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Modifying and Preserving Ferroelectric Lithographic Nanostructures

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Abstract

Nanoscale structures made of silver are modified to improve electrical conductivity and enable transfer from the growth substrate. Precisely fabricated nanowires and nanostructures have potential applications to various technologies including integrated circuits, solar cell efficiency, and spectroscopy. Currently, non-contiguous silver nanowires are being synthesized by ferroelectric lithography at the University of North Carolina Asheville (UNCA) and, after characterization, are wiped clean from the periodically poled lithium niobate (PPLN) so that the substrate can be reused. These particular structures have small gaps between them which make them useful for surface enhanced Raman spectroscopy (SERS). However, due to the discontinuity of the silver nanoparticles in these arrays, they cannot conduct electricity. This work aims to create conductive nanowires by varying the solution concentration and duration of deposition and to improve a method of transferring these nanostructures to another medium so they can be preserved. By encasing the wires in epoxy, they may be preserved and analyzed at a later date or be transferred to another platform for other applications. Polydimethylsiloxane (PDMS) has proven effective in encasing the silver nanoparticles of the non-conductive wires without damaging the crystal substrates. These conductive wires may also be removed from the fragile substrate into a flexible PDMS composite. These composites are then tested for conductivity. Once conductivity is confirmed, the process may be applied to different patterns of substrate to produce various circuitry designs.

1. Foundational Research

The subject of nano-engineering is one of the fastest growing disciplines in the field of physics and, arguably, one of the most applicable to technological and societal progress. Nanostructures are used in such a broad variety of applications due to their tendency to exhibit properties of both quantum and classical physics. This experiment is inspired by an ongoing research project in which high-aspect ratio silver nanostructures are created using a ferroelectric lithographic process. While success has been achieved in understanding the relationship between growth conditions and wire parameters, improved control over the wire characteristics would make ferroelectric lithographic structures more widely applicable. The current nanowires are composed of hemispheroidal structures of silver arranged in long, parallel rows. These structures range from 10 to 200 nanometers in size, but deposition time can vary the shape and size of each silver particle drastically. Different geometries of the structures make them better suited for specific applications. For example, it is theorized that halfway between the centers of two silver, nanoscale spheres a massive intensification of incident electromagnetic radiation may be observed which can also affect analyte molecules located near the nanoparticles. When this increased light intensity is used to amplify Raman scattering cross sections, a technique called surface enhanced Raman spectroscopy (SERS) is possible.[1] SERS is useful in characterizing substances with very low detection limits, even down to single molecule spectroscopy. In ordinary Raman spectroscopy, when an analyte is irradiated with monochromatic light, each chemical compound re-radiates light according to its own unique vibrational energy spectrum. However, these signals are often too weak to detect in

comparison to the much more intense Rayleigh scattering that takes place. By intensifying this Raman signal with the surface enhancement effect caused by the silver nanoparticles, the identifying spectrum may become detectable.

1.1. Synthesis

The current process of synthesizing these wires involves a ferroelectric lithographic process. In this work, the ferroelectric substrate used is periodically poled lithium niobate (PPLN) and the deposition solution is silver nitrate ($AgNO_3$). PPLN is poled to contain electric fields that point 180° relative to each other in a periodic fashion (Figure 1a). At the domain boundary between oppositely poled regions, an anomalously large electric field exists. This field, created by screening charges at the surface, attracts conduction band electrons and causes silver nanoparticles to be preferentially deposited along the domain boundary. The deposition process involves irradiating the PPLN with a mercury lamp at approximately 325 nm. This excites the electrons in the substrate which follow the electric field to the surface of the crystal. PPLN exhibits the most silver deposition along the boundary between electric fields (Figure 1b). Nanoparticle size and shape can be modified by changing the $AgNO_3$ concentration and the deposition time. Previous work concluded that a deposition time of ten minutes with a 10^{-4} M solution concentration created the most uniform, spherical nanoparticles.[2,3,4]

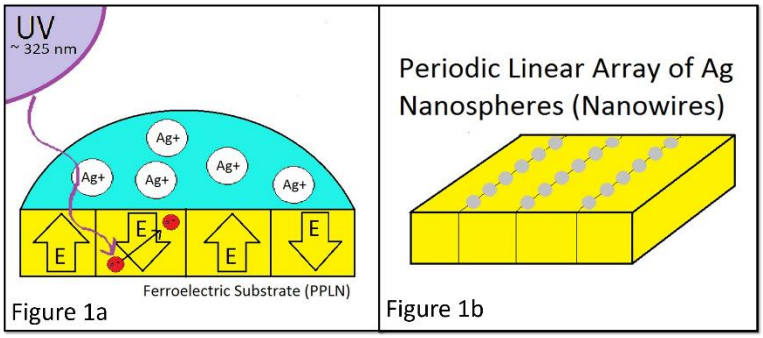


Figure 1. a) Diagram of ferroelectric lithographic process. b) Resultant silver nanowire formation.

