The effect of bonding of a CO molecule on the conductance of atomic metal wires

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Received 5 October 2006, in final form 13 November 2006
Published 3 January 2007
Online at stacks.iop.org/Nano/18/035205

Abstract
We have measured the effect of bonding of a CO molecule on the conductance of Au, Cu, Pt and Ni atomic contacts at 4.2 K. When CO gas is admitted to the metal nanocontacts, a conductance feature appears in the conductance histogram near 0.5 of the quantum unit of conductance, for all metals. For Au, the intensity of this fractional conductance feature can be tuned with the bias voltage, and it disappears at high bias voltage (above ∼200 mV). The bonding of CO to Au appears to be weakest, and associated with the formation of monatomic Au wire.

1. Introduction

The fabrication and characterization of nanostructures have attracted wide attention because of their potential application in atomic-scale electronic devices. The development of fabrication methods such as mechanically controllable break junctions (MCBJ) and scanning tunnelling microscopy has made it possible to fabricate even monatomic metal wires [1, 2]. The properties of the nanowires have been studied in detail by various methods [3]. On the basis of our understanding of metal nanowires, the influence of molecules binding to the metal nanocontacts has been discussed in recent years [4–12]. Li et al reported a change in the conductance of metal nanowires due to adsorbates. The change was attributed to adsorbate scattering and rearrangement of the atomic configuration of the nanowire induced by adsorption [4]. Under specific circumstances a single molecule can be made to form a bridge between metal electrodes just after breaking the nanococontact. The first conductance measurement for a single molecule was performed by Reed et al who investigated 1,4 benzendithiol [5]. Conductance measurements for single molecules have been studied by several experimental techniques, including MCBJ and electromigration break junctions [9], and various interesting phenomena have been observed [6, 9]. Although these results are promising there are large discrepancies between the experimental results obtained by different groups, and between experiments and theory.

One of the reasons for these discrepancies is uncertainty regarding the configuration of the molecule and the nature of the molecule–metal interface. The molecules selected for these studies are usually composed of several carbonyl rings and are anchored to gold metal leads by sulfur groups. In view of these difficulties, it seems natural to step back and focus on an even simpler system, such as H₂ and CO.

Detailed studies have been performed for H₂ on Pt nanocontacts by conductance measurement and point contact spectroscopy. It was found that the conductance of a single H₂ molecule anchored between Pt leads is slightly below 1 $G_0$, where $G_0 = \frac{2e^2}{h}$ is the quantum conductance unit. The configuration of the H₂ molecule in the junction and the number of conductance channels were determined by combined experimental and theoretical studies [7, 8]. The effect of H₂ on metal nanocontacts was also studied for Au, Fe, Co, Ni and Pd [10–12]. Going beyond the simplest molecule, H₂, we concentrate here on CO for the following reasons. First, CO is one of the simplest molecules for which atomic and electronic structures for bonding to metal surfaces are well determined. CO on the metal surfaces can be studied by conventional surface analysis methods, including Auger electron spectroscopy (AES) [13] and low energy electron diffraction (LEED) [14], while H₂ is hard to detect by these methods [15]. We can discuss the results for the metal nanocontacts based on the understanding obtained for flat metal surfaces. Second, both electron donation and back donation from the CO molecule occur at the same time, and are important charge transfer mechanisms for the understanding of chemical interactions between a molecule and a metal. In...
metal, involving electron donation from the 5σ orbital (highest occupied molecular orbital, HOMO) stay near the Fermi level of the metal, involving electron donation from the 5σ orbital to the metal, and back donation from the metal d band to the 2π* orbital. Third, CO is a poisonous gas. If the conductance of the metal nanoncontact is changed in a specific way by CO, it may be applicable in CO gas sensors.

The effect of CO on the Pt nanoncontacts is discussed in more detail elsewhere [11, 16]. The CO single molecule anchored between Pt leads was characterized by conductance measurement and point contact spectroscopy. In the present study, we report on the effect of CO on Ni, Cu, Pt and Au nanoncontacts. While Au and Cu are noble metals, Ni and Pt are transition metals, for which the Fermi level lies inside the metal d band and back donation from the metal to the CO 2π* orbital should play an important role. Reflecting the change in the chemical interaction, the adsorption energy of CO on Ni, Pt, Cu and Au flat surfaces decreases in that order [15]. We discuss the relationship between this adsorption character on macroscopic metal surfaces and the conductance behaviour of metal nanoncontacts. For Au nanoncontacts we present a more detailed analysis of the conductance histograms and conductance traces.

