Study of the Effects of Chemical Etchants on the Quality of Silver Nanowires Cultivated on Periodically Poled Lithium Niobate

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Abstract

Silver nanowires are promising microstructures for various applications such as substrates for surface-enhanced Raman spectroscopy of biomolecules like DNA, and as interconnects in integrated circuits. Ferroelectric lithography is used to prepare such wires on periodically poled lithium niobate (PPLN) crystals, but imperfections in the crystal surface cause unwanted interstitial silver deposition and irregularities in the wires. In this work, several chemical treatments were used to attempt to etch the z-face of the PPLN crystals to an atomically smooth state. HF/HNO₃ preferentially etched the poled domains creating an uneven surface and KOH caused irregular pitting of the surface. However, as confirmed through scanning electron microscopy and energy dispersive x-ray spectroscopy, aqua regia was hypothesized to etch the PPLN surface evenly and laterally, repairing preexisting surface flaws as well as those caused by KOH treatment, improving the quality and size of wires prepared, and reducing interstitial silver deposition. Further investigation is necessary to optimize the treatment parameters of aqua regia exposure time, temperature and other variables to the point of highest possible wire quality. Aqua regia treatment will be investigated in tandem with physical polishing methods, as preliminary tests suggest that ideal results may be achieved via complementary aqua regia treatment and physical polishing methods. Once treatment parameters are optimized, this combination treatment method could be used to prepare newly manufactured wafers for silver deposition, as well as to repair damaged wafers which would previously have been considered waste. If continued research confirms this possibility, then a reliable and efficient new method of synthesizing silver nanowires of usable quality will have been discovered.

Keywords: Ferroelectric Lithography, Periodically Poled Lithium Niobate, Silver Nanostructures

1. Introduction

Ferroelectrics are materials that, when subjected to an external electric field which induces a dipole in the materials' crystal structure, are able to maintain that field permanently even after being removed from the external field. Lithium niobate is a ferrolectric material that, because of its hexagonal crystal structure, exhibits 180 degree domain switching, meaning that it is able to be poled with alternating positive and negative electric field domains across its surface, creating periodically poled lithium niobate (PPLN). Electric field anomalies occur at the boundaries where the field switches rapidly from positive to negative within a very small space, causing a spike in the field's magnitude where a surplus of electrons accrues.

This special property allows for the use of a technique called ferroelectric lithography, which is the preparation of silver nanostructures (wires and pearls) on periodically poled ferroelectric lithium niobate. Silver cations in aqueous silver nitrate solution are photoreduced to elemental silver by ultraviolet light at the sites of high electron density along the electric domain boundaries on a ferroelectric substrate of PPLN.¹⁻⁷ The linear domain boundaries are limited to a width of about 150 nm (20-200 nm) so silver lines with a very small diameter and a high aspect ratio form on the substrate. These lines are known as nanowires.

Nanoscale structures often exhibit very different or exaggerated chemical and physical characteristics compared to their macro counterparts, due to a high surface area to volume ratio. Silver, unlike most other transition metals, maintains its high electrical conductivity even at the nanoscale, so nanowires made of silver will play a significant role in the future of

technology as electronic devices continue to trend toward the nanoscale, as they would serve as excellent interconnects in nanoscale integrated circuits. Silver nanowires may also be used as substrates for surface-enhanced Raman spectroscopy, a technique that allows for nondestructive, high resolution imaging and characterization of biomolecules such as DNA.^{4,6}

Unfortunately, the current quality of nanowires produced on PPLN is too low for use in these applications. PPLN is predominantly used as a waveguide in laser technology,⁸ wherein atomic smoothness of the z-face of the wafers is not required, and in fact sub-surface defects, collectively called the Bielby layer, are preferred as they enhance poling by providing nucleation sites in the crystal.⁸ Thus, PPLN wafers are mechanically polished only to microscopic smoothness after crystal growth and slicing in the manufacturing process,⁸ which creates nanoscale sub-surface and surface defects in the structure, visible in Scanning Electron Microscope (SEM) imaging. These defects result in anomalies within the electric field on and below the surface, which seem to mimic the effects of the anomalies occurring at the domain boundaries, causing undesired silver to preferentially deposit at these interstitial areas and compromising the integrity of the wires.⁹

Only a handful of research groups dedicate themselves to solving this problem, but those who do have found that manipulation of a few key variables in the deposition process can have a great impact on the quality of wires: UV light wavelength,² intensity,³ and exposure time,⁷ and concentration of silver nitrate solution.^{3,7}

