Quantum Contact in Gold Nanostructures by Scanning Tunneling Microscopy

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This paper shows that the nanostructures deposited at room temperature in scanning tunneling microscopy experiments are produced by mechanical contact between tip and sample. Gold mounds are deposited in gold substrates and it is observed that the current flowing between tip and sample is quantized and the resistance can be as low as 100 Ω.

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In the past few years, scanning tunneling microscopy (STM) has been extensively used as a tool to locally modify surface structures. In addition to the growing interest in the physics of small structures, very spectacular results such as the positioning of individual atoms with atomic precision have been reported [1]. A difficulty in many of these results is, however, the incomplete understanding of the underlying phenomena. In this paper we focus our attention on the process of deposition of nanometer-size gold structures, first reported by Mamin, Guethner, and Rugar [2]. Based on the finding of a threshold voltage for deposition which scales with tip-sample separation, the authors conclude that the deposit is formed by atomic emission from the gold tip. In this work we demonstrate that for the same conditions reported in [2], the creation of the nanometer gold structures takes place by the formation of a contact between tip and sample, characterized by an electrical resistance smaller than 100 Ω. This contact is of such a nature that discrete jumps in electrical resistance occur as the contact is broken. We suggest that these jumps are due to the quantization of the resistance.

Our experiment consists of depositing nanostructures with a gold tip on a gold substrate, by applying a voltage pulse at the tunneling position. We used a STM head working at atmospheric pressure and room temperature. The gold tip was prepared by electrochemical etching in concentrated hydrochloric acid (1.5–2 V dc). Either gold balls or gold deposited on top of a mica sheet were used as substrates. In order to obtain more information about the deposition process, we measured the current flowing during the deposition and observed that this current remains saturated at the current limit of 100 nA of our preamplifier, for a time longer than the duration of the voltage pulse. To measure the maximum current that can flow during the process, a new preamplifier is used in order to increase the measurable limit of the current. The new device is made from two I-V converters working with two different gains. The input of both converters is connected to an analog switch with a leak current of 0.25 nA. A synchronized signal switches between the two preamplifiers in less than 150 ns. The low gain converter measures contact resistances as low as 100 Ω, which is the switch resistance, while the high gain preamplifier is used for scanning.

Data characteristic of a typical experiment are shown in Fig. 1. The deposited nanostructure [Fig. 1(a)] can be described as a hillock of 38 nm diameter and 3.1 nm height. The current pulse observed during the fabrication of the structure, right after the voltage pulse, is plotted in Fig. 1(b). In addition, the voltage applied to the Z piezoelectric transducer (Z piezo), indicating the movement of the tip with respect to the sample, is shown in Fig. 1(c). The voltage pulse was 6 V (sample positive) and its duration was 14 μs. The duration of the current pulse is 10 ms, much larger than the duration of the voltage pulse. The saturated current is 1.5 mA, fixed by the characteristics of the low gain preamplifier. Since the bias voltage is in this case 0.4 V, the contact resistance is 267 Ω. This small resistance value can only be explained by a contact established as a consequence of the voltage pulse. Once the pulse is made, the feedback operates with a long time response, which causes tip retraction from the sample [see Z plot in Fig. 1(c)] until the contact is broken. Interestingly, this breaking process is characterized by discrete changes of current or contact resistance. Notice also that the final step which separates contact from tunneling is a resistance jump of 12.9 kΩ, in coincidence with the theoretical quantum unit of resistance ($h/2e^2$). The observed resistances indicate the formation of a contact neck between sample and tip with cross sections varying from 3 to 0.5 nm, although the maximum area of contact is difficult to determine since the I-V converter saturates at 1.5 mA. The observation of steps in the conductance is reproducible in all the experiments, although their values differ. This is a consequence of the different geometry and state of the tip in each deposition and the way in which section varies as the tip retracts. However, the precise values of the steps observed before the contact breaks can always be reasonably interpreted as multiples of $2e^2/h$, as shown in Fig. 2, where another set of data is presented for the sake of