2. Experimental details

The measurements were performed using the mechanically controllable break junction technique [3]. A small notch was cut at the middle of Ni, Cu, Pt and Au wires in order to fix the breaking point. The wires used were 0.1 mm in diameter and about 1 cm long. The wire was glued on top of a bending beam and mounted in a three-point bending configuration inside a vacuum chamber. Once under vacuum and cooled to 4.2 K the wire was broken by mechanical bending of the substrate. Clean fracture surfaces are exposed by breaking and these remain clean for days in the cryogenic vacuum. The bending can be relaxed to form atomic-sized contacts between the wire ends using a piezo element for fine adjustment. CO was admitted via a home-made capillary equipped with a heater wire running along the capillary that prevents premature condensation of the CO gas. After admitting a small amount of CO gas into the sample chamber we waited some time for the gas to diffuse to the end of the insert. About 3000 digitized conductance traces were used to build each conductance histogram in the present study.

3. Results

Figure 1 shows the conductance histograms for Ni, Cu, Pt and Au nanoncontacts before and after admitting CO. The conductance histograms are observed to change by admitting CO, which indicates that CO molecules can diffuse on the surface on metal nanoncontacts as follows. At 4.2 K there is no possibility for diffusion of CO molecules on the metal nanoncontacts. However, the nanoncontacts are locally heated by the current, and mechanical energy is put into the contacts by constantly making and breaking them. The molecules near the contact can migrate to the contact point during contact breaking, and thus we can observe the effect of CO molecules on the metal nanoncontacts at 4.2 K. While the conductance histograms are changed for all metals by admitting CO, the change depends on metals. For Pt, two new peaks appear in the conductance histogram, one near 0.5 $G_0$ and one near 1 $G_0$, in agreement with our previous studies [11, 16]. A peak appears in the conductance histogram near 0.5 $G_0$ for Ni. In both cases the peak for the clean metal that represents a single metal atom contact (at 1.6 $G_0$ for Pt and 1.4 $G_0$ for Ni) is suppressed after admission of CO. Weak features near 0.5 $G_0$ also appear in the conductance histograms for Au and Cu, although the change is much smaller than for Pt and Ni.

For Pt, the 0.5 $G_0$ feature is probably due to the conductance of a single CO molecule anchored between Pt electrodes [16, 17]. For Ni, Cu and Au it is not clear whether the new feature near 0.5 $G_0$ is due to the conductance of a single CO molecule or whether it is due to the conductance of the metal nanowire whose surface is covered by CO. In both cases the conductance of the contact should vary with the type of metal because the electronic structure of the CO–metal bond depends strongly on the metal. Therefore, it is striking that all metals investigated here show a conductance close to 0.5 $G_0$ upon admitting CO. From the limited number of metals investigated it is not clear whether this will hold for metals in general, but this would not be expected.

The importance of the changes in the conductance histograms for Ni, Pt, Cu and Au decreases in that order.
This order agrees with the adsorption properties of CO molecules on metal surfaces [15]. On transition metal (Ni, Pt) surfaces, electron donation from the $5\sigma$ orbital to the metal and back donation from the metal to the $2\pi^*$ orbital occur simultaneously, and a strong chemical bond is formed between the CO molecule and the metals. The present results show that the adsorption properties on macroscopic surfaces reflect the adsorption properties on atomic-scale metal nanostructures. On the other hand, there is a difference in the adsorption properties between the macroscopic surface and the atomic-scale nanostructure. While a CO molecule does not adsorb chemically on macroscopic Au surfaces, CO molecules appear to coordinate to Au nanocontacts judging from the change in the conductance histogram (figure 1(a)). Indeed, novel catalytic properties have been reported for Au nanoparticles [18]. Theoretical calculations support the idea that the Au nanocontact is chemically active, with strong chemisorption of $O_2$ and CO [19].

