# Photoinduced Ag deposition on periodically poled lithium niobate: Wavelength and polarization screening dependence

Cite as: J. Appl. Phys. **109**, 104302 (2011); https://doi.org/10.1063/1.3580509 Submitted: 03 January 2011 • Accepted: 19 March 2011 • Published Online: 16 May 2011

Yang Sun and Robert J. Nemanich

### ARTICLES YOU MAY BE INTERESTED IN

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

Journal of Applied Physics 110, 084303 (2011); https://doi.org/10.1063/1.3647752

Photocatalytic nanoparticle deposition on  ${\rm LiNb}{\cal O}_3$  nanodomain patterns via photovoltaic effect

Applied Physics Letters 91, 044101 (2007); https://doi.org/10.1063/1.2759472

Polarization-dependent electron affinity of LiNbO<sub>3</sub> surfaces Applied Physics Letters **85**, 2316 (2004); https://doi.org/10.1063/1.1790604





J. Appl. Phys. 109, 104302 (2011); https://doi.org/10.1063/1.3580509

 $\ensuremath{\textcircled{}^{\circ}}$  2011 American Institute of Physics.

### Photoinduced Ag deposition on periodically poled lithium niobate: Wavelength and polarization screening dependence

Yang Sun, and Robert J. Nemanich<sup>a)</sup>

Department of Physics, Arizona State University, Tempe, Arizona 85287-1504, USA

(Received 3 January 2011; accepted 19 March 2011; published online 16 May 2011)

This research addresses the wavelength dependence of the fabrication of Ag nanostructures through photoinduced deposition using single crystal ferroelectric lithium niobate as a template. The photoinduced deposition involves ultraviolent light illumination of polarity patterned lithium niobate while immersed in a AgNO<sub>3</sub> solution. The results focus on the differences of the Ag nanostructure formation process on the positive and negative domains and domain boundaries. The results indicate that for below-band-gap excitation, a very low density of nanostructures is observed. However, for all above-gap-excitation wavelengths, deposition occurs on both polarity surfaces and at the domain boundaries. The density is greatest at the domain boundaries and reduced densities of smaller nanostructures are observed to form on both the positive and negative domains. The deposition on the domain surfaces is greatest for the shortest wavelengths, whereas the domain selectivity is increased for wavelengths just above the band gap. The external screening and weak band bending of single crystal lithium niobate introduces an enhanced electric field at the domain boundary. The enhanced electric field leads to migration of electrons to the domain boundary and consequently enhanced formation of Ag nanoparticles along the boundary. The variation in the reduction rate versus illumination wavelength is attributed to the light absorption depth and the competition between the photochemical and photoelectric deposition processes. To explore the transition from surface to bulk screening of the polarization charge, oxygen implanted PPLN surfaces were prepared and used for the Ag photoinduced deposition. Consistent with the transition to internal (bulk) screening, the Ag nanoparticle formation on the oxygen implanted PPLN surfaces showed suppressed boundary nanowire formation. © 2011 American Institute of Physics. [doi:10.1063/1.3580509]

#### I. INTRODUCTION

Ferroelectric materials are characterized by a spontaneous, reversible polarization and polar surfaces, which exhibit a surface bound charge.<sup>1</sup> The different domains present surfaces with different properties including work function, electron affinity, surface charge, and surface potential. A range of technologies have been developed for nanoscale characterization of the electronic properties of ferroelectric domains: the domain polarity has been characterized by piezoresponse force microscopy (PFM);<sup>2</sup> the surface bound charge and screening have been studied with electrostatic force microscopy (EFM);<sup>3</sup> the surface potential has been studied with scanning Kelvin probe microscopy;<sup>4</sup> and the polarization-dependent electron affinity has been studied by UV-photoelectron emission microscopy (PEEM).<sup>5</sup> In addition, patterns of nanoscale domains may be prepared using a direct write process with a scanning probe microscope (SPM) and a conductive tip. The pattern is generated by applying an electric potential between the tip and the back of the crystal.<sup>6,7</sup>