1.2. Imaging

Characterizing these nanostructures employs the use of a scanning electron microscope (SEM). This work employs the use of a FEI Quanta 400 scanning electron microscope (SEM). Typical scanning parameters are: 25-30kV acceleration voltage and a 3.0 spot size. PPLN is a semiconductor, so careful sample preparation is required to produce clear images without charging artifacts. Typically, a conductive medium (carbon tape or colloidal graphite) is adhered to each side of the substrate to create a path for conductivity. This prevents charge from collecting on the surface of the substrate and results in a higher resolution image. Unless otherwise noted, all SEM images employ a secondary electron Everhart-Thornley detector.

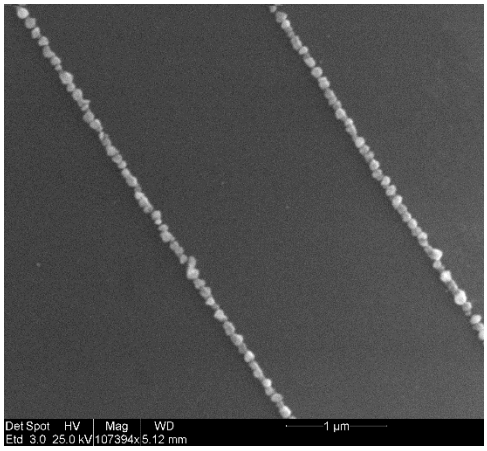


Image 1. SEM image of silver nanowires from a 10 minute deposition with 10^{-4} M $AgNO_3$ solution.

1.3. Cleaning

Normally, after characterization by SEM, the wires are removed through a modified cleaning regimen developed by former researcher, Aaron Mosey, at UNCA.[3] The samples are sonicated in acetone for ten minutes, followed by a sonication in methanol for ten minutes.

Eventually, the substrate becomes scratched due to repeated use (Image 2). This is only a problem due to the fact that unwanted interstitial growth increases with increasing surface imperfections such as scratches. Interstitial growth interferes with SERS and conductivity. A polishing process created by Mosey et al. has proven effective in removing these scratches and is employed when sample images become too scratched for proper characterization.[3]

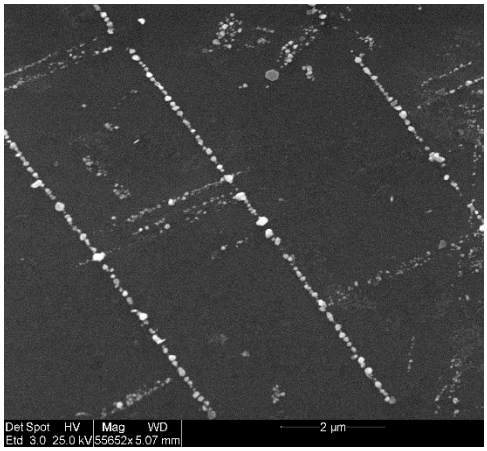


Image 2. SEM image of interstitial growth between domain boundaries.

2. Preservation of Nanostructures

After characterizing the wires in the SEM, the next desired step is to lift these wires from the substrate. This allows the substrate to be cleaned in the regimen outlined above and for the substrate to be reused while preserving the nanowires for further characterization. These substrates are analogous to a mold for growing these wires, so reusing and preserving their condition is paramount to the further study of these nanowires. This means that the mechanism of lifting must be nondestructive to the substrate and must preserve the spacing of the nanoparticles. The method must also be compatible with the cleaning regimen outlined above, leaving no residue on the substrate. Several methods have been tested in order to create this lifting procedure.

The first of these methods employed the use of a variety of two part epoxies and resins. SuperSap by Entropy Resins and RBC3200 by RBC Resins were tested using various cure times and mixing ratios. But all tests showed a common result: highly irregular surfaces at the epoxy-PPLN interface. None of these results indicated either epoxy being a suitable lifting mechanism.

