Selective Photochemical Reduction of Silver on Nanoembossed Ferroelectric Nanowires

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There has been growing enthusiasm for developing novel processes capable of assembling nanostructural elements with chemical or electromagnetic functions into nanostructures toward potential nanodevices by using both highly defined and well controlled method.¹ Ferroelectric devices, for example, with internal dipolar field are able to internally drive apart photogenerated carriers via the bulk photovoltaic effect.² As the ferroelectric domains can be patterned at the nanoscale, the domain modified surface chemistries may provide a method for nanodevices fabrication.³ The concept of using poled ferroelectric domains to direct the growth of nanoparticles is being explored, known as ferroelectric lithography.⁴ Photochemical experiments on ferroelectrics such as $Pb(Zr_x,Ti_1)$ $_x)O_3$, BaTiO₃, and LiNbO₃ have shown that the reduction reactions (for instance, the reduction of Ag^+ to Ag^0) are favored on the surface of domains with positive polarization.⁵ Using a conductive tip under a certain bias in an Atomic Force Microscope (AFM), it has reportedly become a convenient technique to write ferroelectric domains and served as a major method for ferroelectric lithography. However, the limitation of this technique is its slow scan rate and small scan area.

In this work, we propose to use nanoembossing technique to pattern domains in the ferroelectric lithography. Figure 1 describes the embossing process (a) and the resultant imprinted structure in PZT. Photochemical reduction of Ag particles occurs preferentially along the embossed nanowires. By imaging domain configurations of the embossed films using Piezoresponse Force Microscope (PFM), we found that the selectively deposition of Ag particles associates to the underlying ferroelectric domain structures created by the nanoembossing process (Figs. 2-3). Controllable and selective deposition of metal species onto nanoembossed ferroelectric nanostructures without the assistant of external electrical field may provide a new route to nanoferroelectric lithography.

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Figure 1. Schematic illustration of PZT nanoembossing process (a). Embossed topography with ~ 200 nm embossed depth on a ~ 450 nm PZT film (b).



Figure 2. (a) Corresponding out-of-plane (OPP) piezoresonse signal of the embossed sample shows most positive and negative domains clustered on the embossed nanowires. (b) OPP signal of an un-embossed region for comparison, which indicates a featureless domain state in this region. The scale bar in (b) also refers to (a).



Figure 3. SEM pictures of embossed PZT topographies before (a) and after (b) Ag deposition. As shown, Ag particles have selectively grown on the embossed nanowires contributed to the domain patterns created by the nanoembossing.