

PREPARATION OF LITHIUM NIOBATE FOR SILVER NANOWIRE SYNTHESIS BY MECHANICAL POLISHING

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Abstract

Mechanical polishing is shown to reduce interstitial deposition between silver nanowires patterned on a ferroelectric substrate. The hysteretic electric field of periodically poled ferroelectric lithium niobate (PPLN) exhibits an anomaly at the 180-degree domain boundary. Under ultraviolet excitation, net electronic drift at domain boundaries facilitates preferential photoreduction of silver, thereby creating nanowires. Metallic nanopatterned arrays created by this method lend themselves to applications as surface enhanced Raman substrates or conductors in miniaturized integrated circuits. However, imperfections and discontinuities on the PPLN surface cause interstitial silver growth. An easily repeatable mechanical polishing technique is presented to improve surface quality and thus eliminate the unwanted on-domain growth. Wires are characterized using scanning electron microscopy.

Keywords: Lithium Niobate, Silver Nanowire, Polishing

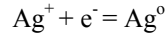
1. Introduction

Recent technological advances require the control of particles down to the atomic scale. This field, called nanoscience, promises immediate engineering applicability in emerging technologies demanding miniaturization. Currently, the research of metallic nanowires has shown great promise due to their applicability in electronic circuits, biosensors and biodetectors¹⁻⁴. In particular, the ability of silver to retain conductivity on the nanoscale as well as exhibit plasmon resonance makes it suitable for use as a Surface Enhanced Raman Spectroscopy (SERS) substrate with increased spatial tunability^{1,2,5}.

Methods for silver nanowire production range in complexity and feasibility as well as scope. Much attention has been given to Ferroelectric Lithography (FL), a liquid-phase deposition process that produces controlled patterned self-assembled silver nanostructures with variable size and aspect ratio parameters³ using a minimum of technical requirements¹⁻⁸. In silver nanowire FL, a periodically domain-patterned ferroelectric crystal is used as a substrate for the controlled photoreduction of silver onto its surface. At the domain boundaries arrays of spherical nanostructures on the order of 30-150nm can be arranged to form wires with characteristics dependent upon light intensity, silver ion solution concentration, deposition time, and temperature^{3,4,9}.

Ferroelectrics exhibit spontaneous polarization⁶ resulting from a net dipole switching due to crystallographic change under coercion of an applied external electric field. An ideal ferroelectric for this process is Lithium Niobate (LN), LiNbO_3 . Crystalline LN exhibits 180 degree domain switching^{7,8} which allows for the establishment of alternating domains of positive (corresponding to +C plane) or negative (corresponding to -C plane) electric field. At the domain boundaries an anomaly is exhibited by the hysteretic electric field. Screening charges on the surface of PPLN allow for nucleation and thus self-assembly of molecules. The localized electronic properties of the domain boundaries, due to electric field anomaly, may be utilized for controlled nanostructure synthesis.

During ferroelectric lithography, the PPLN substrate is immersed in an aqueous solution of AgNO_3 and irradiated by continuous UV light on the order of the LN's excitation bandgap, $\sim 3.9\text{eV}$ causing net electronic drift towards the domain boundaries. Screening charges accumulate at the surface of the domain boundaries precipitating adsorption to the PPLN surface and subsequent nucleation of Ag according to the following reaction:



Conductive properties retained by the metallic silver nanostructures allow electrons to move freely, allowing further nucleation. In this way, self-assembly of silver nanospheres occurs until UV irradiation is discontinued and equilibrium is achieved. Size and shape of resultant nanostructure is mostly dependent upon molecular concentration of AgNO_3 and intensity^{8,4}. Figure one illustrates this process.

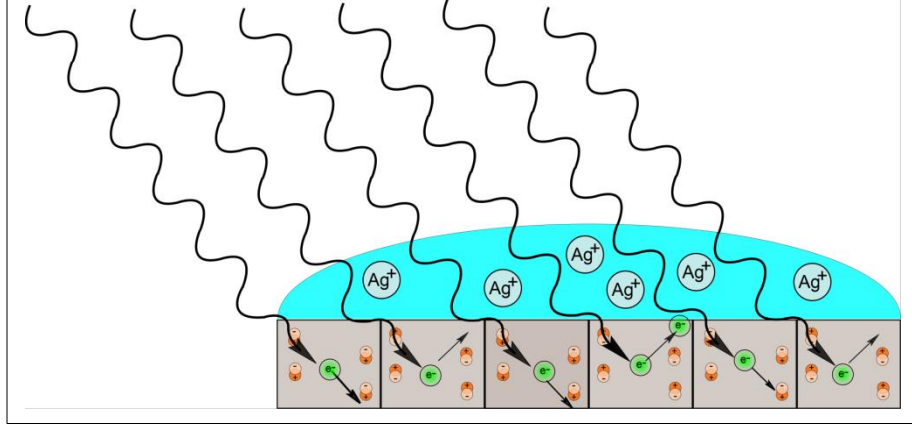


Fig. 1.