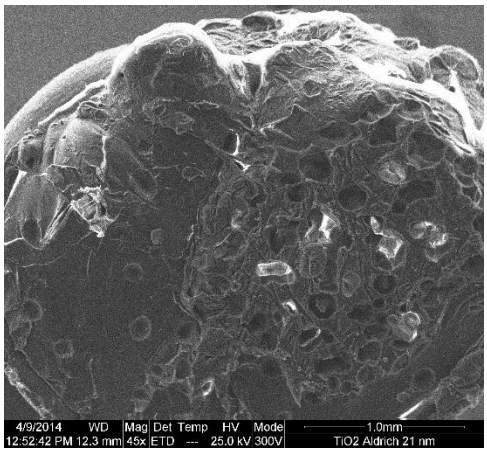


Image 3. SEM image of RBC3200 resin.

After multiple epoxies failed to give the desired results, a "stick and peel" method with carbon adhesive spectroscopy sample mounts such as those made by SpectroTab. The SpectroTab is placed onto an SEM stub and pressed into the top of the substrate (Figure 2). The two are then peeled apart, leaving very little residue on the substrate and lifting the nanoparticles without disturbing interparticle spacing. However, after the first trial, it was discovered that air pockets in the carbon tab collapse under the vacuum of the SEM. For particles lying above these air pockets, the spacing between them is expanded as the surface below them deforms (Image 4).

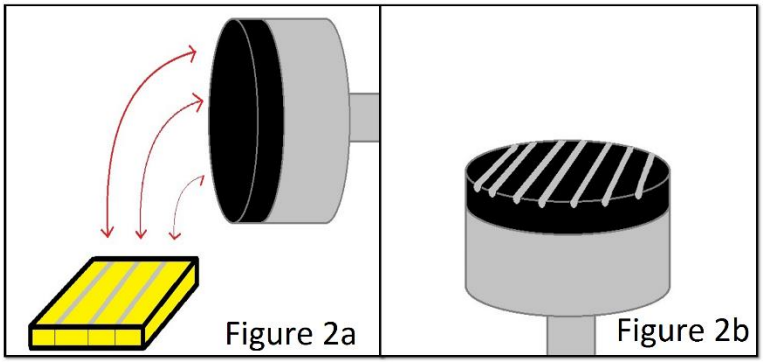


Figure 2. a) Shows silver nanowires being pressed into SpectroTab. b) Nanowires embedded in SpectroTab.

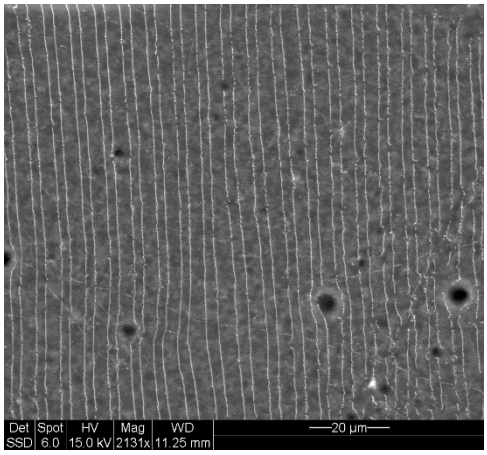


Image 4. SEM image using backscatter electron detector of silver nanoparticles in carbon tab. Dark areas indicate deformation due to SEM vacuum.

An attempt to solve this problem is to vacuum treat the carbon adhesive tab before pressing it into the wires. However, this produces an uneven surface to press the wires into which will miss some entire portions of wires. This leaves even larger gaps in the wires (Image 5). Another problem is the durability of these carbon tabs. They never cure so they are constantly soft and sticky. This can make removal of the substrate and preservation of the wires difficult (Image 6).

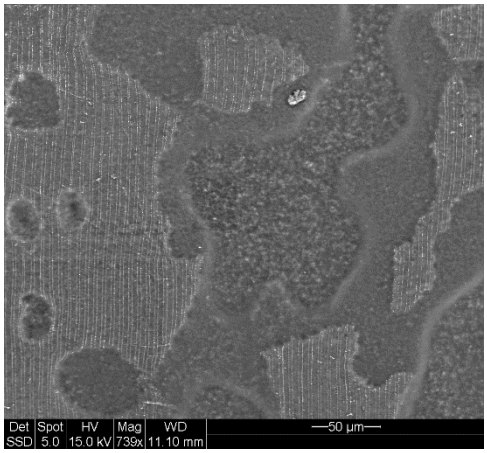


Image 5. SEM image using backscatter electron detector showing missing areas of nanowires embedded in carbon tab.

