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Low-temperature dissociative adsorption of Hydrogen on W, Mo and Ta surfaces studied with Mechanically Controllable Break-Junctions.

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Abstract.
Mechanically Controllable Break-Junctions were used to study the physical adsorption of hydrogen molecules on the surfaces of W, Mo and Ta as well as their subsequent chemisorption and dissociation and diffusion of protons into the bulk of the material. Dissolving of hydrogen into Ta is accompanied by $1/f^\alpha$ resistance noise with $1.2 < \alpha < 1.7$ depending on the contact diameter.

1. Introduction

Mechanically Controllable Break-Junctions (MCBJ) have already proven to be a powerful tool not only for the investigation of the quantum and transport phenomena in metallic nanowires [1] but also for studying the conductance through a single molecule [2, 3, 4]. Application of MCBJ to elucidate the interaction between adsorbed molecules and a metallic surface is an important part of research aimed at development of molecular electronic devices. MCBJ has an exceptionally high stability both in the tunneling and the direct contact regime covering the range of resistances from 10 to 10^{12} Ohm. This provides a unique opportunity to perform a whole series of different measurements in the same experiment.

In spite of the fact that hydrogen atom and molecule are the simplest imaginable adsorbates there is a lot of controversy in experimental data and theoretical models, especially for transition $-d$ metals (see reviews [5, 6] and references therein). Not surprisingly there is a difference in interpretation of the results for Pt MCBJ [7] and Pd MCBJ [8]. In the first case the hydrogen bridge between platinum atoms retains some properties of the hydrogen molecule [9] while conductance through the Pd-H-H-Pd bridge is affected by atomic hydrogen dissolved in Pd.

In this article we report our results on the low temperature adsorbtion of hydrogen on the surfaces of freshly broken tungsten, molybdenum and tantalum contacts.

2. Experiment

In our experiments we used a standard MCBJ technique described elsewhere [1]. For the particular case of W, Mo and Ta the details of sample preparation, characterization and measurements are given in [10].

All measurements were done in the temperature range 4.2 - 6 K either in a cryogenic ultra-high vacuum or in the presence of ultra-pure (99,9999%) hydrogen. The typical amount of hydrogen gas for most of the experiments was between 0.5 and 5 μM. Even though the amount of gas admitted could be accurately determined, the presence of different materials and unavoidable temperature gradients introduce a large uncertainty in the coverage of the surface of the materials under investigation. In addition, the operating area at the electrode surface is roughly 10^{16} times smaller than the total inner area of the vacuum vessel. Although this fact precludes quantitative measurements, MCBJ method gives a unique possibility to study the adsorption process of individual molecules.

3. Results and discussion

The physical adsorbtion of a hydrogen molecule on a metal surface can be detected by measuring the dependence of tunnel resistance on the distance between the electrodes $R(z)$. The effect of physically adsorbed atoms on $R(z)$ was observed for the first time for He [11] and was explained by the decrease of the electron density of states close to the Fermi level in the electrode when approaching the helium atom. The same effect (though less pronounced) was observed in STM measurements in water [12] and attributed to the oscillations of the tunnel barrier height. Regardless of the model in question, the Distance Tunneling Spectroscopy (DTS) gives us a clear indication of the appearance and the distance from the surface of adsorbed species.
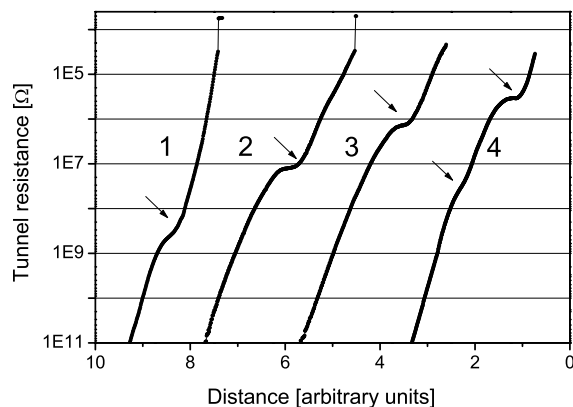

