

Challenges in Colloidal Phase Change Nanoparticle Devices

Marissa A. Caldwell¹, Delia J. Milliron², H.-S. Philip Wong³

*Departments of Chemistry¹ and Electrical Engineering³, Stanford University, Stanford CA 94005
The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley CA 94720*

Abstract

Colloidal nanoparticles offer an attractive route both to investigate the fundamental scaling limits of phase change technology and to act as a solution processable route to phase change material (PCM) deposition. However, the incorporation of a nanoparticle film into a working memory cell faces significant process challenges. Here we describe some of the challenges unique to colloidal nanoparticles and the strategies currently used to circumvent them.

Main Text

While many strategies have been used to minimize the volume of phase change materials¹⁻⁵, until recently, no reports of a colloidal route to nanoparticles of any known

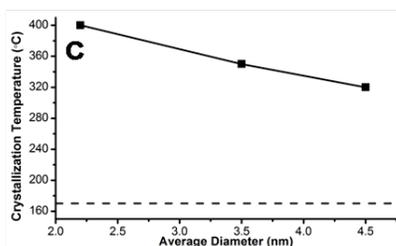
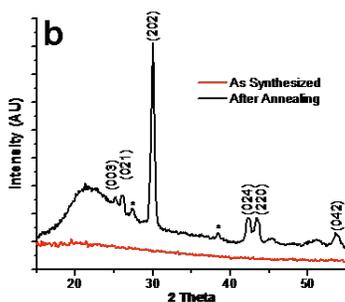
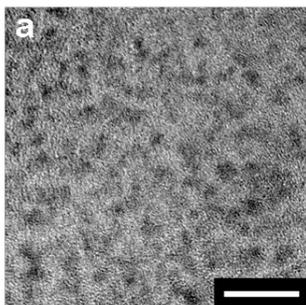
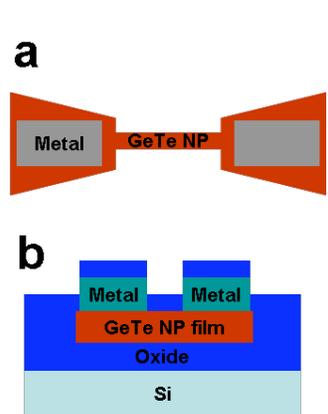


Figure 1 - a) Transmission electron micrograph of GeTe nanoparticles. Scale bar is 10nm. b) Powder x-ray diffraction of nanoparticles before and after annealing at high temperatures. c)

phase change material existed. In the past decade, several other electronic applications such as photovoltaic devices⁶, have become interested in utilizing inorganic colloidal nanoparticles. Increased focus on producing high quality nanocrystals has led to colloidal syntheses of highly regular, monodispersed nanocrystals⁷ aimed at specific applications, but development of analogous systems for PCRAM applications was not reported. Recently, we reported the first colloidal route to PCMs in the form of amorphous GeTe nanoparticles⁸. The nanoparticles ranged in size from 1.7-4nm in diameter and their structure, shape and composition were characterized by standard techniques (Fig 1a,b). In addition, we reported a size selective procedure enabling us to measure the size dependence of the crystallization temperature, and found a dramatic increase in the amorphous stability as the particle size decreased (Fig 1c).

To further investigate the nanoparticle properties, we focused on incorporating the nanoparticles into a PCRAM device, in order to elucidate the electrical switching characteristics of nanoparticle films. For a first generation device, we choose a simple line device geometry (Fig 2). The line geometry is one example of typical phase change cells, which are generally designed to force current through a small volume of PCM in order to generate enough joule



heating to crystallize or melt the PCM⁹. All of the processing is based on standard optical lithography and CMOS processing, with the exception of the PCM deposition (Fig 3a). The colloidal nanoparticles are very stable in non-polar solvents due to their organic capping ligand. In particular, GeTe nanoparticles are exceptionally soluble and stable in toluene. However, the use of toluene as a solvent for spin coating creates two major challenges. The first is good wetting of the substrate. For high quality nanoparticle films, the spin coating solution must wet the substrate well. In the case of our process flow, the last step before particle

deposition is a wet etch of the SiO₂, which makes the surface hydrophilic. To control the surface wetting characteristics, we added an additional vapor prime of hexamethyldisilazane (HMDS) immediate before nanoparticle deposition, and found good wetting characteristics with the nanoparticle solution.

The second process challenge caused by toluene is the nanoparticle film liftoff. In this process flow, liftoff, rather than etching, is used to pattern the PCM. Initial attempts at nanoparticle film liftoff resulted in poor photoresist removal due to hardening. Toluene is known to harden photoresist, which interferes with clean liftoff. To get around this challenge, we added an additional lift off layer (LOL) consisting of a non-photosensitive polymer below the photoresist (Figure 3b). The LOL provides and undercut during photoresist development and allows a clean liftoff despite the hardened resist.

