Ductility at the nanoscale: Deformation and fracture of adhesive contacts using atomic force microscopy

N. Pradeep[a] and D.-I. Kim
National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

J. Grobelny
National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA and University of Lodz, 90-236 Lodz, Poland

T. Hawa
National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA and University of Maryland, College Park, Maryland 20742, USA

B. Henz
U.S. Army Research Laboratory, APG, Maryland 21005, USA

M. R. Zachariah
National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA and University of Maryland, College Park, Maryland 20742, USA

(Received 13 September 2007; accepted 30 October 2007; published online 15 November 2007)

Fracture of nanosize contacts formed between spherical probes and flat surfaces is studied using an atomic force microscope in an ultrahigh vacuum environment. Analysis of the observed deformation during the fracture process indicates significant material extensions for both gold and silica contacts. The separation process begins with an elastic deformation followed by plastic flow of material with atomic rearrangements close to the separation. Classical molecular dynamics studies show similarity between gold and silicon, materials that exhibit entirely different fracture behavior at macroscopic scale. This direct experimental evidence suggests that fracture at nanoscale occurs through a ductile process. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2815648]

The nanomechanical properties of materials become increasingly important as they are used for the fabrication of micro- and nanometer-sized structures with the advent of nanotechnology. Failure of materials—ductile or brittle—at macroscale is determined by the relative amounts of plastic deformation or bond rupture occurring in the material under an external load. Ductile materials demonstrate large amounts of plastic deformation while brittle materials show little or no plastic deformation during fracture. The amount of plasticity depends primarily on the capability for energy dissipation in the material microstructures. At the nanoscale, materials are "perfect" with defect-free structures giving rise to completely different mechanical properties in comparison to their bulk counterparts.[1–3] The conventional use of the terms "ductile" and "brittle" for nanoscale materials is thus questionable. The experimental observations of the fracture behavior of glass at the nanoscale raises an open question:[4,5] What is the fracture behavior of glass at nanoscale? Is it brittle or ductile? The referenced fracture studies are "qualitative" in nature, relying on the topography of the surfaces undergoing fracture without providing any direct information about fracture mechanics within the crack.

Well known ductile and brittle materials were chosen to do alternative nanoscale fracture experiments by making force measurements during the formation and subsequent fracture of nanoscale contacts using atomic force microscopy (AFM). The ability to control the applied load and measure the mechanical response directly between the fracturing surfaces makes an ideal fracture experiment. Microspheres of gold and silica (radius $\sim$12.5 μm) were used to form contacts with flat gold and silica samples in separate experiments. The experiments were carried out in ultrahigh vacuum as the environment can also affect material fracture through the presence of humidity.[6,7] The probes are initially scanned on the surface in contact mode in order to clean the surfaces, until a consistent and reproducible separation force is obtained. With a microsphere attached, the AFM cantilevers (in two separate experiments) were moved toward a countersurface until the probes "snapped on" to form contacts and were subsequently retracted to break the contacts. After the cleaning process, the separation force increased considerably for both gold-gold and silica-silica systems indicating the formation of clean surface contacts. The cantilever was moved at a speed of 150 nm s^{-1} for all the measurements. The mechanical (force) response during the displacement was monitored by measuring the angular deflection of the precalibrated cantilever measured using a laser beam. Figure 1 shows the force-deformation curves obtained from the force versus cantilever displacement data during the unloading cycle until the surfaces are separated.

The mechanics of the adhesive spherical contacts were analyzed by a continuum elastic theory, namely, the self-consistent transition model.[8,9] Transition model is a combination of the adhesion exterior to the contact area modeled by a zone of uniform traction along with that within the contact area by the traction field appropriate to uniform displacement. At the nanoscale, the adhesion forces are often sufficient to cause deformation of the contacting surfaces. The data are described by the model except very close to the point of separation. The model suggests that the contact