The unique properties of ferroelectric surfaces have been used to achieve localized chemical reactions, nanopatterned surface functionalization,<sup>8–12</sup> and electrowetting.<sup>13,14</sup> In particular, localized charge transfer oxidation-reduction chemi-

cal reactions on polarity patterned ferroelectric templates have been used to form patterns of metallic nanostructures.<sup>6,15–17</sup> Specifically, for lead zirconate titanate (PZT) poly-crystalline films and barium titanate crystals, the Ag deposition occurred predominantly on the positive domain surfaces.<sup>15–17</sup> In contrast, for photoinduced deposition on polarity patterned lithium niobate, the results showed enhanced Ag deposition at the domain boundaries along with deposition on the positive domains.<sup>6</sup> The difference in the effects was attributed to a difference in the polarization charge screening of the different materials. For materials like PZT, the concentration of defects due to oxygen vacancies and other surface states is estimated as  $10^{14}$  cm<sup>-2</sup>.<sup>18</sup> The high concentration of defect states results in internal screening of the polarization charges, and the induced built-in field modifies the energy bands near the surface and leads to large band bending [Figs. 1(a) and 1(b)]. This implies that the predominant polarization screening mechanism for PZT is internal screening. However, for materials like lithium niobate having a low density of near surface defects  $(10^{12} \text{ cm}^{-2})$ ,<sup>5</sup> the band bending and built-in field are weak [Figs. 1 (c) and 1(d)], and the polarization charges are mainly externally screened via the surface absorption of charged molecules.<sup>19,20</sup>

The different screening mechanisms also lead to different electron affinities of the positive and negative domains. For lithium niobate with screening attributed to molecular adsorption, PEEM measurements have suggested an electron

<sup>&</sup>lt;sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: robert.nemanich@asu.edu.



FIG. 1. (Color online) Band schematics for negative (a) and positive (b) domains for a material with internal screening (i.e., PZT) and band schematics for negative (c) and positive (d) domains for a material with external screening (i.e., lithium niobate). Internal screening leads to strong band bending due to a high concentration of charged states near the surface. Lithium niobate has a smaller concentration of defect states and exhibits external screening, thus, the band bending that occurs at the surface is smaller and depletion width is longer than for PZT.

affinity of 0.7 eV on the negative domains and 2.3 eV on the positive domains. A recent study has proposed that photoinduced deposition is more efficient if the photon energy results in excitation above the vacuum level.<sup>21</sup> In this case the process was termed as photoelectric reduction, whereas for photoexcitation below the vacuum level the process was termed photoreduction.

In this study, the effects of the polarization charge screening mechanism on the photoinduced deposition process are further explored using periodically poled lithium niobate (PPLN) and oxygen implanted PPLN as templates. To establish the dependence of the illumination wavelength on the process, normalized UV illumination with photon energies above and below the  $\sim$ 3.9 eV band gap are employed to generate Ag deposition. The results are explained in terms of the polarization bound charge screening mechanism, the band bending, the near surface electric field distribution, and the depth that the carriers are created relative to the band bending region.

To establish the effect of the polarization screening mechanism on the process, PPLN surfaces implanted with different oxygen ion doses were prepared, and the Ag deposition process was repeated. The deposition pattern was compared to that on original PPLN. The hypothesis is that oxygen implantation generates increased defect concentrations and the screening mechanism changes from external (surface) screening to internal (bulk) screening. Consequently the electric field pattern will also be changed, and the experimental results indeed present different responses of the photoinduced deposition processes on the original PPLN and oxygen implanted PPLN.

