University of North Carolina at Asheville
Journal of Undergraduate Research
Asheville, North Carolina
May 2013

Effects of Electron Bombardment on the Controlled Synthesis of Silver Nanostructures using Ferroelectric Lithography

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Abstract

This study examines the controlled synthesis of silver nanostructures onto a patterned ferroelectric substrate via photo reduction of aqueous silver nitrate. Effects of electron bombardment incident upon the ferroelectric substrate by scanning electron microscopy (SEM) will be discussed. The ferroelectric substrate is exposed to ultraviolet (UV) radiation in the presence of aqueous silver nitrate during which silver ions in solution are photo reduced at the surface creating adsorbed silver nanostructures. Placement of the nanostructures is directly dependent upon the poled domains of the ferroelectric crystal. Varying several parameters including nitrate molarity, UV source strength, and exposure times can control characteristic size and shape of the nanostructures. Visual analysis of the nanostructures requires the use of scanning electron microscopy, which inadvertently alters the poling characteristics of the substrate.

Keywords: Silver Nanostructures, Electron Bombardment, Ferroelectric Lithography

1. Introduction

This work seeks to improve upon methods of silver nanowire synthesis in an easily reproducible manner for applications in Raman spectroscopy. Specifically to improve the spatial sensitivity of surface enhanced Raman spectroscopy (SERS). SERS is an enhanced spectroscopic method implementing molecular vibration modes[1]. In Raman a sample to be tested, or analyte, has an argon ion laser beam bounced off of it[2]. The reflected beam carries vibrational mode information in the form of a wavelength shift from the incident laser beam. A spectrometer takes the reflected beam and extrapolates the data through precise measurements of the wavelengths and intensities. SERS is the incorporation of a specialized substrate that the analyte is place onto[2]. This substrate contains an array of randomly placed silver nanowires. These wires are of the appropriate size and shape to have a surface plasmon frequency that is nearly identical to the argon laser's wavelength.

The plasmon resonance describes the collective oscillation of the valence band electrons of the atoms[3]. The frequency at which plasmon resonance occurs is controlled through geometric parameters such as size and shape of the particles. A perfectly spherical silver nanoparticle with a 100nm diameter contains approximately 41.8 million silver atoms. The plasmon resonance frequency is also a broad peak such that an accuracy of plus or minus a nanometer wavelength will still result in a high excitation. It is this excitation that leads to a major amplification of the electric field within the immediate vicinity of the nanoparticle[4]. This electric field not only enhances the incident laser beam but it amplifies the emitted Raman signal thus amplifying the Raman scattering by factors of up to 10 billion times. This only works if the analyte is in this immediate vicinity of the enhanced electric field. Creation of an aqueous solution of the analyte and inundating the substrate is a sufficient method of getting the analyte in this enhancement area. Molar concentration requirement of the aqueous solutions that are typically very low (~0.0001M) tend to be sufficient for SERS[3].

Typical SERS substrates do not have spatially dependent surface enhancement. Essentially a macromolecule, such as DNA that is surface enhanced will have all bonding constituents enhanced showing the ATCG bonding but no information that would indicate order of these chemicals, just their existence in the sample[5]. If however there could be a spatially dependent area of enhancement that were small enough to provide enhancement of sections of the macromolecule then perhaps more information can be achieved with SERS.

This research goal is to create the spatially dependent SERS substrate via ferroelectric lithography to be able to obtain structure sequence and arrangement to complement the standard SERS chemical bonding analysis. This may be theoretically accomplished through the synthesis of a nanowire of silver that resembles a pearl-necklace. This linear arrangement of spherical balls of silver is preferred over a continuous cylindrical wire of silver because curvature or aspect ratio is one of the major geometric parameters influencing the resonant plasma frequency. A more desired result is achieved with the pearl-necklace model, however it is not as easy to synthesize as a solid cylinder. A new method that incorporates electron bombardment into the ferroelectric lithographic techniques has been discovered to potentially be quite useful for this research.

