

# Fabrication of metallic nanowires on a ferroelectric template via photochemical reaction

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## Abstract

Fabrication of silver nanowires on a domain-patterned lithium niobate template by inducing a photochemical reaction in an aqueous solution is reported. Silver deposition occurs preferentially along the domain boundaries which separate antiparallel domains. The nanowires can reach lengths of hundreds of micrometres, and their location can be controlled by generating domain patterns of a desired configuration while their width depends on deposition conditions, such as temperature, solution concentration and ultraviolet (UV) light exposure time. The selective deposition process is explained by a combination of the inhomogeneous distribution of the electric field in the vicinity of the domain wall and the polarization screening mechanism of the template material. Controllable and selective deposition of metal species onto nanoscale domain-patterned ferroelectric templates may provide an alternative bottom-up route to lithographic fabrication methods.

Miniaturation of electronic devices requires the development of structural elements of reduced dimensions. Metallic nanowires are attracting great interest due to their application as interconnecting components of nanoscale devices as well as chemical sensors and biological labels [1, 2]. Numerous techniques have been adopted for the growth of metal nanowires. Many of the top-down lithography-based methods provide high-precision positioning and size control, but are limited in downscaling the nanowire diameter below 50 nm [3, 4]. The bottom-up approaches allow fabrication of nanowires with much smaller diameters, but are time consuming, suffer from poor registration, and require special templates that, in turn, involve top-down processing [5].

In this paper, we present a liquid-phase processing method for the fabrication of silver nanowires on a domain-patterned ferroelectric template via a photochemical reaction. We demonstrate that the local reactivity on the ferroelectric surfaces depends not only on polarization but also on the intricate balance between polarization charges, adsorbed charges and defect states near the surface. It is shown that variations in the local surface electronic properties induced by the domain walls leads to preferential deposition of silver along the domain boundaries. As the domain walls in ferroelectrics can be as thin as several unit cells, this approach opens

up the possibility of fabricating metallic wires of nanoscale dimensions.

A unique feature of ferroelectric materials is a spontaneous polarization, the direction of which can be changed by the application of an external electric field [6]. Polar surfaces of ferroelectrics are characterized by the presence of surface charges that can enable a new set of applications, including local molecular self-assembly, local physical adsorption/desorption, local chemical reactions, local charge transfer reactions, and the manipulation of individual molecules. There have been a number of reports on domain-specific deposition of materials on ferroelectric surfaces governed either by the Coulomb interaction or by electrochemical reactions [7–9]. Prior experiments utilizing the effect of ferroelectric polarization on chemical reactivity have demonstrated the viability of this approach for the fabrication of complex nanostructures [10, 11].

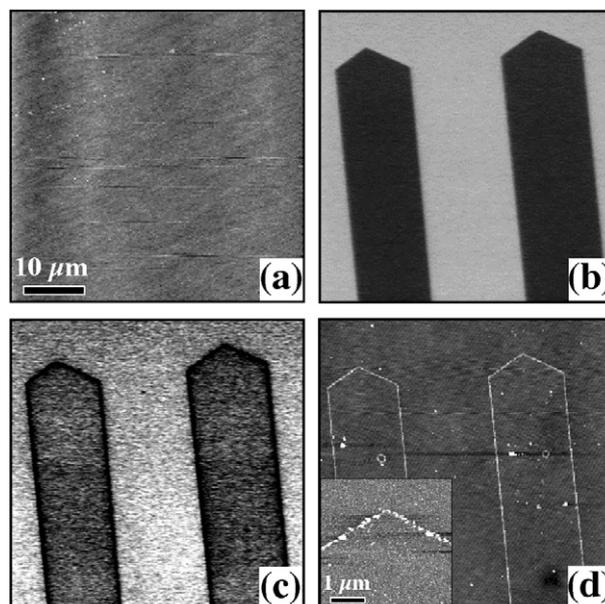
In this work, periodically poled lithium niobate (PPLN) substrates of congruent composition (Crystal Technologies) have been used as ferroelectric templates. At room temperature, lithium niobate exhibits hexagonal symmetry with polarization along the *c* axis, which allows only two possible domain orientations. The samples used in this study were  $3 \times 3 \times 0.5$  mm<sup>3</sup> plane-parallel plates cut normal to the

polar axis. The periodic domain structure (period of  $\sim 28 \mu\text{m}$ ) has been fabricated by depositing a photoresist mask on the  $+c$  sample face and applying a voltage of 10 kV through a fixture with an electrolyte solution. The mask has been removed after poling. In addition,  $c$ -cut  $0.9 \mu\text{m}$  thick crystals of stoichiometric lithium niobate (SLN) have been used in this study. The lower switching threshold field of the SLN samples [12] allows local domain switching using a conductive tip of an atomic force microscope (AFM). Domain patterns of arbitrary configuration have been written in the SLN samples using a computer-controlled Keithley 236 Source Measure Unit and applying a negative bias of 30 V to the sample via a Pt-coated tip (MikroMasch,  $k = 5 \text{ N m}^{-1}$ ). The same tip has been used for visualization of the domain patterns in both samples by means of piezoresponse force microscopy (PFM) [13].