[a]Electronic mail: pradeep.namboodiri@nist.gov

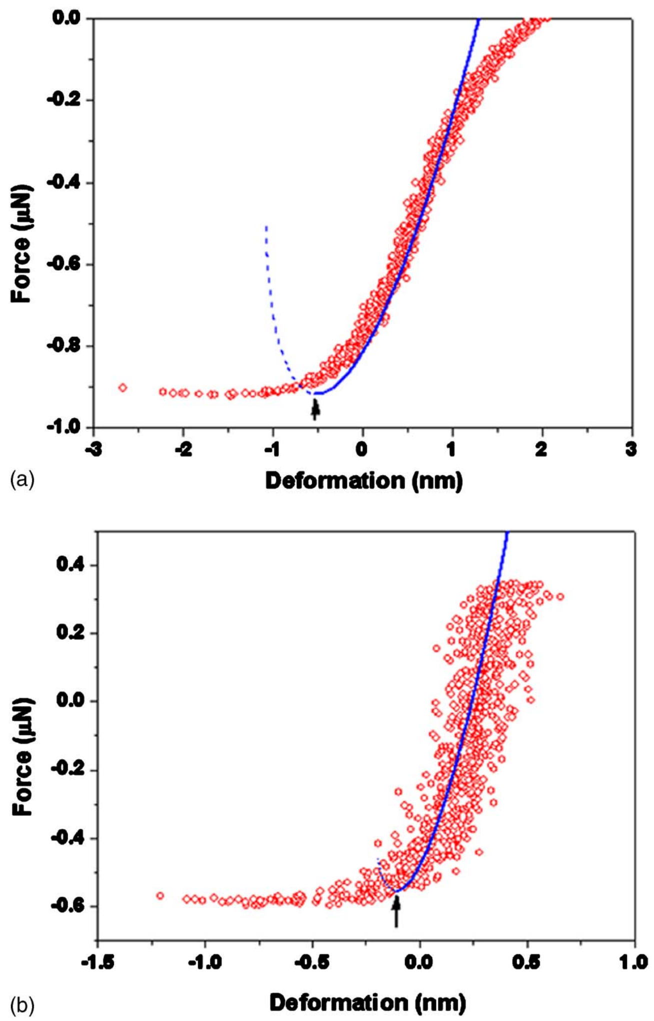

FIG. 1. (Color online) Force-deformation curves for (a) gold, (b) silica contacts derived from the corresponding force displacement curves. Contact deformation is obtained by subtracting the cantilever displacement from the measured cantilever deflection. Dotted line in blue shows the theoretical fit using the transition model. The black arrow indicates the theoretical separation point. The deformation shown in the horizontal axis is based on the transition model and the measured data were shifted horizontally for the best fit.

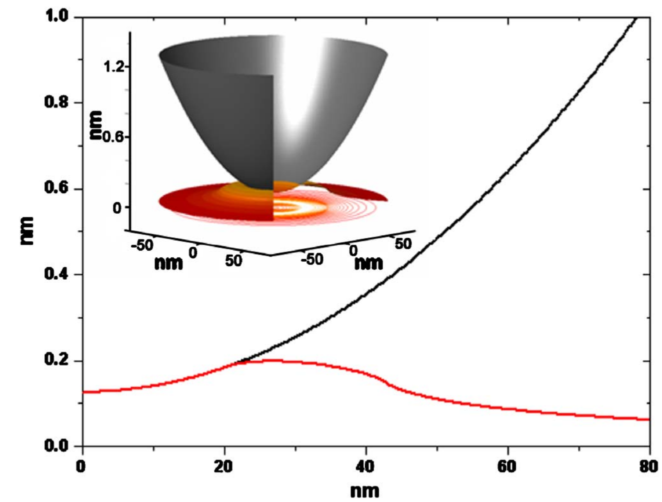

FIG. 2. (Color online) The line profile at the theoretical separation point of the silica sphere and silicon surface computed based on experimental data. The inset shows the representation of the contact obtained using the model.

should break at the point (marked with an arrow in Fig. 1) where the force gradient exceeds the spring constant of the cantilever. The observations suggest that the deformation extends further and form a connective neck with an approximate length of 2.0 nm for the gold and silica contacts. Figure 2 shows the profile of the silica surface at this point calculated using the model. In this region beyond the theoretical separation, the contact stiffness drastically reduces and gives a flat region in the force-deformation curve indicating that stretching occurs almost at constant force. Gold sphere has a smaller adhesion force compared to that in the case of silica due to the influence of relatively high roughness.[10,11]

