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Liquid-like tribology of gold studied by *in situ* TEM

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ABSTRACT

Sliding and indentation between a single asperity tungsten probe and Au (1 1 0) film is studied via *in situ* transmission electron microscopy (TEM) nanomanipulation. A number of mechanisms relevant to the understanding of the tribological behavior of metal–metal interfaces are directly observed, including liquid-like (lubricious) behavior at moderate temperatures (166 °C), gouging and ploughing wear. An *in situ* method for fabricating atomic-sized Au probes is also presented.

1. Introduction

Metal–metal sliding contacts represent the most abundant class of materials where tribological understanding is crucial in a wide variety of applications, including automotive gears, turbine engines, sliding electrical contacts, and biological implants. Sliding between clean metal surfaces is typically associated with very high friction (from high adhesion) and large wear rates, as shown by ultrahigh vacuum experiments [1–3]. The use of solid and liquid lubricants, thus, became the limiting factor in tribological performance between metals. However, in conditions where the use of organic-based lubricants is unfavorable (e.g. vacuum, high temperatures) the use of metals in the form of nanoparticle additives as lubricants is seen as one solution to reduce friction losses and eliminate device failure [4–6].

Here we investigate the behavior of gold sliding contacts by *in situ* transmission electron microscopy (TEM). This technique allows us to drag a single asperity across the surface of an electron transparent sample, while directly observing the interface. In addition to conventional imaging, a number of available analytical techniques may be used to characterize the sliding interface within the microscope, namely transmission electron diffraction (TED), energy dispersive X-ray spectroscopy (EDX), electron energy loss spectroscopy (EELS), dark field, high resolution, and *z*-contrast imaging. In this way, direct structure–friction relationships can be formed by directly imaging the sliding interface. The traditional inability to image or otherwise probe an interface during contact and sliding, known as the "blind interface problem," may be overcome by this technique.

In situ TEM techniques have made it possible to directly measure electrical and mechanical properties of gold contacts, including atomic-sized contacts exhibiting quantized conductance steps associated with atomic rearrangements [7,8] and high resolution visualization of deformation of nm-sized gold interfaces via slip and twining [9]. While most of these studies focus on atomic scale effects at room temperature, they generally do not consider nano- to micron-sized contacts at elevated temperatures: those that bear the most relevance for metal–metal tribological interfaces. Collective effects such as dislocation motion and surface diffusion play a more significant role in determining tribological properties between metals than mechanics of atomic-sized nanowires, because the contact sizes of sliding surfaces are generally larger than a few atomic spacings, thus, allowing the formation of interfacial dislocations [10].

2. Experimental

The HS100 STM-Holder™ stage developed by Nanofactory Instruments (Göteborg, Sweden) was used at Argonne National Laboratory (Argonne, IL USA) on a FEI Tecnai F20ST TEM operated at 200 kV. The sample holder is capable of course and fine three-dimensional motion, with piezo resolutions of 0.2 Å in *XY* and 0.025 Å in *Z*, while coarse motion control gives a wide range of motion: ±1 to 2 mm in *XY* and ±10 μm in *Z*. In addition to

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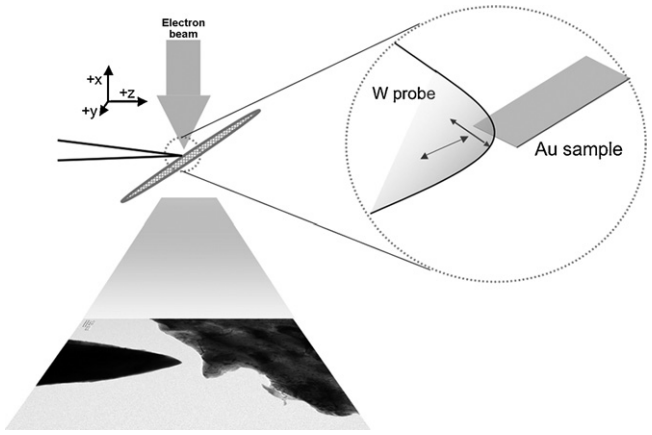

Fig. 1. Schematic of the *in situ* TEM holder.

nanomechanical control, the stage is capable of local electrical characterization and acquiring scanning tunneling images.

