Chemical Physics Letters 509 (2011) 48–50

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Role of the chemical bonding for the time-dependent electron transport through an interacting quantum dot

A. Goker [a], Z.Y. Zhu [b], A. Manchon [b], U. Schwingenschlögl [b],*

[a] Department of Physics, Bilecik University, 11210 Gülümbe Bilecik, Turkey
[b] King Abdullah University of Science and Technology, Physical Sciences and Engineering Division, 23955-6900 Thuwal, Saudi Arabia

ARTICLE INFO

Article history:
Received 10 March 2011
In final form 27 April 2011
Available online 30 April 2011

ABSTRACT

A combination of ab initio and many-body calculations is utilized to determine the effects of the bonding in Au electrodes on the time dependent current through a quantum dot suddenly shifted into the Kondo regime by a gate voltage. For an asymmetrically coupled system the instantaneous conductance exhibits fluctuations. The frequencies of the fluctuations turn out to be proportional to the energetic separation between the dominating peaks in the density of states and the Fermi level. The chemical bonding in the electrodes, thus, drastically alters the transient current, which can be accessed by ultrafast pump–probe techniques.

1. Introduction

Time-dependent electron transport in single electron devices is a subject of fundamental importance in molecular electronics, since it is widely believed that these devices have the potential to replace the conventional MOSFET transistors [1] in the near future thanks to rapid progress in nanotechnology. Detection of electrons in real time [2] is expected to play an important role in the development of quantum computers [3] and single electron guns [4].

The time-dependent current arising from the sudden switching of the gate or bias voltage [5–7] exhibits various time scales [8,9]. Moreover, interference between the Kondo resonance and the sharp features in the contacts' density of states (DOS) emerges in the long timescale, associated with the formation of this many-body resonance [10]. Effective one-electron theories indicate that the transport properties in steady state depend strongly on the electrode metal [11], the contact structure [12], and the contact orientation [13]. The same approach also predicts that the electrode metals alter the rectifying performance of the device [14].

In previous studies of single electron devices both the Green's function approach [15,16] and the non-equilibrium diagrammatic Monte Carlo method [17,18] showed that the electronic structure of the contacts has a significant influence on the shape of the transient current, while these studies were based on unrealistically simple assumptions on this structure for ease in calculations. In molecular electronics devices, however, the transport behaviour is an atomic scale property and therefore governed by the contact geometry. For example, it has been observed for C_{60} buckyballs placed between metallic electrodes that the transport depends on the geometrical arrangement of those electrode atoms which are in direct contact to the buckyballs [19]. Thermopower measurements of metal–molecule–metal junctions indicate that the transport fluctuations are dominated by variations in the contact geometry and therefore in the orbital hybridizations [20], while the transport through molecular field effect transistors is influenced by the symmetry breaking introduced by the gating field [21]. First-principles calculations for atomic-sized aluminium contacts show a strong deviation of the electronic states from bulk fcc aluminium [22]. The transport properties of the Au/benzene-1,4-dithiol/Au molecular contact are largely determined by local modifications of the electronic states [23]. In general, the chemical bonding at the contact is essential for the transport. The transmission coefficient and *I–V* characteristics of Al, Cu, Ag, and Au interfaces thus are governed by vacancies and by the buckling of the interface atomic layers [24]. For the Au–MgO–Au heterostructure deviations from an exponentially suppressed conductance for growing interlayer thickness have been explained by a modified Au–O chemical bonding [25].

In the present Letter, we carry out a comparative study of three prototypical Au contact structures and their influence on the transient current through a single electron device in the Kondo regime. Following the approach introduced in Refs. [10,26], we show that the specific contact geometry has serious effects on the transient current. Without detailed knowledge about the contacts an interpretation of experiments therefore is not possible. On the other hand, our predictions make it possible to conclude on the contact geometry from the results of transport measurements.

---

* Corresponding author.
E-mail address: udo.schwingenschlogl@kaust.edu.sa (U. Schwingenschlögl).