This material extension occurs during separation of nanoscale contacts. When the surfaces are brought into close proximity, the interaction forces which include van der Waals/Casimir or electrostatic forces cause the surfaces to jump to contact leading to the formation of primary bonds.[12] This process is termed as avalanche adhesion where two surfaces collapse and form interatomic bonds when the interfacial spacing falls below a critical distance.[13] However, the potential during the separation is dominated by the number of the primary bonds formed between atoms of contacting surfaces representing the material property at the contact. Because the fracture strength of the bonds is greater than the tensile stress before separation, there could be material flow and plastic deformation leading to material extension.[14] In addition to the large stress during the process of separation, the diffusion barrier at the nanoscale is very small at room temperature,[15] which allows deformation and structural rearrangement of atoms. This is similar to plastic deformation resulting in a stiffness-free stretch demonstrated by the flat region in the force-deformation curve. There have been experimental studies as well as molecular dynamic simulations of gold contacts showing the formation of connective neck during separation.[14] While the observations are reasonable for metals, it is not obvious to be the case for macroscopically brittle materials such as silicon or silicon oxide (glass) that the same things will be true. The observed extension dominated by atomic scale events such as plastic flow and structural rearrangement is beyond the scope of continuum mechanics. Nonetheless, the theory serves to locate the onset of plastic deformation and thereby to determine the length of the extension.

In order to understand the observed extension for the ductile and brittle materials, atomistic simulations were carried out using classical molecular dynamics. Stillinger-Weber[16] and embedded atom[17,18] potentials were used, respectively, for silicon and gold atoms. Due to the limitations of the potential used, silicon was chosen for simulations instead of silica as the materials are similar in their macroscopic behavior. For simplicity of modeling, two spherical particles of radii 5 nm were used to simulate the contact fracture experiments. Minimum energy configuration of the atoms in the particles was obtained by equilibrating the particles at their melting points for about 10 ns and then allowing them to cool down to the simulation temperature of 300 K. The model was initialized by placing two equilibrated nanoparticles next to each other. Once the nanoparticles had sintered, they were pulled apart keeping the temperature constant. The entire separation process took place with a constant strain rate in a time scale of 10–100 ns. The force was calculated by summation of stress in the cross-

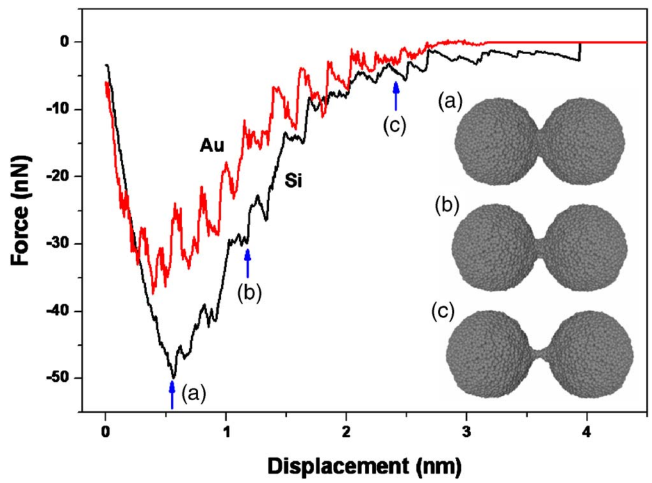

FIG. 3. (Color online) Force-displacement curves for gold and silicon particles, obtained from MD simulations. Snapshot sequences (a)–(c) demonstrate the material extension occurred during the separation for silicon contact.

sectional area of the nanoparticle interconnection and plotted as a function of the displacement in Fig. 3.

The simulations reveal strikingly similar behavior between silicon and gold contacts in terms of the material extension during separation. This similarity is consistent with the experimental observations using AFM suggesting a ductile behavior at the nanoscale for both materials.[19] The "saw tooth" behavior in the force distance curve (0.1–0.2 nm on the displacement scale) near the separation is due to the stress relaxation caused by the rearrangement of atoms in the connective neck.[20] The saw tooth behavior is typical of a single connective neck and is not observed in the experiments because the effect is averaged out due to a larger contact area. Another feature of the results obtained from the simulations is that the force decreases gradually until the separation point as opposed to the experimentally observed constant force region in Fig. 1. The disparity is because of the fact that the simulations, due to computational limitations, are several orders of magnitude faster than the actual crack velocity. This gives rise to high strain rates that does not allow diffusion of atoms to the extension similar to that observed in earlier experiments on nanoscale silicon contacts.[21] If material flow is allowed, the connective neck can grow without having a change in the force consistent with experimental observations. Previous studies[14] concluded that a single atom chain of gold grows by a continuous supply of atoms from the contacting bodies maintaining constant stress. Our experimental observations revealed that the separation process for silica and gold contacts proceeds in a similar manner. Since these experiments are performed in clean UHV environments, it should be noted that the fracture behavior of these materials in ambient conditions will be influenced by the water present in the environment.[22]