Several practical considerations arise during operation, particularly in the process of aligning the tip with the sample. First, the axes of the TEM and STM are identical, meaning that motion in +*Z* (approaching the sample) will inevitably yield some degree of *X*–*Y* displacement. This is monitored on a coarse scale by modulating the tilt about the *Z* axis while positioning the tip in order to reduce 'wobble' in the image, assuming the eucentric height is fixed. A finer approach requires measuring the objective lens focus setting and comparing with the Gaussian focus condition for the scanning probe. Additionally, probes must be fabricated with an adequately high aspect ration to avoid interfering with the sample in an area other than the region of interest.

Au (1 1 0) films were deposited onto cleaved NaCl crystals by evaporation at 335 °C then removed by dissolving in water, placed on 3 mm gold TEM grids, and finally thinned by ion polishing. The samples were mounted onto the TEM holder at an angle of 30° to the horizontal, as illustrated schematically in Fig. 1. This geometric compromise enables simultaneous inspection by the scanning probe and the electron beam—a very powerful technique for directly observing sliding interfaces. Tungsten probes were electropolished from 0.25 mm polycrystalline wire in a 2 N NaOH solution at voltages starting at 5 V, steadily decreasing to 0.1 V over a period of 5–10 min to achieve final radii between 2 and 100 nm. Upon insertion into the TEM column, the tungsten probe was directed to approach and contact the gold film. Although the normal force could not be directly measured, initial contact was established without causing any observable plastic deformation. Film compliance was high, causing the film to bend by tens to hundreds of nanometers (as seen in projection) without any measurable contact deformation. This, however, varies greatly as a result of local film thickness and morphology. A series of normal approaches and separately, lateral sliding passes at speeds of approximately 10–100 nm s^{-1} were carried out and captured on a TV-rate monitor to record the dynamic behavior of the probe-sample interaction.

3. Results

Initial approaches with the tungsten probe showed evidence of strong adhesion between the tip and sample, and subsequent

