

Influence of H₂O molecules on sub-nanometre scale gaps between Au leads

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Abstract

Electric-field induced surface modification of Au is used to create stable sub-nanometre-scale gaps between Au leads. Electron tunnelling current is measured as a function of the molecular environment. We explore the influence of water molecules on tunnelling conductance. At small voltage, water molecules do not influence the conductance. At large voltage, a strong static electric field between the leads induces trapping of H₂O molecules from the water vapour. At room temperature, trapped water molecules increase the tunnelling barrier height, in agreement with the workfunction of water. We estimate that the resistance of a single trapped water molecule at 5 V is of order 100 G Ω .

1. Introduction

The studies of electron transport in molecular scale systems have recently become possible with the use of advanced microfabrication and self-assembly techniques. Investigations of electronic conduction through a self-assembled thiol-molecule monolayer on a gold surface have been demonstrated with scanning tunnelling microscopy [1], micromachined Si nanopores [2] and mechanically controllable break junctions [3].

In this paper we study the transport properties of atomic-scale tunnelling junction with H₂O molecules trapped between two gold leads. The influence of water molecules on sub-nanometre-scale gaps is important in the emerging field of molecular electronics. Since most molecules have relatively high resistance, it is important to find out how H₂O molecules, which are always present in the atmosphere, affect the junction electronic properties, before other molecules are introduced. We show that water molecules in tunnelling junctions are extremely good insulators. The contamination of junctions by H₂O should not be a problem, because parallel channels for conduction through contaminant water molecules have negligibly small transmission.

Junctions with a molecular-scale gap were created by the self-modification of gold films in the presence of strong electric field. The modification of a gold surface by an applied electric field has been studied extensively through scanning

probe microscopy [4–14]. In a strong electric field, applied by a scanning tip, gold atoms on the surface diffuse toward the region of strongest electric field, creating a mound. If this process is left unchecked, and the current is limited, then there will be a rearrangement of gold atoms which produces a neck-type contact between the tip and the surface. For a recent review, see [14]. Such contacts had a resistance of $\sim 200 \Omega$ [7]. In this work we apply an analogous technique to create tunnelling junctions between two Au films on a silicon chip. Then we examine how H₂O molecules at different vapour pressures affect the transport properties of these junctions.

2. Experimental details

2.1. Junction preparation

A schematic of the growth procedure is illustrated in figure 1(A). First, a slit between two insulating silicon nitride substrates is created, according to the recipe in [15]. Figure 1(A) displays a cross-section of the slit with a 50 nm layer of silicon nitride on top of a 200 nm layer of dry silicon dioxide. Through the silicon nitride layer, the width of the slit is approximately 70 nm, with a 120 nm wide undercut in the silicon dioxide layer. Then, by the standard metal vapour deposition technique with a base pressure in the 10^{-7} Torr range, a thin gold film was deposited at a rate of 3 \AA s^{-1} , over an exposed 0.1 mm length of the slit. The undercut serves to

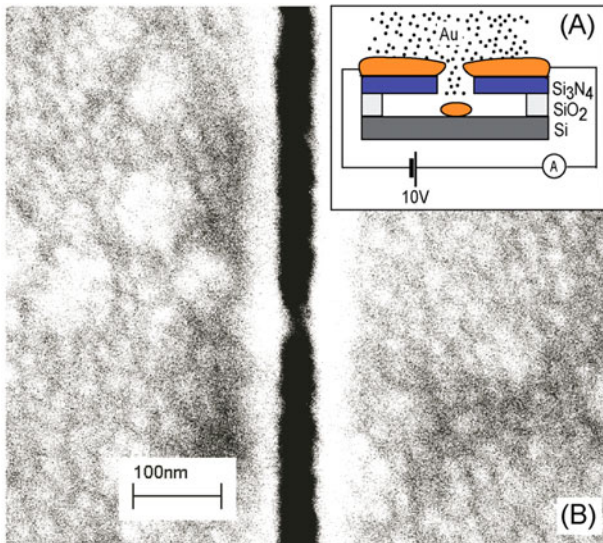


Figure 1. (A) Schematic cross-section of the sample during deposition of gold films onto two silicon nitride substrates, separated by a 70 nm gap. A wider undercut in the silicon dioxide layer serves to prevent contact between the films. The conductance between the films is monitored *in situ*. (B) SEM image of the junction. The protrusions are pulled toward each other from the opposite slit edges. Electrically, the protrusions may be weakly coupled to the parent leads, but for a junction grown at 10 V voltage across the slit, tunnelling between the protrusions determines the junction resistance. The size of different contacts varies in the range 10–100 nm.