0009-2614/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2011.04.086

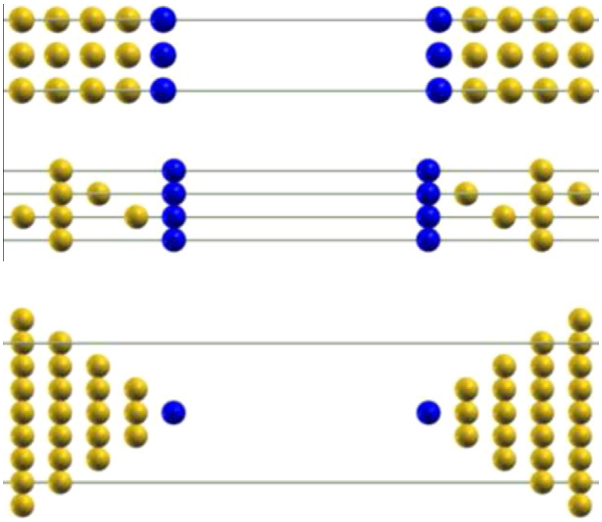

Figure 1. Contact geometries considered for the Au electrodes. Top: (001) surface. Middle: (111) surface. Bottom: (111) pyramide. The topmost atoms shown in blue color (dark gray) determine the transport between the electrodes.

2. Methodology

Density-functional theory (DFT) calculations for obtaining the DOS of the Au contacts have been performed using the full-potential linearized augmented plane wave code WIEN2k [27]. As prototypical fcc contact geometries, we compare the Au (001) surface to the Au (111) surface as well as a mono-atomic Au contact of pyramidal shape, see Figure 1 and Ref. [28] for details. The structures are modeled using atomic slabs of 13 Au layers, where the distance between the two opposite electrodes amounts to 30 Bohr radii. The exchange correlation potential of the generalized gradient approximation in the Perdew–Burke–Ernzerhof form [29] is used in all calculations. Moreover, the plane wave cutoff is determined by $R_{mt}K_{max} = 6.5$ and $l_{max} = 10$. In reciprocal space, meshes of $30 \times 30 \times 3$, $36 \times 36 \times 2$, and $6 \times 6 \times 2$ are applied for the Au (001) surface, Au (111) surface, and Au pyramid, respectively.

We describe the single electron device by means of the single impurity Anderson Hamiltonian

$$H(t) = \sum_{k\alpha\sigma} \left[\epsilon_k n_{k\alpha\sigma} + V_\alpha(\varepsilon_{k\alpha}, t) c^\dagger_{k\alpha\sigma} b^\dagger f_\sigma + \text{H.c.} \right] + \sum_\sigma \epsilon_{dot}(t) n_\sigma, \tag{1}$$

where the operators $f^\dagger_\sigma(f_\sigma)$ and $c^\dagger_{k\alpha\sigma}(c_{k\alpha\sigma})$ create (annihilate) an electron with spin σ in the dot level (ϵ_{dot}) and the left/right $(\alpha = L, R)$ contact, respectively. The corresponding number operators are n_σ and $n_{k\alpha\sigma}$, and the operator $b^\dagger(b)$ creates (annihilates) a massless boson. For time independent hopping V_α, the coupling of the dot to the contacts can be casted as $\Gamma_{L(R)}(\epsilon) = \overline{\Gamma}_{L(R)} \xi_{L(R)}(\epsilon)$, where $\overline{\Gamma}_{L(R)} = 2\pi |V_{L(R)}(\epsilon_f)|^2$ is a constant and $\xi_{L(R)}(\epsilon)$ is the contact DOS.

3. Results and discussion

The DOS of the topmost atoms as obtained from our ab initio calculations is shown in Figure 2. It determines the transport between the electrodes. The Au band width is clearly reduced in the case of the pyramidal contact due to an enhanced decoupling of the topmost atom from the remainder of the electrodes. In order to use the ab initio DOS for the many-body calculations, it is fitted by a linear combination of Gaussians,

$$\rho(\epsilon) = \sum_i \frac{\alpha_i}{\zeta_i \sqrt{0.5\pi}} \exp\left(-2 \left(\frac{\epsilon - \epsilon_i}{\zeta_i} \right)^2 \right). \tag{2}$$