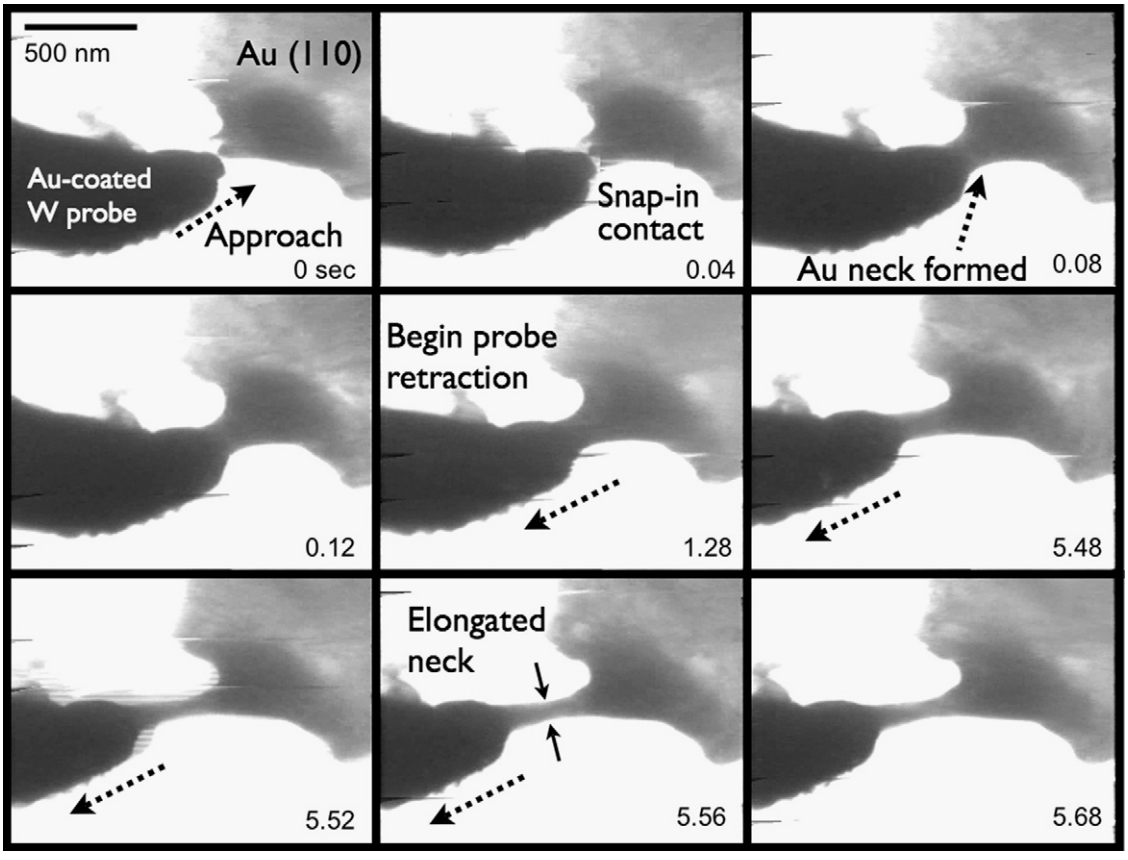

Fig. 2. A series of TV-rate images captured in bright field mode show the sudden formation of a neck between the probe (left) and the gold sample (right). The time scale for this event is within one frame rate (1/25th second). Upon retraction, the neck undergoes a sudden change in width at 5.52 s.

sliding and indenting the surface showed changes in contrast due to bend contours of the compliant thin sample. However, no damage to the contact region was observed, since soft contaminant layers provided a natural protective coating. A bias pulse of 5 V for 100 ms was applied in an attempt to clean the surface of adsorbed hydrocarbon contaminants. This served not only to eject hydrocarbon contaminants from the surface, but also to locally heat the Au, thereby transferring an amount of Au to the W probe, and caused the junction to physically separate. After several minutes without electron illumination, allowing the sample and probe to thermally equilibrate while maintaining a constant probe bias at 100 mV, contact was established once again. This time, rapid formation of a neck region upon contact was observed, reminiscent of the joining of liquid droplets. Highly plastic liquid-like behavior was observed through repeated approach and retraction actuations clearly showing rapid snap-in and pull-off phenomena. After pull-off, sharp asperities (<5 nm tip curvature) were observed on either side of the interface. Fig. 2 shows a sequence of still frames from a TV-rate video capture of the snap-in and resulting elongation of the neck by retracting the probe. Sudden snap-in contact is established with the rapid formation of a neck region; this process takes place within the time of a single video frame (1/25th second). Following the initial contact, the probe was slowly moved (<10 nm s^{-1}) laterally by several hundred nanometers, as to induce sliding. Fig. 3 shows that this lateral motion resulted in the plastic bending and elongation of the neck, evidenced by changes in contrast of the thinning neck region.

In a separate test conducted with zero tip-sample bias, sliding the tungsten probe along the edge of a thin gold sample showed evidence of ploughing deformation—a common explanation for high friction and wear rates between metals. Fig. 4 shows a series of still bright field images from a TV-rate video capture of the gold film being deformed. As the slider passes across the sample, a gouged track is left plastically deformed—a direct demonstration of ploughing on the nanoscale by *in situ* TEM. Fig. 5 shows an indentation series over the course of tens of minutes. Bend contours, some periodic, are observed in the gold sample as the harder tungsten tip is pressed against it. The contact was performed with zero tip-sample bias and lasted 20 min from initial contact to pull off. The presence of 3 nm of contamination is seen in the upper left corner of Fig. 5a. Very small amounts of surface contamination will decrease the surface diffusion coefficient enough to prevent liquid-like motion at room temperature (zero bias). After further increasing the load (Fig. 5b), both the probe and sample are bent to a large degree,

