Solid state nanogaps for differential measurements of molecular properties

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This paper demonstrates the production and probing of solid state nanogaps. These nanogaps can be inexpensively and controllably produced using a combination of molecular and standard photolithography. These nanogaps are implemented for chemical monitoring by using surface enhanced Raman spectroscopy to collect molecular information at the nanogap and current-voltage traces to probe the charge transport of the nanogap. These data show that the oligonucleotides used as the molecular resist are degraded, that some of the degraded oligonucleotides are removed, and then new oligonucleotides are adsorbed. © 2009 American Institute of Physics.

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Solid state nanogaps are scientifically interesting due to their small size, robustness, and versatility. Many insights in physics at the nanometer scale have been made using these types of structures and more are expected in the future. Practically, solid state nanogaps have the potential of detecting chemical species on the near single-molecule scale. This capability is beginning to be studied due to the importance of inexpensive chemical sensing.

Coincidentally, surface enhanced Raman spectroscopy (SERS) is an analytical technique of growing importance that also stands to benefit from the maturation of nanogap technologies. SERS is a variant of Raman spectroscopy that uses roughened metallic substrates to enhance, amplify, and otherwise refine its output signal. However, the difficulty that frequently arises with SERS is creating substrates that have large and very uniform enhancement factors. Ideally SERS substrates should be efficiently and inexpensively fabricated on the wafer scale and will consist of small metallic structures with uniform spacing from a few hundred nanometers to just a few nanometers. More routinely, however, SERS substrates are subject to local unpredictable “hot spots” of enhancement and require advanced nanolithographic patterning to prepare.^{1–3}

Fortunately, the commingling of solid state nanogaps and SERS has increased recently and research is beginning to show that the closely spaced metal features at the nanogap are capable of enhancing the Raman effect.^{4–6} Such discoveries lead to the possibility of using nanogaps for dual function applications—to serve as an electronic detection device and as a SERS platform for chemical characterization.

In the past, nanogap structures have been fabricated with mechanically controlled break junctions,^{7,8} nanowire lithography,⁹ and electron beam lithography with electromigration^{4,10} among others.¹¹ Each method has its own individual advantages and disadvantages though very few offer both the promise of nanoscopic gap-size control and the likelihood of inexpensive and efficient fabrication. In this project, emphasis will be placed on using a hybrid molecular technique to create planar electrodes with separations of about 20 nm. In the future, these structures will be invaluable for investigating molecular electronic candidates, for

researching biological systems, and as a substrate for SERS studies. Here, as a proof of concept experiment, the local molecular environment of the nanogap is monitored using SERS and current-voltage traces immediately after fabrication, then again after an alkanethiol substitution, and finally after a subsequent oligo substitution.

Solid state nanogaps are generated using a variation in previously developed molecular resist strategies.¹² These strategies have demonstrated the ability to use multilayer resists to create structures from just a few nanometers to ~40 nm.¹³ The structures presented here are different in several ways from previous alkanethiol-based solid state nanogaps in that these structures are created with thicker single layer molecular resists and they maintained the capping metallic layer often sacrificed in other papers.

The fabrication methodology for these structures will be briefly explained. In this report, the initial electrode in the electrode pair that composes the nanogap is fabricated on a silicon wafer with 200 nm of silicon oxide (University Wafer) using a conventional photolithography lift-off process with SPR3012 (Rohm&Haas) and LOR5A (MicroChem) resists and then 3 nm of chrome and 40 nm of gold are deposited using electron beam evaporation. The photoresist and unwanted metal are removed with sonication in acetone and an immersion in CD-26 (MicroChem). Next, the electrode is submerged in 5 μ M solution of thiolated oligonucleotide (IDT) for 24 h. Finally, a second photolithographic lift-off process, metallic evaporation, and resist removal are used to pattern the second electrode in the electrode pair. These processes were similar to those used to pattern the initial electrode except 3 nm of chrome and 25 nm of gold were deposited. The oligo resist had the sequence 5'-T₁₀-GC AGC TTA GAA TCA AAT AGC GCG ATA TGC ATC GAT GAC TA-3' and a thiol modification at the 5' terminus. Research suggests an oligo this size should be about ~20 nm in length.¹⁴ Scanning electron microscope (SEM) images were collected to characterize the electrode fabrication process (data not shown) and image analysis confirms that the size of the nanogap is within the expected range of 20 ± 5 nm.