Figure 1. Distance tunneling spectroscopy of the physically adsorbed hydrogen molecules on the surface of Ta. In the course of time H_2 tends to move towards the surface. Curve 4 displays the presence of a second layer of hydrogen molecules.
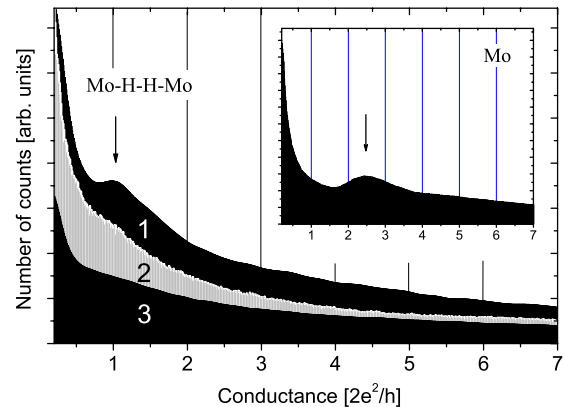
Figure 2. Conductance histogram for Mo in vacuum (inset) and in the case of dissociative adsorbtion of hydrogen. Time evolution (histograms 1,2,3 were taken within 2 - 3 hours) results in the smearing of the conductance peak at 1 G_0.

The results of our measurements for H_2 molecules adsorbed on Ta are presented in Fig.1. The deviation from the exponential behavior (indicated by arrows) occurs in a very large range of tunnel resistances starting from $10\,G\Omega$ and to less than $1\,M\Omega$. The estimated distance of H_2 from the surface ranges from 2.5 to 6 Å. This indicates that the adsorbtion minimum for hydrogen on the surface of Ta is rather flat and shallow, permitting a large range of spacings between H_2 and the surface. We found that the observation of H_2 at large distances is statistically more probable during the initial stage of measurements while after a certain period of time molecules can be found close to the surface. Over the course of hours only physically adsorbed molecules of hydrogen were observed on the surface of Ta in so-called "precursor states" with no indication of H_2 dissociation and chemisorption.

The process of molecular dissociation and the chemisorption of atomic hydrogen could be triggered by admitting an additional amount of hydrogen into the system and thereby increasing the H_2 coverage. With H atoms chemically bound to the metal surface we expect the transition from tunneling to direct contact through the metal - H - H - metal bridge with a characteristic conductance different from the conductance of one-atom metal to metal contact. The most common technique to observe this transition is the conductance histogram method [1] based on conductance measurements of repeatedly fractured contacts. Normally we use more than 10^4 individual conductance traces for each histogram.

In the case of molybdenum the conductance histograms always display the one-atom peak around 2.4 G_0 (inset in Fig.2). Chemisorption of hydrogen results in the fading away of this peak and (similar to the rest of transition metals) the emerging of a peak at 1 G_0. In the course of time this peak considerably smears out and eventually almost disappears, leaving only a faintly visible shoulder. A similar effect of 1 G_0 peak degradation was observed for Ta and W.

The reason for the time evolution of the conductance histograms is the quantum diffusion of hydrogen atoms from the surface into the bulk of the metal. At low temperatures the W-, Mo- and Ta-H_x system is the mixture of two phases - the α-phase (a solid solution of hydrogen in metal) and the chemically ordered β-phase. At low temperatures the α-phase is dominating and the scattering of electrons on dissolved hydrogen atoms results in the large serial resistance to me-H-H-me bridge. We found that the transition from tunneling to direct contact occurs at 0.3 - 10 MΩ and, moreover, conductance traces are totaly irreproducible resulting in featureless histograms.
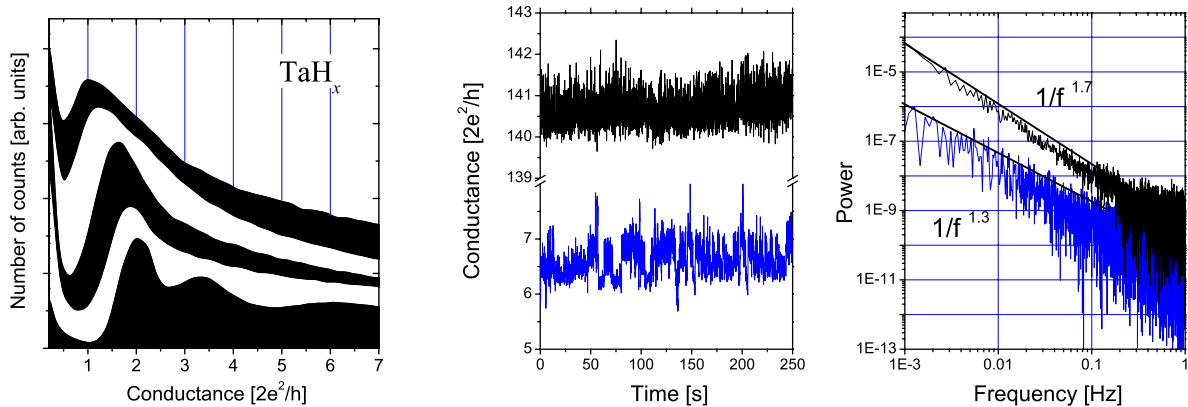