(This figure is in colour only in the electronic version)

prevent connection between the two films during the deposition process. Figure 1(A) also shows the conductance across the slit is monitored during metal film deposition, and our expectation that the metal film sticks out over the slit. The applied voltage is 10 V and the current limit is large (~ 10 mA). While depositing Au, we stop evaporating when electric connection is detected. The typical thickness of the Au layer at this moment is 60–80 nm. The resistance of the samples varies significantly among samples, from ~ 100 k Ω to ~ 50 M Ω .

The sample formation has been examined by a scanning electron microscope (SEM). A pair of corresponding protrusions formed under the influence of the applied electric field, as described in [7, 14], creates a conductive junction. Edge irregularities ('seed' grains) randomly located along the slit may stimulate the protrusion growth. Typically there are several detectable irregularities which may potentially form a junction. By stopping the deposition when electric conduction suddenly appears, we select only one conducting junction. The junction size L along the slit, from the SEM images, is 10–100 nm. Figure 1(B) shows one of the junctions immediately after formation. The protrusions are pulled toward each other from the opposite slit edges. At 10 V, electrical contact between the leads has resistance much larger than $R_Q = h/2e^2 = 12.9$ k Ω ; tunnelling between the protrusions determines the junction resistance. Current through the junction depends exponentially on the gap between the protrusions. As the current increases, effects such as electromigration, and perhaps even melting, oppose the gap reduction. In quasi-equilibrium, at 10 V bias, the spacing

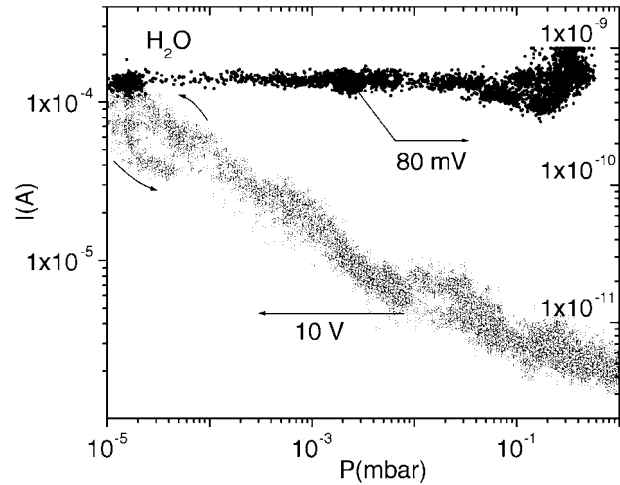


Figure 2. Electric-field induced trapping of water molecules. Current through the contact at 80 mV is independent of water vapour pressure, while current at 10 V decreased by several orders of magnitude with increasing water vapour pressure. These dependences are reversible. The results of two increase/decrease pressure cycles are shown.

between the Au electrodes stabilizes around a minimum distance, which is determined below.

2.2. Trapping of water molecules

A large applied voltage across the junction induces trapping of small polar molecules like water, analogous with electrostatic trapping of small conducting nanoparticles [15]. Water molecules are chosen for the trapping experiment since water is a 'natural' impurity in non-ultra-high-vacuum (non-UHV) systems: there is always some water vapour in the evaporation chamber to begin with. We examine how the increase in water vapour pressure changes the current through the junction.

We introduce a vapour of molecules from a cylinder of high purity liquid water, and measure the current I versus water vapour pressure P . The results are presented in figure 2, showing I versus P for 0.08 and 10 V bias. At 0.08 V, the junction resistance is independent of vapour pressure. However, when the applied voltage is 10 V, the junction current drops by several orders of magnitude as the vapour pressure increases. Thus, the electric field induces the resistance change. The minimum voltage at which current changes as a function of pressure depends on junction resistance: the smaller the resistance, the smaller the minimum voltage. For a junction of resistance 100 k Ω at 1×10^{-7} mbar, the minimum voltage is ~ 7 V. I versus P curves are *reversible*, as shown in figure 2. For some samples, I – P curves measured on the first cycle are different from the rest. The shape of the I – V characteristics changes significantly with P (see the next section).