#### **II. EXPERIMENT**

#### A. Material

The 5 mm  $\times$  5 mm  $\times$  0.5 mm congruent lithium niobate templates are polished, plane-parallel plates cut normal to the polar axis and periodically patterned with positive and negative domains with 180° domain boundaries (Crystal Technologies). The positive domain is defined as having polarization pointing outward leaving the domain surface with a positive polarization charge, and the negative domain having inward polarization and a negative polarization surface charge. A commercial SPM, (Agilent), with a PFM imaging module has been used in these studies. The modulation voltage was applied through a conductive probe (PPP-EFM, Nanosensors, k = 2.8 N/m, first-order resonance frequency  $\sim 70$  kHz). The PFM measurements were done in an ambient environment using an ac modulation  $V_{ac} = 2$  V at 10 kHz. Figure 2(a) shows a topographic image of the surface of a PPLN sample, where features associated with the domain structure are not evident in the image. The PFM phase image of the same area [Fig. 2(b)] displays the periodic structures. The darker zones correspond to the positive domains and the brighter zones are the negative domains.

To explore the role of surface screening versus bulk screening of the polarization bound charge, identical PPLN substrates were implanted with oxygen ions at different doses. Two different PPLN surfaces were implanted with oxygen ions at an energy of ~700 keV and with doses of ~2 × 10<sup>15</sup> and ~6 × 10<sup>14</sup> cm<sup>-2</sup>. The implantation dose and location on the sample is a well controlled process. The oxygen ion beam covers ~16 mm<sup>2</sup> of the sample surface area, which is large compared to the ferroelectric domains and the AFM scan regions. PFM scans after the implantation indicate that the ferroelectric domains are preserved [Fig. 2(c)] and the positive and negative domains are implanted uniformly within the PFM scanning area. Channeling measurements confirmed that the implanted regions were crystalline.



FIG. 2. (Color online) AFM topography image of as-received PPLN (a), PFM phase image of the same region (b), and PFM phase image of the oxygen implanted PPLN (c). The PPLN shows a featureless image in AFM topography, however, the periodic structure of the positive and negative domains are evident in the PFM phase image.

Wavelength (nm)	Photon energy (eV)	Intensity (mw/cm <sup>2</sup> )	Photon flux $(\#/s \cdot cm^2)$	Illumination time (min)	Absorption coefficient ( $cm^{-1}$ )	Penetration depth (µm)
365	3.40	39.0	$\sim\!71.60\times10^{15}$	$\sim 60$	< 10	> 1000
314	3.95	13.5	$\sim$ 21.32 $ imes$ 10 <sup>15</sup>	$\sim 1.5$	$\sim 90$	111
302	4.11	13.4	$\sim\!20.36\times10^{15}$	$\sim 1.5$	$\sim 800$	12.5
291	4.26	5.5	$\sim 8.00  imes 10^{15}$	$\sim 4$	$\sim 3000$	3.33
254	4.90	1.8	$\sim\!2.30\times10^{15}$	$\sim 13$	$> 10^{4}$	< 1

TABLE I. UV light exposure parameters.

## B. Photoinduced deposition and surface characterization

The PPLN 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 a 50  $\mu$ l drop of a 0.001 M AgNO<sub>3</sub> solution. The sample was then exposed to UV radiation using a 100 W Hg lamp with a collimated condensing lens assembly. The spot size was adjusted to approximately 1 cm.<sup>2</sup>

Filters with 254, 291, 302, 314, or 365 nm central bandpass were used to select the corresponding emission lines from the light source. The corresponding full-width at halfmaximum of each filter as measured by the manufacturer is 9.98, 10.35, 11.48, 11.11, and 11.40 nm, respectively. The operational parameters of the UV light source are listed in Table I. For a given wavelength, the light intensity at the surface of the sample was measured (using a calibrated power meter), and the photon flux (number/ $s \cdot cm^2$ ) was determined from the measured intensity. Different illumination times were used during the deposition process such that the total incident photon exposure on the sample was  $\sim 2 \times 10^{18}$  cm<sup>-2</sup> for all of the above-band-gap wavelengths. After the UV exposure, the sample was immersed in de-ionized water for 1 min, blown dry with nitrogen, and imaged using intermittent mode AFM in ambient environment using a nonconducting probe (PPP-NCH, Nanosensors, k = 42 N/m, first-order resonance frequency ~300 kHz). The same photoinduced process was employed for the oxygen implanted surfaces.