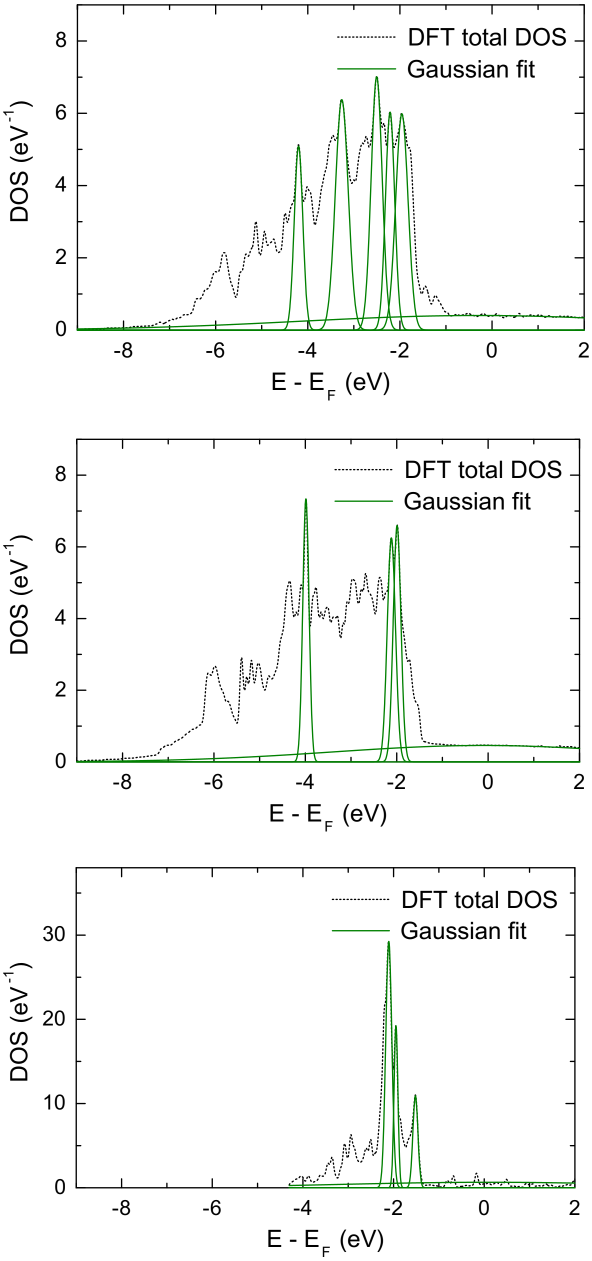

Figure 2. Black dashed lines represent the DOS of the Au (001) surface (top), the Au (111) surface (middle), and the Au pyramid (bottom) calculated using DFT. The energy is given with respect to the Fermi level. The Gaussians dominating the behaviour of the transient current are highlighted by green solid lines.

A broad Gaussian is added in each case to ensure that the DOS at the Fermi level is finite and the entire bandwidth of the material is covered. Figure 2 highlights for the three different geometries the Gaussians which dominate the behaviour of the transient current.

The Kondo effect is a many-body resonance which enhances conductance at low temperatures. The linewidth of the resonance is given by the Kondo temperature

$$T_K \approx \left(\frac{D\Gamma_{tot}}{4} \right)^{\frac{1}{2}} \exp\left(-\frac{\pi |\epsilon_{dot}|}{\Gamma_{tot}} \right). \tag{3}$$

Here, D is the half bandwidth of the conduction electrons and $\Gamma_{tot} = \overline{\Gamma}\xi(\epsilon_f)$. We study the transient current for the case that the

