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Photo-induced Ag deposition on periodically poled lithium niobate: Concentration and intensity dependence

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This research focuses on the formation of Ag nanopatterns on periodically poled lithium niobate (PPLN). The photo-induced process employs UV-light exposure while the PPLN is immersed in a AgNO₃ solution. The Ag deposition was consistent with previous results, showing preferential deposition along the domain boundary as well as an increased density of particles on the positive domain surface in comparison to the negative domain. By tuning the chemical solution concentration and the UV-light intensity, the Ag⁺ ion flux and the electron flux are varied and the deposition pattern could be controlled to either enhance the nanowire-like structures along the domain boundary or create a more uniform deposition pattern over the positive and negative domains. To understand the deposition process, we investigated the relationship between the Ag^+ ion flux because of diffusion and the electron flux initiated by the UV exposure of the ferroelectric surface. The subsequent results suggest that this relationship is responsible for the different deposition patterns. The observed variation of boundary-enhanced or boundary-depressed deposition is explained by consideration of the electric field distribution and the ratio of the Ag⁺ ion and photon flux. The results establish that the ratio can be controlled by varying the solution concentration and/or UV-light intensity to generate enhanced nanowire-like structures along the domain boundary or a more uniform deposition pattern over the positive and negative surface. Moreover, the specific value of the Ag⁺/photon flux ratio where the pattern changes is dependent on other factors including the nucleation limited growth mechanism and the Stern layer on the lithium niobate. © 2011 American Institute of Physics. [doi:10.1063/1.3647752]

I. INTRODUCTION

The use of ferroelectric materials as templates for "growth" of patterns of nanoparticles and nanowires has gained interest because of its potential application for biochemical sensors or reconfigurable electronics.^{1–3} Moreover, as researchers have come to better understand the physics behind this process, it has become evident that aspects of this research could influence other technologies.

Essential to this process is the use of ferroelectric crystals, which exhibit spontaneous and reversible polarization. Consequently, these materials can be patterned with an alternating, external electric field to create a periodically poled substrate and thus obtain a template with a pattern of regions with alternating surface charge. These areas of surface charge are referred to as domains, whereby the negatively and positively charged domains present different properties such as work function, electron affinity, and surface potential.⁴ Moreover, to obtain an energetically stable state, the surface charges undergo external and/or internal screening. Internal screening is distinguished by the formation of a space-charge layer near the surface, whereas external screening is identified by the absorption of charged molecules, or surface states because of the surface layer. These processes can modify the electron affinity as well as band bending.⁵ For example, a positively polarized surface is screened by free electrons, negatively ionized defects, negatively charged surface states, and/or the absorption of negative ions from the atmosphere. (The same is true for a negatively polarized surface except the screening is by holes or positively charged defects, surface states, or molecules.⁶) This intrinsic screening gives rise to an internal electric field and thus band bending near the surface region.⁷ These unique properties of ferroelectric surfaces have been utilized in several processes, including localized chemical reactions, nanopatterned surface functionalization,^{7–11} and electrowetting.^{12,13}

These characteristics are also important to the photoinduced formation of metallic nanostructures, as they allow the ferroelectric to be used as a template.^{14–16} The photoinduced deposition process on these materials typically results in preferential deposition along the domain wall boundary and dispersed deposition on the domain surfaces, where the positive domains exhibit a higher density of metallic particles than the negative. In our research, congruent periodically poled lithium niobate (PPLN) is used as the deposition template. The PPLN template has a bandgap of ~ 3.9 eV.⁴ When the ferroelectric sample is immersed in a chemical solution and exposed to light with photon energy higher than the ferroelectric bandgap (>3.9 eV or <318 nm), the photon absorption process produces electron-hole pairs near the surface. The electrons or holes may migrate or diffuse to the surface where the presence of excess electrons leads to the reduction of metallic cations from the solution onto the surface of the ferroelectric sample. Then the reduced atoms nucleate and continued growth occurs because of the reduction of Ag on the nucleated particles to form larger clusters and particles.¹⁷

The subsequent deposition pattern of these nanostructures depends on the following four factors at room temperature:

photon energy, surface polarization charge screening, flux of photo- generated electrons, and flux of metallic cations. Our previous work investigated how the photo-induced deposition process depended on the photon energy and surface polarization charge screening.¹⁸ The results showed enhanced deposition along the domain boundary and preferential deposition on the positive domain surface. The overall deposition rates decreased with increasing wavelength (decreasing photon energy). The enhanced boundary nanowire formation was suppressed on surfaces that had been modified by oxygen ion implantation. The preferential deposition along the boundary was attributed to the external screening of the surface polarization charge and the resulting strong electric field in the direction of the polar axis near the domain walls. Therefore, it was expected that migration of the photo-generated electrons would be accelerated by the strong electric field and thus enhanced deposition occurs along the boundary. Conversely, the suppression of boundary nanowire formation for oxygen implanted surfaces was attributed to the transition from surface external to bulk internal screening of the polarization charge.