Figures 3(A) and (B) display typical I – V curves of a junction in high vacuum and water vapour, respectively. The I – V curves are obtained by sweeping the voltage from 10 to 0 V and then back to 10 V, in 100 ms. The I – V curve is taken every 10 s; the I versus P curve taken at 10 V is not affected by measuring the I – V characteristics under these conditions.

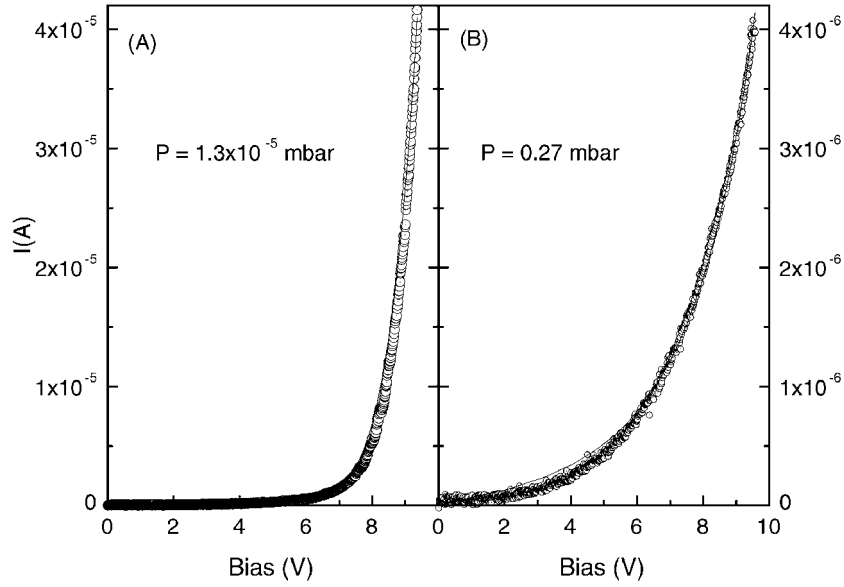


Figure 3. (A), (B) I - V curves of a tunnelling junction in high vacuum and water vapour, respectively. The curves are best fits, obtained in WKB approximation for a tunnel barrier of variable width d and height δ . At high vapour pressure the best-fit value of δ is close to the ionization energy of water, which demonstrates the high packing density of the water monolayer in the trap. At low vapour pressure δ is close to the workfunction of gold, showing the dominant role of electron transport through vacuum in the vacant places.

3. Results and discussion

To characterize our samples, we model the I - V curves by a simple one-dimensional energy barrier with transmission amplitude D obtained in the WKB approximation [16]:

$$D(V, E_x) = \exp\left(-2 \int_0^X \sqrt{\frac{2m(U(x, V) - E_x)}{\hbar^2}} dx\right)$$

where V is voltage, $U(x, 0)$ is a square potential barrier of height δ and width d , at nonzero bias voltage, barrier bending $U(x, V)$ is assumed to be linear, E_x is the kinetic energy associated with the direction of tunnelling and $X = \min(d, \frac{\mu + \delta - E_x}{eV}d)$. Then, considering electrodes consisting of free-electron metals with a well developed Fermi sphere corresponding to Fermi energy μ , we get for current density at $V \gg k_B T/e$ [16]

$$j(V) = \frac{2e\rho_t}{h} \left(eV \int_0^{\mu - eV} D(V, E_x) dE_x + \int_{\mu - eV}^{\mu} D(V, E_x)(\mu - E_x) dE_x \right),$$

where $\rho_t = \frac{2\pi m_t}{h^2}$ is the two-dimensional ‘transverse’ density of states, m_t is the effective electron mass in a plane perpendicular to the tunnelling direction (we consider $m_t = m_0$), e is electron charge, T is the temperature and k_B is Boltzmann’s constant. This formula gives the correct expression in the limits of tunnelling ($V \ll \delta$) and field emission ($V \gg \delta$). The contact area $S = \pi L^2/4$ is estimated from the junction size inferred from the SEM images, and the current $I(V) = S j(V)$. In this model, we assume that the size of the junction does not vary with vapour pressure P . We fix $L = 50$ nm according to the SEM image for a given sample, and vary d and δ as a function of P . (If all three parameters are varied as a function of P , a strong L versus P dependence results: $10 \text{ nm} < L < 100 \text{ nm}$. The strong dependence is an artifact,

reflecting that conductance is much less sensitive to L than to d and δ .)