2. Methods

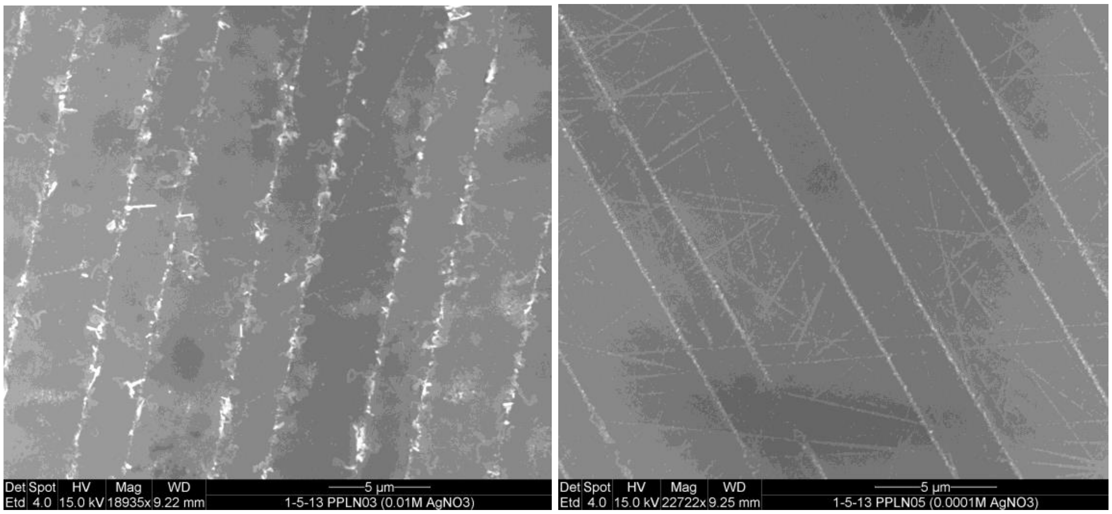
The periodically poled ferroelectric substrate lithium niobate $LiNbO_3$ (PPLN) is pre-cut into wafers of the following dimensions: 2.5mm x 5mm x 0.5mm. The deposition face is either of the larger 2.5mm x 5mm planes of the PPLN. The silver nanospheres are derived from a low molarity solution of aqueous silver nitrate $AgNO_3$. The method of silver nanosphere growth and linear wire formation is achieved simultaneously via photo-reduction at the surface. The PPLN is first cleaned in several ultrasonic baths of acetone $(CH_3)_2CO$ ranging from 5 to 20 minutes each with periodic changing of the acetone. Post ultrasonic bath, the PPLN is thoroughly rinsed in deionized water ~16M ohm-cm, then dried with nitrogen gas, then SEM (scanning electron microscope) analyzed for verification of cleanliness. Then a conductive graphite paste is used as an adhesive to secure the PPLN to a standard mount SEM stub. The sample is then secured in a holding device that secures the stub with the deposition face of the PPLN level and facing up. Next, the sample and stub surface are inundated in aqueous silver nitrate $AgNO_3$ and placed in a chamber that exposes the entire stub and sample to high intensity ultraviolet (UV) light. Post UV exposure, the sample is again rinsed with deionized water and blown dry with nitrogen. At this point the SEM is used to analyze the silver nanostructures that have adsorbed to the surface during the UV exposure. Once a recipe yielding promising nanostructures for SERS has been achieved, the PPLN crystal's ferroelectric properties are altered with electron bombardment from an electron gun in a vacuum.