For Au nanocontacts we observed systematic changes in the conductance behaviour and reproducible conductance traces, characteristic of Au nanocontacts in the presence of CO. For this reason we concentrate on Au nanocontacts in the following. The conductance histogram changes with bias voltage, and the change is continuous and reversible (figure 2). The fractional conductance feature is clearly observed at low bias voltage, and its intensity decreases with bias voltage. Figure 3 shows the intensity of the fractional feature normalized to the intensity of the peak at 1 $G_0$, plotted as a function of the bias voltage. The fractional conductance feature gradually decreases and disappears at a bias voltage of about 200 mV, indicating that the structure having a fractional conductance is unstable at high bias voltage, suggesting that the interaction between the CO molecule and the Au nanocontact is weak. It is noteworthy that the fractional conductance feature appears at low bias voltage, even after it first disappeared at high bias voltage. This indicates that the CO molecule is not blown off the surface but remains bound to one of the two electrodes at high bias voltage.

In order to find evidence as to how the CO molecule is adsorbed on, or incorporated into, the Au nanowire, we have analysed the conductance traces. Figure 4 shows typical breaking and return traces for Au after admitting CO. The stretching length was calibrated with the length histogram of the last conductance plateau for clean Au. There are three characteristics in the conductance traces. The last plateau, by which we mean the part having a conductance near 1 $G_0$, extends for quite a length; the conductance drops abruptly just before breaking to about 0.5 $G_0$, and the conductance smoothly increases with further stretching on this fractional conductance plateau. These characteristics are observed reproducibly and they are typical for Au nanocontacts in the presence of CO. In the following these characteristics are discussed.

First, we discuss the length of the Au nanocontact. Figure 5 shows the length histogram of the last conductance plateau for Au after admitting CO. The length of the last plateau is taken here as the distance between the points at which the conductance drops below 1.2 $G_0$ and 0.2 $G_0$, respectively. The conductance traces are obtained as a function of piezo voltage. It is reported in [2] that the length histogram of the last conductance plateau for clean Au, which is defined as having a conductance between 1.3 $G_0$ and 0.7 $G_0$, shows a number of equidistant maxima, at multiples of 0.257 nm [3]. We use this to determine the ratio between the relative change in piezo voltage with respect to the stretch length, assuming that the inter-peak distance is 0.26 nm in the length histogram for clean Au. The stretch length was calibrated in this way with clean Au before each measurement of the Au in the presence of CO.
of the last plateau. Apart from an offset of 0.5 nm due to the elastic response of the banks [2], the relation is approximately 1:1, suggesting that a fragile structure is formed with a length corresponding to that of the last plateau, which is unable to support itself when it breaks and collapses onto the banks on either side. Long plateaux of over 1 nm length and the 1:1 relation were also observed for clean Au monatomic wires [2], supporting the formation of the monatomic wire in the present case. While clean Au forms a monatomic wire under UHV at low temperature the results show that Au monatomic wires also form in the presence of CO.

Second, we discuss the change in conductance during the breaking process. The conductance drops abruptly down to about 0.5 \( G_0 \) and once this has happened the wire breaks after a small additional increase in length. The conductance drop should be caused by the adsorption of CO on the Au nanowire or incorporation of CO into the Au wire because it is not observed for clean Au. The fast break indicates that the structure with the conductance about 0.5 \( G_0 \) is unstable and CO adsorption or incorporation destabilizes the Au nanowire. This is in contrast with Pt wires in the presence of \( \text{H}_2 \) and Ag wires in the presence of \( \text{O}_2 \), for which the wire can be stretched further even after the conductance drops to a low value [20, 21]. The difference may be explained by a difference in the chemical interaction including the direction and amount of charge transfer and effect of charge transfer on the stability of the metal nanowire.

