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Physical adsorption on ferroelectric surfaces: photoinduced and thermal effects

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Abstract

Selective deposition of charged polystyrene (PS) microspheres from an aqueous solution on domain-patterned lithium niobate is investigated. The selectivity of PS microsphere deposition can be varied by controlling the deposition temperature. Selective decoration of the positive domains (positive polarization surface charges) is achieved at room temperature and is attributed to the electrostatic interaction of the charged nanoparticles and the polarization surface charges of the ferroelectric. In contrast, at elevated temperatures, the particles decorate the negative domains. This process is explained by considering the pyroelectric properties of lithium niobate.

Due to the presence of permanent surface charges, which can be controlled at the nanoscale, ferroelectric crystals such as lithium niobate (LiNbO₃) have been the subject of investigation as template materials for selective polarizationdriven deposition of charged species. Earlier studies by Pearson et al [1] described the electrostatic interaction between charged particles in a colloidal solution and the surface charges of the ferroelectric sample resulting in selective decoration of the ferroelectric domains of specific polarity. Recent studies focused on investigation of surface charge, surface potential and a surface dipole in fundamental processes governing assembling on ferroelectric surfaces [2–4]. It has been demonstrated that metallic nanowires can be grown via a photo-induced chemical reaction on domain-patterned LiNbO3 and BaTiO₃ crystals [2, 4, 5] and lead zirconate titanate (PZT) films [6, 7].

In this paper, we present results of UV-induced liquidphase deposition of carboxyl functionalized polystyrene (PS) microspheres on a periodically poled lithium niobate surfaces (PPLN) at controlled temperature conditions. We show that the decoration of the domains in LiNbO₃ crystals by PS microspheres at elevated temperature is different from the decoration at room temperature. The observed difference is ascribed to the photovoltaic and pyroelectric effects.

Periodically poled lithium niobate of congruent composition with a thickness of 500 μ m (Crystal Technologies) were used as deposition templates. The domain structure of the

lithium niobate samples exhibits polarization along the *c*-axis allowing only two possible domain orientations with 180° domain structure (period ~28 μ m). The LiNbO₃ substrates were 3 × 3 mm² plane parallel cuts perpendicular to the polar axis. The domain structure was provided by the supplier and involved a photolithographic step.

Commercially available PS microspheres (Duke Scientific Polystyrene, Carboxyl Cat# W010HA 0.10 µm) suspended in deionized water were used for selective deposition studies on PPLN. For deposition, the aqueous solution of polystyrene microspheres (hydrophobic) was diluted with deionized water to obtain an adequate concentration (0.004% solids in According to the manufacturer's specifications, solution). the microspheres have a diameter of 100 ± 10 nm and are charged negatively due to their carboxyl-functionalization. The functionalization consists of a carboxyl group -C(=O)OH(or $-CO_2H$) attached to a microsphere. The oxygen has a net negative charge, and the surface charge density, specified in terms of the parking area, is $102-175 \text{ Å}^2/\text{carboxyl-group}$ according to the manufacturer. The parking area describes the space occupied by a carboxyl group. In general the parking area allows comparing particles of different size and charge and is inversely proportional to the surface charge density.

The presence of a net charge at the particle's surface has an impact on the distribution of ions in the surrounding interfacial region. Thus the charged particles become clouded by ions of opposite charge such that an electric double layer is



Figure 1. Distribution of potential of polystyrene spheres in the solution.

formed close to the particle surface. Electrostatic interactions between the charged particles and the electric double layer determine the stability of the colloidal system. Recent studies on hydrophobic particles in aqueous solution proposed a compression of double electrical layers, resulting in a reduction of the electrostatic repulsion of the hydrophobic particles [8].

To confirm the charge state of the functionalized microspheres, measurements of their surface potential have Zeta-potential analysis showed that the been performed. particles in the solution carry a negative potential of -50 mV(figure 1). Zeta potential of PS microspheres was measured with a Malvern Zetasizer Nano ZS instrument using a combination of laser Doppler velocimetry and phase analysis light scattering. Prior to measurements, the water-based suspension of PS particles was sonicated using a horntype sonicator for 2 min. Before deposition the LiNbO₃ samples were cleaned in a sequence of methanol and acetone in an ultrasonic bath. During deposition, the samples were illuminated with a 20 W Hg pen lamp with a dominant emission wavelength of 254 nm, which was placed \sim 3 cm above the sample. According to the manufacturer's specifications the power density reaching the LiNbO₃ is in the range of 1–4 mW cm⁻². The illumination is strongly absorbed by the lithium niobate since its corresponding photon energy is greater than the band gap of LiNbO₃ (\sim 3.9 eV).

To avoid formation of colloidal particles, the original solution was sonicated for 15 min before the dilution. After the dilution, the aqueous solution was sonicated again for 15 min. Deposition of the microsphere solution was done under (i) ambient environment at room temperature and (ii) at elevated temperature (T = 60 °C) accompanied in both cases by UV illumination. During both types of experiments the aqueous solution was air dried on the sample surface. No further cleaning process was done. The time to let the microsphere solution dry varied due to the difference in temperature in both processes; (i) 25 min at room temperature and (ii) 5 min at elevated temperature, respectively. After the solution air dried atomic force microscopy (AFM) and PFM measurements were immediately initiated.