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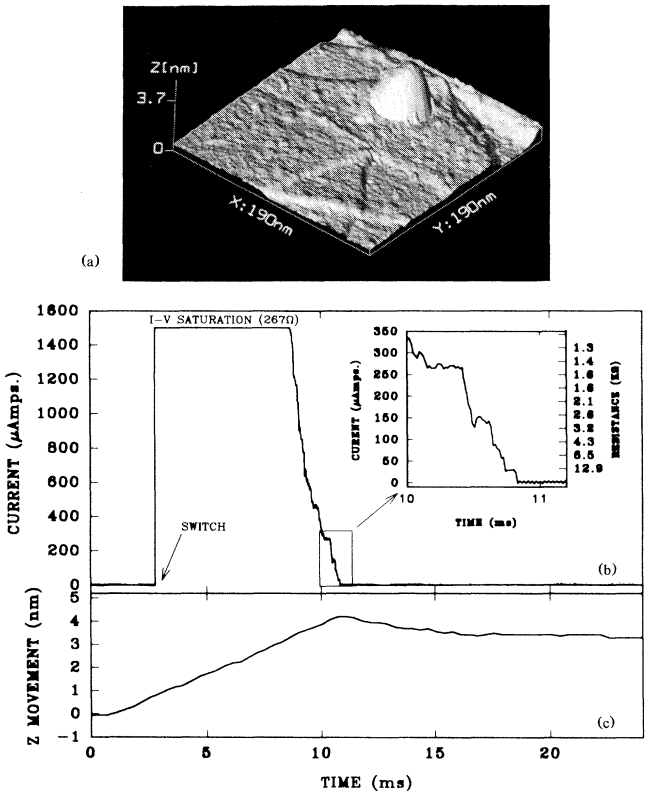

FIG. 1. (a) Nanostructure created by applying a voltage pulse of 6 V amplitude and 14 μs duration starting at time $t=0$. (b) Electrical current flowing after the voltage pulse as a function of time. The current is measured after a short delay ($\sim$2.5 ms) needed to activate the switch (see text); its maximum value is 1.5 mA (I-V saturation value) for a bias voltage of 400 mV. Notice the stepwise character of the curve at high resistances (see inset). (c) Movement of the Z piezo measured simultaneously with the current.

comparison. It is remarkable that we are able to produce conduction channels of atomic size in a metal at atmospheric pressure and room temperature.

More information about the process comes from the analysis of the tip movement as measured by the Z piezo voltage [Fig. 1(c)]. The Z piezo voltage increases linearly first, due to the separation of the tip from the sample. When the contact is broken, the Z piezo goes back slowly until a tunneling current is detected and there it remains constant. The total tip movement, measured in Fig. 1(c) as the difference between the final steady state position and the initial position ($\sim$3.3 nm), is slightly larger than the height of the deposited structure [3.1 nm in Fig. 1(a)]. In other experiments the difference is even larger. This effect arises because when the contact neck is broken, a part of it becomes attached to the end of the tip, thus forming some kind of protrusion. The slight change of the Z piezo voltage, after the break of contact, is a measure of the relaxation of the final structures formed

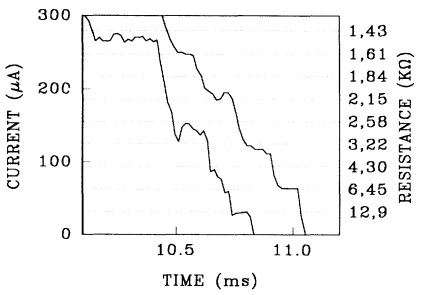

FIG. 2. Jumps in contact current as a function of time measured in two different experiments. Lines parallel to the horizontal axis corresponding to resistance values of $h/2ne^2$ (n integer) are indicated.

on both tip and sample as a result of surface diffusion [3]. The rounded shape of the deposited structures indicates such diffusion.

Our interpretation of the deposition process is shown in Fig. 3. The initial low contact resistance proves the formation of a wide tip-sample contact right after the voltage pulse (step B). As the tip retracts away the contact resistance increases indicating a reduction in the contact cross section as the connecting neck elongates [4] (steps C, D, and E). Step F shows the relaxation of the tip and sample once the contact is broken. From the value of this relaxation a lower limit of the neck length can be estimated (1 nm for results in Fig. 1).