The photoreduction that occurs at the surface is an example of the photoelectric effect. Given that PPLN has a band gap of around 4eV, many of the spectral lines emitted from a typical mercury tube UV source meet or exceed this band gap via wavelength to energy conversion. Upon exposure of the PPLN to the UV, electrons are brought into the conduction band where silver ions in the aqueous nitrate solution are present since the sample is fully inundated. Since the free silver ions in solution have a slight positive charge and the electrons brought to the surface of the PPLN from UV light are negatively charged, the silver ions adsorb to the surface one at a time. The electric poling properties of the PPLN allow wires to form and will be discussed later in the results section.

3. Results

3.1 Nitrate Molarity Dependence

The silver nitrate concentration is a major factor in the determination of what size and shape nanoparticles will be formed at the surface of the PPLN. While holding the UV source intensity constant for all experimentation the only remaining variable factors are nitrate molarity and UV exposure time. Experimental nitrate concentrations used varied between 0.1M AgNO3 and 1.0x10-5 AgNO3 linearly by factors of 10. The concluding result is that given a specific time and UV intensity, there is an ideal molarity of nitrate that will produce close to ideal, spherical silver nanoparticles. In theory and practice, if too high a concentration is used, then ions are photo-reduced out of solution too quickly and the silver grows tall flakes that then fall over due to gravity and nonsymmetric growth. The flakes form because of an excess of silver ions in the solution. During the photo-reduction as soon as an electron migrates to the surface there is a silver ion readily available one after the other and a chain reaction occurs forming the undesirable ‘flaky’ silver features. On the other hand if the nitrate concentration is too weak then the entire process of depositing silver ions take a long time. It is less likely that an ion will be present when the electron is formed such that the entire reaction takes longer overall. This isn’t a problem for the silver nanowires formed; however other areas of the ferroelectric substrate adsorb excess, undesirable interstitial silver. Interstitial silver refers to silver that adsorbs to the PPLN in areas between the domain boundaries where the wires should form. This silver skews the spatially dependent SERS that is to be tested because random areas may have surface enhancing characteristics. Currently this isn’t an avoidable obstacle given the parameters of the poling on the lithium niobate. More on this will be discussed later.



(1a) (1b)

Figure (1a) – Too high a molarity concentration (0.01M $AgNO_3$) yielding ‘flaky’ features.
Figure (1b) – Too low a molarity concentration (0.00001M $AgNO_3$) yielding excess interstitial features

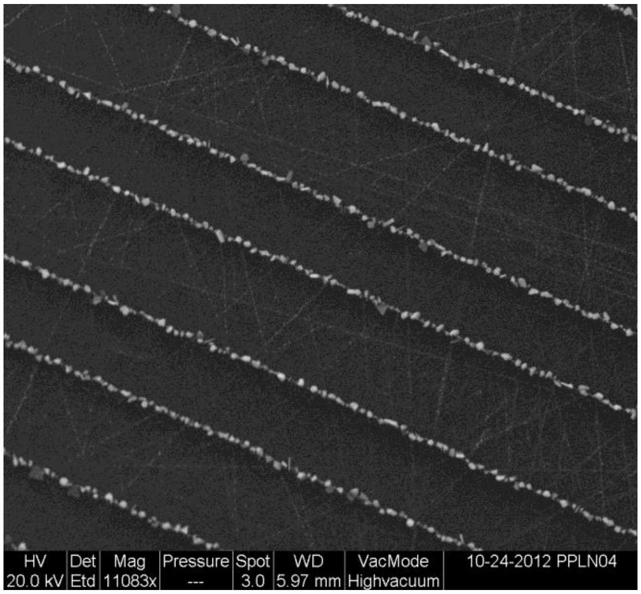


Figure (1c) – A close to ideal nitrate concentration (0.001 $AgNO_3$) for a given UV intensity yielding nice looking ‘pearl-necklace’ wires with minimal interstitial silver.

