Honeycomb Networks of Metal Oxides from Self-Assembling PS-PMMA Block Copolymers

Frank Barrows\textsuperscript{1,2}, Paul Nealey\textsuperscript{2}, Tamar Segal-Peretz\textsuperscript{3}, Liliana Stan\textsuperscript{4}, Jeffrey Elam\textsuperscript{5}, Anil Mane\textsuperscript{5}, Ellie Porath\textsuperscript{6}, Charudatta Phatak\textsuperscript{2}, Amanda Petford-Long\textsuperscript{2}

\textsuperscript{1} Applied Physics Program, Northwestern University, Evanston, IL, USA
\textsuperscript{2} Material Science Division, Argonne National Laboratory, Argonne, IL, USA
\textsuperscript{3} Technion- Israel Institute of Technology, Haifa, Israel
\textsuperscript{4} Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL, USA
\textsuperscript{5} Energy Science Division, Argonne National Laboratory, Argonne, IL, USA
\textsuperscript{6} Physics Department, University of Chicago, Chicago, IL, USA

To fully understand the stochastic nature of resistive switching in memristive oxides such as TiO\textsubscript{2} and HfO\textsubscript{2}, it is necessary to observe the formation and dissolution of conduction pathways at sequential points during the set and reset operations. Understanding the role of microchemical and microstructural factors on the variability of the resistance states is critical in order to enable control of resistive switching phenomena \cite{1}. In this work, we present a unique method to produce nanopatterned resistive switching oxide networks via block copolymer (BCP) self assembly and sequential infiltration synthesis (SIS) that will allow for probing the mechanisms by which conduction pathways are formed in the networks using techniques such as in-situ TEM.

Our process consists of two steps: (1) Self-assembly of block copolymers to define the patterns and (2) Infiltration of metal oxides into the pattern using atomic layer deposition (ALD) as discussed in Segal-Peretz \textit{et al.} \cite{2}. An anchor layer of random PS-PMMA, polystyrene poly(methyl methacrylate), was spin coated followed by annealing at 250°C for 30 minutes and quenching on an aluminum block. We then spin coated a 3 wt.% BCP PS-b-PMMA solution and annealed the sample at 270°C for one hour before quenching. Ellipsometry measurements showed the BCP thickness to be ~50 nm after annealing. Using the SIS process, we infiltrated the metal oxides into the PMMA by sequential pulsing metal precursor and subsequently oxidizing the metal by exposure to H\textsubscript{2}O. After the metal oxide infiltration, the residual polymer was etched away with O\textsubscript{2}, leaving a BCP-templated metal oxide nanostructure with a honeycomb pattern (Fig 1).

Analysis of the AlO\textsubscript{x} honeycomb network in Fig 1 showed that the connected alumina bars have a width of ~20 nm. It is important to limit the oxide bar cross-section so they will accommodate a single conducting pathway of diameter ~10 nm for HfO\textsubscript{x} as reported in the literature \cite{3}. As a result, we will be able to investigate the resistance change behavior of the entire network through percolation like switching as opposed to multiple pathways forming in a single link.

The significance of this approach is that it is readily scalable, and the geometry of self-assembled PS-PMMA BCP can be controlled, thereby allowing control of the oxide network geometry \cite{4}. Fig 2 shows the BCP honeycomb phase deposited between Pt electrodes separated by 180 nm. We will present results on fabrication of networks of other oxides such as HfO\textsubscript{x} and TiO\textsubscript{x}. We will discuss the resistance switching behavior of these networks and the characterization using multi-modal imaging with conductive AFM, electron tomography, and in-situ TEM \cite{5}. 

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References:

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Figure 1. SEM image of Alumina infiltrated into PS-b-PMMA which has been etched away.

Figure 2. a) SEM image of Pt electrodes. b) SEM image of PS-b-PMMA between platinum electrodes.