#### C. Analysis

The Ag nanoparticle size and density were determined from visual analysis of the AFM images. To obtain the particle density, three different regions with areas of 400  $nm \times 400$  nm were selected in each domain, and the particles were visually counted. Features (particles) that visually appeared much smaller than the average size were excluded. For example, particles with height < 2 nm 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 and on the negative domain surface, whereas 40 isolated particles are selected on the positive domains. Then a cross-section profile across the center of each selected particle is obtained using the AFM software. Particle diameter and height are determined from the cross section profile. The average size (volume) is calculated based on the volume of a section of a sphere using  $v = (1/6)\pi h[(3/4)D^2 + h^2]$ , in which D presents the diameter and h is the height. The uncertainty is the root-meansquare deviation of the volume of the 20 or 40 particles. For photoinduced deposition using the shortest wavelengths, coalescence of adjoining particles was observed, and in some cases it was difficult to identify and select isolated particles. This analysis was also limited by the fact that nanoparticles smaller than the tip diameter are not accurately represented. Although we made every effort to minimize this effect (by using sharp tips) it seems likely that the smaller particles are not accurately reflected.

The deposition for each wavelength has been repeated several times to minimize errors and obtain consistent results. For every repeated experiment, the visual inspection identified the same phenomena, and the quantitative analysis was consistent. The small variance in the absolute value of silver particle size and density did not change the interpretation of the experimental results.

#### **III. RESULTS**

#### A. Ag deposition on congruent PPLN surfaces

AFM images of the undoped congruent PPLN surfaces after the photoinduced deposition process are displayed in Fig. 3. Noting again, all surfaces were prepared the same way, and the UV exposure time was calibrated such that the total photon exposure was the same for each wavelength (with the exception of the below-band-gap 365 nm exposure). Figure 3 includes a low resolution image of the positive and negative domains, a higher resolution image near a domain boundary, and a line scan across the domain boundary that displays the relative height of the features.

Figure 3(a) displays the topography of the undoped congruent PPLN surface after Ag photoinduced deposition with 254 nm light. This is the shortest wavelength employed in this study, and it is evident that nanowire-like structures assemble along the boundaries of the positive and negative domains. However, the higher magnification image [Fig. 3(b)] reveals that the "nanowires" are formed from a series of ~100 nm rounded islands, some of which are separated by gaps of ~10 nm. The surfaces of the positive and negative domains were also both densely covered by smaller sized nanoparticles (25–50 nm).

Figures 3(c)-3(j) display the results for photoinduced Ag depositions using longer wavelengths of 291, 302, and 314 nm. The periodic domain patterns and their boundaries are evident for all of these above-band-gap wavelengths. Upon analysis of the corresponding 2  $\mu$ m × 2  $\mu$ m images, we find that the positive domains exhibit a higher density of Ag



FIG. 3. (Color online) AFM topographic images of a PPLN surface after Ag photoinduced deposition using 254 nm (a) and (b), 291 nm (c) and (d), 302 nm (e) and (f), 314 nm (g) and (h), and 365nm (i) and (j), illumination. (a), (c), (e), (g), and (i) are 40  $\mu$ m × 40  $\mu$ m scans and (b), (d), (f), (h), and (j) are 2  $\mu$ m × 2  $\mu$ m higher magnification images (insets: height profiles of the higher magnification images).

nanoparticles than the negative domains, and that larger nanoparticles are densely aligned along the boundaries forming nanowire-like structures.

Figure 4 presents a quantitative analysis of the Ag nanoparticle size (volume) and density. The response to the different excitation wavelengths is summarized in the following.