We will now discuss the destabilization mechanism of the Au nanowire by CO in terms of the charge transfer between the CO molecule and Au, and in relation to the stabilization mechanism of the Au monatomic wire. The Au d band is located below the Fermi level, and thus the electron back donation from the Au d band to 2\( \pi^* \) orbital of CO does not play an important role. The donation from the 5\( \sigma \) orbital of CO to the metal is dominant, and the electron would be transferred from CO to Au. The charge transfer between CO and Au was studied for Au nanoparticles deposited on TiO\(_2\), which showed novel catalytic properties [22]. Adsorption of CO on Au particles induces charge transfer from Au to TiO\(_2\), suggesting that the electron is transferred from CO to Au. A monatomic wire is formed only for 5d metal as a result of the following mechanism. For 5d metals, the s occupation increases at the expense of the d electrons due to relativistic effects in electronic structure. Since the top of the d band consists of states with anti-bonding character that are now partially depleted, the d bond becomes stronger. While the d electrons tend to compress the lattice, the s electrons exert an opposing Fermi pressure. At the surface, the spill-out of the s electron cloud into the vacuum relieves some of the s electron pressure, and allows a strengthening of the bonds at the surface. The monatomic wire geometry allows for an even larger relief of s pressure. Therefore, the bond in the wire is much stronger than the bond in the bulk, and monatomic wires are formed for 5d metals, Ir, Pt and Au [3, 23]. When CO adsorbs on the surface of the Au monatomic wire, spill-out of the s electron cloud into the vacuum will be inhibited. Furthermore, the density of states (DOS) near the Fermi level with anti-bonding character will increase due to the charge transfer from CO to Au. These mechanisms will decrease the bond strength of the Au in the wire, and the Au monatomic wire will be destabilized by CO adsorption or incorporation.

Third, we discuss the increase in conductance with the stretch length after the conductance drops down to near 0.5 \( G_0 \). The increase in conductance can be discussed in terms of a change in the DOS or in terms of the molecular orientation. The elongation of the metal nanowire induces a change in the atomic and electronic structure of the wire including the energy and width of the metal band and the DOS at the Fermi level. When the elongation of the nanowire induces an increase in the DOS at the Fermi level, the conductance of the nanowire increases. Actually, an increase in the conductance with elongation is observed for Al nanocontacts [24]. This increase is explained by the narrowing of the sp\(_x\) band and a concomitant increase in the DOS at the Fermi level induced by the elongation. Another possibility is the change in the molecular orientation. Since a similar increase in the conductance with elongation is observed for the Au monatomic wire in the presence of \( \text{H}_2 \) [25] and the effect of the molecular orientation on the conductance is well studied with density functional theory (DFT) calculations, we discuss this possibility based on the AuH\(_2\) system. The conductance of the perpendicular configuration, for which the molecular axis is perpendicular to the contact axis, was calculated to be about 0.1 \( G_0 \), and the conductance of the parallel configuration increased up to 0.25 \( G_0 \) [26]. Based on these calculation results, the following models are proposed. First, the \( \text{H}_2 \) molecule incorporates into the Au wire in the perpendicular configuration with density functional theory (DFT) calculations, we discuss this possibility based on the AuH\(_2\) system. The conductance of the perpendicular configuration, for which the molecular axis is perpendicular to the contact axis, was calculated to be about 0.1 \( G_0 \), and the conductance of the parallel configuration increased up to 0.25 \( G_0 \) [26]. Based on these calculation results, the following models are proposed. First, the \( \text{H}_2 \) molecule incorporates into the Au wire in the perpendicular configuration
configuration and then the molecule turns toward an orientation parallel to the contact axis, which shows up as an increasing conductance as the electrodes are pulled apart. Since both H$_2$ and CO are linear molecules, the increase in conductance with elongation observed in the present study may be explained by similar change in the molecular orientation.

4. Conclusion

We have studied the conductance of Ni, Cu, Pt and Au nanocontacts in the presence of CO. In all cases a fractional conductance feature appears in the conductance histogram near 0.5 $G_0$ after admitting CO. The change in the conductance histogram for Ni, Pt, Cu and Au decreases in that order, in agreement with the adsorption properties on macroscopic metal surfaces. For Au, the intensity of the fractional conductance feature continuously and reversibly changes with the bias voltage. The feature disappears at a bias voltage of 200 mV, indicating that the CO–Au bond is weak. The results give evidence that formation of the Au atomic chain persists in the presence of CO, but bonding of a CO molecule weakens the chain and gives rise to a drop of the conductance to about 0.5 $G_0$.

Acknowledgments

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by NOW. MK has been supported by the Yamada Science Foundation.

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