Metallic Adhesion in Atomic-Size Junctions

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(Received 2 April 2004; published 10 September 2004)

We report high resolution simultaneous measurements of electrical conductance and force gradient between two sharp gold tips as their separation is varied from the tunneling distance to atomic-size contact. The use of atomically sharp tips minimizes van der Waals interaction, making it possible to identify the short-range metallic adhesion contribution to the total force.

DOI: 10.1103/PhysRevLett.93.116803 PACS numbers: 73.23.–b, 68.35.–p, 68.65.–k

Metallic adhesion at the atomic level is of fundamental importance in many physical phenomena and is also of practical importance for nanotechnology. However, in spite of the many works devoted to this phenomenon, we are still far from having a quantitative understanding. On the experimental side [1–4], accurately measuring minute atomic forces while still achieving sufficient mechanical stability is technically difficult. In addition, special care must be taken to avoid sample contamination. On the theoretical side, this is also a difficult problem [5–9] due to the many different aspects that must be taken into account such as atomic configuration and motion, electronic band structure, and electrodynamics. In order to deal with this problem simplifying assumptions that, hopefully, capture the essential physics must be made. The validity of these assumptions can then only be checked by quantitative comparison with corresponding experimental results. Such comparisons have rarely been carried out successfully. In this Letter, we present new simultaneous force and conductance measurements on gold atomic contacts and junctions which are of increased stability and sensitivity and permit better quantitative comparison with theoretical calculations.

The mechanically controlled break junction (MCBJ) technique has been used to investigate electron transport properties of single-atom contacts [10] and atomic chains of single atoms [11,12]. In a MCBJ setup a notched wire is fixed on a flexible substrate. Controlled mechanical bending of the substrate allows the wire to be repeatedly broken at the notch and subsequently brings the two facing electrodes back into contact in a stable, controlled manner. Key advantages of using the MCBJ setup over STM are the mechanical stability and the initial absence of contaminants at the freshly exposed surfaces.

Here we use a variant of the MCBJ setup which incorporates a force sensor in the following way. The notched gold wire (99.99% purity) is not directly glued onto the flexible substrate but instead one of its ends [electrode A in Fig. 1(a)] wire is glued to one prong of a miniature piezoelectric quartz tuning fork (TF) whose base (CASE) is soldered to the flexible copper-beryllium substrate so that the prongs of the fork are freely standing parallel to the substrate. Electrode B of the notched wire is soldered onto a support electrically isolated from the substrate and levelled with the prongs of the TF. The force gradient or stiffness k of the interaction between the electrodes is proportional, with a factor $\alpha = \Delta f/k$, to the shift of the resonance frequency Δf of the TF if excited with vanish-

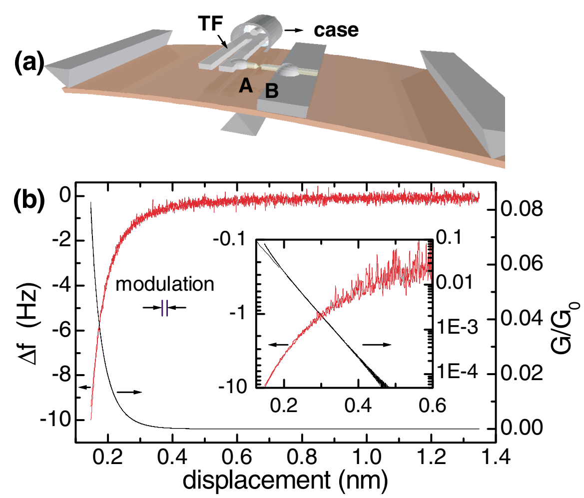

FIG. 1 (color online). (a) 3D view showing our modified MCBJ setup. (b) Typical simultaneous measurement of the frequency shift of the TF and of the tunnel conductance of a junction as the gap between the electrodes is varied in the tunnel regime. Here the data shown (data set #1 in Table I) correspond to opening and subsequently closing the junction, in a triangular ramp lasting on the order of a minute. The curves are lying one on top of the other, demonstrating the extreme stability of this setup. The peak-to-peak amplitude of the modulation applied to the TF, which limits our spatial resolution, is also depicted. The eigenfrequency of the tuning fork when the junction is opened is 30 636.89 Hz. Inset: Semilogarithmic plot of conductance and frequency shift.

ing amplitude. This resonant frequency is tracked by implementing a phase locked loop oscillator [13].

