High-Yield Production of Ultralarge Bar0.8Sr0.2TiO3 Capacitors Hinges Upon Pt Dewetting

Cracks. Pinholes. Inclusions. Any of these can be a materials researcher’s nightmare foretelling the end to a capacitor. J. Daniels, J. Ihlefeld, W. Borland, and J-P. Maria, however, designed a cost-effective process to develop electrodes that are tolerant of cracks and defects that would normally short circuit a capacitor. Contrary to conventional procedure, they sputter Pt electrodes onto thin-film Bar0.8Sr0.2TiO3 (BST) dielectrics before the annealing process that crystallizes and densifies the ceramic layer. During the 900°C anneal, Pt atoms migrate away from microstructural defects but remain wetted to the rest of the film surface. The researchers from North Carolina State University and Dupont Electronic Technologies say the high-yield process can normally short circuit a capacitor. Conventional procedure, they sputter Pt electrodes onto thin-film Bar0.8Sr0.2TiO3 (BST) dielectrics before the annealing process that crystallizes and densifies the ceramic layer. During the 900°C anneal, Pt atoms migrate away from microstructural defects but remain wetted to the rest of the film surface. The researchers from North Carolina State University and Dupont Electronic Technologies say the high-yield process can be used with other oxide–metal combinations to manufacture large-scale, low-cost capacitors.

As the researchers describe in their article in the July 2007 issue of the Journal of Materials Research (p. 1763; DOI: 10.1557/JMR.2007.0272), “Because the probability of depositing an electrode over such a defect scales with capacitor dimension, limitations in yield [traditionally] can be traced to defect area density.” Thus, in the absence of clean room processing, producing millimeter- to centimeter-scale thin-film capacitors is a tremendous challenge. Using the phenomena of Pt dewetting, the group routinely achieved 5-µF capacitors that were 1 µm in thickness and 2.5 cm in lateral dimension. Functional capacitors had a dielectric loss tangent of <0.15 (lower values typically mean better quality capacitors). The procedure provides dramatic yield improvement of large-scale, functional capacitors without using costly clean room environments and specialized equipment to prevent defects.

The success of the procedure hinges upon the naturally high metal–oxide surface energy. Because of the high interfacial energy, thin films of Pt will dewet a dielectric surface at sufficiently elevated temperatures. Daniels and colleagues found that Pt electrodes at least 150-nm thick provide continuous Pt coverage and avoid dewetting and beading during a 900°C anneal. At this Pt thickness and anneal temperature, however, Pt retreats from the immediate vicinity of cracks or surface asperities, which often lead to short circuit pathways and capacitor failure. The researchers hypothesize that high physical curvature at these potential defect sites drives the electrode rearrangement.

The process updates established low-cost fabrication routes to provide high-yield, thin-film capacitors. The researchers believe the success of electrode deposition followed by sintering will apply to capacitors with other metal–oxide combinations having high interfacial energy.

Ashley Predith

One-Dimensional Ag Nanoparticle Arrays Formed by Decomposition of Precursor Nanowires

Assembling one-dimensional (1D) nanoparticle arrays is more challenging to achieve than generating other nanoparticle arrays because of their isotropic structure and nondirectional interaction. J. Nishijo and co-workers from the Institute for Molecular Science, Japan, produced diameter-controlled, 1D Ag nanoparticle

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arrays by decomposing recrystallized silver phenylacetylide nanowires, as they reported in the September 19 issue of Chemistry of Materials (DOI: 10.1021/cm701688i).

The researchers succeeded in recrystallizing silver phenylacetylide by using the ligand dissociation of Me3P–Ag–C≡C–Ph. It crystallized as thin wire-shaped crystals because of its highly anisotropic crystalline structure. A fast PMe3 dissociation rate in a high-polarity solvent produced thin silver phenylacetylide nanowires (39 ± 11 nm in EtOH), whereas slow crystal growth in a lower-polarity solvent brought thicker nanowires (94 ± 12 nm in 1-BuOH). The aspect ratio was ~30–40, which increased to more than 100 when CH3CN was used as a solvent. The strong reducing power of ethynyl anions present in the wires converted the raw material into an assembly of Ag nanoparticles under mild conditions when they were irradiated with ultraviolet (UV) light, while the phenylacetylene molecules formed during the decomposition process polymerized. This generated an organic matrix that surrounded the Ag nanoparticles, protecting them from oxidation while keeping the original shape of the wire, without using any template. After 15 minutes of irradiation, the surface plasmon resonance band of Ag nanoparticles appeared at 485 nm, slightly red-shifted with respect to typical Ag nanoparticles because of the dipole–dipole interaction caused by the short distance between nanoparticles (1 nm for 15 min of irradiation and 3 nm for 3 h of irradiation). Additionally, the high dielectric constant of the matrix can also reduce the plasmon frequency, the researchers said. Particle size was independent of the wire diameter and increased with irradiation time. Transmission electron microscope images recorded by the researchers showed the conversion of a nanowire into a 1D array of homogeneously distributed Ag nanoparticles after irradiation (see Figure 1).

Heating silver phenylacetylide nanowires at 110°C for 3 h was an alternative for obtaining 1D arrays of Ag nanoparticles with a diameter of 2.4 ± 0.7 nm, similar to that obtained after UV irradiation for 15 min. By using higher temperatures, however, the organic part of the decomposed nanowire melted and evaporated and the Ag nanoparticles spread on the substrate without keeping the 1D array structure. This process was used by the researchers to fix the 1D Ag nanoparticle arrays on a substrate after irradiating the original nanowires with UV light.

JOAN J. CARVAJAL

Computational Model Shows Stark Shifts Induce Ultrafast Current in Molecular Wires

The characterization of molecular wires as essential components of nanoelectronic devices traditionally focuses on electronic transport properties at metal–molecule junctions subject to a bias voltage. Laser radiation with frequency components ω and 2ω, chosen such that ω+2ω is on or near resonance, are known to induce currents in spatially symmetric systems. In addition to creating laser-induced rectification, the multiphoton absorption transfers electrons into mobile states. At the junctions, however, most molecules exhibit strong vibronic couplings that introduce ultrafast coherence loss and internal relaxation into the electronic dynamics. Recently, however, I. Franco and P. Brumer from the University of Toronto, Canada, and M. Shapiro from Weizmann Institute, Rehovot, Israel, investigated computationally an alternative mechanism that induces...