Sample preparation for silver deposition was as follows: the sample was sonicated for 20 min first in acetone and then for 20 min in methanol. After cleaning, the sample was placed in a petri dish, and the surface was covered with an aqueous  $\text{AgNO}_3$  solution of 0.01 M concentration. The sample was then illuminated with a 20 W Hg pen lamp placed above the sample. Two different Hg pen lamps were used in the experiments, one with the predominant emission at 254 nm, which corresponds to strong optical absorption, and another with the predominant emission at 365 nm, which has a photon energy less than the  $\sim 3.9 \text{ eV}$  band gap of lithium niobate. According to the manufacturer's specifications, the power density at a distance of 2 cm from the lamp is  $\sim 1\text{--}4 \text{ mW cm}^{-2}$ . The irradiation time was varied in the range from 1 to 30 min. Immediately following illumination, the sample was immersed in deionized water for 1 min, and then blown dry with nitrogen. After deposition, the samples were imaged in non-contact mode AFM (NC-AFM) in order to preserve any structures that had formed on the surface.

Figure 1(a) displays an AFM topographic image of the surface of the PPLN sample, which shows no apparent surface features associated with the domain structure. The PFM images of the same area (figures 1(b) and (c)) reveal a pattern of periodically poled  $180^\circ$  domains of  $\sim 14 \mu\text{m}$  wide. Analysis of the contrast variation in the PFM phase image allows the identification of domain polarity: dark contrast indicates  $+c$  domains (with positive surface polarization charges), while bright contrast corresponds to  $-c$  domains. In the PFM amplitude image, the boundaries between antiparallel domains appear as dark lines about 150 nm wide. (We note parenthetically that this result, which confirms the previously reported data on domain wall width in lithium niobate, presents an unsolved problem: while the first-principle calculations suggest that the width of the  $180^\circ$  domain wall should be just one to two unit cells [14], the experimental observations by means of x-ray synchrotron imaging [15] and PFM [16–18] show significant broadening of the walls. It is speculated that this phenomenon might be a result of a strong residual stress in the vicinity of the wall associated with Li vacancies.)

In the previously reported studies, deposition occurred on the negative or positive surfaces of the domains, depending on the sign of the charge carried by the particles or the type of the chemical reaction (reduction or oxidation) [8–11]. However, in our case, the deposition pattern turns out to be quite different. Illustrated in figure 1(d) is a typical

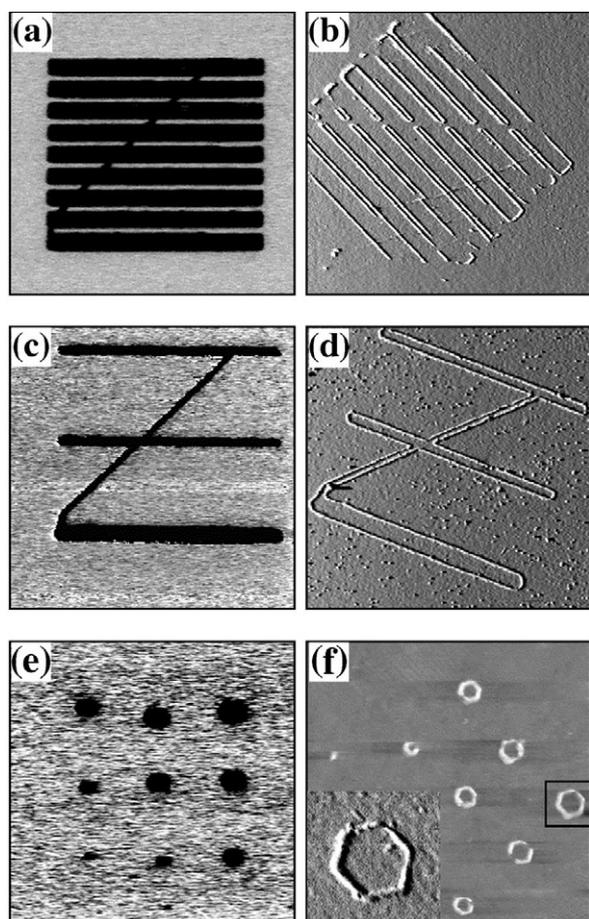


**Figure 1.** (a) Topographic image of the PPLN sample before deposition; (b), (c) corresponding PFM phase and amplitude images, respectively, of the PPLN sample; (d) topographic image of the same sample after deposition (inset: higher-resolution topographic image illustrating the structure of the lines as formed by silver particles).