In order not to perturb the stability of the junction, the oscillation amplitude of the TF was set to less than 6 pm rms. The electrical conductance of the junction is measured with a voltage biased (10 mV) current amplifier connected to electrode B.

The experiment is performed at 4.2 K in cryogenic ultrahigh vacuum (UHV). At this low temperature atomic mobility is much reduced and thermal drifts of the setup are avoided. Cryogenic UHV is achieved by means of a carbon sorption pump preventing contamination of the electrodes when the junction is opened.

Compared with previous measurements of atomic contact forces using atomic force microscope (AFM) cantilevers, the use of a TF has a series of advantages. First, the stiffness (≈ 2000 N/m) of the lever supporting the contact is high enough to prevent early jump to contact. Second, TF has a very high quality factor (larger than 10^4 in the experimental configuration in vacuum at low temperature), permitting a precise measurement of the frequency shift. Third, it allows for a low power electrical measurement of the resonance which is particularly convenient for low temperature experiments. Fourth, in our setup one can control the interelectrode distance using the piezoelectric effect of the TF itself by applying a dc voltage in addition to the ac drive. This piezoelectric motion shows no measurable creep and was calibrated at room temperature using an optical interferometer yielding a displacement 0.74 ± 0.03 nm/V [14]. This setup avoids the usual uncertainties on the calibration of the interelectrode distance in MCBJ experiments.

In the data we present subsequently, we use a calibration of $\alpha = -3.75$ Hz/(N/m) which would be valid for a balanced TF [13] and which is consistent with the known magnitudes for the forces [15]. We estimate the accuracy of this determination to be 20% because of the imbalance of the prongs.

We present experiments in which the interaction between the electrodes is studied by measuring simultaneously the force gradient and the current as the interelectrode distance is varied. Different atomic configurations of the junction are measured by making a large contact and breaking it again. As the distance is reduced a jump to contact takes place. This jump is not related to the force sensor but to the elastic and yielding properties of the junction. This limits the distance range in which the interaction can be measured.

We will first focus on experiments in which the interelectrode distance is kept large enough in order to avoid jump to contact. In Fig. 1 we show a representative simultaneous measurement of the junction tunnel conductance and of the resonance frequency of the TF. We find that the approach and retraction curves are identical and reproducible, that is, current and frequency vs distance are reversible. As the junction gap is reduced, there is a nearly exponential increase of the current and a lowering of the resonance frequency of the TF indicating a negative force gradient. Deviation from exponential behavior can be explained by the elasticity of the electrodes themselves which shortens the distance between the two apex atoms as the electrodes are brought closer to each other. In order to obtain the actual separation between the apex atoms we correct the distance axis modelling the electrode compliance as a linear spring of fixed stiffness k_s. Spring stiffnesses varying between 5 and 60 N/m (see Table I), depending on junction realization being adequate to obtain an exponential current vs distance dependence.

In Fig. 2(a), we plot the current for various realizations of the junction using the corrected distance axis. For each curve, the displacement axis origin is defined so that the distance z is zero when extrapolating the conductance to one quantum of conductance, $G_0 = 2e^2/h$, expected for one-atom contact of gold. Since the apparent tunneling barrier is expected to decrease as the distance between the two tip atoms is reduced, [16,17] assuming a strict exponential dependence of the conductance with displacement will result in an overestimate of the stiffness of the electrodes. Still, this is a convenient definition to compare experimental and theoretical results. The slopes of the exponentials yield an apparent barrier height of 3.3–4.3 eV for all contacts, which is in good agreement with that of clean gold surfaces [17]. The dispersion of values of the apparent barrier height and electrode stiffness reflects the variations in the tip geometry.

