Nanoscale Ga liquid menisci behaviour examined by AFM and in-situ TEM

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Nanoscale liquid metal droplets are increasingly being used in micro-electromechanical systems (MEMS) switches [1] and for several chemical processing techniques such as vapour-liquid-solid (VLS) growth of 1D nanostructures [2]. As liquid droplets decrease in size, surface effects such as oxidation and impurity deposition can have a significant effect on their properties leading to changes in wettability and adhesion. Here the mechanics of nanoscale liquid droplet contacts of Ga metal have been investigated under both air and vacuum conditions using nanoscale probes to interact with the liquid and measure the behaviour during the formation and separation of liquid nano-bridges.

In this study, scanning probe techniques have been used to investigate the mechanical behaviour of nanoscale droplets of liquid Ga metal, with particular interest paid to the surface interaction under different environmental conditions. Ga metal was heated to >100°C on a hot plate. It was then transferred in air to an atomic force microscope (AFM). A standard silicon cantilever was used to perform a number of separate indentations on the liquid metal [3]. The loading and unloading curves into the liquid Ga droplet revealed a stepwise instability due to strong surface interactions with a solid-like skin (Fig. 1). Stick-slip behaviour occurred during loading as the tip was periodically driven though this skin before rupturing into the bulk liquid droplet. On unloading the tip again underwent stick-slip behaviour with repeated fracture of the outer solid skin until complete loss of contact. Imaging by scanning electron microscopy (SEM) showed the liquid droplet with a solid-like skin resembled a partially deflated balloon (Fig. 1, insert).

Liquid Ga droplets were then contacted in-situ in TEM using a NanoLAB triboprobe [4] and an etched tungsten (W)-tip. Ga droplets were heated to >100°C and deposited along the side of another tungsten wire fixed to a sample support on the TEM holder. The etched W-tip was mounted on a mobile nanomanipulator opposite the fixed Ga droplets. Under a vacuum <10^{-5} Pa, the W-tip was pushed into a Ga droplet. Initially, the first few contact events did not show true liquid like behaviour, with a solid skin being pulled from the droplet surface using the W-tip. After this skin had been removed, a clean liquid surface was revealed and successive contacts behaved in a liquid like manner. Once in contact with the liquid droplet, no stepwise displacement behaviour as seen previously by AFM occurred during either the loading or unloading sequences.

During in-situ pulling of liquid gallium metal from a continuous liquid reservoir, a nano-volume (0.25 atto-litres) of gallium was first pulled into a bridge [5] (~350 nm long and 740 nm in diameter) spanning between the continuous reservoir and the W-tip used to perform the pulling experiment (Fig. 2). As the separation gap was increased at a rate of 20 nm s^{-1}, Ga then slowly receded back towards the reservoir, reaching a minimum neck diameter w_m of 560 nm (Fig. 2c) before rapid (within 0.04 s) division occurred. The minimum neck diameter obtained in all experiments of this type was $w_m = 0.88w_c$, where w_c is the contact diameter. Molecular dynamic simulations in the literature of a non-Ga fluid suggest that a liquid division may have a reduced neck diameter down to only a few atoms [6] (i.e. $w_m/w_c \to 0$), as in Figure 3, however this was not observed here. It was noted that there was a linear behaviour between w_m/w_c and the surface-to-volume ratio S/V (Fig. 4). A maximum S/V ratio of 4.96×10^6 m^{-1} was obtained at $w_m/w_c = 0.88$, increased from an original value of 4.48×10^6 m^{-1} (~11% increase).

Ga is known to form an oxide skin [7], and there will also be some degree of Ga solidification as the droplet slowly cools to below its melting point. In this experiment, we have clearly identified that this solid skin plays a key role in the contact mechanics of a liquid Ga droplet. It was directly observed that after removing this skin, and in a vacuum environment, the primary contact mechanics behaviour was liquid like [8].

