University of North Carolina Asheville
Journal of Undergraduate Research
Asheville, North Carolina
May 2018

Techniques for Studying the Lithographic Development of Silver Nanoparticles on a Periodically Poled Ferroelectric Template

Daniel Gallimore
Department of Physics
The University of North Carolina Asheville
One University Heights
Asheville, North Carolina 28804 USA

Faculty Advisor: Dr. James Perkins

Abstract

This research develops techniques for studying the lithographic development of silver nanoparticles on a periodically poled ferroelectric template. These include an algorithm for tracking POIs on the surface of the substrate following a change in the substrate's position and orientation, and a verified procedure for removing residual silver nanoparicles from the surface of the substrate. This will allow future research to better control nanoparticle development, particularly the shape and size of the nanoparticles, an essential step in facilitating a technique called surface-enhanced Raman spectroscopy (SERS), which has applications in detecting single macromolecules[1].

1 Introduction

Raman spectroscopy uses the inelastic, or Raman, scattering of light to infer the presence of molecules within a sample. However, the infrequency of an individual photon scattering inelastically restricts the usefulness of this technique—in small samples, the Raman scattering events number too few to be detectable. SERS modifies the standard technique, causing light to scatter inelastically much more frequently, enabling researchers to identify molecules present in only trace amounts. SERS has even been used to correctly infer the presence of single macromolecules[1].

When a photon scatters from a molecule, the scattering event is inelastic if the energy of the outgoing photon differs from the energy of the incident photon. In Stokes Raman scattering, the photon exits the scattering event at a lower energy than it arrived with. The energy lost by the photon is gained by the molecule, causing the molecule to rotate and/or vibrate[2]. However, the precise amount of energy lost by the photon is uniquely determined by the molecule it scattered from. Thus, the molecule involved in the scattering event can be identified by the "fingerprint" it leaves on the outgoing light.

By contrast, light incident on a molecule typically experiences elastic, or Rayleigh, scattering. In this scenario, the outgoing photon has the same energy as the incoming photon. Hence, Rayleigh scattered light provides no indication of the molecules it scattered off of. At 1000 times the intensity of Raman scattered light, Rayleigh scattered light also masks the molecular signatures written in each inelastic scattering event[2].

One way to address this problem is to simply increase the sample size: even though it is rare for any single molecule to scatter light inelastically, a large enough sample will still produce enough Raman scattering events to be detectable. However, SERS is a more sophisticated approach that increases the likelihood of Raman scattering near the sample, making much smaller sample sizes viable. This can be accomplished by including metallic nanoparticles in close proximity to the sample, which locally enhance Stokes Raman scattering[2].

In past research, metallic silver nanoparticles were developed for the purpose of locally increasing the likelihood of Raman scattering[3]. However, that research did not produce a method for developing nanoparticles with the specific dimensions needed to facilitate SERS. In this research, techniques are discussed that allow researchers to exert more control over the development of silver nanoparticles. These include a technique for relocating POIs after the orentation

of the substrate has been altered, as well as a cleaning procedure that allows the same substrate to facilitate consecutive, independent depositions.

2 Methods

In this research, a 10^4 M AgNO3 solution is photoreduced onto the electric domain boundaries of a periodically poled lithium niobate substrate using a UV light source. The UV light is absorbed by loosely bound valence electrons, causing them to conduct. Free electrons then move preferentially toward the electric domain boundaries of the substrate due to the strong electric field at these locations. When a silver cation encounters an electron near a domain boundary, silver is selectively photoreduced onto the substrate. This creates closely-spaced metallic silver nanoparticles aligned along the domain boundaries.

The nanoparticles are imaged using scanning electron microscopy (SEM). Before being inserted into the microscope, a substrate is attached to a plastic stage using a mix of graphite and isopropyl alcohol. A small rectangle of conductive tape connects a small section of the top surface of the substrate to the dried graphite to prevent excessive charging effects from the microscope. The microscope identifies points in its observation area with coordinates on a Cartesian grid, which is useful for relocating POIs after changing the orientation of the substrate.

The initial procedure for cleaning the substrate was to sonicate the plastic stage (with substrate attached) in acetone for 5 minutes, or until the substrate separated naturally from the stage. The substrate was then sonicated on its own for an additional 15 minutes in acetone, followed by 15 minutes in methanol. In the course of this research, this cleaning procedure was shown to be inadequate. A revised cleaning procedure is included later in the article.

3 Results

3.1 Locating the Nanoparticles

Consider a POI on the surface of the substrate with coordinate P. Given two corners of the substrate, A and B, define a vector $\boldsymbol{u}$ from A to P and a vector $\boldsymbol{v}$ from A to B. Following a change in the position and orientation of the substrate—e.g., after being removed from the microscope and inserted some time later—the POI will no longer be at P. Using the new positions of the corners, A' and B', one can determine the new position P' of the the POI.