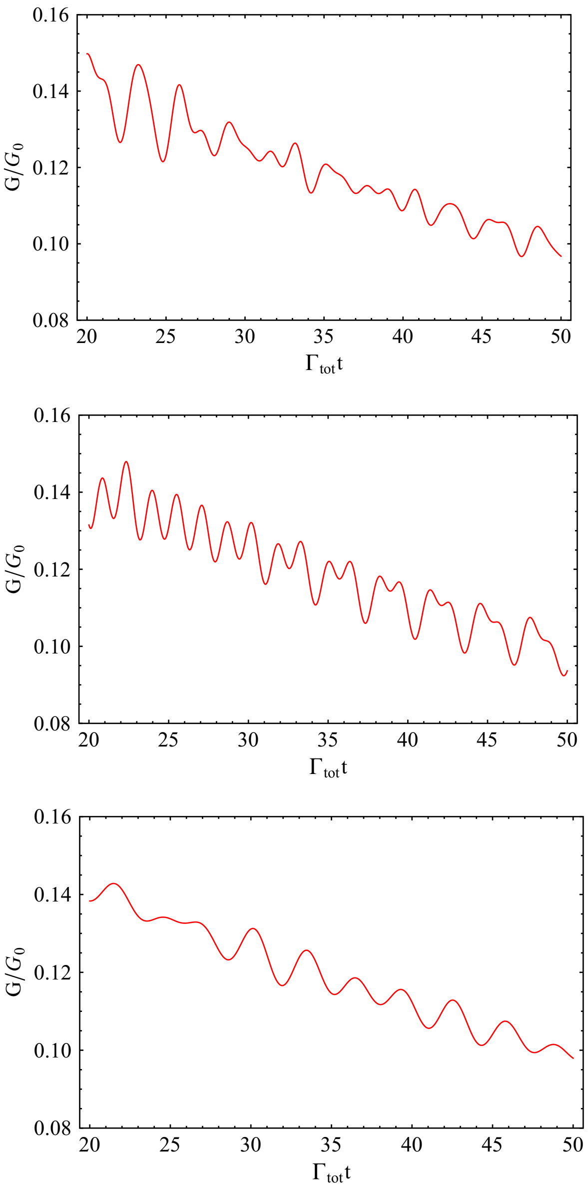

Figure 3. Panels from top to bottom show the instantaneous conductance versus time in the Kondo timescale after the dot level has been switched to its final position for the Au (001) surface, the Au (111) surface, and the Au pyramid. An asymmetry factor of 0.9 is used at $T = 0.009\Gamma_{tot}$ in infinitesimal bias.

dot level is switched from $\epsilon_1 = -4\Gamma_{tot}$ to $\epsilon_2 = -2\Gamma_{tot}$ at $t = 0$ by a gate voltage. For all three geometries, a transition from a non-Kondo state to a Kondo state takes place. We note that the Kondo temperature in the final state is a bit lower for the Au pyramide than for the other two geometries as a result of the reduced conduction electron bandwidth, see Figure 2.

In Figure 3 the transient current in the Kondo timescale is depicted for all our geometries after switching to the final dot level in infinitesimal bias. We here will not deal with the short timescale where the conductance reaches a maximum before it starts to fall for large asymmetry factors, due to the similarity with previous findings [10]. Most remarkably, we observe in Figure 3 drastic differences in the conductance fluctuations. This effect is purely due to the differences in the band structure of the contacts, since all other parameters are held constant. Note that the slight difference in the Kondo temperatures of the Au pyramide and the other two geometries does not change the relative behaviour of the fluctuations, because T/T_K alters only the amplitude of the fluctuations but not the overall pattern of the transient current.

It is clear that the observed fluctuations result from a mixture of sinusoidal oscillations with different frequencies and amplitudes. These frequencies might be extracted by taking the Fourier transform of the current. We find for each of our systems that the frequencies are proportional to the energetic separation between the main DOS peaks and the Fermi level, explaining why the transient current for the Au (001) surface exhibits a more erratic pattern as compared to the others: five distinct frequencies are involved. The other peaks appearing in the DOS turn out to have negligible contributions to the fluctuation patterns. The oscillation amplitudes associated with them are too small to have a discernible effect. The reason for the latter is that they either are located far away from the Fermi level or the peaks are not prominent enough with respect to the surrounding DOS structure.

In conclusion, we have demonstrated that the contact geometry can strongly alter the fluctuations of the transient current through a single electron device operating in the Kondo regime. Since the contact geometry in fact dominates the fluctuation pattern, it must be taken into account in detail when interpreting experimental results. In turn, the specific band structure of a molecular switch may be probed by measuring the transient current flowing through it. Experimentally, transient current fluctuations in the femtosecond timescale are accessible by the ultrafast pump–probe technique [30,31]. Together, this paves the way for the designing of custom switches for future organic computers.