All Raman spectra presented in this paper were collected with a custom-built Raman microscope. Raman scattering was excited using a 12 mW, 632.8 nm HeNe laser (Thorlabs) coupled to an inverted microscope (Nikon, Diaphot) with a 100 $\times$ (Nikon) dry objective. The reflected Raman signal was

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FIG. 1. (Color online) Raman signal from a nanogap created using single-stranded oligonucleotides as a molecular resist in the structure's fabrication. (a) shows a portion of the Raman spectra collected at the electrode interface as fabricated, after a DDT substitution, and then after thiol functionalized oligonucleotides (Oligos) were added to the solid state nanogap. (b) and (c) are the spectra that result from subtracting the as fabricated trace from the DDT trace and from subtracting the DDT trace from the oligonucleotide trace, respectively. These latter spectra are used to highlight the change in condition between two states.

analyzed through an imaging spectrograph (PI Acton, SpectraPro SP-2156) and detected with a liquid nitrogen cooled charge-coupled device (CCD) camera (PI Acton, Spec-10:100BR/LN). The laser power at the sample measured 3 mW and the laser spot was $\sim 2 \mu\text{m}$ in diameter. Collection times were 20 s. GRAMS/AI 8.0 software (Thermo) was used for analysis and correction.

The electronic properties of the nanogap were also collected as they provide a quick, qualitative measure of variation in the nanogap. While electronic property measurements are fast and inexpensive, they provide little molecular information. For this reason, SERS was also performed. The electronic properties and Raman spectra for these structures were recorded at three time points during the experiment: (1) immediately after fabrication, (2) after substitution of dodecanethiol (DDT) into the gap, and (3) after immersion in a 50-mer thiol terminated oligonucleotide. Note that the Raman information was collected in a confocal format at the nanogap enabling the data to be collected from nominally the same position during each step of the experiment.

Figure 1 shows portions of the Raman spectra from a representative solid state nanogap and Fig. 2 shows the current voltage traces for the same solid state nanogap at the same time points. The dark blue trace in Fig. 1 shows the as fabricated condition. Note that while spectra recorded away from the nanogap show little signal or perhaps small contributions from the Si substrate (data not shown), the portion of the spectrum from the nanogap shown in Fig. 1 has two strong peaks at 1342 and 1585 relative cm^{-1} . These peaks are

FIG. 2. (Color online) Current-voltage characteristics for the electrode as fabricated, after the DDT substitution, and then again after the final oligonucleotide addition. The electrode conducted 350 nA as fabricated, 18 nA after the alkane substitution, and 130 nA after the oligo substitution, all at +0.5 V of applied bias.

very similar to those observed in pyrolyzed photoresist or for glassy carbon with two strong bands around 1360 relative cm^{-1} [disordered (*D*) band] and 1600 relative cm^{-1} [graphitic (*G*) band].^{15,16} These features alone are typical of sp^2 bonding within a graphitic carbon matrix whereas oligo systems typically have several additional characteristic peaks present.^{17,18} This suggests that some of the oligonucleotide being used as a molecular resist degraded during the fabrication process. The dark blue trace in Fig. 2 shows the electronic properties of the as fabricated nanogap. Through SEM imaging, the separation of the nanogap was observed to be $\sim 20 \text{ nm}$ with a roughness on the order of 5 nm. At this length scale, no charge transport is expected from ballistic tunneling¹² but as can be seen in the current voltage trace, significant charge transport was observed for this system. It is expected that this charge transport was through the oligos or through the degraded oligos, which appear graphitic from the molecular information collected by Raman spectroscopy. Note that oligonucleotides and DNA once thought to be insulators have since been shown to enable long range charge transfer when dry, though the exact mechanism is still debated.^{19,20}