(1) Domain boundary structures: For all above-band-gap excitation, the domain boundaries are decorated with larger



FIG. 4. Average Ag nanoparticle size (volume) (a) and (b) and density (c) vs wavelength. The lines are from point to point and are not fits to the data.

Ag clusters that form nanowire-like structures. The nanowire width is ~85 nm; the height is ~27 nm for 254 nm exposure [Fig. 3(b)], ~60 nm width and ~16 nm height for 291 nm exposure [Fig. 3(d)], ~55 nm width and ~15 nm height for 302 nm exposure [Fig. 3(f)] and ~15 nm width and ~4 nm height for 314 nm exposure [Fig. 3(h)]. It is evident that the size of the domain boundary nanoparticles decreases with increasing wavelength.

- (2) Selectivity on domain surfaces: for the shortest wavelength 254 nm exposure, Ag nanoparticles are formed on both positive and negative domains with a similar density. However, for 302, 291, and 314 nm exposure, the nanoparticle density on the positive domains is enhanced over that formed on the negative domains. Overall, the relative difference of the particle density on the positive and negative domains increases with increasing wavelength.
- (3) Nanoparticle size: For all above-band-gap wavelength exposures, Ag nanoparticles on the domain boundary are larger than nanoparticles on the domain surfaces. The size ratio of boundary nanoparticles over domain surface nanoparticles decreases with increasing wavelength.
- (4) Below-band-gap excitation: For 365 nm exposure, nanoparticle formation was not detected in the AFM images when the same integrated photon flux was used. However, if a longer exposure was employed, Ag deposition was observed, which was predominantly on the positive domain surface. The results are shown in Figs. 3(i) and 3(j). It is evident that the distribution of Ag nanoparticles is very sparse, and there is no evidence of enhanced deposition at the domain boundary. This below-band-gap deposition may be due to defects and/or weak aboveband-gap illumination due to the bandpass function of the filter.

#### B. Ag deposition on oxygen implanted PPLN surfaces

AFM images of Ag deposition on the oxygen implanted PPLN surfaces with the lower dose of  $\sim 6 \times 10^{14}$  cm<sup>-2</sup> are displayed in Figs. 5(a) and 5(b) for 254 nm exposure and Figs. 5(c) and 5(d) for 314 nm exposure. The Ag nanoparticles are evident on both the positive and negative domain surfaces, and there is also evidence of enhanced deposition at the boundary. The boundary nanowire-like structures are suppressed compared to those that form on the unimplanted PPLN surfaces. AFM images of Ag deposition on PPLN implanted with the higher dose of  $\sim 2 \times 10^{15}$  cm<sup>-2</sup> are displayed in Figs. 5(e) and 5(f) for 254 nm and Figs. 5(g) and 5(h) for 314 nm. As displayed in the images, the density and average height of Ag nanoparticles on the negative domains is less than on the positive domains, the combination of these effects results in a  $\sim 2$  nm increase in the average height on the positive domains. This difference is clearly evident in the lower magnification scans. However, the boundary nanowire-like structures are hardly evident. This implantation process is repeatable and the same experimental results are found under the same implanting energy and dose level. These results are in many ways similar to the results for photoinduced deposition of Ag on PZT, where it has been proposed that internal screening leads to significant band bending and internal fields that drive the photoexcited electrons toward the positive domain surfaces.<sup>15–17</sup>

#### **IV. DISCUSSION**

The photoinduced deposition process involves illumination with above-band-gap light ( $\sim$ 3.9 eV or 318 nm) to pro-



FIG. 5. (Color online) AFM topographic images of the oxygen ion implanted PPLN surfaces after Ag deposition: (a)–(d) low dose implant ( $\sim 6 \times 10^{14}$  cm<sup>-2</sup>) and (e)–(h) higher dose implant ( $\sim 2 \times 10^{15}$  cm<sup>-2</sup>). For each dose level, photoinduced deposition with two illumination wavelengths is used: 254 nm [(a), (b), (e), and (f)] and 314 nm [(c), (d), (g), and (h)]. The scan sizes are 25  $\mu$ m × 25  $\mu$ m for the left images and 2  $\mu$ m × 2  $\mu$ m for the right higher magnification images.