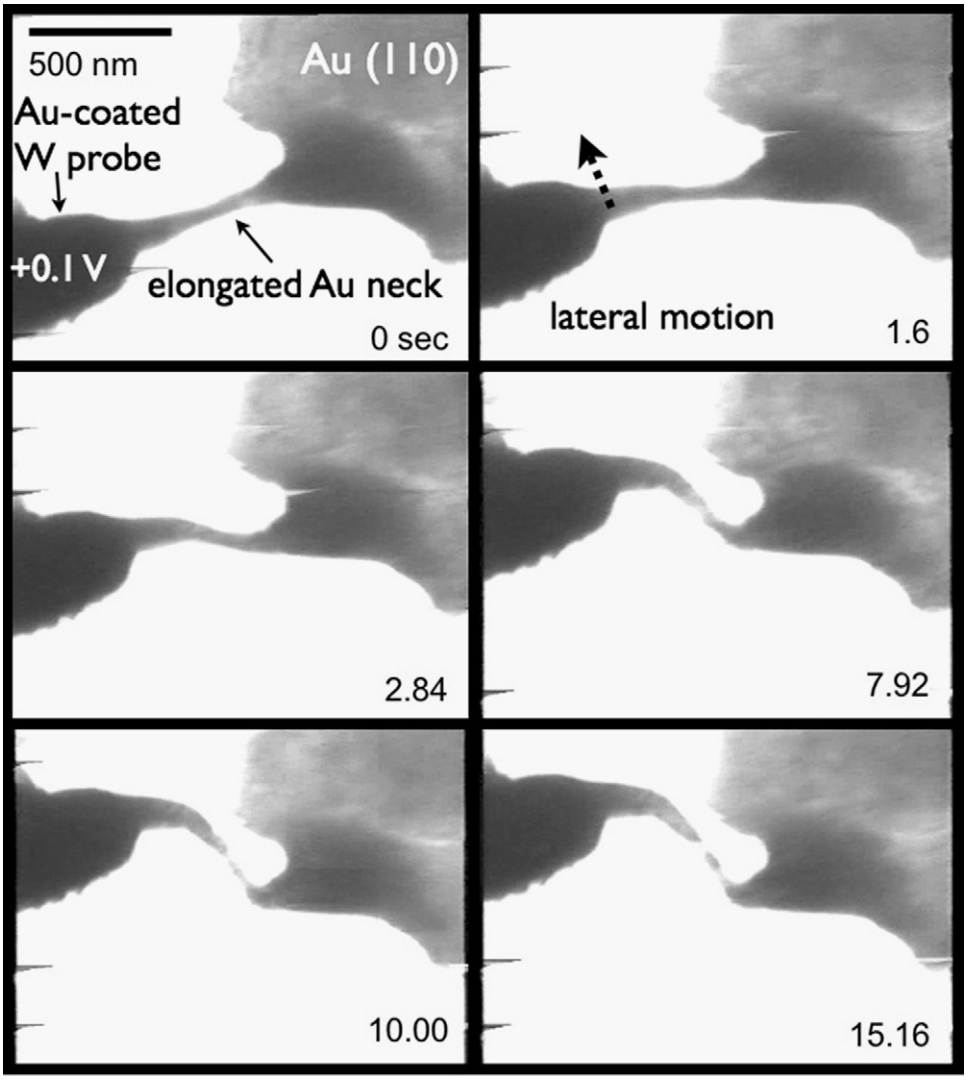

Fig. 3. Liquid-like deformation of the neck region at 100 mV. Individual TV-rate frames are captured at times shown in seconds. The neck width has been reduced to less than 50 nm by displacement of the probe away from the initial contact region.