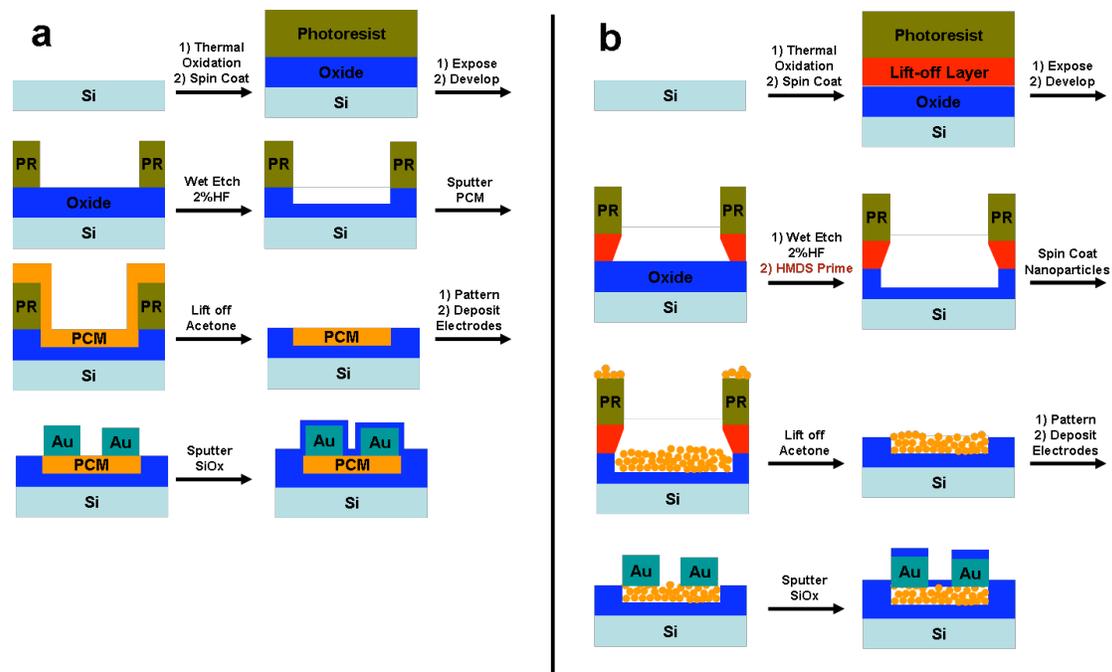


Figure 3 - Process flows for a) standard line device fabrication with a physical deposition of PCM and b) modified fabrication to incorporate colloidal nanoparticles

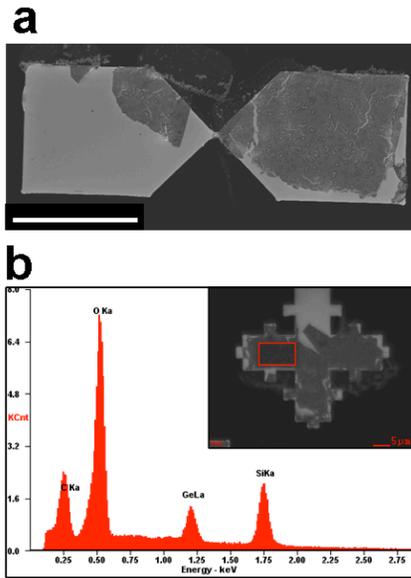


Figure 4 - a) SEM image illustrating nanoparticle film delamination. Scale bar is 100µm. b) EDAX data indicating the location of the nanoparticle film. The peak not

Once the major process challenges were solved, several attempts at making devices were made. However, no working devices were fabricated. A major problem remained with the liftoff of the nanoparticle film. Despite optimizing the nanoparticle film thickness, the film delaminates from the patterned regions of the devices, despite the rather mild liftoff conditions (Figure 4). Delamination generally occurs due to poor surface adhesion of the film, suggesting that while the HMDS surface prime aids in solvent wetting, it does not form a strong enough interaction with the nanoparticles as compared to the interparticle interaction of the film. The organic ligands provide very favorable interactions between nanoparticles creating forces strong enough for the film to delaminate, rather than remain on the surface. The ligands also created another challenge with the line geometry. The device geometry demands a very large area interface between the nanoparticles and the electrodes. Making good electrical contact to nanoparticle films is not easy due

to the insulating effects of the ligand shell.

Given the current and line geometry, we have cell phase change cell multiple advantages, contact area of the addition, we believe that cell will prevent many of encountered with the first design leverages the fill high aspect ratios more physical deposition vehicle to demonstrate one colloidal nanoparticles

In conclusion, while a unique opportunity to properties of PCMs, they must be addressed when incorporating them into a PCRAM device geometry. Many of these challenges can be circumvented by relatively minor modifications of the process flow, but intelligent design of the geometry itself is required.

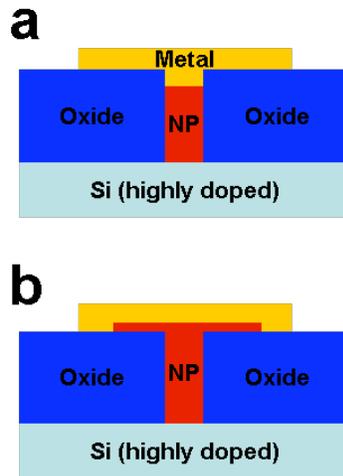


Figure 5 - Pillar geometry where nanoparticles a) underfill and b) overfill via. In either case, electrical switching should occur.

predicted problems with the begun fabricating a new, pillar (Figure 5). This geometry has including minimizing the electrode/nanoparticle film. In the higher aspect ratio of the the lift off problems generation design. The new solution processing ability to efficiently than traditional processes and will provide a of the many advantages that provide.

colloidal nanoparticles provide investigate the scaling bring specific challenges that

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