivated pores are resistant against electrochemical reduction and thus we do not expect pore widening when the TiN electrodes are used in a wet electrolyte/solvent environment at voltages of down to -4.5 V continuously for up to 24 h. We also found that water decomposition and subsequent bubble generation inside passivated pores are eliminated for these conditions by using a 0.1 M solution of KCl in 90% glycerol. An HDPA-coating process for previously passivated nanopores was also tested, but the results did not suggest any further protection over 24 hours of voltage application. When possible we replicated our results between three and five times, finding consistent outcomes. Our results show that a DNA-transistor employing a trapping potential of +4 V can successfully be protected against electrochemical reactions and bubble formation inside the pore.

Acknowledgments

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Figure 1. Schematic of the device and experimental setup, including device structure and measurement apparatus.

Figure 2. TEM images of a 13-nm-diameter TiN nanopore (a) before and (b) after a 20 s passivation by oxygen plasma. Images were taken at $600\,000\times$ magnification; scale bars are 5 nm.

Figure 3. Passivating oxide layer thickness as a function of plasma oxidation time. Each data point comes from 5 to 10 pores in TiN, and error bars represent standard error.

Figure 4.

TEM top-view images of the same nanopore (a) right after drilling, (b) after passivation, and (c) after passivation and coating. Coating is done in a wet environment and only minimal flushing of the chip was performed after coating to avoid damaging the membrane. As a result, the coating layer thickness in (c) appears to be thicker than 1.9 nm and also shows inhomogeneities.

Figure 5.

Final-to-initial conductance ratios for all test schemes: while non-passivated pores were electrochemically oxidized in both solutions, neither passivated nor passivated and coated pores did. Bubble generation was only observed in water but not in 90% glycerol solutions. Error bars reflect standard error. Both 24 hour tests were done with one pore each, and the results fall within the standard error margin of the corresponding one-hour-long test results.

Figure 6.

TEM top-view images of the same non-passivated nanopore before execution of a type I(a) test run (left) and afterwards (right): Strong surface oxidation of membrane and pore after voltage application can clearly be observed. The pore was flushed extensively with water before TEM imaging to remove potential salt residues from all surfaces. Successful salt removal was ensured by monitoring and minimizing the ionic background current through the pore while flushing it.

Figure 7.

TEM top-view images of the same nanopore: (a) after drilling and before passivation, (b) after passivation and before execution of a type II test run, and (c) afterwards. Due to the protective passivation layer the pore diameter has not changed after applying a voltage of 4.5 V to the membrane for 24 h. Hints of salt residues inside the pore and especially at its edges are visible which could not be completely flushed away after the test.

Table 1

Overview of all executed electrochemical oxidation test schemes. Each test type was performed on 3 to 4 different pores for one hour. Two 24 hour-long tests were performed using p34 and p43 again after the initial one-hour-long test.

test type	pore ID	solvent	[KCl] *	time at 4.5 V
type I(a)	p11	water	1 M	1 hour
non-passivated in water	p12			
	p13			
	p14			
type I(b)	p21	90% glycerol 10% water	0.1 M	1 hour
non-passivated In 90% glycerol	p22			
	p23			
	p24			
type II	p31	90% glycerol 10% water	0.1 M	1 hour
passivated 1.75 nm oxide	p32			
	p33			
	p34			
	p34			24 hours
type III	p41	90% glycerol 10% water	0.1 M	1 hour
passivated & coated 1.75 nm oxide & 1.9 nm HDPa	p42			
	p43			
	p43			24 hours

* 1 M KCl in 90% glycerol/10% water can not be created due to solubility constraints. 0.1 M KCl in 90% glycerol is the maximum molarity that can be achieved.