structure consisting of Ag lines observed after the aqueous photoreduction procedure using the 254 nm UV light on the PPLN sample. Comparison of the topographic image of the silver lines with the corresponding PFM images shows that silver deposition occurred preferentially along the domain boundaries, with silver lines following the perimeter of the negative domains. The line width can be controlled in the range from 70 to 300 nm by changing the UV exposure time from 1 to 30 min. Furthermore, it has been found that the deposition process is sensitive to the light wavelength: silver deposition was not observed on the sample surface illuminated with below-band-gap 365 nm light.

Topographic imaging at a higher magnification reveals that the lines are formed by clusters of 30–150 nm silver particles (inset in figure 1(d)). The formation of continuous Ag lines with a high aspect ratio (nanowires) can be achieved by performing the photoreduction process at elevated temperature ( $T \sim 80^\circ\text{C}$ ). Figure 2 shows several examples of nanowire formation using different domain patterns generated in the SLN sample by the conductive AFM tip. It is evident that the aqueous photoreduction process using domain-patterned templates allows fabrication of nanowire arrays with control over their position, shape and aspect ratio.

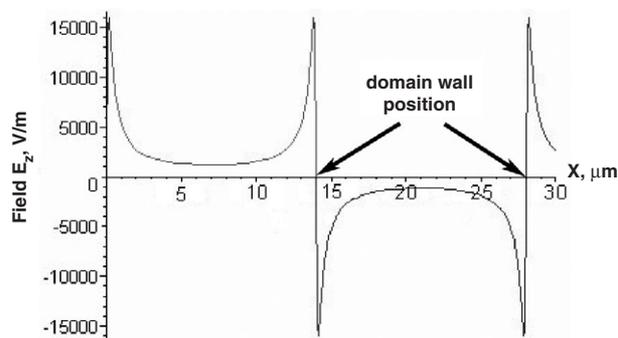
In prior deposition experiments employing particles in solution [9], it has been assumed that the interaction between the deposited ions or charged particles and the ferroelectric surface is electrostatic in nature and results from the fact that the ferroelectric holds a surface charge arising from its spontaneous polarization. However, in an aqueous solution, the formation of an electric double layer due to the adsorption of water dipoles or different ionic species should lead to essentially complete screening of the polarization charges.



**Figure 2.** ((a), (c), (e)) PFM images of domain patterns generated in the SLN sample by a conductive AFM tip. ((b), (d), (f)) Corresponding topographic images of silver nanowires fabricated by aqueous photoreduction at 80 °C. Topographic images are rotated by 30°–45° clockwise with respect to the PFM images. The scan size in ((a)–(f)) is  $15 \times 15 \mu\text{m}^2$ . The inset in (f) shows a zoomed image of the area marked by the black block. The scan size of the inset is  $2 \times 2 \mu\text{m}^2$ .

Because of this fact, surface decoration techniques described several decades ago usually work only when insulating organic liquids are used [7]. In this case, charged colloidal particles are attracted to the surfaces of the polar domains.

The fact that, in our experiments, silver is deposited along the domain boundaries can be, in principle, attributed to the dipolar interaction of charged particles with the field gradient existing in the vicinity of the domain wall. Decoration of domain walls has been observed in colloidal solutions containing particles with high dielectric constants [7]. In this case, the non-uniform electric field interacting with the field-induced polarization in the particles would provide a force tending to move them towards the domain boundaries (a process related to the dielectrophoretic effect). However, the fact that, without UV irradiation, silver deposition was not observed indicates that the dielectrophoretic effect cannot explain the domain wall decoration with silver. In addition, the size of the ions in the solution is far smaller than the minimum particle size (of the order of several hundred nanometres) required for an appreciable dielectrophoretic effect.



**Figure 3.** A calculated distribution of the normal component of the electric field for the periodically poled lithium niobate at a distance of 100 nm below the surface.