References

[1] Committee I R 2004 International Technology Roadmap for Semiconductors, Japan Electronics and Information Technology Industries Association, Tokyo.
[2] W. Lu, Z. Ji, L. Pfeiffer, W. West K, A.J. Rimberg, Nature 423 (2003) 422.
[3] J.M. Elzerman, R. Hanson, L.H.W. van Beveren, B. Witkamp, L.M.K. Vandersypen, L.P. Kouwenhoven, Nature 430 (2004) 431.
[4] G. Feve et al., Science 316 (2007) 1169.
[5] P. Nordlander, M. Pustilnik, Y. Meir, N.S. Wingreen, D.C. Langreth, Phys. Rev. Lett. 83 (1999) 808.
[6] M. Plihal, D.C. Langreth, P. Nordlander, Phys. Rev. B 61 (2000) R13341.
[7] J. Merino, J.B. Marston, Phys. Rev. B 69 (2004) 115304.
[8] M. Plihal, D.C. Langreth, P. Nordlander, Phys. Rev. B 71 (2005) 165321.
[9] A.F. Izmaylov, A. Goker, B.A. Friedman, P. Nordlander, J. Phys. Condens. Matter 18 (2006) 8995.
[10] A. Goker, B.A. Friedman, P. Nordlander, J. Phys. Condens. Matter 19 (2007) 376206.
[11] H. Kondo, J. Nara, H. Kino, T. Ohno, J. Phys. Condens. Matter 21 (2009) 064220.
[12] H. Kondo, H. Kino, J. Nara, T. Ozaki, T. Ohno, Phys. Rev. B 73 (2006) 235323.
[13] L.H. Wang, Y. Guo, C.F. Tian, X.P. Song, B.J. Ding, J. Appl. Phys. 107 (2010) 103702.
[14] X.Q. Deng, J.C. Zhou, Z.H. Zhang, G.P. Tang, M. Qiu, Appl. Phys. Lett. 95 (2009) 103113.
[15] Y. Zhu, J. Maciejko, T. Ji, H. Guo, J. Wang, Phys. Rev. B 71 (2005) 075317.
[16] J. Maciejko, J. Wang, H. Guo, Phys. Rev. B 74 (2006) 085324.
[17] P. Werner, T. Oka, A.J. Millis, Phys. Rev. B 79 (2009) 035320.
[18] T.L. Schmidt, P. Werner, L. Muhlbacher, A. Komnik, Phys. Rev. B 78 (2008) 235110.
[19] G. Schull, T. Frederiksen, A. Arnau, D. Sánchez-Portal, R. Berndt, Nat. Nano. 6 (2011) 23.
[20] J.A. Malen, P. Doak, K. Baheti, T.D. Tilley, A. Majumdar, R.A. Segalman, Nano Lett. 9 (2009) 3406.
[21] T.M. Perrine, B.D. Dunietz, J. Am. Chem. Soc. 132 (2010) 2914.
[22] U. Schwingenschlögl, C. Schuster, Chem. Phys. Lett. 432 (2006) 245.
[23] U. Schwingenschlögl, C. Schuster, Chem. Phys. Lett. 435 (2007) 100.
[24] M. Fadlallah, C. Schuster, U. Schwingenschlögl, T. Wunderlich, S. Sanvito, J. Phys. Condens. Matter 21 (2009) 315001.
[25] M. Fadlallah, C. Schuster, U. Schwingenschlögl, I. Rungger, U. Eckern, Phys. Rev. B 80 (2009) 235332.
[26] A. Goker, Z.Y. Zhu, A. Manchon, U. Schwingenschlögl, Phys. Rev. B 82 (2010) 161304(R).
[27] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, L. Luitz, WIEN2K, an augmented plane wave + local orbitals program for calculating crystal properties, Technical University, Vienna, 2001.
[28] U. Schwingenschlögl, C. Schuster, Chem. Phys. Lett. 439 (2007) 143.
[29] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[30] Y. Terada, S. Yoshida, O. Takeuchi, H. Shigekawa, J. Phys. Condens. Matter 22 (2010) 264008.
[31] Y. Terada, S. Yoshida, O. Takeuchi, H. Shigekawa, Nat. Photon. 4 (2010) 869.