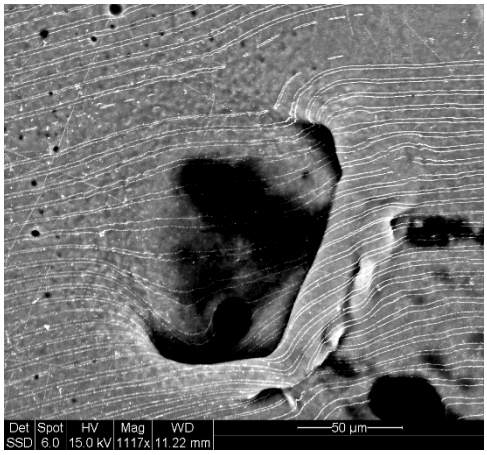


Image 6. SEM image using backscatter electron detector of nanowires disturbed by removal of PPLN substrate from carbon tab.

After conceding to the fact that epoxies, resins, and carbon tape were not the solution to this particular problem, the area of polymers began to look promising. So, polydimethylsiloxane (PDMS) was introduced. PDMS is an optically clear, two part silicon polymer. This particular polymer undergoes a crosslinking reaction during the curing process that creates a flexible polymer, very similar to vulcanized rubber. This reaction does not outgas, so there are no gas bubbles to get trapped in the polymer. This leaves a smooth surface at the interface between the substrate and polymer, a desired characteristic absent in the SpectroTab trials. The PDMS kit used for this application is the Sylgard 184 Silicone Elastomer Kit by Dow Corning Inc.

PDMS comes in two parts: the polymer and a crosslinker. For this application, a ratio of 10:1 (polymer:crosslinker) by volume is used and the crosslinking reaction takes 24-48 hours. However, varying this ratio can change the properties of cured polymer. Due to the small amounts used for each lift, the total volume of mixed polymer is kept to roughly 1.1mL (1mL of polymer and 0.1mL of crosslinker). Because PDMS is non-conductive, graphite may be added to the mixed polymer to reduce charging for future SEM imaging. Adding graphite at a ratio of .02-.04 g/mL of polymer is sufficient for SEM imaging.

When crosslinked, PDMS completely encapsulates the silver particles, preserving their positions. And, similar to most household silicone products, PDMS exhibits non-stick properties. This makes PDMS an ideal polymer to fully encapsulate and lift the silver particles from the substrate without leaving behind a residue. After lifting the wires, the silver-PDMS composite is imaged in the SEM.

Simply mixing the polymer and pouring it over the substrate with wires disturbs the positions of the particles (Image 7). Since the SpectroTab trials proved effective in lifting all the wires without displacing their positions, the same "peel and stick" method was modified to work with much more viscous polymer mixture. To prevent the displacement of the particles, the PDMS must be shaped as the SpectroTab and be pressed into the substrate (Figure 3). To create a thin layer of PDMS mixture, a lab-made spin coater is created out of a recycled computer fan, a 12V power source, and CD case as a splatter chamber. This spin-coater was not calibrated for exact speed or film thickness, but produced an ideal surface to lift the nanoparticles (Image 8). A small drop of PDMS mixture is placed on the center of a SEM sample stud and spun until the PDMS reaches the edge of the stud. After the PDMS covers the stud, the wires are pressed into the and the polymer is allowed to cure before removing the substrate, leaving the silver nanoparticles encapsulated in the PDMS and the PPLN surface free of silver and polymer residue.

Image 7. SEM image of silver nanoparticles randomly dispersed in PDMS.

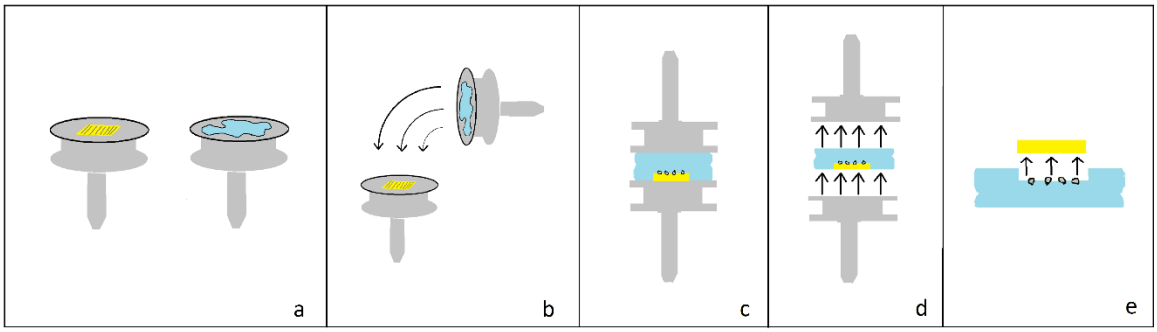


Figure 3. a) Left: PPLN with wires. Right: PDMS spin coated on stud. b) Wires pressed into PDMS. c) PDMS allowed to cure. d) After cure, studs are removed. e) PPLN is removed from PDMS leaving behind wires.

