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Structural and electronic properties of gold nanowires

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Abstract. We have used high resolution transmission electron microscopy to determine the structure of gold nanowires generated by mechanical stretching. Just before rupture, the contacts adopt only three possible atomic configurations, whose occurrence probabilities and quantized conductance were subsequently estimated. These predictions have shown a remarkable agreement with conductance measurements from a break junction operating in ultra-high-vacuum, corroborating the derived correlation between nanowire atomic structure and conductance behavior.

PACS. 68.65.La Quantum wires – 68.65.-k Low-dimensional, mesoscopic, and nanoscale systems: structure and nonelectronic properties – 73.63.-b Electronic transport in mesoscopic or nanoscale materials and structures

1 Introduction

Nanometric systems are attracting a great interest in the scientific and technological community due to the novel physical and chemical properties that appears in materials in this size range. Among several phenomena, the quantum conductance of metal nanowires (NWs) is concentrating a great research effort. NWs can be generated by bringing into contact two surfaces which are subsequently pulled apart; during the contact stretching and just before rupture, the conductance display flat plateaus connected by abrupt jumps whose value is approximately a conductance quanta $G_0 = 2e^2/h$ (where e is the electron charge and h is Planck's constant) [1]. Although the simplicity of this experimental approach, we must take into account that a different nanowire is generated for each elongation procedure and also, that the conductance changes reflect a complex superposition of structural and electronic effects; then it is rather difficult provide a detailed interpretation [2].

In this work, we have studied the atomic arrangement of gold NWs *in situ* in a high resolution transmission electron microscope (HRTEM) and, we have observed that during their elongation, the contacts adjust themselves to adopt merely three possible atomic arrangements in order to maximize the NW cross section atom packing. We have modeled the structures, predicted their occurrence probabilities and conductance behavior. Using an independent experiment, a Mechanically Controllable Break Junction (MCBJ) [3] operating in ultra high vacuum (UHV), we performed electrical transport measurements showing a remarkable agreement with our predictions. This approach provides a novel framework to analyze individual conductance curves of gold NWs generated by mechanical stretching. We have also studied in detail the atomistic processes involved in the formation and elongation of suspended chain of gold atoms.

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2 Experiment

We have generated NW *in situ* in a HRTEM (JEM3010, UHR, 300 kV) using the method developed by Takayanagi's group [4,5]. The procedure consists in focusing the microscope electron beam (current density 120 A/cm^2) on the sample to perforate and grow neighboring holes until a nanometric bridge is formed between two of them. We have used a self-supported polycrystalline gold thin film (5 nm thick, deposited on a holey carbon grid) in order to generate NWs between apex of different orientations and elongate them in different directions [6]. Atomic resolution image acquisition has been performed after reducing the electron beam intensity to its usual value (30 A/cm^2). A digital camera (Gatan MSC794, acquisition time 1 s) was used to acquire micrographs and a high sensitivity TV camera (Gatan 622SC, 30 frame/s) associated with a conventional video recorder was used to register NW real-time evolution.

The procedure described above, allows us to generate NW with a remarkable stability, because the NW, its apexes and the surrounding thin film regions form a monolithic block, and in consequence, the NWs formed by a few atomic layers usually show a long life time (1-10 minutes). Although this stability, the generated NWs elongate spontaneously, get thinner and then break due

to the relative slow movement of the NW apexes. This apexes displacement are probably due to a film deformation induced by thermal gradients between parts of the sample, as usually observed in TEM thin film work. A critical aspect when studying such tiny nanostructures is the presence of contaminants, the most critical one in TEM is amorphous carbon. However, we must keep in mind, that the intense electron irradiation transforms carbon into bucky-onions and finally clean the gold surface [7].

The electric transport properties of gold NWs were studied using an independent instrument specially designed for this purpose, namely an UHV-MCBJ [8]. In this approach, a macroscopic gold wire (99.99%, $\phi = 75$ μm) is glued in a flexible substrate in two points; then it is fragilized in a point between the two fixing parts by a incomplete cut. By bending the substrate *in situ* in the UHV, we break the wire and produce two clean gold surfaces; using the same bending movement, the fresh tips are put together and separated repeatedly in order to generated and deform NWs. Its important to remark that in this configuration the NWs are generated from surfaces obtained in UHV ($< 10^{-8}$ Pa), so it is expected to have a clean sample for few hours [8]. This care with vacuum conditions is extremely important to generate reliable experimental measurements on NW properties [6,9].