In the present experiment, the expectation was that the reduction of silver ions by the excess electron charge generated by UV light would lead to selective silver deposition on  $+c$  domains similar to the previously reported results of photochemical reactions on surfaces of barium titanate  $\text{BaTiO}_3$  (BTO) crystals and  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT) films [10, 11]. To explain this significantly different pattern of selective deposition in lithium niobate, we consider the difference in electronic properties of lithium niobate and the perovskite ferroelectrics used in the previous studies and additionally take into account the distribution of the electric field in the vicinity of the domain wall.

In PZT films, oxygen loss during high-temperature annealing of the film typically produces a high concentration of oxygen vacancies. This high concentration of defect states near the surface in PZT estimated as  $10^{14} \text{ cm}^{-2}$  (see [19]) leads to a significant contribution of internal screening, which compensates the polarization charges and leads to strong band bending at the surface. The absorption of the above-band-gap light leads to the generation of electron–hole pairs across the PZT film. In PZT, the strong band bending results in an electric field which separates the electron–hole pairs generated by the UV light with electrons moving to the surface towards the positive domain end and holes drifting away from it. The electron charges can then participate in the photochemical reduction of ionic  $\text{Ag}^+$  to metal  $\text{Ag}^0$ . Given that the defect density near the film surface is two orders of magnitude higher than in the bulk of the PZT film ( $10^{-20}$  versus  $10^{-18} \text{ cm}^{-3}$ , respectively) [19], it can be assumed that the regions close to the surface provide most of the electrons for the photochemical reaction on the surface.

In the lithium niobate crystal, a low concentration of defect states near the surface ( $10^{12} \text{ cm}^{-2}$ ) [20] implies that the predominant mechanism of polarization screening is external via the surface absorption of charged molecules. The band bending thus will occur over a length scale that is large compared to the UV absorption length [21, 22]. Because of the weak electric field near the surface, the separation of the electron–hole pairs is less efficient and there will be dynamic equilibrium of the generation and recombination processes. However, calculation of the electric field near the surface of the lithium niobate following the approach used in [23] and assuming complete external polarization screening shows that the field distribution is nonuniform (figure 3). Indeed,

a strong electric field,  $E_z$  (where  $z$  delineates the direction along the polar axis, or the normal component of the field) resulting from the superposition of the fields of polarization and screening charges exists in the vicinity of the  $180^\circ$  domain wall, while away from it the field is almost zero (figure 3). Thus, it may be expected that, as a result of the inhomogeneous field distribution, separation of the photoinduced electron–hole pairs will occur only in the vicinity of a  $180^\circ$  domain wall with excess electron charge accumulating on the surface along the domain wall. Since lithium niobate has a band gap energy of  $\sim 3.9$  eV [20], only light with a wavelength less than 318 nm can be used for the optical generation of electron charge, which explains the absence of any selective silver deposition on the sample illuminated with 365 nm UV light. It should be noted that irradiation for a longer period of time or with high-power UV light leads to silver deposition on the positive surfaces of the domains, which can be explained by gradual accumulation of the photoinduced charges on polar surfaces.

In principle, there is an additional mechanism that can result in strong local electric fields, which is related to the defect structure of lithium niobate. It has been shown that domain walls are stabilized by the slow reorientation of defect dipoles consisting of niobium antisites ( $\text{Nb}_{\text{Li}}$ ) and lithium vacancies. This process can lead to the formation of local electric fields of the order of several  $\text{kV cm}^{-1}$  [24] and stronger band bending. In addition, an in-plane component of the electric field  $E_y$  due to defects [25] can allow the migration of the carriers across the domain wall, which will serve as a sink for the accumulating positive charge. Investigation of the effect of defect concentration on the selective deposition process is continuing in our group.

In summary, we have developed a liquid phase processing method for the fabrication of silver nanowires on a domain-patterned ferroelectric template via a photochemical reaction. Variations in the local surface electronic properties induced by the domain walls leads to preferential deposition of silver along the domain boundaries. The observed behaviour is explained by the local reactivity on the ferroelectric surfaces, which depends not only on polarization but on the intricate balance between polarization charges, adsorbed charges and surface states. As the domain walls in ferroelectrics can be as thin as several unit cells, this approach opens up the possibility of fabricating metal nanowires of nanoscale diameter. Furthermore, this approach allows the fabrication of nanowires of any aspect ratio by developing domain patterns of desired configuration and by adjusting the temperature, solution concentration and irradiation time. This is important for many applications, which are dependent on the nanowire aspect ratio. Using this approach, nanowires could be assembled into complex two-dimensional structures, and nanowire segments of different metals could potentially be fabricated by using solutions containing different metal ions.

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