Let $\boldsymbol{u}'$ and $\boldsymbol{v}'$ extend from A' to P' and A' to B', respectively. Following the theme established so far, the primes indicate that these are the vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ following a change in the position and orientation of the substrate (relationships between the unprimed and primed quantities are summarized in Figure 1). Denote the angle between $\boldsymbol{v}'$ and $\boldsymbol{v}$ with θ. Since $\boldsymbol{v}$ has not moved relative to the substrate, this is actually the angle through which the entire substrate is rotated. Thus, θ is also the angle between $\boldsymbol{u}'$ and $\boldsymbol{u}$.

Let $\boldsymbol{v} = \langle v_1, v_2 \rangle$ and $\boldsymbol{v}' = \langle v_1', v_2' \rangle$. These components are known since $\boldsymbol{v}$ and $\boldsymbol{v}'$ are determined by A, B, A', and B'. Let φ and φ' be the angles made by $\boldsymbol{v}$ and $\boldsymbol{v}'$, measured counterclockwise from the positive horizontal axis. In this method, these angles are defined such that $\tan\varphi = v_2/v_1$ and $\tan\varphi' = v_2'/v_1'$. To prevent the tangent function from blowing up, the values of φ and φ' are restricted exclusively between $-\pi/2$ and $\pi/2$. (There is a small but finite possibility that the substrate will be placed such that φ or φ' equals $-\pi/2$ or $\pi/2$, which is not compatible with this method. To ensure that this method remains viable, the substrate is always inserted into the microscope diagonally.) For vectors lying in the right half of the plane, this method measures φ and φ' with respect to the positive horizontal axis as anticipated. However, for vectors lying in the left half of the plane, these angles are measured counterclockwise with respect to the *negative* horizontal axis. Thus, a vector with a positive angle in the left half of the plane will actually lie *below* the negative horizontal axis. Since θ is the angle between $\boldsymbol{v}'$ and $\boldsymbol{v}$ (that is, counterclockwise *from* $\boldsymbol{v}$ to $\boldsymbol{v}'$), knowing φ and φ' gives a description of θ:

$$\theta = \varphi' - \varphi. \tag{1}$$

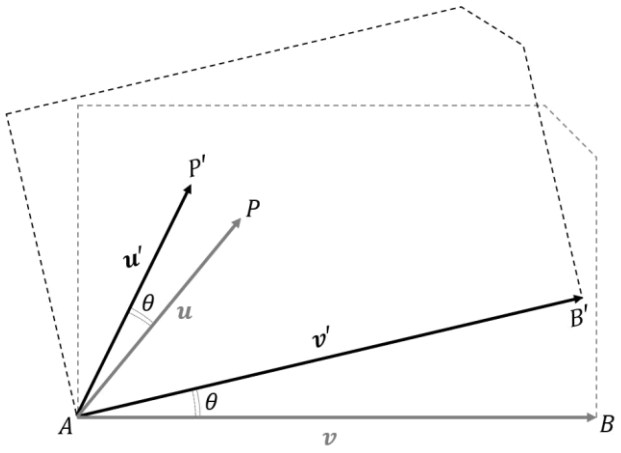


Figure 1: To emphasize the angles between vectors, A is set equal to A'. However, the two will in general differ. Note that the angle between $\boldsymbol{v}'$ and $\boldsymbol{v}$ is also the angle between $\boldsymbol{u}'$ and $\boldsymbol{u}$.

For the following, refer to Figures 2a and 2b. If sgn $v_1 =$ sgn v_1' (that is, both vectors lie in the same half of the plane), then rotating $\boldsymbol{v}$ counterclockwise by θ aligns it parallel to $\boldsymbol{v}'$. However, if sgn $v_1 = -$sgn v_1', then rotating $\boldsymbol{v}$ counterclockwise by θ aligns $\boldsymbol{v}$ *anti*parallel to $\boldsymbol{v}'$. Multiplying the resulting vector by -1 completes the transformation. Note that this is the same transformation that takes $\boldsymbol{u}$ parallel to $\boldsymbol{u}'$. Mathematically, the transformation (assuming sgn $v_1 = -$sgn v_1') takes the following form:

$$R(\varphi' - \varphi) = \begin{pmatrix} \cos\varphi' & -\sin\varphi' \\ \sin\varphi' & \cos\varphi' \end{pmatrix} \begin{pmatrix} \cos(-\varphi) & -\sin(-\varphi) \\ \sin(-\varphi) & \cos(-\varphi) \end{pmatrix}. \tag{2}$$

We invite the reader to verify this numerically. We arrive at this combination by substituting $\varphi' - \varphi$ in the counterclockwise (vector) rotation matrix $R(\theta)$. Note that the counterclockwise rotation matrix for an angle of $-\varphi$ is applied to the vector first. While the two rotation matrices commute in this context, rotating first by $-\varphi$ takes $\boldsymbol{v}$ to the positive horizontal axis (assuming $\boldsymbol{v}$ starts in the right half of the plane), making it easier to visualize the destination of the next rotation by φ'.