For a junction in high vacuum, we obtain $d = 7.5 \text{ \AA}$ and $\delta = 6.4 \text{ eV}$, which is close to the workfunction of Au in bulk, 5.1 eV . As the vapour pressure increases, the barrier height changes smoothly. The I - V curve at $P(\text{H}_2\text{O}) = 0.27 \text{ mbar}$ is displayed in figure 3(B). The best-fit parameters are $d = 5.0 \text{ \AA}$ and $\delta = 11.2 \text{ eV}$. This best-fit value for barrier height is in good agreement with the measured workfunction of water molecules, $\sim 12.6 \text{ eV}$, and water clusters, $\sim 11.5 \text{ eV}$ [17].

In general, the barrier height in tunnelling junctions is the bandgap of the insulator [16]. A tunnelling process involves an intermediate state, in which an excited electronic state is virtually occupied. Usually, in dielectrics, the excited states form an empty conduction band, with a negligible charging energy for an excess electron. By analogy, one may expect that the barrier height in a molecular junction is the energy of the lowest electronic excited state. The lowest electronic excited state, which is 8.8 eV in a water molecule [18], is much smaller than the measured δ .

The excess barrier height arises presumably because the charging energy is added to the excitation energy. The charging effects have already been confirmed in tunnelling through molecular junctions formed by self-assembly of molecules into a monolayer [3].

In H_2O molecules, the charging energy could be significant. Intuitively, the barrier height with charging energy included should be comparable to the ionization energy, 12.6 eV . The absence of extended excited states indicates that water molecules are separated relatively far from each other, so that the spatial overlap between the excited states of different molecules is weak. Yet, $\delta = 11.2 \text{ eV}$ suggests that the packing of water molecules is dense enough to prevent leakage through vacuum, where the barrier height is smaller ($\delta = 5.1 \text{ eV}$).

The polarization energy of water molecules in the applied field of $10 \text{ V}/5.0 \text{ \AA}$ significantly exceeds the thermal energy

$k_B T$ at room temperature and the hydrogen bond energy. Thus, we expect the molecules are polarized and parallel with each other.

The spacing between two water molecules that form a hydrogen bond, in liquid or ice, is 2.8 Å. Hydrogen bonds are nonexistent in a parallel orientation of molecules. As a result, we expect the spacing between molecules to be significantly larger than 2.8 Å. We speculate that the spacing between water molecules in a parallel orientation is comparable to that of the next-nearest neighbours in ice or liquid, ~ 4.5 Å. In the parallel orientation, only a monolayer can fit in the gap of $d = 5.0$ Å.

Some water molecules are unavoidably present in the non-UHV system, where our experiments are performed. This is probably the reason that the best-fit value of barrier height, at the base pressure of our system, slightly exceeds the workfunction of Au. However, at low water vapour pressure, the density of water molecules in the gap is not high enough to block the tunnelling through vacuum channels and electron transport properties are close to that of tunnelling with an expected barrier height of 5.1 eV.

If we repeat the vapour-to-vacuum cycles at high bias voltage, the low-pressure value for barrier height is ~ 2 eV more than initially measured, and remains so for all subsequent cycles. This additional increase of the barrier height is caused by the increase of water molecules density in the gap—once water vapour is introduced, the junction is never as ‘clean’ as before. At high water vapour pressure, for each vapour-to-vacuum cycle, the high-pressure values of fitting parameters are about the same, since water molecules fill practically all vacancies in the gap and tunnelling is possible only through the water molecule monolayer. Considering dense packing of water molecules in the monolayer within the 50 nm size gap we estimate the effective resistance of a single electrically trapped H₂O molecule of 280 GΩ at 5 V bias (see figure 3(B)), which is much higher than the characteristic resistance 9–22 MΩ of a single dithiol molecule [3, 19, 20].

4. Conclusion

We have generalized the technique of electric-field induced modification of a gold surface, to create tunnelling junctions with atomic-scale gaps on a silicon chip. At the base pressure of our system (10^{-6} mbar), tunnelling through vacuum dominates with a barrier height close to the workfunction of gold. At low voltage, H₂O molecules in the environment do not affect the junction resistance. The junctions trap water molecules from the environment only if the applied voltage is large. At high vapour pressure and high voltage, water molecules form a dense monolayer between the leads with the tunnelling barrier height comparable to the ionization energy of a single water molecule. Since water molecules decrease tunnelling current from that in vacuum, the presence of H₂O

molecules in the gap should not pose a problem in molecular electronics, where molecules of higher conductance are used.

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