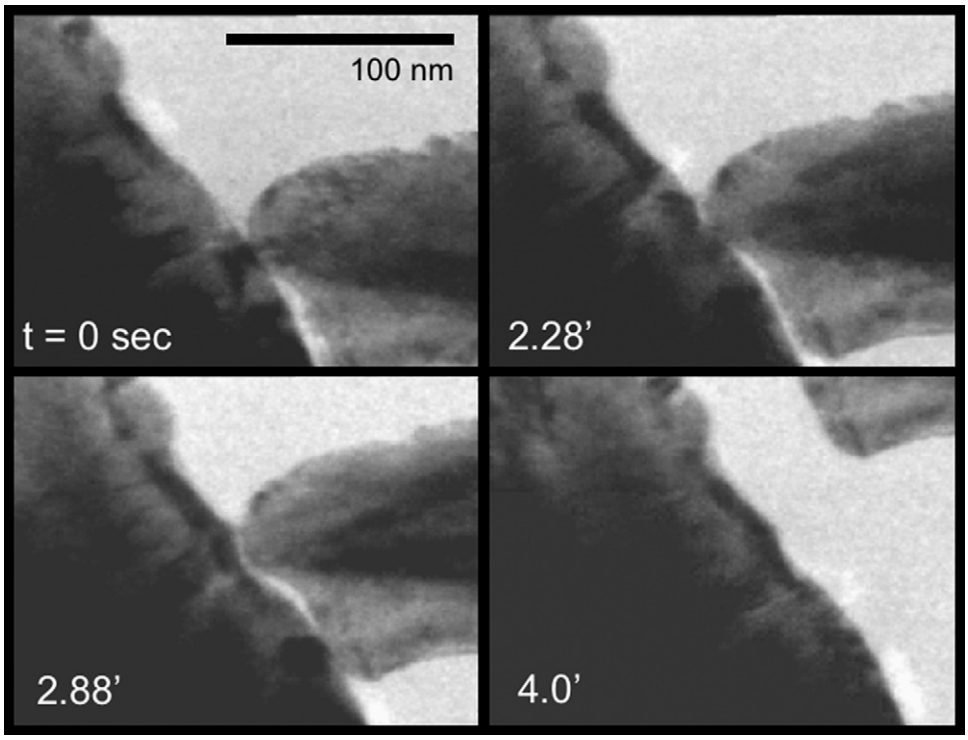

Fig. 4. Video stills showing evidence of ploughing wear between a tungsten asperity and gold sample. Time is given in seconds.

showing increased bend contour motion in the sample, with little or no observable local plastic deformation via indentation of the tip. Upon moving the tip laterally (parallel to the sample edge) to induce sliding, the interface suddenly ruptured, removing a 50 nm × 15 nm piece of the gold film, which remained strongly attached to the tip (Fig. 6). This large amount of adhesion and ensuing wear is consistent with high static friction phenomena between metallic surfaces, and is related to gouging wear behavior.

4. Discussion

Employing a method of calculating Joule heating at small electrical contacts used by Erts et al., we solve for the temperature at the junctions observed *in situ* [11,12]. The Wiedemann–Franz law relates electrical resistivity, ρ, to heat conductivity, k, via temperature, T, and the Lorenz number, L:

$$\rho k = T L$$

It follows that the maximum local temperature at the point of contact, T_{loc}, and the surrounding ambient temperature, T_{am}, may be related by the expression

$$T_{loc}^2 = T_{am}^2 + V^2/4L$$

where V is the applied potential. For a gold contact initially at room temperature, a bias of 100 mV corresponds to a maximum contact temperature of 166 °C, far below the melting point of gold (1064 °C). This leads to the conclusion that the observed behavior is indeed a process known as liquid-like growth, as seen *in situ* by Pashley et al. during stages of thin film growth at elevated temperatures [13]. This phenomenon appears to behave in a similar way to the coalescence of liquid droplets, whereby a neck region forms very quickly between two particles, followed by slower, more gradual growth into a single particle by reducing the surface free energy. However, liquid-like growth only depends on the high mobility of surface atoms. Bulk diffusion is not a significant contributor, as the time scales for bulk diffusion at small length scales (nanometers to microns) is several orders of magnitude longer than for surface diffusion.