While deposition occurs on the domain boundaries, it also occurs interstitially preferentially on the +C (fig. 2) face as well as by the formation of trans-domain structures which resemble scratches (fig. 3) and other surface imperfections. Screening charge accumulation on the +C face and in discontinuities on the face of the wafer contribute to and cause unwanted interstitial growth. Commercially prepared PPLN has particularly poor surface conditions inherent from its manufacturing process. It is therefore necessary to develop a method of mechanical polishing in order to reduce interstitial growth. It is shown that imperfections and discontinuities contribute to interstitial growth and that the method of mechanical polishing developed in this paper greatly reduces the unwanted interstitial deposition. Furthermore, during characterization by scanning electron microscopy, surface polarization is reduced⁹. Mechanical polishing can refresh the surface and improve nanowire quality.

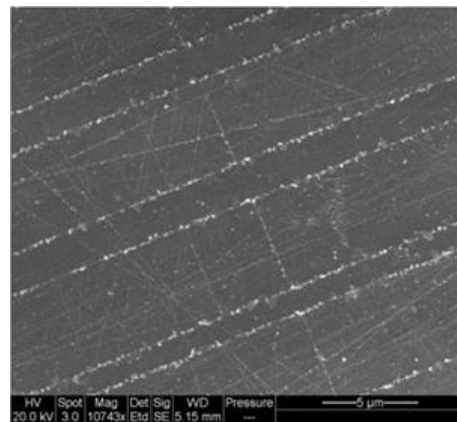
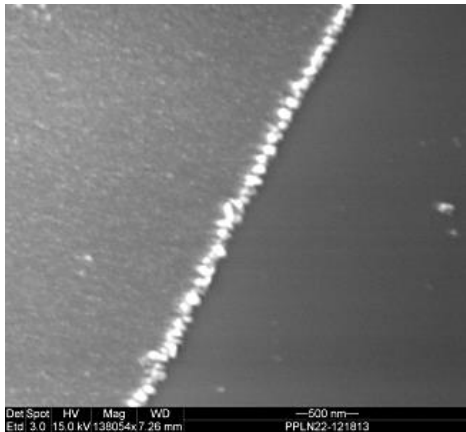


Fig. 2

Fig. 3

2. Method

Silver nanowire synthesis was achieved using the Hanson³ method on commercially prepared samples of .5mm × 1.5mm × 2.5mm crystalline PPLN (Crystal Technologies). Interstitial silver growth was observed in the forms of randomly spaced wires or lines which often bisected wires grown on known domain boundaries. Interstitial growth was also observed as uniform preferential deposition in the +C domain. The uniform deposition on the +C domains can be explained by the presence of screening charges due to net electronic drift from domain polarization in the +C direction. The randomly spaced and angled lines of interstitial growth are shown to be due to surface irregularities and imperfections in the form of scratches.

0.05 micron commercially prepared Alumina slurry (Buehler) was used in an attempt to change surface conditions. It was observed that interstitial growth increased as a result of imperfections from abrasion by the alumina slurry (Fig 4). Impregnation of the alumina into the PPLN surface also occurred. Images taken of a region in which the deposited silver had been wiped away showed that removal of deposited silver reveals scratches (Fig 5). These two results allow for the confirmation that interstitial growth in the form of random trans-domain lines or wires can be the result of scratches and discontinuities on the surface of the wafer and that in order to achieve ordered deposition a method of surface polishing should be developed along with a chemical treatment to minimize polishing compound impregnation.