Electrical measurements were done using a home-made voltage source, and current-voltage converter powered with isolated batteries to reduce electrical noise. Data acquisition was based on a 8 bits digital oscilloscope (Tektronic TDS540C, 2 GSample/s, Bandwidth 500 MHz); this electronic systems was developed with the aim of improving the conductance measurement precision, yielding values with a relative error of $(\Delta G/G) \sim 10^{-4}$.

The applied voltage was 100 mV, and the conductance was measured in the [0, 2.7] G_0 range to improve the detection of the last two quantum conductance plateaus.

3 Results

We have analyzed several hundreds of NWs breaking processes by means of HRTEM images and also the dynamical behavior by means of video recordings. The main conclusions that could be derived from the observation of the last stages of elongation (just before breaking) are: a) gold NWs are crystalline and free of defects [10]; b) they show only three NW atomic arrangement because the neck region adjusts its atomic configuration to get that one of the [111]/[100]/[110] gold zone axis is parallel to the elongation direction (Fig. 1). In simple terms, the first observation is explained because defects are not energetically favored in nanostructures [10], and the second one because the three adopted orientations maximize the atomic packing in the NW cross section [6].

Besides, these three NW types display substantial differences concerning the constriction morphology and mechanical behavior. NWs along [111] and [100] directions show a by-pyramidal shape, and evolve to form one-atom-thick contacts (Figs. 1a, 1b), what can be described as a ductile behavior. These two kinds of NWs, usually form a

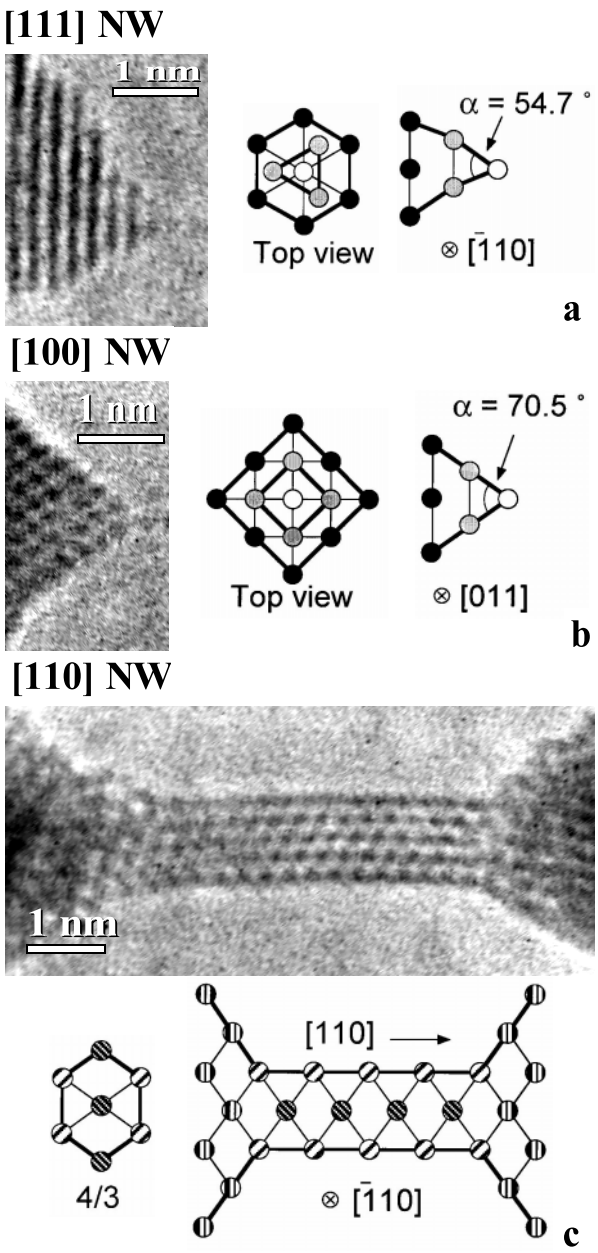

Fig. 1. HRTEM images of gold NWs, atomic positions appear dark. a) [111] atom-chain NW; b) [100] NW; c) rod-like [110] NW. Schematic representations of suggested atomic arrangement for the gold NWs are also shown, top and side views are displayed and opening tip angles (α) are indicated.

suspended atom chain structure as the ultimate thinnest contact [4,11,12]. On the other side, NWs that are formed along [110] direction display a rod like morphology [5] with aspect ratio in the 3-6 range (Fig. 1c), and they break abruptly, as being brittle, when they are rather thick, ordinarily 3-4 atomic layers.