It is evident from the TV-rate images that coalescence between the tip and sample occurs within the time scale of one frame (1/25th second). Let us take a look at the time scales on which surface and bulk diffusion act for relevant length scales. Conservative values for surface diffusion rates, albeit obtained with some inconsistency, are in the neighborhood of 300 $nm^2\,s^{-1}$. Expressions from sintering theory as reported by Pashley et al. for gold yield significant differences in the time of initial coalescence depending on the transport mechanism used [13]. For a particle with a radius of 100 Å, volume diffusion acts on the order of milliseconds, where surface diffusion acts much faster time scale, on the order of 10^{-7} s. It should be noted that these periods are unrealistically small; nanoparticles do not equilibriate this rapidly. The source of this discrepancy is unknown. Scaling up to a larger particle radius of 1000 Å yields time scales of 1 s for volume diffusion and 10^{-3} s for surface diffusion. This remains consistent with our observations of an instantaneous "snap-in" event with an upper limit of 0.04 s.

We now make a numerical estimate of the relative drag forces at a liquid-like viscous contact compared to a solid-like contact, based on the propagation of dislocations at a sliding crystalline interface. Details of this type of calculation may be found in Reference [10] and are not within the scope of a detailed development here. In essence, the solid-like dislocation friction model includes two terms, one that is constant with velocity (radiation friction) one that is linear with velocity (viscous drag). For the purposes of the current estimate, we are interested in comparing the viscous drag coefficients directly, and therefore do not include the radiation term. Furthermore, radiation drag is only dominant at low temperatures and low velocities.

The surface diffusion rate, D, of 300 $nm^2\,s^{-1}$ for gold, may be converted to an effective viscosity, and thereby produce an

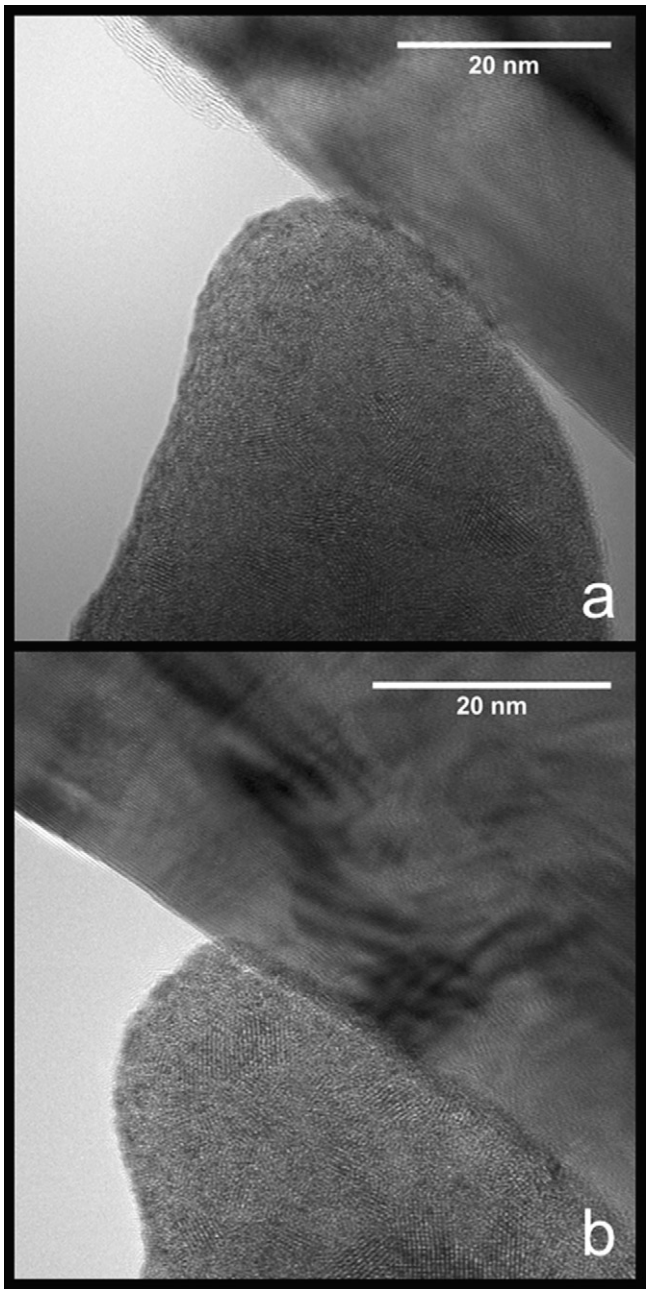

Fig. 5. High resolution TEM images of the tungsten tip contacting (a) and bending (b) the gold film upon increasing the load. Approximately 10 min between exposures.