In an effort to remove some of the degraded oligonucleotide, the sample was immersed in a solution of 1 mM DDT in ethanol and heated at 60°C for 1 h. The sample was then slowly returned to room temperature over several hours. Then the Raman spectrum and electronic properties of the same nanogap were collected again. The results are shown in the brown trace of Fig. 1 for Raman spectroscopy and the brown current voltage traces in Fig. 2. Experiments in our laboratory have not shown significant characteristic SERS scattering from DDT. This is expected since Raman activity is enhanced in molecules with some π -bonding or with large cross-sectional areas.^{21,22} Thus, because DDT is a straight chain, sp^3 hybridized system, a great reduction in Raman activity is expected when it is used to replace the more complex and aromatic, π -bonded environment of the oligonucleotide system. From Fig. 1 it can be seen that Raman activity indeed dropped significantly after the alkanethiol substitution, including activity from the graphitic peaks. This point is highlighted specifically by subtracting the “as fabricated” trace from the “DDT” trace. The resulting Fig. 1(b) shows large negative peaks at 1342 and 1585 cm^{-1} that have been attributed to the *D* and *G* bands of carbon.^{15,16} In Fig. 2 a significant reduction in the charge transfer through the nanogap is also shown. It can be deduced from this information that some (though not all) of the degraded oligonucleotide has been removed from the solid state nanogap. Repeated aggressive sonication in strong solvents like dimethylformamide can be used to remove more of the molecular species at the nanogaps, resulting in a Raman spectrum that is featureless except for a small peak at 530 cm^{-1} that represents the silicon substrate. Unfortunately, this process is time consuming and its adverse effects to the electrodes limit overall device yield.

Finally, the alkanethiol-substituted oligo sample was immersed in a 5 μM aqueous solution of thiol modified 50-mer oligonucleotide and heated to 60°C for 1 h. The sample was removed, rinsed, and the electronic and Raman spectrum were again recorded and are shown as green traces in Figs. 1 and 2. The conductivity of the sample increased while still remaining nonlinear with respect to applied voltage (see Fig.

2). Figure 1(c) shows the Raman spectrum created by subtracting the “oligonucleotide” spectrum from the DDT spectrum. The resultant spectrum shows characteristic nucleic acid peaks for cytosine (at 619 and 1023 cm^{-1}),²³ adenine (at 1332 cm^{-1}),²⁴ thymine (at 992 cm^{-1}),²³ and guanine (at 1315 and 1602 cm^{-1}).²⁴ This information verifies that some oligonucleotide was added to the solid state nanogap. It is expected that this corresponds to a significant Raman enhancement factor. Unfortunately, to date Raman spectra for single stranded oligonucleotide is notoriously difficult to obtain²⁵ and by our hands none have been collected on other substrates for comparison. Notice also that while all conditions share similar peaks in the range of the sp^2 bands, besides the additional peaks below 1200 relative wavenumbers, the oligo sample exhibits a significant shift in the 1342 cm^{-1} peak to lower wavenumbers and a shift in the 1585 cm^{-1} peak to higher wavenumbers. This can be observed easily in Fig. 1(c). It is hypothesized that these features are due to the convolution of peaks from the remaining degraded oligonucleotide from the fabrication process and some overlapping peaks from the added oligonucleotide. It is expected that the shifts predominantly indicate the presence of C–N stretching and NH_2 deformations, respectively.¹⁸

In conclusion, the probing of electronic and optical properties for nanogaps created using a combination of oligo-based molecular lithography and conventional photolithography has been shown. Because of the advanced state of common oligonucleotide preparation techniques, theoretically the oligonucleotide length and thus a single layer molecular resist thickness can be easily tailored to size specifications from just a few nanometers up to realistically tens of nanometers. These nanogaps are not only capable of sensitive electronic detection for quickly and inexpensively probing charge transfer at the nanogap, but may also be analyzed for molecular information using SERS.

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