In this study, PPLN surfaces were illuminated with 254-nm light (photon energy of 4.9 eV), and the effects of the intensity dependent electron flux, J_e , and the flux of metallic cations, J_b , were investigated. The electron flux reaching the template surface is mainly determined by the UV-light intensity and the corresponding photon flux. The metallic cation flux depends on the concentration and mass of the solute. For Ag deposition, the chemical solution concentration determines the metallic cation flux. By varying the concentration of the solution and intensity of the light, we are able to observe the relative effects of the Ag⁺ cation flux and the electron flux. It is hypothesized that the relationship between these two fluxes can account for the variations in the relative deposition on the domain boundaries and surfaces of the ferroelectric template. Through varying the relative values of these two fluxes, different deposition patterns of boundary enhanced nanowire formation or domain surface Ag nanoparticle coverage on +c and -c surfaces are expected, even without changing the external screening to bulk internal screening. The Stern layer at the ferroelectric surface and the Ag nanoparticle nucleation and growth mechanism are also considered in explaining the observed results.

II. EXPERIMENT

This study employs congruent, single-crystal lithium niobate as the ferroelectric template. At room temperature, lithium niobate is characterized by hexagonal symmetry with polarization along the c axis. As a result, there are only two possible domain orientations with 180° domain boundaries. In this experiment, 6 mm × 4 mm × 0.5 mm plane-parallel plates cut normal to the polar axis were used. The PPLN is periodically patterned with ~15 μ m positive and negative striped domains separated by 180° domain boundaries. The positive or negative domains (+c or -c) have a positive or negative surface charge of (+or -) 71 μ c/cm² (4.44 × 10¹⁴ e/cm²).¹⁹ PPLN displays a low density of defects near the surface, which results in predominantly external screening and nearly flat bands near the surface.⁵

Immediately prior to the photo-induced deposition, the lithium niobate template was sonicated in acetone and methanol for approximately 20 min each. After the cleaning process, the sample was immersed into an aqueous solution of AgNO₃. The thickness of aqueous solution above the lithium niobate template is ~2 mm. The solution concentrations were varied from ~10⁻³ to ~10⁻⁷ M. To investigate the effect of intensity on the deposition pattern, the surfaces were illuminated by UV light with a high intensity of ~1400 μ W/cm² and a low intensity of ~25 μ W/cm². The light source is a 100-W Hg lamp with a 254-nm bandpass filter. The different intensities were achieved by tuning the focus of the lamp or by changing the distance between the lithium niobate template and the lamp. The full width at half maximum of the filter as measured by the manufacturer is ~10 nm.

After numerous preliminary photo-induced deposition experiments, we selected four different combinations of solution concentration and UV intensity to be presented here, which are listed in Table I. For each case, the corresponding metallic cation flux and photon flux are estimated. The flux of electrons reaching the template surface is mainly determined by the UV-light intensity and the corresponding photon flux. The photon flux, J_e (photons/cm²·s), is given by

$$J_e = \frac{I_0 \cdot \lambda}{h \cdot c},\tag{1}$$

where I_0 is the UV intensity, λ is the wavelength, *h* is Planck's constant, and *c* is the speed of light.

To determine the ion flux, we followed an approach presented by Anderson and Feldberg.²⁰ They argued that the chemical flux density of a solute is given by

$$J_b = v_o C_o, \tag{2}$$

where ν_o is the average velocity toward or near a surface of a particle in solution and C_o is the concentration of the particles in solution near the lithium niobate surface.²⁰ The average velocity, ν_o , is considered as the surface collision velocity within a mean free path distance from the surface. Note that this velocity is not dependent on solvent properties such as the viscosity. Then, much like a gas, ν_o can be approximated as

$$v_o = \sqrt{kT/2\pi m},\tag{3}$$

where k is the Boltzmann constant, T is temperature in Kelvin, and m is the mass of the particle in the solution. For this

TABLE I. Solution, UV light, and Ag particle size parameters.