estimate of the friction force, using the contact area and thickness observed in the TEM. This can be achieved by approximating the contact as sliding parallel surfaces with a confined viscous liquid, as is the case in Couette flow. Of note, this is a rough estimate, and is not intended to be a detailed numerical analysis of the nanoscale dynamics. Converting D ($300\,\mathrm{nm^2\,s^{-1}}$) to a viscosity at 166 °C yields a value of $\nu = 1.61$ Pa s, which is approximately one order of magnitude greater than air at the same temperature. For a contact area of $0.008\,\mu\mathrm{m}^2$, the Couette drag coefficient is calculated to be $B_{\mathrm{Couette}} = 1 \times 10^{-11}\,\mathrm{N\,s\,m^{-1}}$.

This value may now be compared to a drag coefficient for a solid-like interface. If we take the same size crystalline interface (perfectly clean, flat, uncontaminated), we can calculate the friction force or drag coefficient based on a number of moving dislocations present and moving at the interface. Doing so yields a value of $B_{\mathrm{Dislocation}} = 5 \times 10^{-4}\,\mathrm{N\,s\,m^{-1}}$, giving a ratio of $B_{\mathrm{Couette}}/B_{\mathrm{Dislocation}} = 2 \times 10^{-8}$. This is quite a large difference, indicating a much higher solid-like friction term compared to liquid-like viscous friction—an intuitive result. It must be noted that the liquid-like term has not taken into account capillary forces, which would serve to reduce this ratio. A more detailed analysis must be performed to accurately assess the liquid-like viscous drag force, as the simplified calculation here cannot accurately model the complex edge effects of the mechanical properties of liquid–solid interfaces on this small scale. Nonetheless, a lower boundary for comparing solid-like to liquid-like viscous friction forces has been established.

The notion that a metal must be liquid (i.e., above the melting temperature) to be lubricious – the basic concept in designing inorganic lubricants – is not a requirement, as demonstrated by the high mobility of surface atoms for gold and other metals at small length scales (single asperities). The present work has shown experimental evidence for the liquid-like behavior of gold at temperatures far below the melting point and significantly below other direct observations of this effect. Pashley et al. predicted that liquid-like behavior should exist at room temperature [13]. However, the steady buildup of contamination under the electron beam limited their experimental range to temperatures above 350 °C. This limitation was circumvented in our study, for we were able to locally clean the region of interest through a series of bias pulses and then reestablish contact before significant amounts of contamination developed. The observation of liquid-like behavior at 166 °C, therefore, a further validation of Pashley's theory.

Finally, a practical benefit was realized from the observation of liquid-like behavior of gold. Upon retracting the probe rapidly from the sample after coalescence, very sharp gold tips protruding from the freshly broken interface were formed, much in the way it was suggested in the comprehensive molecular dynamics and scanning probe work on metallic nano-contacts by Landman et al. [14]. The radii of the tips were consistently found to be smaller than 5 nm, offering a means for fabricating highly localized probes. Fig. 7 shows two tips formed by this method of retracting the tip after bias pulsing (~5 V) the contact and re-approaching at a lower potential

