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doi:10.1017/S1431927615007254 Paper No. 0646 Microsc. Microanal. 21 (Suppl 3), 2015

Design of a Heated Liquid Cell for *in-situ* Transmission Electron Microscopy

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Microfabricated, silicon-based chips developed for advanced capabilities in sample holders have recently led to a broad expansion of *in-situ* transmission electron microscopy (TEM) experiments involving materials' responses to increased temperature, electrical bias, or mechanical stress. By including freestanding, electron-transparent silicon nitride membranes, a thin environmental chamber for gases or liquids can be created in the TEM allowing new insights into the nanoscale processes involved in electrochemical, catalytic, or biological systems. Heated gas environments in the TEM have been previously demonstrated with microfabricated chips [1-2], but little work has been done with heated liquid environments. With control over the thermal environment, systems that activate at increased temperature (e.g. nanoparticle growth, protein denaturation, corrosion) or systems that degrade with temperature cycling (e.g. battery materials) can be studied.

We have developed a custom TEM liquid cell optimized for quantitative control of pA-level electrical currents [3]. The chip design is shown in Figure 1. The bottom chip contains ten insulated electrical leads converging to the center over a 40-μm diameter, 50-nm thick silicon nitride membrane seen in Figure 1(c). The lid chip likewise contains a central window as well as etched-through fluid fill ports. After adding the materials and electrolyte of interest, the assembly is hermetically sealed with epoxy and connected to the TEM holder stub as shown in Figure 1(b). The fluid chamber thickness is laterally uniform and has been measured to be 100-200 nm thick by electron energy loss spectroscopy; the small window size and relatively thick nitride membranes reduce the bowing commonly seen in TEM liquid cells. Therefore, there are no changes in the background contrast when moving around the liquid cell, and optimal imaging can be done anywhere within the viewing window.

The bottom chip is easily customized using electron-beam lithography. Here we demonstrate a resistive heater near the center of the silicon nitride membrane. As seen in Figure 2(a), a bottom chip with widely separated electrode tips was patterned to create two 50-nm thick resistors out of Al metal. One serpentine resistor acts as a heater, while the straight-line resistor measures the nearby temperature. The thermometer's temperature dependence over the relevant 20-100 °C range was calibrated in air in an oven as shown in Figure 2(b) using a four-point resistance measurement. As expected, resistance is a linear function of temperature. Additionally, the power input to the serpentine heater required for a local temperature rise at the heater is shown in Figure 2(c). This localized sample heating draws little power and thus ensures fast response and minimal spatial drift due to thermal expansion.

Because the bottom chip contains up to 10 independent electrodes, many electrodes are still available for electrical biasing after the heater has been fabricated. The remaining electrodes were used for electrochemical experiments; for example, thermal runaway in Li-ion batteries is related to decomposition at solid-liquid interfacial layers at elevated temperatures. Additionally, electrochemical nanowire growth is often enhanced at elevated temperatures. The voltage drop across the serpentine heater to achieve 100 °C is less than 0.5 V, and the heater can additionally be electrically isolated by masking with an insulating layer if needed.

Temperature control in a TEM liquid cell will open up new insights into solid-liquid interfaces, allowing *in-situ* determination of activation barriers of the processes imaged. The custom design shown here can be adapted to a wide variety of geometries depending on the requirements of the electrochemical, biological, or chemical system under study [4].

References

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[4] This work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. We thank Dr. J. Sullivan and M. Shaw for design and fabrication discussions and contributions.

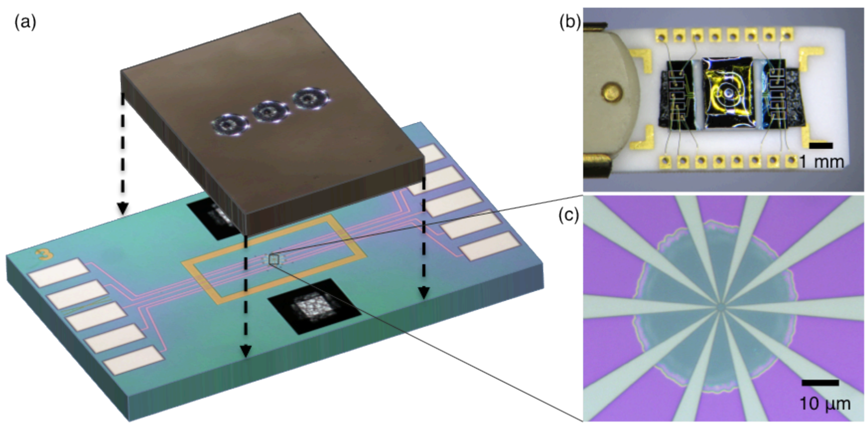

Figure 1. (a) TEM liquid cell layout, (b) assembled and sealed chip at the TEM holder tip, and (c) optical micrograph of the electrode tips converging over the circular silicon nitride membrane.

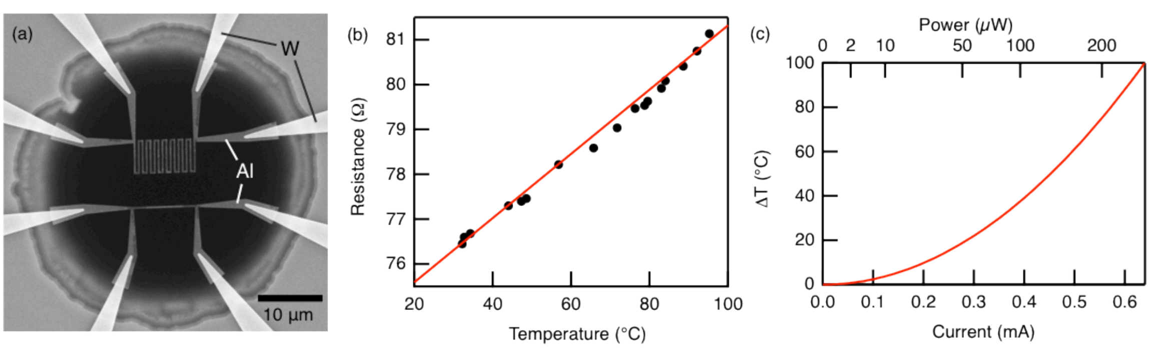

Figure 2. (a) Scanning electron microscope image of a serpentine heater (top) and thermometer (bottom) patterned with 50-nm thick Al. (b) Thermometer resistance as a function of temperature, where the line is a linear fit to the experimental data points. (c) Temperature rise at the heater calculated as a function of serpentine heater current assuming cylindrical geometry and a liquid/membrane total thickness of 200 nm with composite thermal conductivity of 1.5 W/(m K).

https://doi.org/10.1017/S1431927615007254