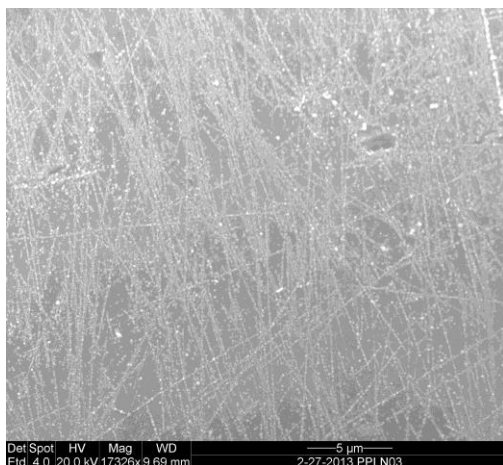


Fig. 4

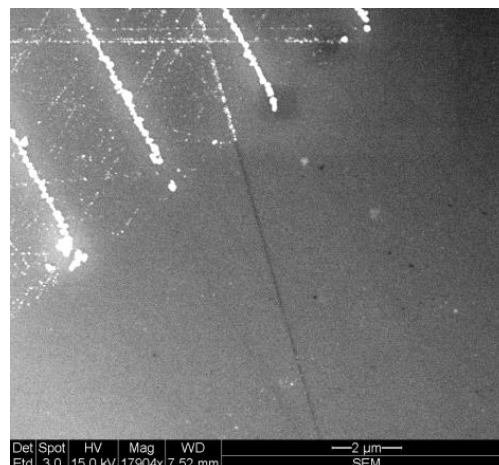


Fig. 5

In order to assess initial surface quality, a photodeposited PPLN wafer was characterized by Scanning Electron Microscopy (SEM). First, the PPLN wafer was sonicated for 20 minutes in acetone followed by a rinse with De-Ionized water (DI), sonication in methanol for 20 minutes followed by DI rinse, and then blown dry with compressed nitrogen. The wafer was then glued to an aluminum SEM stub with a conductive alcohol-based colloidal graphite adhesive. Photodeposition was carried out by immersion in 10^{-4} M aqueous AgNO_3 in conjunction with irradiation by a constant mercury UV source wavelength $\sim 259\text{nm}$ at a distance of 29.4 mm for 10 minutes. Sample was then rinsed with DI water and blown dry with compressed nitrogen.

SEM characterization was carried out by a Quanta 4000 SEM using Everhart-Thornley detector with acceleration voltages between 15-25 kV and spot size 3. Prior to imaging, nylon tweezers were swiped across the face of the wafer to remove deposited silver and provide a region of contrast.

Imaging revealed interstitial growth which suggested scratches and discontinuities on the surface of the LN wafer. Upon inspection of the region wiped free of silver it was shown that interstitial silver in the form of lines is a result of surface irregularities.

After initial imaging the sample was again cleaned using the acetone-methanol treatment outlined above. We polished the sample using a progression of diamond based slurries and then finished with 0.05 μ m silica slurry. Polishing was done by hand using moderate pressure. The first step consisted of a 3 minute polishing session with 3 μ m microcrystalline diamond suspension (MetaDi, Buehler) on a lightly napped polishing pad (MicroCloth, Buehler). Sample was rinsed thoroughly with DI. We then polished with a 1 μ m microcrystalline diamond paste (MetaDi II Buehler) for 3 minutes on a lightly napped polishing pad (MicroCloth, Buehler). Sample was thoroughly rinsed with DI. Final polishing was achieved by a 2 minute polish with 0.05 μ m silica abrasive slurry (MasterMetII, Buehler) on a ChemoMet (Buehler) pad.

Prior to deposition, our sample was sonicated by acetone for 20 minutes and rinsed with DI, methanol for 20 minutes and rinsed with DI, then treated in aqua regia (nitro-hydrochloric acid, $\text{HNO}_3 + 3 \text{HCl}$) for 10 minutes to remove any impregnated abrasives as well as to provide slight etching of the surface. Photodeposition with parameters as follows was used: Immersion in 10^{-4} M aqueous AgNO_3 and photoexcitation for 10 Minutes by constant Hg UV source.

In order to demonstrate repeatability and show that a surface could be renewed after multiple depositions, PPLN #22, which had undergone multiple depositions, and PPLN #31, a brand new sample, were chosen for this paper. In both cases it was necessary to go through the process twice. Figure 5 shows a flow chart for the treatment of PPLN #22. After the first iteration of the process, large scratches were still noted on the face of the wafer. Repetition of the process produced desired results.