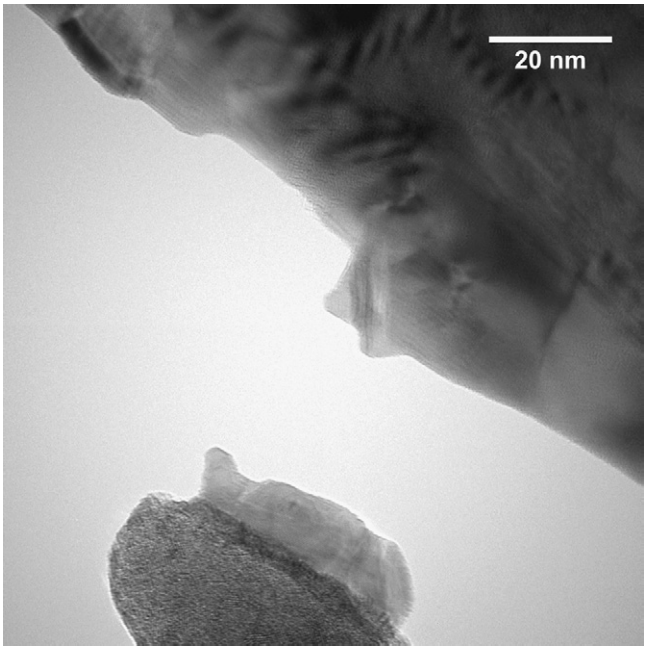

Fig. 6. Gold is removed and remains attached to the probe after moving the tungsten probe laterally (parallel to the sample edge) as viewed in Fig. 5.

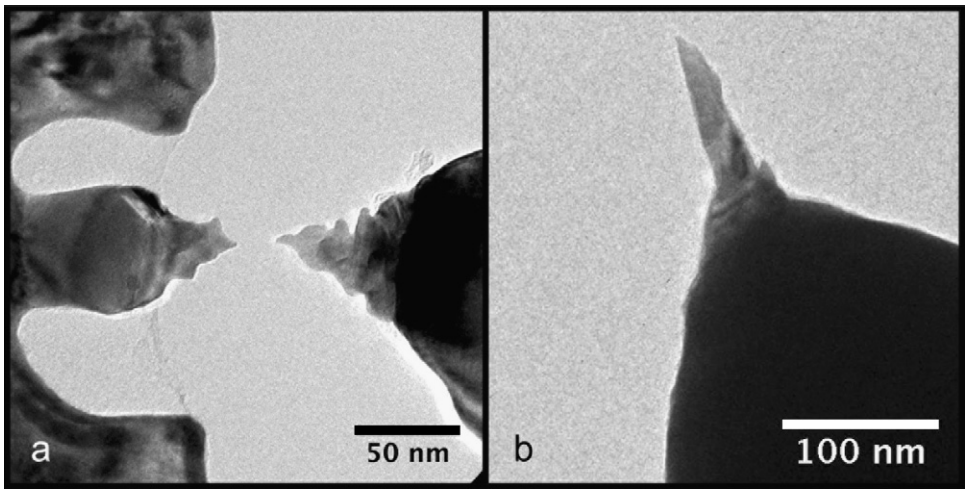

Fig. 7. Atomic-sized Au probes ($r < 5$ nm) fabricated by an *in situ* pulsing and manipulation technique.

(~100 mV). Electron dispersive X-ray spectroscopy (EDX) was performed to confirm that these were indeed gold tips. Small probes are very useful in a variety of applications targeted at mechanical, scanning and electrical characterization of nanostructures and surfaces. This method of renewable probe fabrication presents an alternative to costly carbon nanotube probes with the advantage that when a gold tip is damaged, it may be repaired *in situ* to a sharp radius again.

5. Conclusions

In this report we have presented direct observations of nanoscale tribological phenomena between a tungsten single asperity probe and gold surfaces through *in situ* TEM manipulation and characterization. The observation of ploughing on the nanoscale, effects of contamination, and strong metal–metal adhesion were captured in real time as a scanning probe contacted and slid across a gold sample. Direct evidence of liquid-like behavior of gold was seen at 166 °C, below that of previous experimental techniques. This was accomplished only after locally cleaning an area by pulsing the tip. This result points directly to the applicability of metallic lubricants at sub-melting point temperatures as alternatives or additives to traditional organic based lubricants.

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