Supporting Information for: "Toward the Ultimate Tribological Interface: Surface Chemistry and Nanotribology of Ultrananocrystalline Diamond", A. V. Sumant *et al.*

For analyzing adhesion from AFM measurements, the interface is considered to possess an energy per unit area $\gamma = \gamma_1+\gamma_2-\gamma_{12}$, where γ_1 and γ_2 are the tip and sample surface energies and γ_{12} the interfacial energy.[1] γ is the Dupré energy or work of adhesion, *i.e.* the work per unit area required to separate the surfaces from contact to infinity. γ encompasses all interfacial forces, and can be used to predict the force of adhesion in multi-asperity interfaces[2] such as those in MEMS devices.[3, 4] For an elastic, paraboloidal tip in contact with a flat elastic surface, the behavior spans a spectrum from the Johnson-Kendall-Roberts (JKR) model[5] (for large tips and compliant materials with strong, short range adhesion), to the Derjaguin-Müller-Toporov (DMT) model[6] (for small tips and stiff materials with weak, long-range adhesion). γ is determined from the force F_{PO} required to pull the tip out of contact with the surface:

$$\gamma = \frac{-F_{PO}}{\chi \pi R}$$

where χ ranges monotonically from 1.5 (JKR) to 2 (DMT). To select which position between these two limits applies, we evaluate Tabor's parameter[7, 8]

$$\mu_T = \left(\frac{16R\gamma^2}{9K^2 {z_0}^3}\right)^{1/3} = \left(\frac{16{F_{PO}}^2}{9\chi^2\pi^2 RK^2 {z_0}^3}\right)^{1/3}$$

where R is the tip radius, and K is the contact modulus, given by: $K = \frac{4}{3}\cdot\left(\frac{1-\nu_1^2}{E_1}+\frac{1-\nu_2^2}{E_2}\right)^{-1}$.

E_1, E_2 are the Young's Moduli, and ν_1, ν_2 the Poisson's ratios of the tip and sample respectively. z_0 is the equilibrium surface separation in contact and represents the length scale of the interfacial forces. $\mu_T > 5$ ($\mu_T < 0.1$) implies the JKR (DMT) limit. Unfortunately, z_0 is not known *a priori*. However, an upper bound estimate of μ_T is made by assuming the smallest reasonable value of z_0 =0.154 nm (the C-C bond distance in diamond). AFM tips were fabricated from silicon and coated with a tungsten carbide film that is partially oxidized. Thus, we use a conservatively low tip modulus of 357 GPa (50% of the value of tungsten carbide), and the smallest possible value of χ=1.5, and then solve for μ_T from the measured pull-off forces.

Poisson's ratio for the tip was taken to be 0.24.[9] Young's modulus and Poisson's ratio for UNCD were taken to be 960 GPa [10] and 0.07 [11] respectively. The tip shape and radius were measured *in-situ* by the inverse imaging method[12] using a TipCheck(c) calibration standard (Aurora Nanodevices, Edmonton, AB, Canada) and then applying deconvolution software.[13] A paraboloidal shape was confirmed. To reduce the possibility of tip wear, F_{PO} was measured on various locations at least 35 times per tip without any scanning. Uncertainty was reduced by performing the measurement with two different tips, and there was no measurable difference in γ between them. Choosing the cases that exhibited the larger values of F_{PO}, Tabor's parameter does not exceed 0.08-0.09 even using the most extreme assumptions. Thus, we are firmly in the DMT regime, *i.e.* χ=2 and γ can now be determined from the pull-off force. We also used the DMT model to calculate the work of adhesion for the silicon sample. Accounting for the most extreme possible case for silicon of μ_T=0.2 changes work of adhesion within the experimental error.

References:

[1] J. N. Israelachvili, *Intermolecular and Surface Forces,* 2nd ed. (London: Academic Press London) **1992.**

[2] D. Maugis, *J. Adhes. Sci. Technol.* **1996**, *10,* 161.

[3] K. Komvopoulos, W. Yan, *Trans. ASME J. Tribology* **1997**, *119,* 391.

[4] M. P. de Boer, D. L. Luck, W. R. Ashurst, R. Maboudian, *J. Microelectromech. Syst.* **2004**, *13,* 63.

[5] K. L. Johnson, K. Kendall, A. D. Roberts, *Proc. Roy. Soc. London A* **1971**, *324,* 301.

[6] B. V. Derjaguin, V. M. Muller, Y. P. Toporov, *J. Colloid Interface Sci.* **1975**, *53,* 314.

[7] K. Johnson, J. Greenwood, *J. Colloid Interface Sci.* **1997**, *192,* 326.

[8] D. Tabor, *J. Colloid Interface Sci.* **1977**, *58,* 2.

[9] J. F. Shackelford, W. Alexander, J. S. Park, *CRC Materials Science and Engineering Handbook,* 2nd ed. (Boca Raton: CRC Press) **1994.**

[10] H. D. Espinosa, B. C. Prorok, B. Peng, K. H. Kim, N. Moldovan, O. Auciello, J. A. Carlisle, D. M. Gruen, D. C. Mancini, *Experimental Mechanics* **2003**, *43,* 256.

[11] C. A. Klein, *Materials Research Bulletin* **1992**, *27,* 1407.

[12] J. S. Villarrubia, *Surf. Sci.* **1994**, *321,* 287.

[13] J. S. Villarrubia, *J. Res. Natl. Inst. Stand. Technol. (USA)* **1997**, *102,* 425.