Case	1	2	3	4
Concentration (M)	10^{-3}	10^{-5}	10^{-5}	10^{-7}
Ag^+ flux $J_b (1/cm^2 \cdot s)$	10^{21}	10^{19}	10^{19}	10^{17}
UV intensity (μ W/cm ²)	1400	1400	25	25
Photon flux J_e (1/cm ² ·s)	10^{15}	10^{15}	10^{13}	10^{13}
Flux ratio (J_b/J_e)	10^{6}	10^{4}	10^{6}	10^{4}
Deposition time (min)	8	8	100	160
Size ratio (boundary/domain)	19.5	9.0	21.2	4.5

analysis, we employed the bulk concentration in the solution to obtain the Ag^+ ion flux values listed in Table I. This analysis suggests that the chemical flux of metallic cations is proportional to the concentration and inverse square root of the solute mass. We note that the concentration near the surface could be reduced because of deposition of the impinging ions.

After UV exposure, the sample was immersed in deionized water for 1 min, blown dry with nitrogen, and imaged using intermittent mode AFM in ambient environment using a non-conducting probe (PPP-NCH, Nanosensors, k = 42 N/m, first-order resonance frequency ~300 kHz). The Ag nanoparticle size was determined from visual analysis of the AFM images. Features (particles) that visually appeared much smaller than the average size were excluded. To determine the average particle size on the boundary and domain surfaces, 20 isolated particles were visually selected along the boundary nanowire structure, whereas 40 isolated particles were selected on the domains. The same statistical analysis described in Ref. 18 was applied here to determine the average particle size on domain boundaries and domain surfaces, respectively.

III. RESULTS

The PPLN was immersed in solutions of various concentrations of AgNO₃ and illuminated with two different intensities as summarized in Table I. For case 1, the Ag⁺ flux, J_b , was $\sim 10^{21}$ /cm²·s and the photon flux, J_e , was $\sim 10^{15}$ /cm²·s. Thus, the Ag⁺ flux, J_b , is six orders of magnitude greater than the photon flux, J_e . The resulting deposition pattern is displayed in Figs. 1(a) and 1(b). The images show preferential deposition along the domain boundary and a distribution of smaller particles on the positive and the negative domain surfaces. The Ag boundary nanoparticle size is ~ 20 times larger than that on the domain surfaces.

Next, the same growth was repeated but with a lower $(\sim 10^{-5} \text{ M})$ concentration of AgNO₃ under the same high illumination intensity of 1400 μ W/cm². In this case, the Ag⁺ flux, J_b , is only four orders of magnitude greater than the photon flux, J_e . The deposition results are shown in Figs. 1(c) and 1(d). The particle density is similar to the previous results; however, the Ag nanoparticle size along the boundary is decreased to ~10 times larger than the Ag particles on the domain surfaces demonstrating that the domain boundary growth is reduced in comparison to the high concentration deposition.

The photo-induced deposition was repeated using a reduced concentration of 10^{-5} M, while also reducing the UV intensity to ~25 μ W/cm². This deposition condition restores the ratio of the Ag⁺ to photon flux, J_b/J_e , to 10^6 as employed in the first case. Figures 1(e) and 1(f) show that the deposition pattern with preferential deposition along the boundary is restored, and the size ratio of the Ag particles on the boundary in comparison to that on the domain increases to ~21.

Finally, the experiment was repeated using the low UV intensity, 25 μ W/cm², and further decreasing the solution concentration to 10⁻⁷ M. The Ag⁺ to photon flux ratio, J_b/J_e ,

is thus decreased to 10^4 , which is the same as in the second case. As shown in Figs. 1(g) and 1(h), the boundary growth is again suppressed and a uniform pattern is observed on the surfaces. Here the size ratio of boundary to surface particles is decreased to ~5.

IV. DISCUSSION

The electric field distribution has been calculated near the surface of domain boundaries on lithium niobate with the assumption of complete external screening.²¹ The results indicated a non-uniform distribution with a strong electric field in the vicinity of the 180° domain boundaries. Away from the boundary, the field, because of the polarization and screening, decreases rapidly.²¹ Figure 2(a) shows a vector plot of the below-surface electric field distribution within the \sim 300-nm vicinity of the domain boundary. The length of the arrow represents the electric field magnitude and the arrow orientation represents the direction of the electric field. Figure 2(b) shows E_z , the normal component of electric field, at a distance of 50 nm under the surface. The value of the normal component amplitude at the boundary varies with distance below the lithium niobate surface, and Fig. 2(c) plots this variation. The calculation indicates that the boundary normal electric field decreases with distance into the bulk, whereas the domain surface normal electric field is $\sim 0.17 \times 10^4$ V/m and varies little with distance into the bulk. The normal component of the electric field at the boundary is roughly 10-30 times larger than that at the domain surface as shown in Fig. 2(c). For many semiconductors, it is estimated that the photo-excited electron-hole pairs have a recombination time of the order of 100 ps.²² The electron mobility of congruent lithium niobate is $\sim 0.8 \text{ m}^2/\text{V} \cdot \text{s}^{23}$ and, with these assumptions, the photo-generated electrons could migrate to the surface under the influence of the electric field distribution profile. Within a typical 100-ps recombination time, it is straightforward to show that electrons generated around the domain boundary region would migrate to the surface from a depth of ~ 40 nm while on the domains, the same analysis indicates that electrons generated within <2 nm would migrate to the surface. Thus, although the photon flux is uniform across the surface, the photo-generated electrons at the surface are not uniformly distributed. It follows that the distribution of electrons will reflect the magnitude of the electric field.