The three observed neck morphologies can be understood by using the geometrical Wulff construction [13] to model the expected morphology of the apexes along the three observed zone axis. A [111] NW pyramidal apex

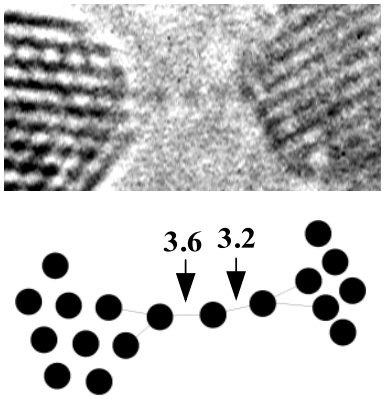

Fig. 2. Atomic resolution image of an atom chain formed by 3 gold atoms (upper part). Atomic positions appear as dark dots. A schematic view is displayed at the lower part, distances are marked in Å (± 0.2 Å).

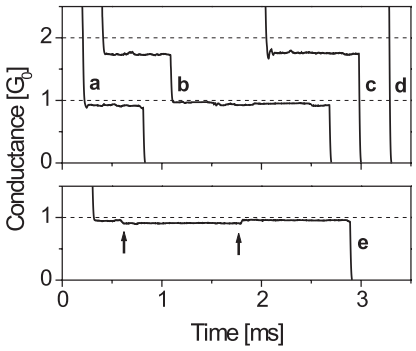

Fig. 3. Conductance behaviors of gold NWs measured using the UHV-MCBJ. a) Merely one plateau at $1G_0$; b) curve with a stair-case profile, plateaus at $2G_0$ and $1G_0$; c) last conductance plateau lying close to $2G_0$; d) abrupt NW rupture; e) conductance curve plateau close to $1G_0$ showing substructures (indicated by arrows).

would be generated by alternating 3 (111) and 3 (100) facets (Fig. 1a); in a similar way, a gold pyramid along [100] would be limited by four (111) facets (Fig. 1b). The rod like shape of NWs along [110] axis can be explained by the existence of two families of low energy (111) planes that lie parallel to this direction (Fig. 1c).

As mentioned above, [111] and [100] NWs usually form one-atom-thick constrictions (atom chains, ATCs) whose length is in the 2-4 atoms range. These chains may last several tens of seconds, what is surprising for such a tiny structure. However, the most unexpected fact on ATCs is the interatomic bond lengths which is in the 0.30-0.36 nm range (Fig. 2) [4,11,12], being much longer than the nearest neighbor distance in bulk gold (0.289 nm). The bonds and ATC lengths measured in this work are in full agreement with previous data obtained within the ultra clean environment of an UHV-TEM [4].

Time resolved atomic resolution observations of ATCs have revealed that although the ATCs seem to be strongly bounded to the tips, their sticking point can move rather easily on the apex surface, what may help to accommodate apex movements [12]. This behavior is analogous to gold atoms on (111) surfaces where the surface potential display a shallow corrugation inducing a low diffusion barrier (0.1 eV [14]).

Figure 3 shows some examples of conductance curves acquired with the UHV-MCBJ; as in most metal NW experiments, we can not control the kind of generated nanowire, then all curve profiles are different [3,15,16]. The conductance curves display horizontal plateaus and abrupt jumps between them; the plateau values are very close to the expected integer multiples of G_0. From the conductance range measured in this work, four different curve profiles can be identified and are presented in Fig. 3: a) a single plateau at $1G_0$; b) plateaus at 1 and $2G_0$; c) a single plateau at $2G_0$; d) no plateaus below $2.7G_0$. It is important to note that when the NW breaks, all the conductance curves always attain the zero value, and this is an indication of cleanness. When some contamination is present (ex: by just waiting many hours after the wire break in UHV), we usually observe the appearance of small short plateaus at $0.1\text{-}0.2G_0$ and also curves displaying a single and long $1G_0$ plateau appear more frequently. Except this detected evolution of the curve profiles with time (6-24 hours), a quick analysis do not reveal any major differences with conductance measurements in experiments performed with poorer vacuum levels or even at ambient conditions.