References

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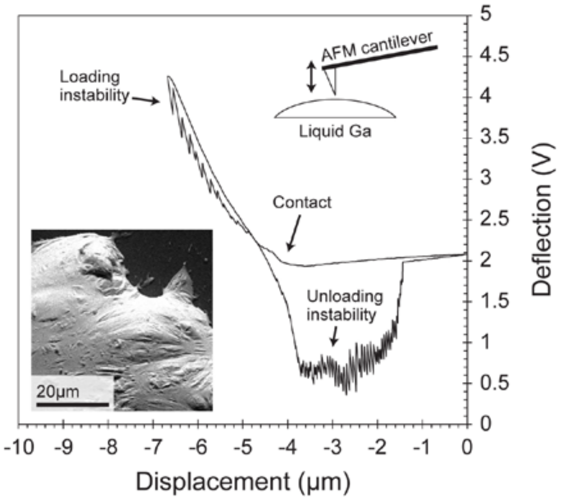

Figure 1. *AFM displacement-deflection plot of an indentation into a liquid-Ga droplet. Instability in the loading and unloading sections is caused by tip interaction with a solid 'oxide skin'. Insert: SEM image of the droplet.*

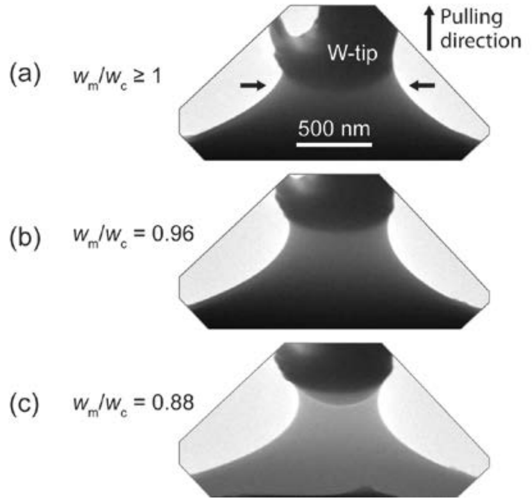

Figure 2. *In-situ TEM image sequence taken from a recorded video of a liquid Ga bridge pulled under tension. After (c), the bridge divides and the liquid recedes back into the liquid droplet within a single video frame (0.04 s).*

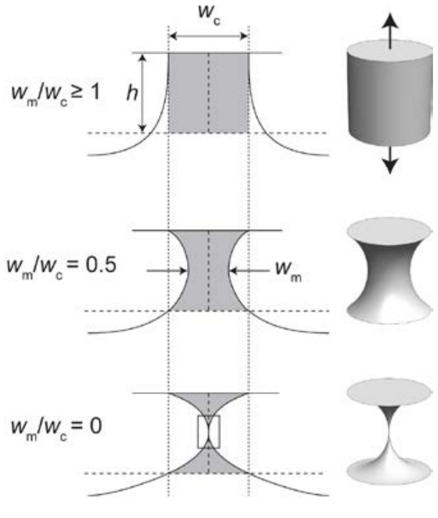

Figure 3. *Representation of a liquid bridge during division as predicted using molecular dynamic simulations [5]. Experimentally, Ga nano-bridges in a vacuum ($<10^{-5}$ Pa) with oxide removed divided at $w_m/w_c = 0.88$.*

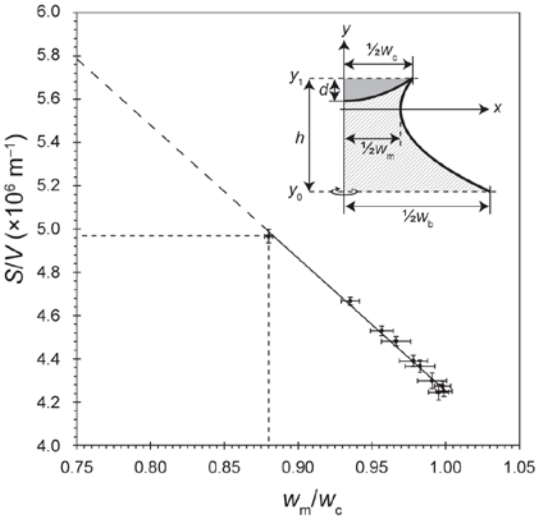

Figure 4. *Surface area-to-volume ratio is linearly proportional to w_m/w_c with a minimum neck existing at $w_m/w_c \geq 0.88$.*