Carville et al investigated the dependence of deposition quality and quantity on the variables of silver solution concentration and UV light exposure time, on periodically proton exchanged lithium niobate. It was known that a silver reduction reaction happens at the domain boundaries where electron density is highest, but the effects of variables like time, concentration, intensity, wavelength, etc. on initial nucleation sites and saturation of domain boundaries were not fully understood. A variety of deposition times and concentrations were tested, and it was found that the speed of deposition is greatest in the beginning of a deposition with a high concentration silver solution and that exposure time is less relevant here, but that with a low concentration solution, deposition begins slowly and then exponentially increases over time so that it occurs very rapidly by the end of treatment, and exposure time is important here in controlling the height and width of wires. That initial nucleation occurs at domain boundaries was confirmed (there is always some interstitial deposition, but this research confirmed that it is not "preferred" by the silver).

Sun et al explored the dependence of silver deposition on wavelength of UV light source. It was found that wavelengths below the band gap of lithium niobate result in little to no silver deposition anywhere on the surface, whereas all wavelengths above the band gap result in silver deposition across all domains, but concentrated primarily along the domain boundaries. Interstitial deposition is greatest at shorter wavelengths, and deposition becomes more selective to the boundaries at higher wavelengths.

Some other groups have also explored the variable and often destructive effects of acid etchants on the periodically poled domains of PPLN.¹⁰⁻¹² For example, Argiolas et al explored a preferential etchant used to map the domains of a poled crystal.² The research details the necessity of consistent poling through the body of the PPLN crystal. PPLN, when used as a laser waveguide, requires very precise widths of periodic domains. Since the etch rate of the negative z-face is faster than that of the positive z-face when using a preferential etchant, preferential etching is used to map the domain distribution across the crystal before packaging. After etching, the difference in domain poles is made obvious topographically. Since spatial resolution of the imaging device must be at least 1% of the width of the domains, a very high resolution instrument must be used to maximize accuracy of measurement, such as a scanning force microscope. The literature describes the crystal growth and poling process, after which a sample crystal is submerged in 1:2 HF:HNO₃ solution at 80°C for a variety of times. The depth of etching is also used to measure crystal bulk hardness, until the time variable reaches 3 minutes, when etching ceases to be normal to the surface and begins to progress laterally. No chemical explanation is given for the difference in etch rates. The acid mixture used here etches in exactly the way that is undesirable to our research, and so can be excluded from consideration.

To date, no research groups have investigated the possibility of using a carefully chosen etchant (that etches laterally across the surface, smoothing imperfections, rather than down into the bulk, and which does not etch the positive and negative domains at different speeds) to smooth the surface of PPLN wafers and eliminate interstitial imperfections which become undesired silver nucleation sites.

The goal of UNCA's nanowire research group was to investigate treatment of the PPLN surface with several chemical etchants, including KOH and aqua regia (one part nitric acid to three parts hydrochloric acid). Scanning electron microscopy and energy dispersive x-ray spectroscopy was used to confirm whether the surface was etched laterally and evenly, whether interstitial deposition was reduced and whether wire quality was improved after treatment. When an appropriate etchant was found, the next step was to work toward optimizing the treatment parameters of chemical exposure time, temperature and other variables to the point of highest possible wire quality. Ideal wires consist of lines of evenly spaced, equally sized, perfectly spherical silver pearls along domain boundaries, with no silver deposition in the interstice between those lines. Once the best possible results are achieved using chemical treatment alone, a new course of investigation will begin to determine an effective combination of physical and chemical polishing techniques for successful, repeatable creation of an atomically smooth PPLN surface. The ultimate goal of this research is to completely eliminate interstitial silver deposition caused by defect-induced electric field anomalies in the wafer, so as to increase repeatability of successful silver nanowire growth, as well as reusability of PPLN wafers, thereby reducing costs

associated with continued research in this area and creating further opportunity for research in the wires' electrical conductivity and efficacy for use in SERS.

2. Methodology

Five wafers were treated in these experiments: 2 previously extensively used and 3 unused. Prior to each chemical treatment and deposition, wafers were sonicated for 20 minutes each in acetone and methanol, to remove organic debris and previously deposited silver, then rinsed with deionized water and dried with nitrogen gas.¹⁻⁵

Chemical treatment involved submerging sonicated wafers in a beaker filled with the chosen chemical, usually for precisely 10 minutes (one treatments involved longer exposure time).

For the deposition process, 0.001 M AgNO₃ solution was freshly prepared for each deposition session using acid-washed glassware to eliminate variability of molarity of solution stored in glass. Sonicated and treated wafers were submerged under approximately 1 mL of silver solution and placed under a UV lamp at a fixed distance for precisely 10 minutes, then rinsed with deionized water and dried with compressed air.