Although the experiments above are based on formation and fracture of nanoscale contacts, the scenario described could be much different in the case of the nanoscale view of fracture in macroscopic samples. While the conflicting reports on fracture of glass[4,5] are based on AFM imaging providing information only from the region close to the surface, it must be noted that most of the fracture takes place within the bulk of the material. Surface atoms are mobile and can diffuse even at room temperature[23] contributing significantly to the superficial layers, and possibly modifying the fracture mechanism close to the surface. It is likely that the cavity formation observed during fracture of glass in earlier studies[4] is purely a superficial phenomenon. Within the bulk, fracture must be proceeding via bond rupture typical of brittle materials. On the other hand, for nanoscale objects with large surface to volume ratio, fracture mechanics is dictated by diffusion of atoms. This makes the fracture of a macroscopic material distinctly different from that of nanoscale contacts, where surfaces play a crucial role allowing material flow. It is misleading to extrapolate the observation of ductile nature of silica at nanoscale to macroscopic scales. At the nanoscale, diffusion of atoms causes structural rearrangements for all materials before bond rupture similar to plastic deformation and leads to ductile fracture.

[1] J. Schiotz,. F. D. Di Tolla, and K. W. Jacobsen, Nature (London) **391**, 561 (1998).
[2] A. M. Minor, S. A. Syed Asif, E. A. Stach, E. Cyrankowski, T. J. Wyrobeck, and O. L. Warren, Nat. Mater. **5**, 697 (2006).
[3] W. A. Soer, J. Th. M. De Hosson, A. M. Minor, Z. Shan, S. A. Syed Asif, and O. L. Warren, Appl. Phys. Lett. **90**, 181924 (2007).
[4] F. Celarie, S. Prades, D. Bonamy, L. Ferrero, E. Bauchoud, C. Guillot, and C. Marliere, Phys. Rev. Lett. **90**, 075504 (2003).
[5] J.-P. Guinn and S. M. Wiederhorn, Phys. Rev. Lett. **92**, 215502 (2004).
[6] S. M. Wiederhorn and L. H. Bolz, J. Am. Chem. Soc. **53**, 543 (1970).
[7] J. Grobelny, N. Pradeep, D.-I. Kim, and Z. C. Ying, Appl. Phys. Lett. **88**, 091906 (2006).
[8] D. Maugis, J. Colloid Interface Sci. **150**, 243 (1992).
[9] K. L. Johnson, Proc. R. Soc. London, Ser. A **453**, 163 (1997).
[10] G. Palasantzas and J. Th. M. De Hosson, Phys. Rev. E **67**, 021604 (2003).
[11] P. J. van Zwol, G. Palasantzas, and J. Th. M. De Hosson, Appl. Phys. Lett. **91**, 144108 (2007).
[12] U. Landman, W. D. Luedtke, N. A. Burnham, and R. J. Colton, Science **248**, 454 (1990).
[13] J. R. Smith, G. Bozzolo, A. Banerjea, and J. Ferrante, Phys. Rev. Lett. **63**, 1269 (1989).
[14] G. Rubio-Bollinger, S. R. Bahn, N. Agraït, K. W. Jacobsen, and S. Vieira, Phys. Rev. Lett. **87**, 026101 (2001).
[15] L. Bitar, P. A. Serena, P. Garcia-Mochales, N. Garcia, and V. T. Binh, Surf. Sci. **339**, 221 (1995).
[16] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).
[17] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).
[18] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).
[19] M. L. Falk, Phys. Rev. B **60**, 7062 (1999).
[20] N. Agraït, G. Rubio, and S. Vieira, Phys. Rev. Lett. **74**, 3995 (1995).
[21] T. Kizuka and K. Hosoki, Appl. Phys. Lett. **75**, 2743 (1999).
[22] P. J. van Zwol, G. Palasantzas, and J. Th. M. De Hosson, Appl. Phys. Lett. **91**, 101905 (2007).
[23] R. Van Gastel, E. Somfai, W. Van Saarloos, and J. W. M. Frenken, Nature (London) **408**, 665 (2000).