4 Discussion

The fact that HRTEM has revealed that, before breaking, gold NWs adopt merely three kinds of atomic arrangements with two different mechanical properties, represents a fundamental information to try to get a more deeper understanding of the origin of the different conductance curve profiles observed experimentally. Firstly, these observations limit to a few the numbers of possibilities to analyze, and secondly the constriction morphology and its evolution provide us with a very good basis for modeling the atomic structure.

A first point to be considered is the final size of a NW before rupture and if it is possible to deduce the related conductance. In these terms, it has been shown that one-atom-thick gold contacts should have a conductance close to a single quantum [1]; then NWs along [111] and [100] (Figs. 1a, 1b) should show their lowest conductance as a plateau close to $1G_0$. On the other hand, rod-like [110] contacts should not display the $1G_0$ plateau because they break abruptly when formed by 3-4 atomic layers.

As in our conductance experiments, there is no control on the orientation of the NW apexes nor of its elongation direction [6], there should be no preferential orientation for the NWs and the final adopted structure would be the closest zone axis to the elongation direction. This should be valid for constrictions where both apexes have the same

Table 1. Statistical analysis of conductance curves.

	Plateau at $1G_0$	Plateau at $1G_0$ and $2G_0$
Expected values	54% (7/13)	31% (4/13)
Series 1	$(52 \pm 2)\%$	$(34 \pm 2)\%$
Series 2	$(56 \pm 2)\%$	$(33 \pm 2)\%$
Series 1	$(50 \pm 2)\%$	$(31 \pm 2)\%$

crystallographic orientation or not; for the second case the apex which is closest to a zone axis will prevail over and, dominate the neck thinning process. Then, for each NW type, the appearance rate would be proportional to the multiplicity of its zone axis, namely 3 for [100] NWs, 4 for [111] NWs and 6 for [110] NWs. In this way, a 7/13 percentage ([111] and [100] NWs) of the conductance curves should display a $1G_0$ plateau.

In order to verify this prediction, we have counted how many conductance curves showed a last plateau at $1G_0$ (ex. curves a and b in Fig. 3), from series formed by 500 measurements. Table 1 displays the result of the analysis and a remarkable agreement with our prediction can be verified. In addition, from the obtained results, we can deduce that the last plateau for a rod-like NW is $2G_0$. In order to try to differentiate the [111] and [100] NWs, we can consider that the conductance curve profile is somewhat related to the contact cross section variation [15,17]. In this sense, [111] NWs have a lower opening angle and they can be supposed to show both 2 and $1G_0$ plateaus, then we would expect that 4/13 of the curves show this profile. The analysis of the conductance curve series again shows a remarkable agreement, corroborating the proposed correlation between atomic arrangement and conductance behavior [6].

Frequently, conductance curves display plateaus whose value is close to integer multiples of the conductance quanta, and in particular they show substructures and small steps as exemplified in Fig. 3e for the $1G_0$ plateau. As discussed above, the $1G_0$ plateau corresponds to one-atom-thick contact and possibly to an ATC, then the subplateaus should correspond to discrete changes in the electron transmission through the NW. These small conductance jumps may be attributed to the ATC fixing points movement on the contact surfaces, as revealed by the dynamical HRTEM [12].

As a final comment, we would like to emphasize the importance of keeping the gold surface free of contamination when performing NW studies. Although gold is a noble metal, the surface become covered with many molecular species that may produce significant changes in the electron transmission coefficients [18]. In fact, the agreement between the appearance of curve profiles and our structural model is only obtained during the first hours after generating the surface in UHV [6]. Also, quite different non-linear behaviors have been observed between NW generated from clean surfaces prepared in UHV and other conditions such as ambient, poorer vacuum, or incomplete surface cleaning [9].

5 Conclusions

We have used two independent experiments (HRTEM and UHV-MCBJ) to study structural and electrical properties of gold nanowires.

We have observed that just before rupture NWs are crystalline and free of defects, adopting merely three types of atomic configurations where one of the [100], [110] or [111] zone axis lies approximately parallel to the elongation direction. We have also revealed a correlation between the conductance curve profile and the NW atomic structure [6]. For ATCs, we have observed that they present extremely long interatomic bonds (0.30-0.36 nm), and that their attachment point are capable of moving rather easily on the tip surface [12].

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