In Fig. 2(b) we see that the force gradient changes markedly between realizations. In a metallic junction there are three main forces to be considered: a short-range metallic force, a long-range van der Waals (vdW) force, and a long-range electrostatic force. This last force can be neglected in this experiment because the electrodes are of the same material (no contact potential) and the applied bias voltage (10 mV) and junction capacitance are small. The large variations in the observed forces can be attributed to the changes in the vdW interaction for different shapes of the electrode in the vicinity of the junction. We model the junction as two facing paraboloidal tips which we assume identical

TABLE I. Analysis of the experimental data sets.

set #	1	2	3	5	31	32	35	33	34	36
k_s (N/m)	7	8	5	7	26	4	17	53	53	27
λ_T (pm)	40	41	41	40	46	40	44	47	54	45
λ (pm)	43	48	48	43	45	44	45	48	48	48
$-z_m$ (pm)	90	85	95	90	72	85	72	120	140	-25
E_b (eV)	0.7	0.7	0.6	0.7	0.5	0.4	0.5	0.4	0.5	0.7
R (nm)	0.70	0.37	0.44	0.70	1.26	1.10	1.26	1.54	5.20	6.40
$-z_0$ (pm)	300	390	320	300	240	300	240	320	420	370

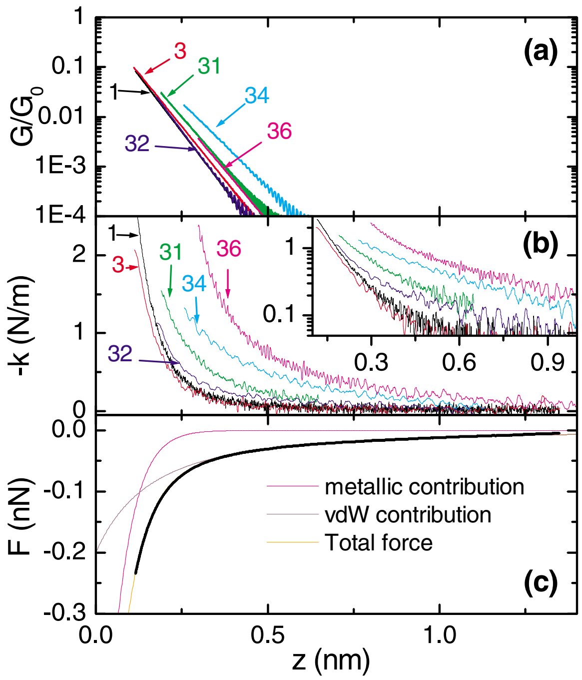

FIG. 2 (color online). (a) and (b) Semilogarithmic plot of the conductance and stiffness of various junction realizations (data sets # 1, 3, 31, 32, 34, 36 in Table I) as a function of the corrected distance axis (see text). (c) Forces obtained by integrating the stiffness for data set #1 showing the vdW and metallic contributions.

for simplicity. In this case the vdW force is given by $F_{vdW} = -A_H R/12(z - z_0)^2$ [18,19], where R is the radius of curvature of the tips and $A_H = 4.4 \times 10^{-19}$ J is the Hamaker constant for gold [20]. z_0 is the correct origin for vdW force and should be close to minus twice an atomic radius [21]. Taking R, z_0, and the frequency shift origin as fitting parameters (see Table I) we obtain excellent fits for the junction stiffness for large z ($> 0.3 - 0.5$ nm, depending on the realization). The lower lying curves (smaller stiffness) correspond to the smallest values of R, and are typically obtained after repeated indentation, which in ductile metals like gold usually results in nanocontact necking which upon breaking yields sharp tips [22].

For short distances ($z < 0.3 - 0.5$ nm), an excess stiffness is observed. We attribute it to a short-range metallic interaction, which is predicted to follow a universal behavior [6]. Expressed in terms of energy, $E = -E_b(1 + x)e^{-x}$, with $x = (z - z_m)/\lambda$. E_b is the binding energy, z_m is the separation at $E = -E_b$, and λ is a scaling parameter that gives the range of the metallic interaction. Consequently we fit the stiffness to the sum of d^2E/dz^2 and the vdW contribution. Taking $E_b/\lambda = 1.5$ nN as determined from the breaking force of a one-atom contact of gold [15], we can extract z_m and λ from the fit. We find $z_m = -80 \pm 40$ pm and $\lambda = 45 \pm 3$ pm. The resulting binding energy is $E_b = 0.7 \pm 0.2$ eV, which is consistent with the results of density functional theory calculations for atomic chains of gold [23]. In Fig. 2(c), we represent the force obtained by integration of the stiffness and the vdW and metallic forces resulting from the above fit for the data set #1 in Fig. 2(b). In Table I we present the parameters for each of the experimental curves.

