Direct Writing of Silver Nanostructures and Painting on Phosphate Glass with Electron Beam Irradiation

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We report on a novel but simple process for directly coloring transparent $AgIAgPO_3$ glasses at the nanoscale using an electron beam. This process also is capable of direct extraction of silver nanoparticles on the substrate surface. $AgIAgPO_3$ glass belongs to a family of solid state superionic conductors with high conductivity of Ag^+ ions.[1] The availability of Ag^+ ions at room temperature allows for simple, single-step patterning of Ag nanostructures through solid state electrochemical interaction with incident electrons. The localized irradiation of the surface of the glass by an electron beam causes charge transfer to the surface and subsequently localized electrochemical reduction of silver. In this report the processes is characterized using high conductivity $AgIAgPO_3$ glass and low conductivity $AgPO_3$ glass subjected to beams with acceleration voltages ranging from 1-12kV for varying amounts of electron fluence ranging from 50 pC/μm^2 to 35 nC/μm^2.

For fluences less than 2.5nC/μm^2, the reduced silver altered the optical properties of the glass, creating intense colors in reflection. Varying the fluence allowed for fine tuning of colors, while the beam acceleration voltage controlled the wide range of colors produced. In comparison, low conductivity $AgPO_3$ glass displays a very limited set of colors. Though Marquistaut[2] has demonstrated limited color patterning with femtosecond lasers, the appearance of color requires an additional annealing step to increase ion mobility. Figure 1a demonstrates the high contrast capability in a simple bicolor pattern displaying high color uniformity. Figure 1b displays the flexibility of the process by integrating both voltage and fluence control allowing fine-tuned color control.

At larger fluence, the quantity of silver extracted was sufficient to generate well defined bulk-like reflective silver films protruding from the surface. In contrast, patterning $AgPO_3$ glass results in uncontrolled dendritic silver growth. By using a lithography package to control the e-beam scanning, the process can direct-write silver films of arbitrary shape. The localized extraction of silver allows adjacent features to be formed with gaps as small as 50nm in films over 200nm tall as shown in Figure 2. These types of features are especially suited for the direct creation of engineered silver structures such as NSOM apertures and SERS substrates.

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[1] **Bhattacharya S, Dutta D, Ghosh A**. Dynamics of Ag+ ions in Ag_2S -doped superionic $AgPO_3$ glasses. *Phys Rev B: Condens Matter Mater Phys.* 73: 104201, 2006.
[2] **Marquestaut N, Petit Y, Royon A, Mounaix P, Cardinal T, Canioni L**. Three-dimensional silver nanoparticle formation using femtosecond laser irradiation in phosphate glasses: Analogy with photography. *Adv Funct Mater* 24: 5824-5832, 2014.

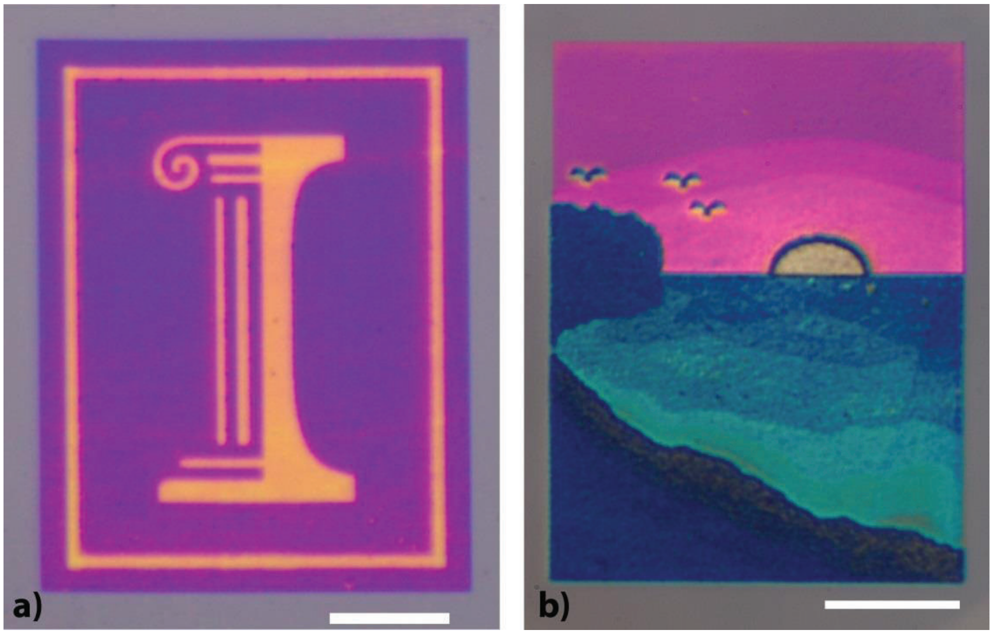

Figure 1: Microscope optical images on $AgIAgPO_3$ produced by patterned electron beam irradiation: a) Optical image of high-contrast bicolor graphic. Patterned in two passes: 5 kV and 7 kV V_{acc}. b) Optical image of gradient painting pattern in two passes: 4 kV and 6 kV V_{acc}. Scale bars are 25 microns.

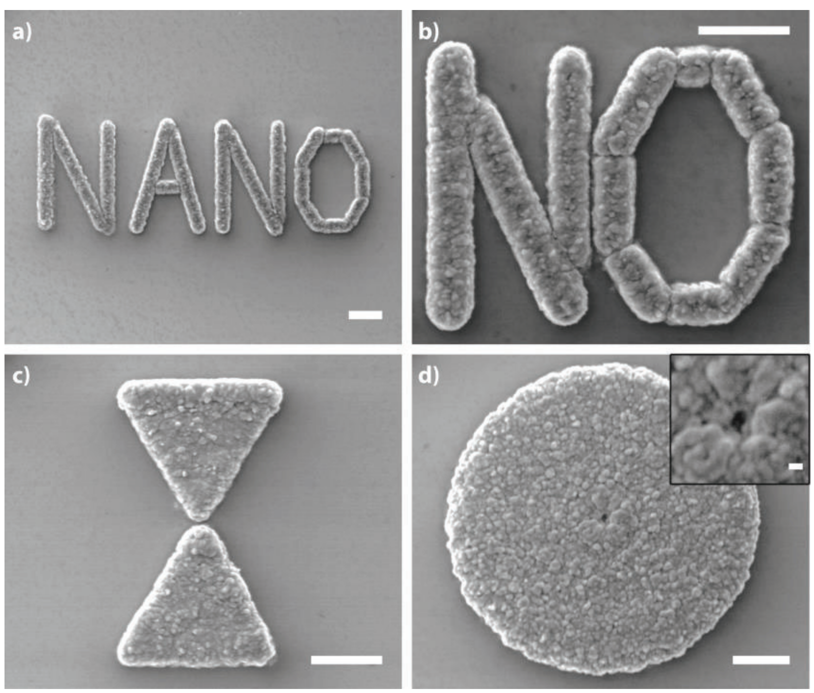

Figure 2: High resolution silver structures patterned on $AgIAgPO_3$: a)Lateral resolution test of lines written at 5kV and 3.9nC/µm b) Silver lines patterned with a 50nm gap. c) Bow tie antennae with 55nm gap d) 150nm NSOM aperture in 280nm thick silver film. Scale bars 1 µm, inset scale bar 100nm.