A Nanoaquarium for in situ Electron Microscopy of Liquids

CNF Project # 1542-07
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Abstract:

We have developed a nanofluidic platform for in situ transmission (TEM) and scanning transmission (STEM) electron microscopy of liquid samples called the nanoaquarium. Dynamic processes involving particle and fluid motion are imaged with high resolution, in real-time, by TEM/STEM. The nanoaquarium consists of a hermetically-sealed, liquid-filled chamber sandwiched between two freestanding silicon nitride membranes. Embedded electrodes are integrated into the device for sensing and actuation.

Summary of Research:

The transmission (TEM) and scanning transmission (STEM) electron microscope are among the most powerful nanoscale imaging tools available to the scientific community, with resolution in the nanometer or even sub-nanometer range. These high resolution imaging tools cannot readily be used to observe dynamical processes occurring in liquid media without addressing two significant barriers: sample thickness and sample evaporation.

Typically, the TEM/STEM requires very thin samples on the order of 100 nm to minimize electron scattering through the sample and provide high contrast images. Additionally, liquid samples must be confined in a leak-free, hermetically-sealed vessel to prevent evaporation in the high vacuum environment of the TEM/STEM chamber. There are many nanoscale dynamical processes, such as colloidal crystal formation, aggregation, nanowire growth, electrochemical deposition, and biological interactions, whose understanding would benefit greatly from real-time, direct imaging with a TEM/STEM.

We have developed a nanofluidic platform for in situ TEM/STEM of liquid samples called the nanoaquarium. The nanoaquarium consists of a hermetically-sealed, 100 nm tall, liquid-filled chamber sandwiched between two freestanding, 50 nm thick silicon nitride membranes. Embedded electrodes are integrated into the device for sensing and actuation. Figure 1 depicts the cross-section of the device and Figure 2 is a top view of a completed device. The fabrication approach, which is based on direct wafer bonding, affords thinner cross-sections than in any previously reported devices and enables improved contrast and resolution. Additionally, our wafer-scale fabrication approach allows for high-yield mass production of devices.

Double-side polished silicon wafers were coated with thin layers of stoichiometric silicon nitride. Gold electrodes were deposited on the silicon nitride by e-beam evaporation and patterned by lift-off. A layer of silicon oxide was deposited on top of the electrodes. The silicon oxide layer was planarized with a chemical mechanical polisher to remove steps from the embedded electrodes. Conduits and chambers were patterned in the silicon oxide layer. Strict tolerances
of bow/warp, total thickness variation (TTV), surface roughness, and cleanliness of the wafers were maintained to enable spontaneous, room temperature direct wafer bonding at low force in the absence of an electric field.

As part of the bonding process, wafers were cleaned in Piranha (H₂SO₄:H₂O₂ = 1:3 for 10 min) followed by a modified RCA1 solution (NH₄OH:H₂O₂:H₂O = 0.25:1:5 for 10 min at 80°C). Wafers were then treated with oxygen plasma (30 seconds at 60 mTorr with a gas flow of 50 sccm and platen power of 15 W), rinsed in DI water, and bonded manually by hand. Plasma treatment of the wafer surfaces allowed bond annealing to be performed at 250°C. Low processing temperatures and use of a dielectric spacer material facilitated direct integration of electrodes onto the chip. The technique can produce liquid chambers as thin as a few tens of nanometers. Membrane windows and vias were etched into the backsides of bonded wafers using KOH. Full details of the fabrication process are presented elsewhere [1].

Device performance was validated with aqueous solutions containing 5 nm gold (Au) particles (EM.GC5, BBI Life Sciences), 50 nm Au particles (EM.GC50, BBI Life Sciences), and 50 nm fluorescent polystyrene particles (Fluorescent Yellow Particles, Spherotech). Devices were filled by placing a droplet of solution at the inlet and letting the solution fill the conduit by capillary imbibition. Once the conduit was filled, another droplet was placed at the opposite end and the device was clamped in a titanium fixture with O-rings that sealed the inlet and outlet.

Sealed devices remained filled with solution for several days with no apparent loss of fluid. Images and videos of the liquid-filled chamber were taken with a FEI Quanta 600 FEG Mark II SEM with STEM detector, operated in high vacuum mode with an acceleration voltage of 20 kV. Diffusive motion of the particles in solution was apparent. Individual particles as well as aggregates were seen diffusing through the field of view, sometimes bumping into each other to form larger aggregates (Figure 3).

An *in situ* liquid TEM/STEM device was successfully fabricated. The nanoaquarium allowed us to obtain high contrast images of nanoparticles suspended in liquid and to monitor particle motion and aggregation. The hermeticity of the device was excellent; the device was effectively leak-proof, both in the vacuum chamber of the microscope for periods of hours, and at room conditions for periods of days.

**Acknowledgments:**

Fabrication was carried out at the Cornell NanoScale Facility, a member of the National Nanotechnology Infrastructure Network, which is supported by the National Science Foundation (Grant ECS-0335765). Electron microscopy was performed at the Penn Regional Nanotechnology Facility. Dr. Lolita Rotkina of the Penn Regional Nanotechnology Facility provided valuable assistance with electron microscopy. Dr. Frances M. Ross of IBM’s T.J. Watson Research Center provided encouragement and advice. Sumant Sood of SUSS MicroTec shared expertise on wafer bonding. Peter Szczesniak of the MEAM Machine Shop at the University of Pennsylvania assisted in constructing the device holder.

**References:**