To simplify our analysis, we assume that one Ag^0 atom is generated when one electron combines with one Ag^+ cation, and that the process is 100% efficient when both an electron and Ag^+ cation are present at the surface.

For case 1 and case 3, the presence of the enhanced nanowire boundary formation suggests that the electron distribution in response to the internal electric field determines the Ag deposition pattern. The domain boundary particles are ~ 20 times larger than the particles on the domain surface, which is similar to the ratio of the electric field at the domain boundary and surface. As shown in Table I, for cases 1 and 3, the Ag⁺ flux, J_b , is projected to be six orders of magnitude greater than the photon flux, J_e , which means for each electron migrating to the surface, there are Ag⁺ ions



FIG. 1. (Color online) AFM images of Ag deposition patterns on PPLN using 254-nm illumination with the following solution concentrations and UV-light intensities: (a) and (b) 10^{-3} M and 1400 μ W/cm², (c) and (d) 10^{-5} M and 1400 μ W/cm², (e) and (f) 10^{-5} M and 25 μ W/cm², and (h) and (g) 10^{-7} M and 25 μ W/cm².

available resulting in the formation Ag^0 atoms. This situation is schematically shown in Fig. 3(a). The consequence is that the resulting Ag^0 atom density and distribution reflects the electron distribution as determined by the electric field distribution (Fig. 3(b)). Because there are more Ag^+ ions and fewer electrons, the efficiency of Ag^+ ion reduction is reduced under the conditions for case 1 and case 3. In fact,

the efficiency of Ag^+ ion reduction essentially determines the pattern on the surface.

Although the Ag^0 deposition reflects the electric field distribution for cases 1 and 3, when the ratio between the Ag^+ ion flux and photon flux, J_b/J_e , is decreased to 10^4 as for cases 2 and 4, the formation of boundary nanowire-like structures is suppressed (Figs. 1(c) and 1(d)) and a more



FIG. 2. (Color online) (a) Vector plot of the belowsurface electric field distribution within the \sim 300-nm vicinity of the domain boundary. The arrow length represents the electric field magnitude and the orientation represents the electric field direction. (b) Calculation of the normal component of the electric field, $E_{z,}$, at a distance of 50 nm below the LiNbO₃ surface (Ref. 21). (c) Domain boundary electric field, E_z (left scale), and the ratio between E_z at the domain boundary and E_z at the center of the domain surface (right scale) vs distance below the LiNbO₃ surface.

uniform pattern of nano-islands is observed (Figs. 1(g) and 1(h)). This transition of patterns suggests that the Ag^0 atom deposition is not distinctly determined by the electron distribution. The other component in the $Ag^+ + e^- = Ag^0$ reaction is the Ag^+ flux. Here, we presume that the Ag^+ ion flux is the same for the positive domains, negative domain, and domain boundaries. Although the calculated Ag^+ ion flux is four orders of magnitude greater than the photon flux for cases 2 and 4, later we will suggest factors that could reduce the Ag^+ ion flux impinging on the surface to be less than the electron flux. Then for each Ag^+ ion impinging on the sur-

face, there is always a supply of electrons available to produce an Ag^0 atom. Conversely, for each electron migrating to the surface, there may not be an Ag^+ ion available (Fig. 3(d)). Thus, in this situation, the Ag^0 atom distribution is determined by the Ag^+ ion flux, which is uniform over the lithium niobate surface (Fig. 3(e)).

It is evident that there is a delicate balance that determines the deposition pattern. Moreover, because of the low solution concentration and/or low UV-light intensity for cases 3 and 4, it is necessary to lengthen the time of the deposition process as indicated in Table I.