Image 8. SEM image of silver nanowires in PDMS.

3. Modification of Nanostructures

This research aims to create conductive nanowires by modifying the deposition time and solution concentration of the lithographic procedure outlined above. In order to characterize the wires, the samples will be imaged in the scanning

electron microscope. After characterization, a conductivity test will be performed on the silver-PDMS composite to check for conductivity through the wires.

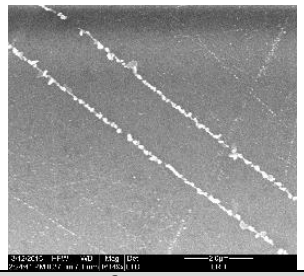
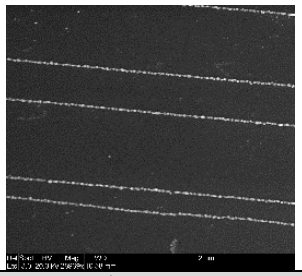
3.1. Procedure

The concentration and deposition time of the ferroelectric lithographic procedure will be varied with each deposition. The solution concentrations range from 10^{-3} M to 10^{-5} M $AgNO_3$ by powers of ten. The deposition times are five, ten, fifteen, and twenty minutes with each solution to develop a relation between wire size, deposition time, and solution concentration.

3.2. Results

A pattern emerges from these depositions: less silver in the solution requires longer deposition times to create similar wires to high concentrations at short times. This leads us to the conclusion that concentration of silver in solution is the limiting factor in this process. Below is a small sampling SEM images illustrating this correlation (Table 1). Contiguous wires, however, were not observed.

Table 1. SEM images of various solution concentrations and deposition times.

	
10^{-3} M, 5 min	10^{-4} M, 10 min

Solution concentrations and deposition times are listed below corresponding SEM image.

3.3. Conductivity Test

Even though none of the combinations of deposition times and solution concentrations used in this work produced contiguous wires, a procedure and set of materials to test conductivity have been developed. Figure 4 shows the circuit that would be used to test conductivity by measuring small currents. To connect the nanowires into the circuit, a lead is created for each sample through the use of a SpectroTab which has had a thin strip cut from the center using a 3D printed stencil (Image 9). This setup allows the spacing between the conductive leads to be carefully maintained between tests. Once contiguous wires are observed, this circuit and procedure will be capable of measuring conductivity of any 2D system of nanostructures.

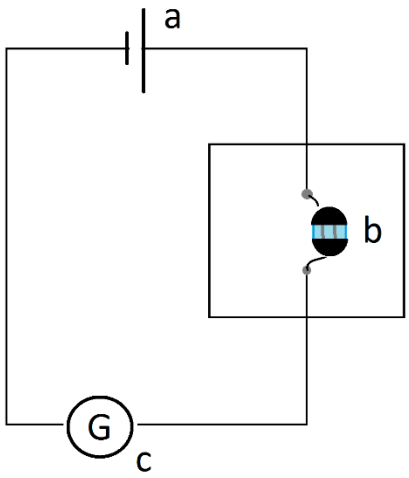


Figure 4. a) 12V DC power supply. b) PDMS sample with silver nanowires and carbon tab lead. c) Galvanometer.

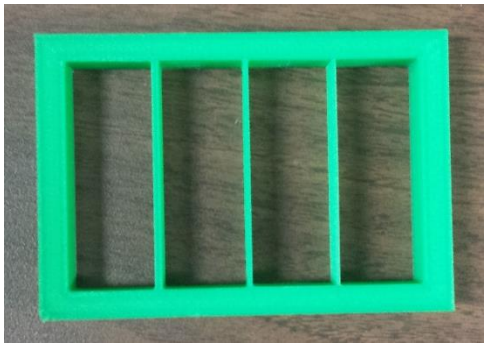


Image 9. Stencil manufactured to create sample leads. Slice size from right is 1.5mm, 1mm, and .5mm.

4. Conclusion

PDMS is an excellent polymer to lift ferroelectric lithographic nanostructures from their growth substrates. In fact, this lifting method could be applicable to other bottom up nanostructures. While much progress was made in lifting the nanostructures, the modification of such structures into conductive, contiguous wires requires more work. It has been shown that by varying solution concentration and deposition time, the shapes of and spacing between the nanoparticles may be changed. It seems that lower concentrations of solution have more promise of producing contiguous wires than higher solutions. Also, longer deposition times create larger structures with complex and undesired shapes (like platelets). Whether these two variables may be finely balanced enough to produce continuous silver nanowires must be left to future work.

5. Acknowledgements

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6. References

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