duce electron-hole pairs near the surface. Free electrons can be separated by the presence of an internal field or through diffusion. The electrons can migrate toward (or away from) the surface due to the electric field or through thermal diffusion to/from the surface. With the 0.001 M AgNO<sub>3</sub> solution the flux of Ag ions  $(10^{19-20}/\text{s cm}^2)$  to the surface is significantly greater than the photon flux  $(10^{15-16}/\text{s cm}^2)$ . Consequently, the deposition process is limited by the availability of electrons at the surface. The presence of the nanoparticles indicates that nucleation limits the process, and that growth apparently occurs due to reduction of the Ag on the nucleated particles. The presence of the large nanoparticles at the boundary suggests that the electron distribution in response to the internal electric field determines the growth pattern. Presumably, the free electrons migrate or diffuse toward the surface, collect on nucleated nanoparticles and further growth proceeds through reduction of Ag ions at the nanoparticle surface.

In order to explain the wavelength dependence of the Ag deposition process and the differences of Ag deposition on original PPLN and implanted PPLN, we consider three aspects, which are addressed in the following subsections.

#### A. Surface charge screening and electric field distribution

Based on the deposition model described above the photoinduced deposition pattern will depend on the electric field distribution in the ferroelectric material that arises from the internal or external screening of the polarization and the domain pattern. Consequently, the density of photo-generated carriers near the surface will differ substantially at different regions of the surface. Moreover, for similar polarization domain patterns, the screening mechanism can lead to significantly different electric field distributions. For doped materials or materials with a high density of charged defects, internal screening will become important, and the electric field due to the polarization bound charge and charged defects (or dopants) leads to significant band bending. Studies have determined the electric field distribution with the assumption of complete internal screening.<sup>19,22</sup> The results indicate significant electric fields near the domain surfaces, which drive electron migration toward the positive domain surfaces. These studies do not indicate a significantly enhanced electric field along the domain boundary. Thus, the deposition on these templates showed uniform coverage predominantly on the positive domain surfaces without evidence of enhanced deposition along the domain boundaries.<sup>15–17</sup>

In order to explain the nanowire-like structure along the PPLN domain boundaries, the electric field distribution has also been calculated near the surface of domain boundaries of lithium niobate<sup>6,19</sup> with the assumption of complete external screening. The results indicated a nonuniform field distribution with a strong  $E_z$  component of the electric field in the vicinity of the 180° domain boundaries. Away from the boundary, the field due to the polarization and screening decreases rapidly. It is expected that the photoexcited electrons in the vicinity of the boundary electric field. Consequently, enhanced Ag deposition is observed along the domain boundary and nanowire-like structures are observed. In Fig. 6, a sequence of images for above-band-gap 314 nm illumination

displays the accumulation of Ag nanoparticles on the surface over a time period of 4 min. It is evident that the formation is most rapid at the boundaries followed by the positive domains and then the negative domains. Or in other words, more electrons are available at the boundaries than on the domain surfaces during the same irradiation time. Thus, the Ag deposition at the boundaries reflects predominantly the effect of the field induced migration, whereas the deposition on the domain surfaces is due to both diffusion and field induced migration (due to the relatively weak field).

The experiments related to the ion implanted PPLN surfaces were designed to explore the effects due to a change in screening mechanism while preserving the other properties of the materials to the extent possible. The oxygen implantation introduces defects into the PPLN, which can contribute to the screening of the polarization bound charge. The presumption is that the defects are within the band gap and can screen both positive and negative polarization charges consequently enhancing band bending in both positive and negative domains. Depending on the implantation level, the surface of the PPLN changes from external screening, low defect density and weak band bending (< 0.1 eVfrom XPS measurements) for un-implanted surfaces to enhanced internal screening, high defect density and stronger band bending. The latter case is similar to the expected screening for PZT, and the resulting Ag deposition structures were expected to also be similar. This was indeed confirmed by the Ag deposition results shown in Fig. 5. The results showed that the boundary deposition was substantially reduced for the lower dose implantation and was essentially completely suppressed in the higher dose implantation. There was more deposition on the positive surfaces indicating the effects of the field induced migration.