We can confirm that the measured metallic interaction corresponds to the interaction between just two atoms by further reducing the tunneling junction gap. As the gap is reduced, there is a spontaneous jump to contact during which both the conductance and the resonance frequency have an abrupt jump. A similar behavior is observed upon retraction (jump out of contact) as shown in Fig. 3(b). The conductance of the contact is close to G_0, see Fig. 3(a), indicating a one-atom junction. The frequency shift can be analyzed in terms of a short-range metallic and vdW interactions, as explained above. However, in this case there are discontinuities at the jumps, and the force curve has disconnected tunneling and contact portions. From the contact portion, we can obtain directly k_s, which for the curve in Fig. 3, is 5.8 N/m, compared to the value of 8 N/m obtained by assuming a strictly exponential dependence of conductance vs distance. This provides direct evidence that using the conductance to estimate k_s systematically overestimates the stiffness of the electrodes (typically by about 30%). The effect on λ, z_m, and E_b can be assessed by repeating the analysis for the different data sets for smaller stiffness. For example, for set #1, if k_s is reduced by 30% we obtain $\lambda = 55$ pm, $z_m = -160$ pm, and $E_b = 1.0$ eV. This is an indication that

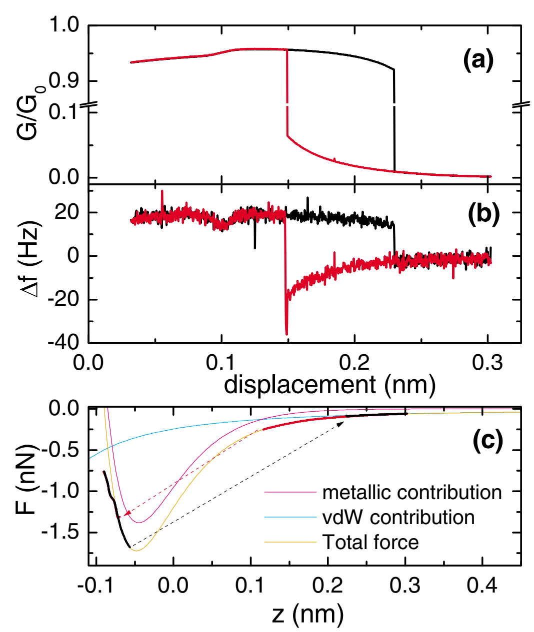

FIG. 3 (color online). Simultaneous (a) conductance and (b) frequency shift measurements for a one-atom junction. (c) Force, with vdW and metallic force components.

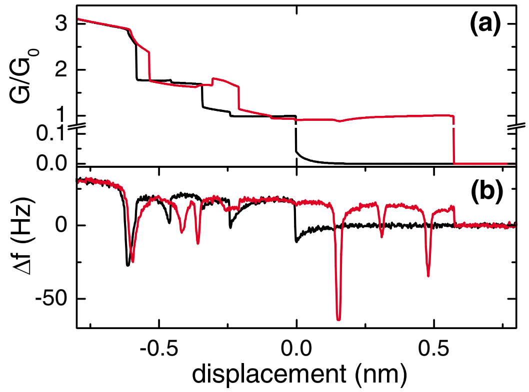

FIG. 4 (color online). Simultaneous (a) conductance and (b) frequency shift measurements for a larger indentation resulting in atomic chain formation.

the values of λ, z_m, and E_b in Table I are likely to be too small by about 30% .

Our results for λ are in quantitative agreement with the theory of Rose *et al.* [7] for metallic adhesion, which predicts that the range of the metallic interaction should be given approximately by the Thomas-Fermi screening length whose theoretical value is for the gold surface 54 pm. In contrast, previous experiments in Al-Au [4], Si-Cu [24] and W-Au [2,3] gave decay lengths from five to 10 times larger than the theoretical value.

In a metallic junction, the metallic adhesion force and the conductance are both due to the overlap of the electronic wave functions. Using a simple perturbative approach, Chen [25] obtained that the metallic interaction force should be proportional to the square root of the conductance for large distances. This implies that the range of the force λ should be twice the range of the conductance λ_T. In contrast, recent *ab initio* calculations find a conductance proportional to the force [9]. We obtain a value of λ close to λ_T but somewhat larger.