A commercial scanning probe microscope (SPM), ThermoMicroscopes CP-Research, with a piezoresponse force microscopy (PFM) imaging module has been used in these studies. The modulation voltage was applied through a conductive tip (NSC-14 MikroMasch, $k = 5 \text{ N m}^{-1}$). The PFM measurements were done in ambient environment using an ac modulation $V_{ac} = 2 \text{ V}$ at 12 kHz.

Topographic characterization of the PPLN surfaces after drying the microsphere solution was performed in non-contact mode AFM (NC-AFM). Figure 2(a) shows the topographic image of the surface of a PPLN sample before the deposition of the microsphere solution where no significant surface features are observed. Figure 2(b) shows the topography image of the same area after the UV-assisted deposition of the microsphere solution at room temperature. A PFM phase image taken of the same area is shown in figure 2(c). Dark contrast in the PFM phase image indicates +c domains with positive surface polarization charges, whereas bright PFM phase contrast indicates -c domains with negative surface polarization charges. Comparison between the topographic and PFM data in figure 2 indicates that the PS microspheres preferentially decorate the surface of the +c domains with positive surface polarization charges.

To explore the temperature dependence the next experiment was performed by heating the PPLN sample to a temperature of T = 60 °C immediately before and during the deposition. The solution of spheres was not heated prior to the deposition, but since the temperature was maintained during UV illumination, the solution on the sample also reached a temperature of T = 60 °C. After the deposition process, the surface topography was examined with non-contact atomic



Figure 2. (a) AFM topographic image of the PPLN surface before deposition, (b) non-contact AFM topographic image of PPLN after deposition of microspheres and (c) corresponding PFM phase image of the area (the scan size of all images is $15 \times 15 \ \mu\text{m}^2$).



Figure 3. (a) NC-AFM topographic image of the PPLN surface before deposition, (b) NC-AFM topographic image of the PPLN sample after deposition of microspheres at elevated temperature of $T = 60 \,^{\circ}$ C and (c) corresponding PFM phase image of the area (the scan size of all images is $40 \times 40 \,\mu$ m²).

force microscopy (NC-AFM). To verify which polar surface, +c or -c domain surface, was decorated, PFM imaging of the same area was performed.

Figure 3(a) shows the topographic image of the clean PPLN surface before deposition, while figure 3(b) shows topography of the same area after the deposition process. The dark features in the upper right and lower left corner of figures 3(a) and (b) are topographic features used as markers to establish the exact same location for AFM imaging. The PFM phase image of the domain pattern is shown in figure 3(c). In contrast with the experiments at room temperature, the PS microspheres now preferentially decorate the surface of the negative domains. In addition, an enhanced deposition of microspheres along the domain boundary can be clearly seen.

Selective deposition of the PS microspheres on the +cdomain surfaces at room temperature can be explained by a photovoltaic effect along the polar axis of the lithium niobate crystal. In stable conditions, polarization charges of the PPLN sample are completely compensated via a combination of charge adsorption on the surface (external screening) and internal charge accumulation beneath the The low concentration of surface (internal screening). defects in the lithium niobate $(10^{12} \text{ cm}^{-2})$ [9] implies that the predominant mechanism of polarization screening is the external one. Photoelectron emission microscopy (PEEM) measurements indicate a variation of the electron affinity that was attributed to the external screening [10] (figure 4). Residual internal screening resulting in band bending is also anticipated from these results, leading to the formation of a space charge region below the surface.

In order to quantitatively examine the properties of the ferroelectric surface the degree of screening of the polarization charge, σ_{pol} , due to (internal and/or external) screening charges, σ_{scr} , has to be addressed. Four cases can be distinguished [11]: (i) unscreened polarization charge, with $\sigma_{scr} = 0$, (ii) partial screening, $\sigma_{pol} > \sigma_{scr}$, (iii) complete screening $\sigma_{pol} = \sigma_{scr}$, and (iv) overscreening of the polarization charge with $\sigma_{pol} < \sigma_{scr}$. The latter three cases of partial, complete and overscreening will be discussed further. The entire unscreening of σ_{pol} is not an energetically favorable state [12, 13], whereas overscreening is expected to occur in non-equilibrium states such as domain switching or heating [14].



Figure 4. Schematic band structure of the (a) +c domain and (b) -c domain of the LiNbO₃.