3.2 UV Exposure Time Dependence

Theoretically using too long of a UV exposure time utilizing ultra low concentrations will be less ideal than a short exposure using significantly higher nitrate concentrations. This is due to the creation and migration of electrons within the lithium niobate crystal. Because of the electric fields induced in the crystal, the electrons will actually be forced toward different areas of the crystal after being brought to the conduction band. The wires form preferentially at the domain boundaries of the poled crystal. This is the narrow region between an area poled upward (+C plane) and orthonormal to the surface of deposition and an area poled downward (-C plane) and orthonormal to the surface of deposition. At the domain boundaries the electric field must be continuous as defined by gauss' law therefore the electric field becomes very strong here where the polarity of the electric field reverses. This strong electric field causes more electrons to migrate toward the area, yielding the potential for a preferential adsorption of silver nanowires.

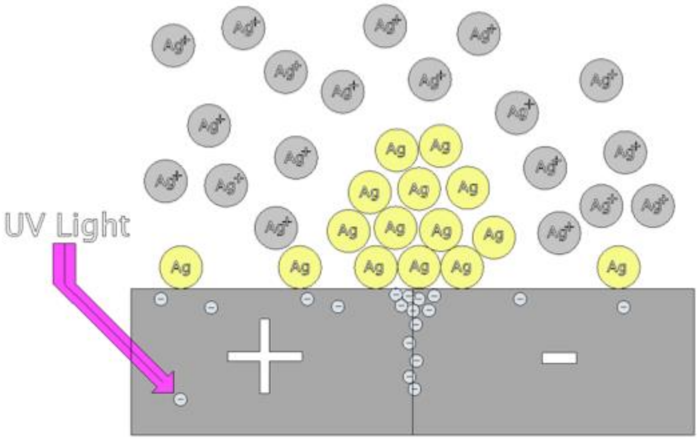


Figure (2a) – The +C plane accrues a higher concentration of deposition surface electrons than the –C plane (see figure 2b). The yellow silver ions represent successful adsorption to the surface. The gray silver ions are positively charged and potentially available for adsorption in the presence of an electron at the deposition surface.

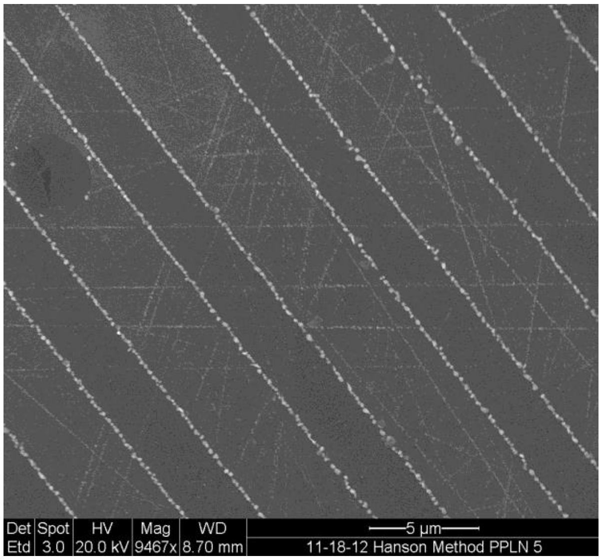


Figure (2b) - Evidence that agrees with figure 2a is visible in this deposition. Notice that the +C plane accumulates a higher amount of interstitial silver when compared to the –C domains.

3.3 Electron Bombardment Effects

During experimentation the reusability of each crystal is financially important. Continual SEM analysis was theoretically suspected to potentially have negative effects on the electrical poling. To test such a hypothesis, an area of the PPLN was selected and bombarded with electrons from the SEM electron gun under high vacuum for approximately 12 hours at 30kV accelerating voltage. Post bombardment, the PPLN was deposited using the same experimental parameters and techniques used that yielded the results in figure (2b). Then the sample was re-examined to confirm or deny negative SEM effects applicable to our experimentation techniques.