We show in Fig. 4 curve a representative simultaneous measurement of stiffness and current during contact formation and breaking of an atomic chain [11,12,23]. The current shows a stepwise behavior in the contact regime related to atomic rearrangements [26]. The enhanced resolution over previous direct force measurements [15,22,23] shows that the contact stiffness of the elastic stages is not constant with applied stress. The atomic rearrangements result in sudden drops in the stiffness which reflect bond weakening due to extreme strains close to yield. These drops are also observed during the atomic chain formation, whose conductance, in contrast, remains close to G_0 [27]. This mechanical behavior is consistent with the observed longitudinal phonon frequency decrease in one-atom contacts and chains [28] and agrees with direct force measurements in atomic chains [23].

In summary, we have measured the interaction between two sharp Au tips in the tunnelling and contact regime simultaneously with the conductance. The tips are atomically sharp and form an atomic contact when they touch. This was done under cryogenic UHV conditions with a new device: an MCBJ supplemented with a tuning fork. This setup allows for unprecedented precision, stability and cleanness. It furthermore allows formation of extremely sharp tips minimizing vdW forces, which must be taken nevertheless into consideration, and to extract the metallic interaction. In contrast to most previous experiments on metallic junctions, our results for the decay length λ and the binding energy E_b are in quantitative agreement with what is expected from the theory of metallic adhesion of Rose *et al* [7].

We thank S. Vieira and C. Urbina for useful comments and discussions. This work has been supported by the MCyT (MAT2001-1281 and HF2002-0168), CAM (07N/0053/2002 and 07N/0039/2002), and MECD (SB2000-0007).

[1] U. Dürig *et al.*, Phys. Rev. Lett. **65**, 349 (1990); U. Dürig *et al.*, Europhys. Lett. **23**, 147 (1993).
[2] G. Cross *et al.*, Phys. Rev. Lett. **80**, 4685 (1998).
[3] A. Schirmeisen *et al.*, New J. Phys. **2**, 29.1 (2000).
[4] B. Gotsmann *et al.*, Phys. Rev. Lett. **86**, 2597 (2001).
[5] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555, (1970).
[6] J. H. Rose *et al.*, Phys. Rev. Lett. **47**, 675 (1981).
[7] J. H. Rose *et al.* Phys. Rev. B **28**, 1835 (1983).
[8] S. Ciraci *et al.*, Phys. Rev. B **46**, 10411 (1992).
[9] W. A. Hofer *et al.*, Phys. Rev. Lett. **91**, 036803 (2003).
[10] N. Agraït *et al.*, Phys. Rep. **377**, 81 (2003).
[11] A. I. Yanson *et al.*, Nature (London) **395**, 783 (1998).
[12] H. Ohnishi *et al.*, Nature (London) **395**, 780 (1998).
[13] J. Rychen *et al.*, Appl. Surf. Sci. **157**, 290 (2000).
[14] The fact that the electrical parameters of a tuning fork barely change upon cooling down (apart from the quality factor) indicates that this calibration remains valid at low temperature.
[15] G. Rubio *et al.*, Phys. Rev. Lett. **76**, 2302 (1996).
[16] N. D. Lang, Phys. Rev. B **37**, 10395 (1988).
[17] L. Olesen *et al.*, Phys. Rev. Lett. **76**, 1485 (1996).
[18] F.J. Giessibl, Phys. Rev. B **56**, 16010 (1997).
[19] M. A. Lantz *et al.*, Science **291**, 2580 (2001).
[20] G. L. Klimchitskaya *et al.*, Phys. Rev. A **61**, 062107 (2000).
[21] E. Zaremba and W. Kohn, Phys. Rev. B **13**, 2270 (1976).
[22] N. Agraït *et al.*, Phys. Rev. Lett. **74**, 3995 (1995).
[23] G. Rubio-Bollinger *et al.*, Phys. Rev. Lett. **87**, 026101 (2001).
[24] M. Guggisberg *et al.*, Phys. Rev. B **61**, 11151 (2000).
[25] C. J. Chen, J. Phys. Condens. Matter **3**, 1227 (1991).
[26] U. Landman *et al.*, Science **248**, 454 (1990).
[27] During the atomic chain formation there are small conductance jumps related to force relaxations, but their magnitude is much smaller than G_0.
[28] N. Agraït *et al.*, Phys. Rev. Lett. **88**, 216803 (2002).