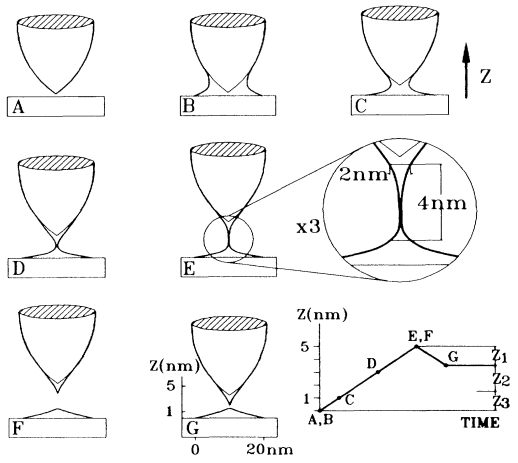

FIG. 3. Creation of a deposit by formation of a neck between tip and sample. A: Initial state (tunneling position). B: Contact after applying a voltage pulse. C, D, and E: Tip withdraw of 1, 3, and 5 nm, respectively. The neck formed before breaking is about 4 nm long and less than 2 nm thick (see enlarged drawing). F: Relaxation of the neck after the contact is broken due to diffusion. G: Tip returns to tunneling position. The typical Z piezo movement after the voltage pulse is plotted at the lower right part of the figure. Z_1 corresponds to the relaxation distance and Z_2 and Z_3 are the heights of the protrusions on tip and sample.

We have also measured the dependence of the process on the amount of current flowing between the two electrodes. This is made by changing the I-V saturation current from 15 nA to 1.5 mA in tenfold steps. In all cases, the mounds obtained were similar, showing the same height, the same threshold voltage, and with the same probability of formation. The current always remained saturated at its respective limit, while the Z piezo behaved in the way described previously. Therefore, we assume that contact occurs in every case. We take this as an indication that heating of the contact region by current is not essential in the formation of the deposits in the conditions we mentioned above.

Since contact occurs unambiguously during the voltage pulsing process, a logical question is whether such voltage pulsing is actually necessary in order to form the structure. We have performed an experiment starting at the tunneling position and then acting on the Z piezo voltage in order to produce a tip-sample contact. The contact is detected by a strong increase of the flowing current. The result of this operation is the formation of a hillock which is essentially the same as that obtained by applying a voltage pulse. Figure 4 shows mounds subsequently fabricated with and without voltage pulse.

The experimental evidence reported above shows that the contact between tip and sample is the main requirement for the formation of gold nanometer-size deposits by STM. The question is why the voltage pulsing produces such a contact and why there is a threshold voltage [2], as we have also verified. The possibility that atomic emission from the tip is the physical process responsible for the threshold voltage is unlikely. Taking the size of the deposits (typically 10–20 nm wide and 2–3 nm high) and the time duration of the pulse (600 ns according to [2]), we obtain an atomic emission intensity of 1.6×10^{10} ions/s. This rate is extremely high compared with the metallic ion emission from gold nanotips (10^5 to 10^6 ions/s) reported by Thien Binh and García [5]. The threshold voltage value is also anomalously low when compared with typical data from field evaporation [6].

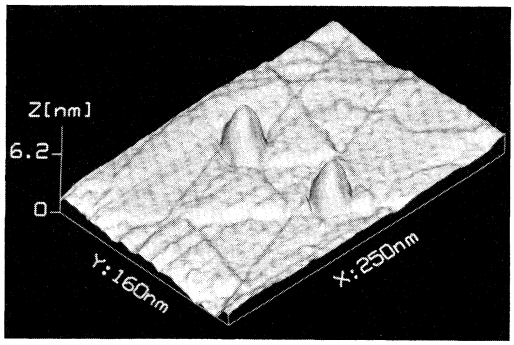

FIG. 4. Deposits subsequently fabricated by applying a voltage pulse (lower one in the figure) and by acting on the Z piezo in order to lead tip and sample to contact.

A possible way to establish the contact could be the formation of a protrusion by the high electric field, as has been reported in field emission experiments [5]. Notice that, in terms of electric field, the roles of tip and sample are equivalent in the tunneling regime due to the small gap distance. Therefore, a protrusion could arise on the sample and/or the tip.

Another explanation is to attribute the contact to mechanical deformation by the attractive electrostatic force between tip and sample [7]. The finding of a threshold voltage can be explained by the V^2 dependence of the electrostatic force. An additional argument is the independence of the process with respect to the voltage polarity [2]. The dependence on the tip-sample distance D can also be explained since the electrostatic force for very low D values ($D \ll R$) goes like R/D, with R being the radius of the tip [8].

With independence of the actual mechanism leading to the contact, it seems clear from our data that the surface structure formation is a result of the adhesion between the surfaces of tip and sample. In this way, another interesting point is the fracture process of the contact, which can be thought of as a uniaxial tensile test experiment performed at the nanometer scale and room temperature. Given the ductile nature of gold the deduced necking process [9] preceding the fracture seems very reasonable. This experiment could be taken as a starting point for investigating mechanical properties at the atomic level.

