Dispensing and Surface-Induced Crystallization of Zeptoliter Liquid Metal Alloy Drops

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Scientific Thrust Area

This work is based on in-situ transmission electron microscopy and is carried out primary in the CFN's *Electron Microscopy* facility (E.S.) in collaboration with the *Interface Science and Catalysis* theme (P.S.).

Research Achievement

The controlled delivery of fluids is a key process in nature and in many areas of science and technology, where pipettes or related devices are used for accurately dispensing well-defined fluid volumes. Existing pipettes are capable of delivering fluids with attoliter (10^{-18} L) accuracy at best. Studies on phase transformations of nanoscale objects would benefit from the controlled dispensing and manipulation of much smaller droplets. In contrast to nanoparticle melting whose fundamental pathway was studied extensively, experiments on crystallization, testing classical nucleation theory, are hindered by the strong influence of support interfaces which tend to induce the premature nucleation of the solid phase. Experiments on free-standing fluid drops (e.g., using levitation to avoid melt-support interactions) are extremely challenging.

Here we demonstrate the operation of a pipette specialized for the controlled delivery of individual nanometer sized drops of liquid metals or metal alloys, which is about three orders of magnitude more sensitive than the finest 'universal' pipettes. The pipette, assembled and operated in–situ in a transmission electron microscope (TEM) [1, 2], consists of a semiconductor nanowire (NW), constituting the pipette body, whose tip provides a reservoir of metal semiconductor (Au-Ge) alloy (Figure 1). The entire NW and the Au-Ge reservoir are encapsulated in-situ in a self-assembled multilayer shell of graphene sheets that drives the actuation of the pipette.

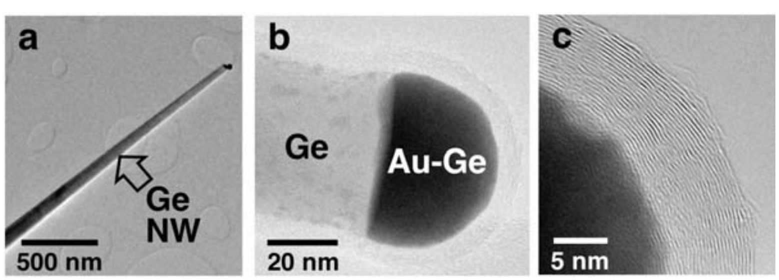

Figure 1: a – Ge nanowire pipette body. b – Fluid reservoir at the pipette tip: Au-Ge alloy melt encapsulated into a multilayer carbon shell (T = 425ºC). c – Pump: carbon shell, made of multiple curved graphene layers, builds pressure on the liquid Au-Ge reservoir.

The device delivers metal alloy melt with zeptoliter (10^{-21} L) resolution (Figure 2). We use this exquisite control to produce nearly free-standing Au-Ge drops suspended by an atomic-scale meniscus at the pipette tip, and to image their phase transformations with near-atomic resolution. Our observations of the liquid-solid transition challenge classical nucleation theory by providing experimental evidence for an intrinsic crystallization pathway of nanometer-sized fluid drops that avoids nucleation in the interior, but instead proceeds via liquid-state surface faceting as a precursor to surface-induced crystallization.

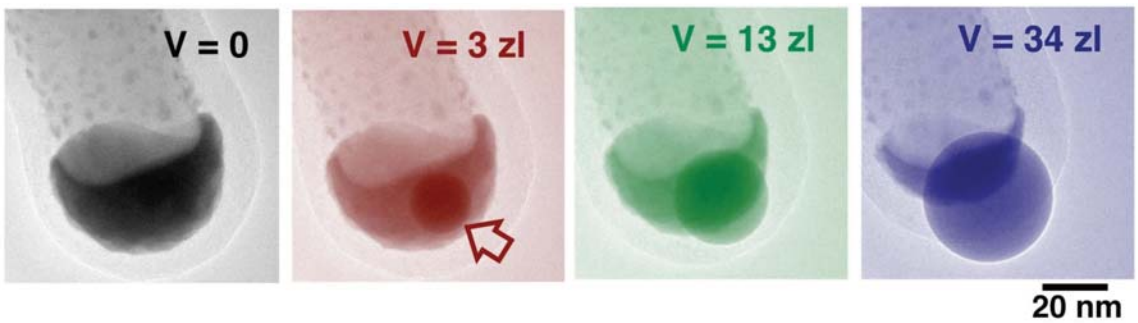

Figure 2: Expulsion of a Au-Ge melt drop during operation of the zeptoliter pipette at 425ºC.

Future Work

Future work will proceed in two main directions – i. graphene shell formation on nanowires from different materials and development of pipettes based on them and ii. establishing the atomic structure of the template for surface-induced crystallization.

Publications

1. P. Sutter and E. Sutter, Nature Mater. **6**, 363 (2007).
2. E. Sutter and P. Sutter, Adv. Mat. **18**, 2583 (2006).
3. BSA 07-37 patent pending.
4. BSA 08-13 patent pending.
5. H. Chiu, S. Kauzlarich, E. Sutter, Langmuir **22**, 5455 (2006).
6. E. Sutter, P. Sutter, R. Calarco, T. Stoica, and R. Meijers, Appl. Phys. Lett. **90**, 093118 (2007).