Illumination of lithium niobate with above band-gap UV light affects the amount of internal screening charge at room temperature. As a result of the band bending photo-induced electrons migrate preferentially in +Z direction and contribute to the internal screening of the positive polarization charges of +c domains (figure 4(a)), for the -c domains the electrons move towards the bulk. Due to the weak electric field near the surface, separation of electron-hole pairs is not very efficient. Furthermore, the wavelength of the UV light ($\lambda =$ 254 nm) is assumed to be absorbed only in the very vicinity of the surface. Hence, we conclude that the electron flux generated by the photovoltaic effect is much lower, compared to previous studies [4]. The increase in internal screening results in a decrease of the density of the charges adsorbed on the surface. After UV illumination is turned off, electronhole recombination processes result in incomplete screening of the positive polarization ($\sigma_{\rm pol} > \sigma_{\rm scr}$), which leads to the negatively charged microspheres moving to and decorating the positive domain surface at room temperature. Liu et al [4] pointed out the importance of a continuous supply of electrons to be transferred towards the surface. They achieved this by polishing their samples down to a thickness of 800 nm to achieve illumination throughout the sample. In addition to that an Au electrode was deposited on the backside of the sample and contacted to a power supply. This ensured the supply of electrons which were needed for the catalytic deposition of silver in their experiments.

The decoration of the negative domain at elevated temperature can be attributed to the pyroelectric property of the LiNbO₃. Heating of the LiNbO₃ crystal results in a decrease of

the spontaneous polarization P_s [15] and overscreening of the polarization (figure 4). Hence the surface potential, which is strongly affected by the polarization charge and the screening charges, changes with temperature. In the case of the negative domains (figure 4(b)) there is an excess of positive screening charges. Electrostatic interaction between the negatively charged PS microspheres and the excess positive screening charges is assumed to cause decoration of the negative domain at T = 60 °C. For the positive +c domains, heating yields a correspondingly excess of negative charges and, consequently, no microsphere deposition. Comparing the measurements at room and elevated temperatures, we observed also an enhanced decoration of the domain wall at T = 60 °C. Based on a previous study of photo-chemical deposition [2], the enhanced decoration of the domain walls at $T = 60 \,^{\circ}\text{C}$ can be explained by the nonuniform electrical field distribution.

These qualitative measurements are supported by studies of the surface potential using heat-treatment [16], where the predominant contribution of screening charges at elevated temperatures (up to 393 K) was observed, while at room temperature the contribution of the polarization charges was predominant. Time dependence of the surface potential at constant temperature was also studied, showing conservation of screening charges for several hours (~50 h) in vacuum. Kalinin *et al* reported similar behavior of BaTiO₃ surfaces in air [17].

In conclusion, we have investigated the deposition of charged polystyrene microspheres in aqueous solution on periodically poled lithium niobate surface. By varying the temperature of the sample during the deposition process, we could control the location of the charged microspheres on the surface of the LiNbO₃. The observed behavior is explained by two main effects: the photovoltaic effect and the pyroelectric properties of the LiNbO₃. UV illumination and heating of the LiNbO₃ crystal disturbs the balance between the surface polarization charges and the screening charges resulting in selective deposition of the negatively charged microspheres. Whereas the photovoltaic effect is responsible for the decoration of the positive domains at room temperature,

the pyroelectric effect is the dominant mechanism contributing to the particle deposition on the negative domains at elevated temperatures. The electrostatic interaction is assumed to be the driving force for both decoration processes.

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References

- Pearson G L and Feldmann W L 1958 J. Phys. Chem. Solids 9 28
- [2] Hanson J N, Rodriguez B J, Nemanich R J and Gruverman A 2006 Nanotechnology 17 4946
- [3] Ke C, Wang X, Hu X P, Zhu S N and Qi M 2007 J. Appl. Phys. 101 101
- [4] Liu X, Kitamura K, Terabe K, Hatano H and Ohashi N 2007 Appl. Phys. Lett. 91 044101
- [5] Giocondi J L and Rohrer G S 2001 Chem. Mater. 13 241
- [6] Jones P M and Dunn S 2007 Nanotechnology 18 185702
- [7] Kalinin S V, Bonnell D A, Alvarez T, Lei X, Hu Z and Ferris J H 2002 Nano Lett. 2 589
- [8] Mishchuk N 2008 J. Colloid Interface Sci. 320 599
- [9] Yang W C, Rodriguez B J, Gruverman A and Nemanich R J 2004 Appl. Phys. Lett. 85 2316
- [10] Yang W C, Rodriguez B J, Gruverman A and Nemanich R J 2005 J. Phys.: Condens. Matter 17 S1415
- [11] Kalinin S V and Bonnell D A 2001 Phys. Rev. B 63 125411
- [12] Dunn S, Jones P M and Gallardo D E 2007 *J. Am. Chem. Soc.* **129** 4946
- [13] Fridkin V M 1980 Ferroelectric Semiconductors (New York: Consultants Bureau)
- [14] Chen X Q, Yamada H, Horiuchi T, Matsushige K, Watanabe S, Kawai M and Weiss P S 1999 J. Vac. Sci. B 17 1930
- [15] Fatuzzo E and Merz W J 1967 *Ferroelectricity* (Amsterdam: North-Holland)
- [16] Liu X, Terabe K and Kitamura K 2006 J. Electroceram. 16 399
- [17] Kalinin S V, Johnson C Y and Bonnell D A 2002 J. Appl. Phys. 91 3816