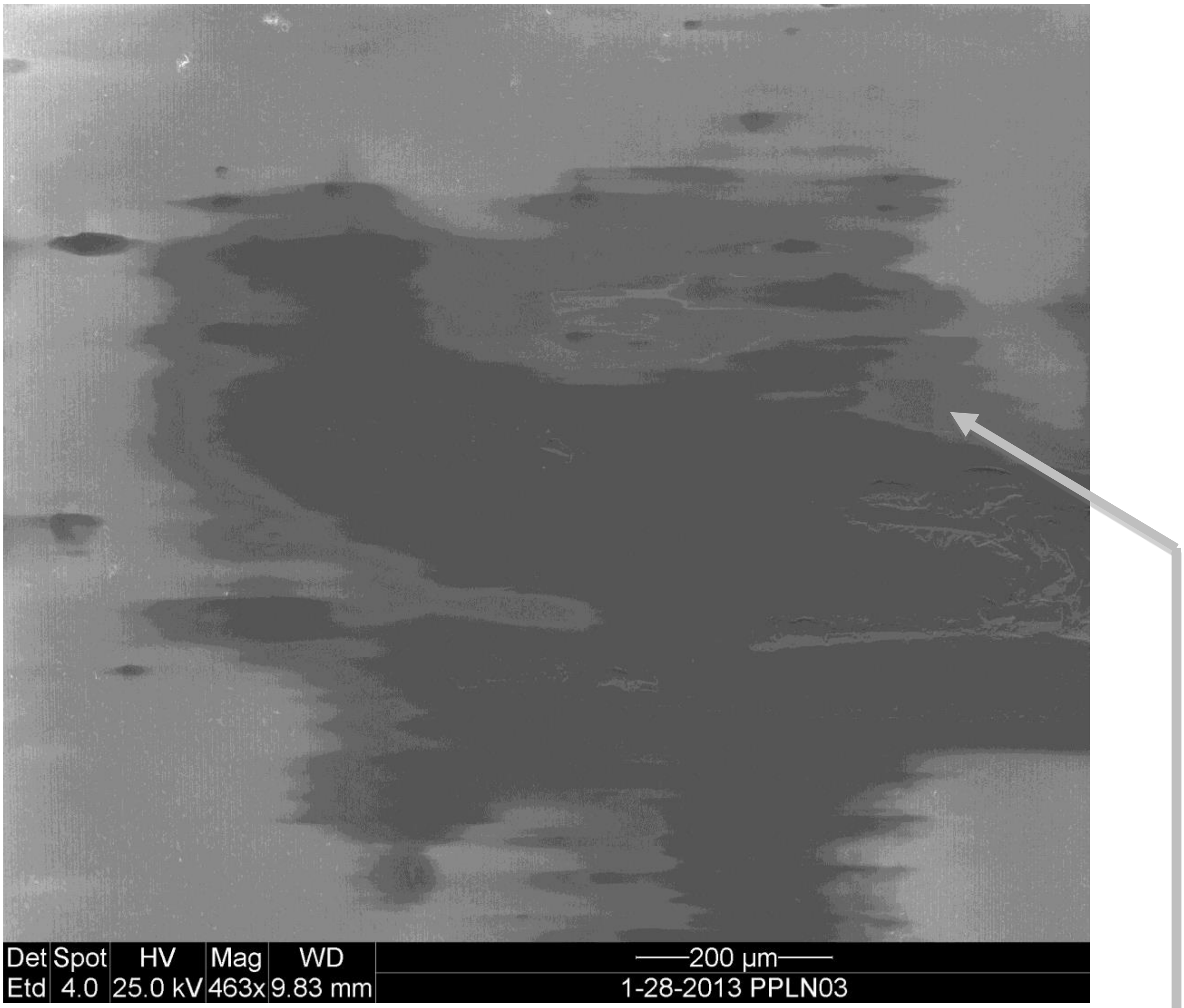


Figure (3a) – The square of electron bombardment is slightly visible under low magnifications and was placed next to a surface scratch (right) so that it could be easily located later. The dark areas are artifacts due to excess surface charging as the PPLN is a non-coated semiconductor it's imaging characteristics are less than ideal for SEM.