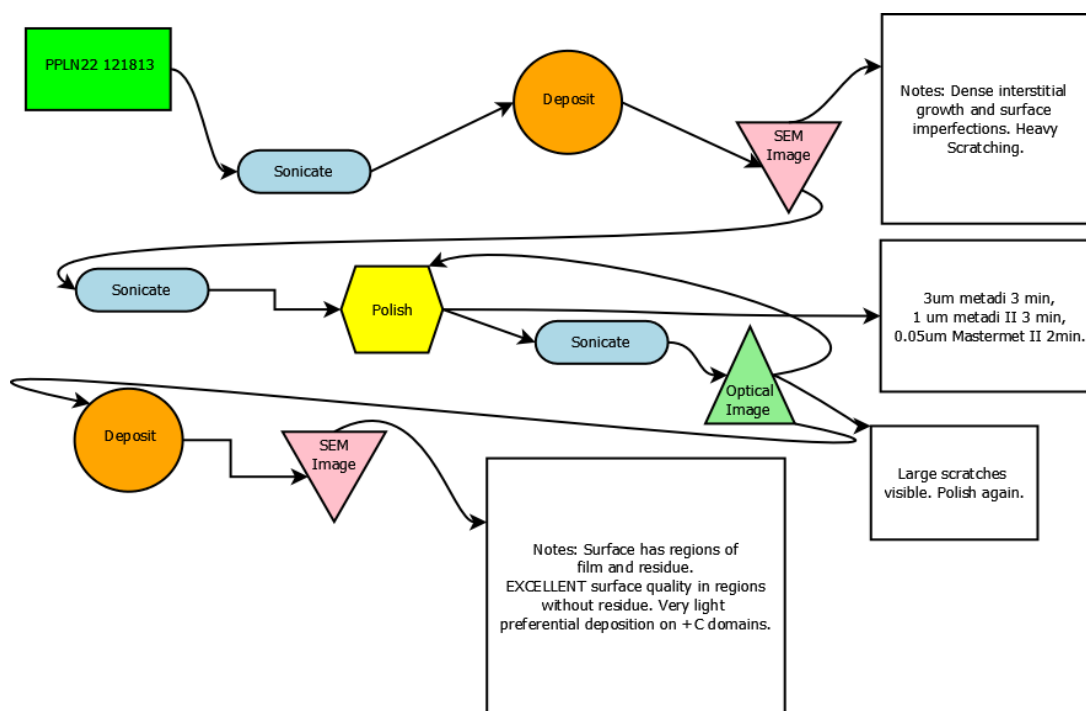


Fig. 5

3. Results

Imaging provided clear evidence of surface improvement and curbed interstitial growth on PPLN#22. Large areas in contrasted regions (Figures 7 and 8) are observed to be free of interstitial growth in the form of trans-domain lines. Random interstitial structures were greatly reduced. Preferential interstitial deposition on the +C domains was still observed. Treatment with aqua regia removed any impregnated residuals from the polishing process.

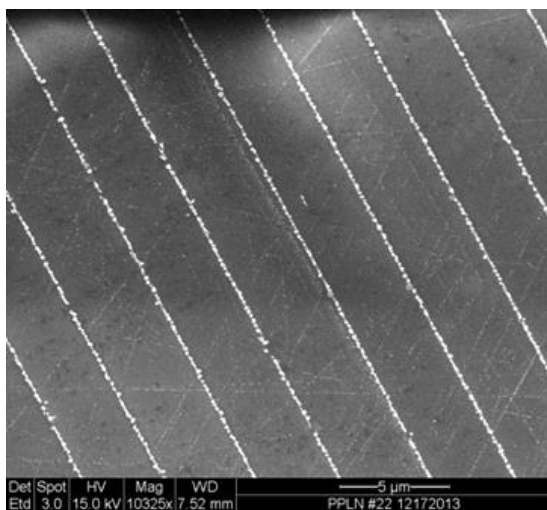


Fig. 7

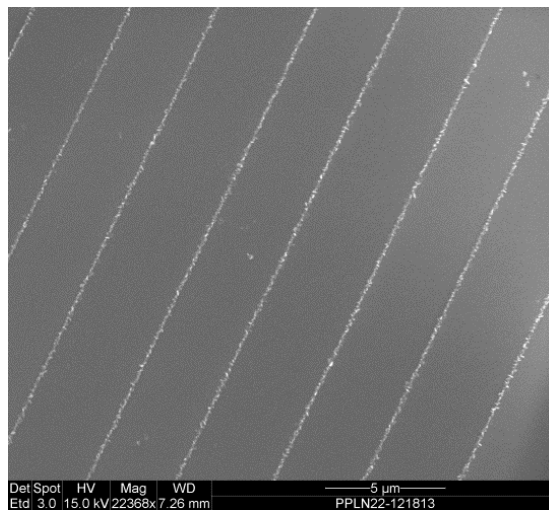


Fig. 8

Upon initial deposition to assess the surface quality of PPLN#31 interstitial growth due to scratches was prevalent. Treatment was performed in two iterations using the same parameters for polishing compounds and times. Interstitial growth was relieved in a similar manner producing a viable substrate capable of silver nanowire synthesis with minimal interstitial growth. Figures 9 and 10 show corresponding regions of PPLN#31 before and after polishing.