FIG. 3. (Color online) Schematic drawings for deposition cases with different Ag^+ ion and photon flux ratios. (a) The deposition situation for case 1 and 3. For each electron migrating to the surface, there is an Ag^+ ion available to combine and produce an Ag^0 atom. (b) The resulting Ag^0 atom density and distribution reflects the electron distribution as determined by the electric field distribution. (c) The corresponding AFM image of the deposition pattern. (d) The deposition situation for case 2 and 4. For each Ag^+ ion impinging on the surface, there is always a supply of electrons available to produce an Ag^0 atom. Conversely, for each electron migrating to the surface, there may not be an Ag^+ ion available. (e) The Ag^0 atom distribution is determined by the Ag^+ ion flux, which is uniform over the lithium niobate surface. (f) The corresponding AFM image of the deposition pattern.

Besides the reduction of the Ag⁺ concentration by deposition, two additional possibilities are considered for reducing the effective Ag^+ flux. The first is the Ag particle growth mechanism. The presence of the nanoparticles in the AFM image indicates that nucleation limits the process. Photoexcited electrons from regions around the nucleation site are collected at the nucleation sites. The particles grow because of reduction of the Ag, which deposits on the nucleated particles. The flux of Ag⁺ ions impinging onto available nucleation sites is less than the total flux impinging on the surface as calculated from Eq. (2). The second effect is the Stern layer at the ferroelectric surface. Because of electrostatic forces, the bound surface charge of the ferroelectric domains is compensated by ions and polarized H2O molecules of opposite charge.²⁴ In an aqueous AgNO₃ solution, the layer on the positive domain will consist of NO₃⁻ ions, free electrons, and polarized H₂O molecules, and on the negative domain, it will consist of Ag^+ ions and polarized H_2O molecules. Another layer of opposite charge then screens this first layer, creating a second layer of screening charge; this is commonly referred to as the "electrical double layer" (EDL) or Stern layer.²⁵ For Ag⁺ cations outside the Stern layer to reach the lithium niobate surface, there must be a disturbance in the Stern layer such that the screening molecules will diffuse from the surface. On the positive domain surface, when photo-excited electrons migrate to the surface, the surface potential is changed and the Stern layer may be disturbed, and thus the NO₃⁻ ions and polarized H₂O molecules disassociate from the surface enabling transport of the Ag^+ ions to the surface, which allows reduction by the available electrons. On the negative domain surface, Ag^+ ions also contribute to the screening of the surface charge; however, the reduction mechanism is the same as on the positive domain. In other words, the Stern layer effectively decreases the Ag^+ flux at the surface. As a result, the actual flux of Ag ions may be much smaller than the calculated value. Our experimental results suggest that the combined effect of the nucleation limited growth mechanism and the Stern layer reduces the effective Ag^+ flux by a factor of $\sim 10^4$ from the calculated value.

From the above analysis of the role of the Stern layer, it is also evident that regions of enhanced electron accumulation will alter the surface charge and lead to a greater disturbance of the Stern layer and thus more efficient Ag deposition. In comparing the deposition parameters of case 2 and case 4, although they have the same Ag^+ ion to photon flux ratio of $\sim 10^4$, the nanowire structures are still evident in case 2 but are not distinct in case 4. We suggest that this difference stems from the effect of the enhanced photon flux, which leads to enhanced electron accumulation at the surface. For case 2, the photon flux is 100 times larger than that for case 4, and the greater density of photo-excited electrons at the surface more effectively disturbs the Stern layer. Consequently, the Ag⁺ ion flux is reduced more effectively in case 4 suggesting the role of the Stern layer. The result is that in case 2, the nanowire structures are still evident.

V. CONCLUSION

We have investigated the solution concentration and UV-light intensity dependence of a liquid-based photoinduced deposition process for the synthesis of Ag nanostructures on a periodically poled lithium niobate template. The observed variation of boundary-enhanced or boundarydepressed deposition is explained by consideration of the electric field distribution and the ratio between the Ag⁺ ion and photon flux. The results establish that the ratio can be controlled by tuning the solution concentration and UV-light intensity to generate enhanced nanowire-like structures along the domain boundary or a more uniform deposition pattern over the positive and negative domain surfaces. This can be better understood by considering the Ag⁺/photon flux ratio, where the nucleation limited growth mechanism and the Stern layer on the lithium niobate surface are responsible for decreasing the effective Ag⁺ ion flux near the surface. These results also support the photo-induced deposition model where the process is limited by carrier generation and the cation reduction occurs at the surface. These findings will hopefully provide a foundation to employ ferroelectric templates for assembly and patterning of inorganic, organic, biological, and integrated structures.

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