#### B. Illumination penetration depth

A significant effect related to the wavelength is that the illumination generates carriers at different depths from the surface and that the carrier density near the surface will also depend on the wavelength. Table I lists the absorption coefficient and depth for the different illumination wavelengths.

As the illumination photon energy decreases to the band gap, an increasing fraction of electrons are generated



FIG. 6. (Color online) AFM images after Ag photoinduced deposition on PPLN using 314 nm illumination for 60 s (left), 100 s (middle), and 240 s (right). The scan size is 2  $\mu$ m × 2  $\mu$ m for all three images.

relatively deep in the sample, and these electrons will have a lower probability of diffusing or migrating to the surface before recombination or trapping. Consider first the size of the boundary nanoparticles where the size of these particles increases monotonically with increasing illumination photon energy [Fig. 4(a)]. A similar effect is observed for the deposition on the positive and negative domains [Fig. 4(b)]. The difference in the deposition on the positive and negative domains is ascribed to the relative effects of field induced migration. It is evident that as the wavelength decreases, the field induced migration becomes relatively less significant compared to diffusion.

For 254 nm illumination the diffusion effect is most evident. The photons are strongly absorbed within a depth of  $\sim 100$  nm. The electrons generated in both the positive and negative domains have a high probability of diffusing to the surface, and field induced migration is less significant. Consequently, Ag nanoparticles are formed at a similar density on the positive and negative domain surfaces.

#### C. Photoreduction and photoelectric deposition

As noted in Sec. I, recent research on photoinduced deposition on lithium niobate has suggested that photoelectron emission processes could be significant in the process.<sup>21,23</sup> The effect would be important for the negative domains where the 0.7 eV electron affinity and 3.9 eV band gap would lead to a threshold of 4.6 eV for photoelectron emission, whereas on the positive domain the threshold is anticipated at 6.2 eV.<sup>5,22</sup> All wavelengths employed in our experiment are significantly below 6.2 eV, thus the photoinduced reduction process would not involve photoelectron emission. However, the 4.9 eV photon energy of the 254 nm illumination is above the anticipated photo threshold of 4.6 eV of the negative domains. However, we do not observe a significant difference in the deposition rate on the negative domains for this excitation suggesting that the effect is less significant for these PPLN surfaces as compared to those of Refs. 22 and 23. The most evident difference between the results reported here and those of Refs. 22 and 23 is that they employed an illumination source with higher photon energies (cutoff at 200 nm), which would enhance the photoelectron emission. In addition, if the screening is different between the materials of the two studies, then the photothreshold would be affected. Band bending and internal screening could also enhance the photoelectric effect or limit its observation.

#### V. CONCLUSION

We have investigated the wavelength and screening dependences of a liquid-based photoinduced deposition process for the synthesis of Ag nanostructures on a periodically poled lithium niobate template. The observed variation of deposition rate and domain/boundary location was explained by consideration of the polarization screening mechanism and the resultant electric field distribution, the penetration depth of illumination, and the photochemical and photoelectric emission deposition mechanisms. The results establish that shorter wavelength illumination enhances the role of carrier diffusion over field induced migration. It is shown that implantation can be employed to tune the polarization screening between external and internal screening mechanisms, which substantially affects the internal electric field distribution. The results also support the photoinduced deposition model where the process is limited by carrier generation and the cation reduction occurs at the surface. This study provides quantitative results and analysis of the physics of polarization screening and the photoinduced Ag nanostructure formation process on ferroelectric materials. The results provide a foundation to employ ferroelectric templates for assembly and patterning of inorganic, organic, biological, and integrated structures.