For the imaging process, trial and error was used to determine optimal settings, and the SEM was set to a working distance of 10 mm, a spot size of 3, and a voltage of 15.00 kV, using the Everhart-Thornley scanner. Each wafer was divided into octants, and a spot was chosen at random within each octant. The first image within each octant was taken at a magnification of 10,000x. Barring technical difficulties such as charge buildup in the chosen area, subsequent images were taken in the same spot at magnifications of 20,500x, 40,000x 105,000x. Exemplary images were then chosen to represent the average state of each wafer.

3. Results and Discussion

Wafer #1, previously unused, was exposed to aqua regia for 10 minutes before every deposition. Figure 1 shows a typical image of deposition after aqua regia treatment. The alternating domains appeared to etch at the same rate, and aqua regia was assumed to etch laterally as there was no evidence of downward etching, though time limitations and available equipment did not allow for confirmation. Wafer #1's final experiment was exposure to aqua regia for 60 minutes, in attempt to establish an upper limit for aqua regia effectiveness. This extended exposure resulted in what seemed to be complete depoling of the surface of the wafer, and no silver deposition even in what was once interstitial area. Mechanical polishing scratches, along which silver would previously have deposited interstitially, are clearly visible on the clean surface of the wafer, the most evident of which is the dark vertical line through the center of the image in Figure 2.



Figure 1: wafer #1 after 10 min. aqua regia treatment



Figure 2: wafer #1 after one hour aqua regia treatment

Wafer #2, previously used, was exposed to KOH, then aqua regia for 10 minutes each before deposition. KOH was shown to produce pitted scars in the surface of the wafer (Figure 4), and it was hypothesized that aqua regia may be able to use these scars as a starting point from which to etch the surface laterally, and perhaps under the right conditions, even remove the entire Bielby layer. Figure 5 shows the improved typical deposition after aqua regia exposure. However, these treatments together offered no improvement over the original condition of the used wafer, shown in Figure 3.



Figure 3: wafer #2, prior to chemical treatment Figure 4: wafer #2 after 10 min. in KOH Figure 5: wafer #2 after 10 min. in aqua regia

Wafer #3, previously used, was first treated with KOH and aqua regia, in attempt to duplicate the results found with wafer #2. Figure 6 shows the wafer before treatment, Figure 7 after KOH, and Figure 8 after aqua regia. Like wafer #2, the result was that aqua regia substantially repaired the surface from the scarring caused by KOH.



Figure 6: wafer #3 prior to chemical treatment Figure 7: wafer #3 after 10 min. in KOH Figure 8: wafer #3 after 10 min. in aqua regia

Wafer #4, previously unused, was untreated for several depositions, for the purpose of observing wire degradation over time on untreated wafers. However, after 6 depositions, of which Figure 9 is a typical example, no change in wire quality was noticeable. The wafer was then exposed to aqua regia. Figure 10 shows a typical deposition after treatment: wires are much smaller but generally more uniformly shaped, there is less interstitial deposition, and less evidence of deposition in polishing scratches. The wires are not perfect, as there are some visible gaps between silver particles, and interstitial deposition is still present, but aqua regia is clearly a promising candidate for reparation of PPLN surface imperfections. More evidence of this becomes obvious when Figure 9, a previously unused, untreated wafer is compared to Figure 1, a previously unused aqua regia treated wafer. Figure 9 clearly shows several times more interstitial deposition than Figure 1.





Figure 9: typical deposition on wafer #4 prior to chemical treatment

Figure 10: wafer #4 after 10 min. in aqua regia

Wafer #5, previously unused, was used to demonstrate again the improvement of wire quality and decrease in interstitial deposition after aqua regia treatment. Figure 11 shows deposition before treatment, and Figure 12 after. Though again, wire quality is not perfect and a small amount of interstitial deposition remains, it is clear that aqua regia treatment has positive effects on deposition quality. Results from wafers #4 and #5 suggest that scarring first with KOH is probably unnecessary.



Figure 11: typical deposition on wafer #5 prior to chemical treatment



Figure 12: wafer #4 after 10 min. in aqua regia

4. Conclusion

Aqua regia was established as a promising chemical etchant for future investigation. Aqua regia treatment caused decrease in wire diameter, but silver particles became more spherical and uniform in size. Interstitial deposition noticeably decreased after one treatment of 10 minutes in aqua regia. Continued work will explore refinement of aqua regia treatment parameters, as well as the effectiveness of a combination of physical polishing methods and aqua regia etching. Physical and chemical treatments together are hypothesized to produce the highest quality wires and nearly eliminate interstitial growth.

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