The arrow indicates the upper right hand corner of the area of electron bombardment. The rest of the square is darker than the surrounding region due to a lack of silver deposition.

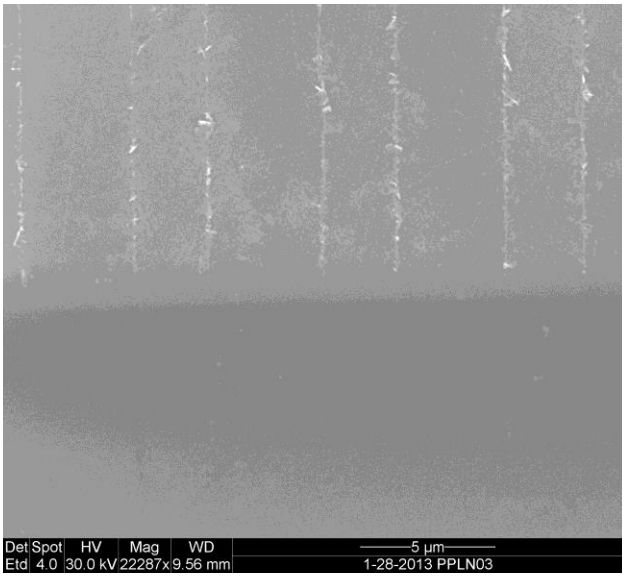


Figure (3b) – A zoom in of the area of electron bombardment shows that the disruption to the electric field does have a low diffusion lapse rate linearly across the surface of the PPLN (~ 3-4 microns).

4. Discussion

4.1 Analysis of De-poling PPLN via SEM

In theory it has been deduced that the de-poling effects are a result of the interaction volume produced from the incident electron beam. It has been shown that even after a 24 hour bombardment, the penetration of the de-poling does not continue all the way through the crystal to the other side, which would require a penetration depth of approximately 0.5mm. Since the interaction volume is proportional to the accelerating voltage but is still limited to a depth of approximately 0-6 microns this would account for the one-sided de-poling of the PPLN. This follows since within the interaction volume is an area of high electron activity. Upon interaction with the solid the electrons begin scattering on impact and cumulatively move in all directions within the interaction volume. The individual movement of the electrons must electrically pole the lithium niobate in the direction of travel; however, the cumulative movement of all the incident, secondary and backscattered electrons leaves no net poling of the crystal due to scattering geometry. As for the continual imaging of the PPLN, it has been shown that as little as 5 hours of 30kV electron bombardment at a medium raster rate significantly harms the potential for wire formation in the region of bombardment. In conclusion if repeatability of the PPLN is to be successful, rapid imaging techniques should be employed to minimize the de-poling effects. Approximately 2 hours of imaging in one area at 30kV would cause enough damage to require the retirement of a sample. Imaging different areas of the sample after each deposition should allow the reuse of samples many times. Therefore a properly implemented plan of rapid and progressive imaging will allow repeatable depositions to be made to a single sample without significant alterations to the wires.

4.2 Electron Bombardment Induced Lithographic Techniques

Discovery of the SEM's ability to de-pole the ferroelectric lithium niobate has led to the idea of using it to eliminate interstitial silver. Through a multistage process of depositing and creating two de-poled areas, a single isolated nanowire could be placed between the de-poled regions without the presence of interstitial silver in the immediate vicinity. Future work hopes to show that this can be accomplished to create a single silver nanowire suitable for spatially dependent SERS analysis and testing.

5. Acknowledgements

I would like to thank my research colleagues Aaron Mosey and Athby Al-Tawhid. I would also like to thank my advisor and mentor Dr. James R. Perkins for his continued support and guidance. Without these people and without the support of the university's undergraduate research program this study would not have been possible.

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