Figure 3. Dependence of conductance histograms on bias voltage for TaH$_x$. From the bottom to top V_b is equal to 400, 300, 250, 200 and 175 mV.

Figure 4. Typical pattern of conductance fluctuations for TaH$_x$ junctions for $G = 6.5\ G_0$ and $G = 140.5\ G_0$. The noise power spectra for the same junctions display $1/f^\alpha$ law at $f \leq 1\ Hz$ with $\alpha = 1.3$ and 1.7 respectively. In all cases $V_b = 10\ mV$.

When both elastic and inelastic mean free paths are considerably smaller than the contact diameter d (so-called thermal limit) there is a linear dependence between the applied bias voltage and the temperature in the center of contact $eV = 3.63 k_B T$ [13]. Overheating of the contact causes desorption of hydrogen atoms both from the surface and from the bulk of the metal. Conductance histograms taken at elevated (up to $V_b \approx 0.5V$) bias voltages show the restoration of their shape to that of pure W, Mo or Ta. For Ta we found that the restoring of the conductance histogram shape occurs at $V_b \geq 400$ mV (estimated temperatures 1000 - 1200 K). The gradual decrease of V_b causes the shift of the one-atom peak towards lower conductance (Fig.3). This occurs due to the incomplete segregation and desorption of hydrogen from the bulk of electrodes

and emerging of the serial resistance of the order of a few kΩ. The surface of the electrodes, however, remains sufficiently free from chemisorbed H atoms so that this peak can be observed down to $V_b \approx 150 - 175 mV$. This voltage corresponds to the temperature of approximately 450 - 550 K and is in reasonable agreement with the thermodesorption spectra.

Conductance versus voltage dependencies $G(V)$ for TaH_x junctions are exhibiting considerable noise. This noise is directly related to the quantum diffusion - the motion of hydrogen ions between neighboring interstitial sites. The relative amplitude of noise increases with the decrease of the contact conductance (while the absolute amplitude remains of the order of $1 G_0$). The typical conductance fluctuation patterns for contact with conductance of 6.5 and 140.5 G_0 are presented in Fig.4. The noise power spectra were derived from the long term (2-3 hours) conductance fluctuation measurements at fixed bias voltage. We found that the low frequency noise (1 mHz - 1 Hz) is following the $1/f^\alpha$ law with α ranging mostly from 1.2 to 1.7. The general trend for contacts with $G \geq 100 G_0$ α is α tending to be larger than 1.5 while for the contacts with conductance below 10 G_0 the index α usually drops to 1.2 - 1.3. In the last case we have a quasi-one dimensional situation of a "short nanowire" and our results are similar to those observed for $1/f$ resistance noise in Pd-H films [14]. Saturation of the electrodes with hydrogen takes 3-5 hours for W and Mo and more than 20-30 hours for Ta. After that time only the random walk of protons resulting in $1/f^2$ noise can be observed.

Concluding, the dissolving of H in the W, Mo and Ta electrodes results in considerable scattering of electrons accompanied by $1/f^\alpha$ resistance fluctuations. This hinders detailed measurements of conductance through the metal-H-H-metal bridge. At the same time it gives us the opportunity to study the diffusion of protons, the transition between ordered and disordered phases in MeH_x and the influence of hydrogen on the superconductivity in Ta. All these effects are currently under investigation. With the increasingly refining of experimental procedures and proper theoretical background the MCBJ technique can be considered as a powerful tool for studying the interaction between adsorbed molecules and the surface.

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