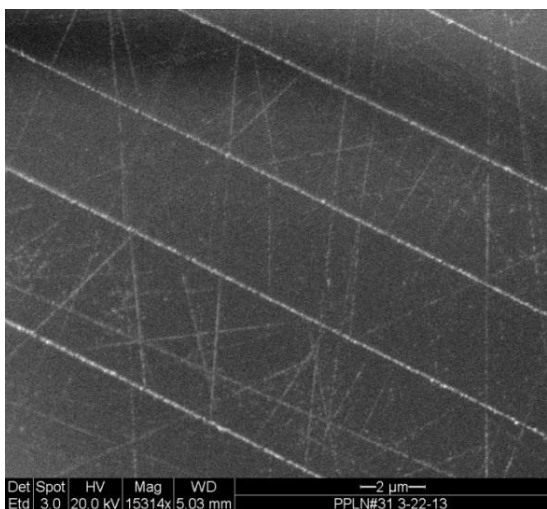


Fig. 9

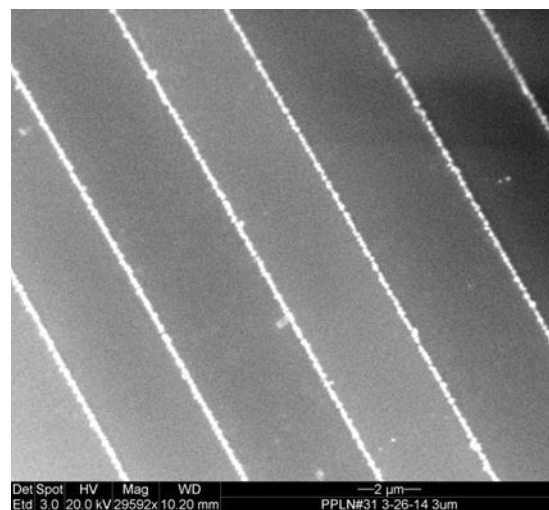


Fig. 10

4. Conclusion

Discontinuities and imperfections on the face of the ferroelectric growth substrate greatly contribute to unwanted interstitial growth. Scratches cause transdomain depositions which may resemble random aperiodically patterned nanowires. Control of errant interstitial deposition can be improved upon by methodical surface conditioning via an easily repeatable technique. Mechanical polishing followed by chemical treatment has been shown to effectively prepare the surface of the PPLN substrate for optimized silver nanowire synthesis.

A readily repeatable process has been shown for the surface preparation of periodically poled ferroelectric lithium niobate silver nanowire growth substrate. Scratches and other discontinuities will contribute to unwanted interstitial growth. These imperfections are present initially as a consequence of the manufacturing process but may also be accrued over time due to handling and repeated depositions. Virtual elimination of transdomain wire-like structures can be achieved through this polishing technique. However, preferential deposition on the +C domains is still present. This growth may be able to be limited by adjustment of deposition parameters^{8,9}.

5. Future Works

A method for an easily repeatable process to produce silver nanowires is feasible. Examination of the tunability of the wires as a SERS substrate can be investigated. Removal of the wires from the substrate could be part of this repeatable process.

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7. Reference

- 1 A. Haussmann, P. Milde, C. Erler, L.M. Eng., *Nano Lett.* **2009**, 9, 763-768.
- 2 S. Damm *et al.*, *Jour. Phys. Chem.* **2012**, 116, 26543.
- 3 J. Hanson, B.J. Rodriguez, R.J. Nemanich, A. Gruverman., *Inst. Phys. Pub.* **2006**, 17, 4946-4949.
- 4 N.C. Carville *et al.*, *Jour. App. Phys.* **2013**, 113, 187212.
- 5 D.D. Evanoff, G. Chumanov, *ChemPhysChem*, **2005**, 6, 1221-1231.
- 6 L. Dongbo, D.A. Bonnell, *Annu. Rev. Mater. Res.*, **2008**, 38, 351-68.
- 7 A.M. Prokhorov, Y.S. Kuz'minov, *Physics and Chemistry of Crystalline Lithium Niobate*. IOP Publ. Ltd., New York, 1990.
- 8 Y. Sun, B.S. Eller, R.J. Nemanich, *Jour. App. Phy.* **2011**, 110, 084303.
- 9 R.E. Morris, *UNCA Jour. Und. Res.* **2013**.