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## Solution-Phase Deposition and Nanopatterning of GeSbSe Phase-Change Materials

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*Chalcogenide films with reversible amorphous-crystalline phase transitions have been commercialized as optically rewritable discs, and intensive effort is now focused on integrating them into electrically addressed nonvolatile memory devices (phase change random access memory, or PCRAM). While optical data storage is accomplished by laser-induced heating of local spots within continuous films, electronic memory requires integration of discrete nanoscale phase-change material features with read/write electronics. Currently, phase-change films are most commonly deposited by sputter deposition, and patterned by conventional lithography. We are exploring an alternative, solution-phase deposition method for metal chalcogenide phase-change materials.*

Soluble precursors for metal chalcogenide thin films are synthesized in the reducing solvent hydrazine. Isolated by removing the solvent, the resulting powders contain metal-chalcogen clusters, spaced apart by hydrazine molecules and hydrazinium ions. For phase-change material development, two precursors were synthesized: one containing Sb and Se, and another containing Ge and Se. These precursors decompose at low temperature (<200 °C), forming the extended bonding networks of metal chalcogenide materials. Upon thermal annealing, the Sb-Se precursor yields crystalline Sb<sub>2</sub>Se<sub>3</sub>, and the Ge-Se precursor yields an amorphous powder.

To deposit thin films, the precursors are dissolved and spin coated, then thermally annealed to form the phase-change material, an alloy of Ge, Sb, and Se. The precursors may be combined in solution in different ratios to tune the composition of the final film. For example, Ge-Se and Sb-Se precursors are mixed to prepare GeSbSe films, which are amorphous as deposited, while films of Sb<sub>2</sub>Se<sub>3</sub>, like the associated powder, are crystalline after annealing to decompose the precursor.

Crystallization of the phase-change films is characterized at the NSLS by continuously monitoring diffraction peaks during ramped thermal annealing. The crystallization temperature at which peaks first appear can be tuned by adjusting the level of Ge doping in GeSbSe films (**Figure 1a-d**). Higher Ge content stabilizes the amorphous state until crystallization is no longer observed above about 15% Ge.

Contrast in electrical resistivity between the amorphous and crystalline phases indicates the state of a PCRAM device – a digital 1 or 0. We

characterize the resistivity contrast of our phase-change materials by measuring the resistance across two contacts as we thermally anneal the film. Since conduction is thermally activated, the resistance of the amorphous film drops slowly as it is heated. At the crystallization temperature, the resistance drops sharply since the crystalline state is more conductive. Upon cooling, the material remains in the crystalline state and the resistance is reduced from its initial value.

The kinetics of the amorphous-crystalline transition are probed by annealing local areas of the film with laser pulses and observing the time-dependent reflectivity. Enhanced reflectivity is indicative of crystallization, while decreased reflectivity indicates amorphization. A GeSbSe film is deposited on a 40 nm thick layer of Al<sub>2</sub>O<sub>3</sub>, which moderates heat transfer to the silicon substrate so that local areas may be melt-quenched and frozen in the amorphous state following a high-powered laser pulse. The amorphous spots formed by melt-quenching can be recrystallized by moderately powered laser pulses. The observed minimum recrystal-



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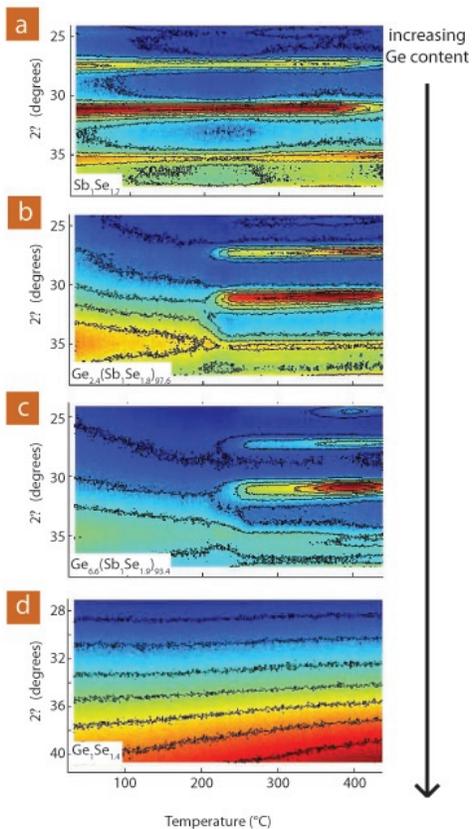
lization time is about 100 ns.

During deposition of the precursor film, capillary forces can be leveraged to fill nanoscale patterns. Nanodot patterns of phase-change material can be formed using a block copolymer template (**Figure 2a**). The resulting phase-change nanodots (**Figure 2b,c**) crystallize in the same orthorhombic phase as the bulk film (**Figure**

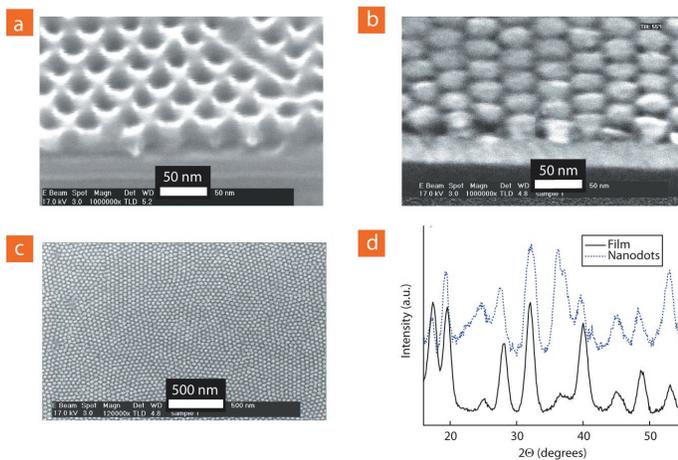
**7d**), at a crystallization temperature reduced by 35 °C. Capillary filling can also fill high-aspect ratio via structures. Filling such vias with phase-change material can potentially reduce the critical RESET current in a PCRAM device.

We have demonstrated solution deposition of phase-change materials with tunable composition and crystallization temperature. Fast (~100

ns) switching is possible in spin-on GeSbSe films. Small- and/or high-aspect ratio vias can be filled easily with phase-change material deposited from solution. Next, we plan to integrate spin-on materials into prototype PCRAM devices and to explore new applications for spin-on metal chalcogenide materials.



**Figure 1.** Thermal crystallization of GeSbSe films followed by temperature-dependent x-ray diffraction.



**Figure 2.** Nanopatterns of GeSbSe phase-change material formed using a block copolymer template.