A second point of interest is the study of the electrical transport through the contact. As stated above, the dimensions of the observed contact are of few nanometers, smaller in any case than the mean free path of electrons for bulk gold at room temperature (14 nm). So, the transport is ballistic. Furthermore, when the constriction diameter is of the order of λ_F (0.5 nm), conductance is presumed to be governed by quantum mechanics rules.

In our experiment, the transport shows a stepwise decrease of the conductance (similar observations have been reported in point contact experiments at liquid helium temperature [10,11]). This behavior is associated with the discrete variation of contact cross section. It has been shown previously [4] that the neck elongation process is produced in the form of atomic rearrangements as the tip retracts, resulting in discrete jumps in ballistic conductance [12]. However, when the contact area is only a few atoms wide, we observe steps in conductance only at integer values of $2e^2/h$ (Fig. 2). At this point, the connective neck is presumed to be long compared to λ_F (Fig. 3), and thus the quantum transport is expected to occur in the form of discrete channels [13–15]. Since the conductance associated with one atom is less than $2e^2/h$ [16], the number of channels is not directly related to the number of atoms. This argument indicates that the steps observed in our experiment, immediately before the neck breaks, should be related to the existence of a quantized

resistance. So, our data support the observation of quantized resistance in metallic contacts.

In conclusion, it has been shown that nanostructures are created by adhesion when a contact is produced between tip and substrate. Low resistance (or high current) measured for periods much larger than the duration of the pulse and quantized steps give evidence of this contact. The final rounded shape of the nanostructure is due to the diffusion in the system.

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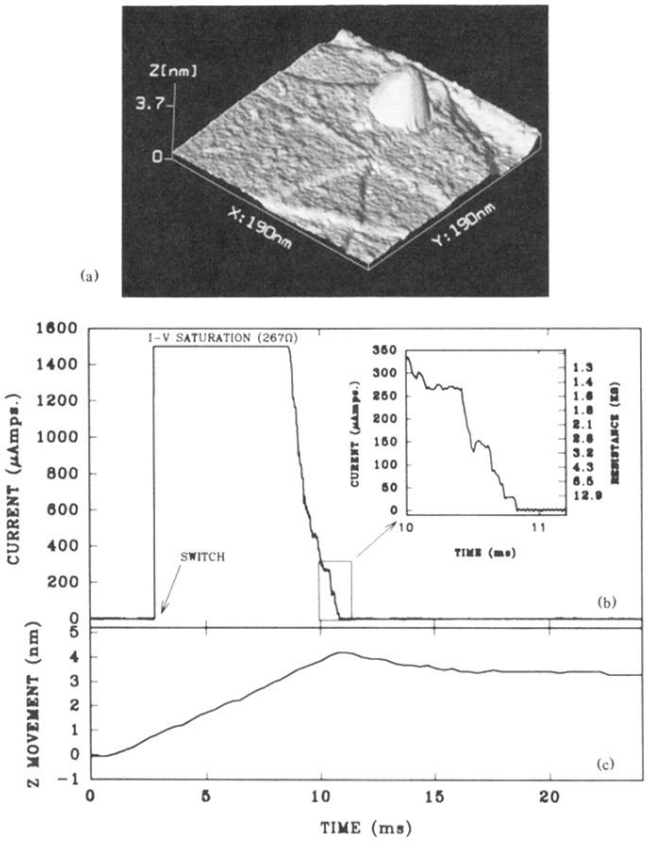
[16] For wide constrictions the number of these channels is of the order of atoms in the cross section, but it has been shown theoretically [14,15] that for very narrow point contacts the increase in conductance, when one atom is added, is less than $2e^2/h$, and when the conductance is quantized, the number of channels is not related to the number of atoms.



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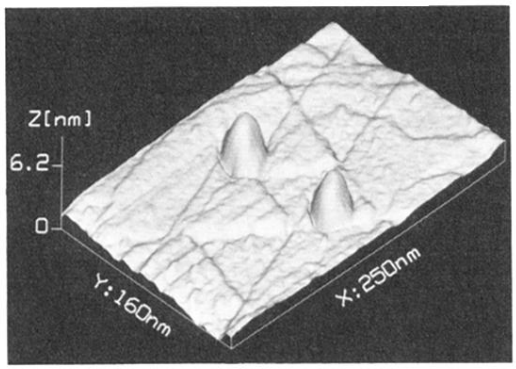

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