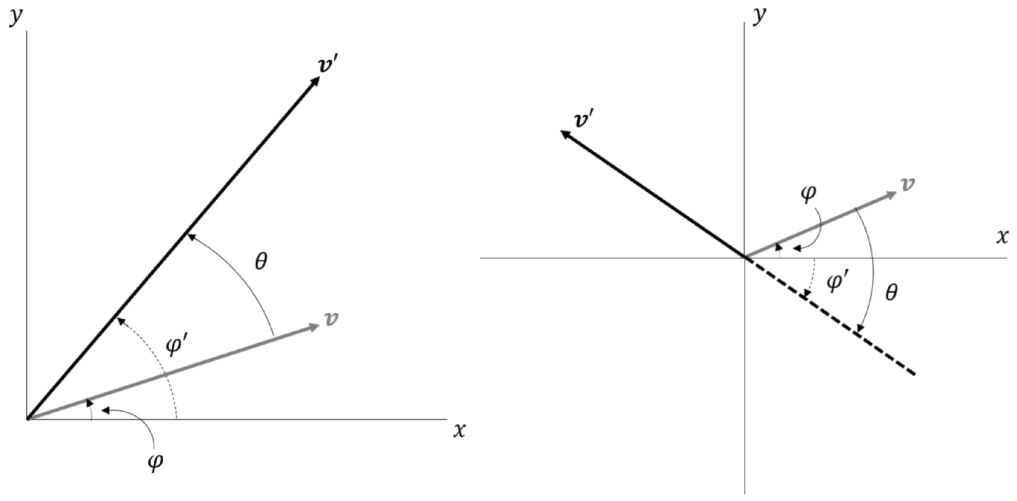
Applying this transformation to $\boldsymbol{u}$ will give us the direction of $\boldsymbol{u}'$. However, it will also reveal one final problem. Due to the challenge of consistently positioning the sample tray the same distance from the microscope objective, $\boldsymbol{v}$ will in general be scaled differently from $\boldsymbol{v}'$. Thus, after rotating $\boldsymbol{u}$, multiply by $\|\boldsymbol{v}'\|/\|\boldsymbol{v}\|$ to correct for the change in scale. This successfully transforms $\boldsymbol{u}$ into $\boldsymbol{u}'$, which finally gives the new position of the POI relative to A' since $P' = A' + \boldsymbol{u}'$.

3.2 Cleaning the Substrate

A section of lintless cloth is saturated with (95.9%) acetone and wiped across the surface of the substrate in one motion. This is done three times, after which the cloth is discarded. The substrate is then sonicated for 20 minutes in acetone and again for 20 minutes in (99.9%) methanol. A new section of lintless cloth is soaked in acetone, and the procedure is repeated two more times.

4. Discussion

In practice, the POI locating algorithm will not exactly locate the the new positions of POIs after reorienting the substrate due to a lack of precision in the coordinate system of the microscope itself. It is more useful for monitoring small regions of the substrate than it is for tracking individual points.



(a) (b)

Figure 2: Arrows at the end of arcs emphasize that angles measured counterclockwise are positive. Arrows pointing in the clockwise direction indicate negative angles. In (a), sgn $v_1 = \text{sgn } v_1'$, whereas in (b), sgn $v_1 = -\text{sgn } v_1'$.

However, the algorithm was used to determine that the cleaning procedure used in previous research[3]—which only used sonication in acetone and methanol for a brief period of time, and used no abrasive—was not sufficient for completely removing silver nanostructures. After this cleaning procedure was applied, it was often the case that scattered patches of nanoparticles were removed, with most remaining intact. In addition, particularly prominent silver structures could be relocated exactly. After meticulously reviewing the progress of various cleaning procedures at regular intervals, the procedure proposed in Section 3.2 was developed. This procedure allows a single substrate to be used for consecutive, independent depositions, creating a more controlled environment in which to analyze the nanoparticles' development.

In the future, the POI locating algorithm could be used to develop a more effcient cleaning procedure. It could also be used to closely monitor the development of specific regions of nanoparticles under different growth conditions.

5. Acknowledgments

The author wishes to express his appreciation to Adviser Dr. James Perkins, the UNCA Undergraduate Research program, and the UNCA Physics Department.

6. References

1. Katrin Kneipp et al, “Single Molecule Detection Using Surface-Enhanced Raman Scattering (SERS),” Physical Review Letters 78, no. 9 (1997): 1667.
2. James Perkins, “Raman Spectroscopy: in situ Characterization of Growth and Surface Processes” (PhD diss., North Carolina State University, 2007), 2-8.
3. Robert E. Morris, “Effects of Electron Bombardment on the Controlled Synthesis of Silver Nanostructures using Ferroelectric Lithography,” adv. James Perkins, University of North Carolina at Asheville Journal of Undergraduate Research (2013): 508-514.