#### ACKNOWLEDGMENTS

This research is supported by the National Science Foundation through Grant No. DMR-0805353.

- <sup>1</sup>A. M. Prokhorov and Yu S. Kuz'minov, Physics and Chemistry of Crystal-
- line Lithium Niobate (Taylor and Francis, London, 1990).
- <sup>2</sup>A. Gruverman, O. Auciello, and H. Tokumoto, Annu. Rev. Mater. Sci. 28, 101 (1998).
- <sup>3</sup>X. Y. Liu, K. Kitamura, and K. Terabe, Appl. Phys. Lett. **89**, 132905 (2006).
- <sup>4</sup>K. Terabe, X. Y. Liu, X. J. Li, and K. Kitamura, Ferroelectrics **340**, 121(2006).
- <sup>5</sup>W. C. Yang, B. J. Rodriguez, A. Gruverman, and R. J. Nemanich, Appl. Phys. Lett. **85**, 2316 (2004).
- <sup>6</sup>J. N. Hanson, B. J. Rodriguez, R. J. Nemanich, and A. Gruverman, Nanotechnology **17**, 4946 (2006).
- <sup>7</sup>B. J. Rodriguez, R. J. Nemanich, A. Kingon, A. Gruverman, S. V. Kalinin, X. Y. Liu, and K. Kitamura, Appl. Phys. Lett. 86, 012906 (2005).
- <sup>8</sup>G. L. Person and W. L. Feldmann, J. Phys. Chem. Solids 9, 28 (1958).
- <sup>9</sup>G. I. Distler, V. P. Konstantinova, Y. M. Gerasimov, and G. A. Tolmacheva, Nature **218**, 762 (1968).
- <sup>10</sup>S. Dunn, D. Cullen, E. Abad-Garcia, C. Bertoni, R. Carter, D. Howorth, and R. W. Whatmore, Appl. Phys. Lett. 85, 3537 (2004).
- <sup>11</sup>S Habicht, R. J. Nemanich, and A. Gruverman, Nanotechnology **19**, 495303 (2008).
- <sup>12</sup>D. Ehre, E. Lavert, M. Lahav, and I. Lubomirshy, Science **327**, 672 (2010).
- <sup>13</sup>P. Ferraro, S. Grilli, L. Miccio, and V. Vespini, Appl. Phys. Lett. 92, 213107 (2008).
- <sup>14</sup>S. Grilli, L. Miccio, V. Vespini, A. Finizio, S. D. Nicola, and P. Ferraro, Opt. Express 16, 8084 (2008).
- <sup>15</sup>A. Haussmann, P. Milde, C. Erler, and L. M. Eng, Nano Lett. 9, 763 (2009).
- <sup>16</sup>S. V. Kalinin, D. A. Bonnell, T. Alvarez, X. Lei, J. H. Ferris, Q. Zhang, and S. Dunn, Nano Lett. 2, 589 (2002).
- <sup>17</sup>J. L. Giocondi and G. S. Rohrer, Chem. Mater. **13**, 241 (2001).
- <sup>18</sup>J. F. Scott, *Ferroelectric Memories* (Springer, Berlin, 2000).
- <sup>19</sup>S. V. Kalinin and D. A. Bonnell, Phys. Rev. B 63, 125411 (2001).
- <sup>20</sup>W. C. Yang, B. J. Rodriguez, A. Gruverman, and R. J. Nemanich, J. Phys.: Condens. Matter 17 S1415 (2005).
- <sup>21</sup>S. Dunn and D. Tiwari, Appl. Phys. Lett. **93**, 092905 (2008).
- <sup>22</sup>S. V. Kalinin, C. Y. Johnson, and D.A. Bonnell, J. Appl. Phys. **91**, 3816 (2002).
- <sup>23</sup>S. Dunn, P. M. Jones, and D. E. Gallardo, J. Am. Chem. Soc. **129**, 8724 (2007).