A Theoretical Analysis of Metal−Molecule Contacts

Jorge M. Seminario,* Cecilia E. De La Cruz, and Pedro A. Derosa

Department of Electrical Engineering
University of South Carolina
Columbia, South Carolina 29208

Received February 12, 2001
Revised Manuscript Received April 10, 2001

A major task in molecular electronics is the precise determination of the molecule−metal interface characteristics. This problem has to be solved before any design approach is adopted for molecular circuits. Due to their intrinsic nature, metal and single molecules have unavoidable electrical mismatches for which there is not yet an established way to evaluate them. Even with the intrinsic barrier that the contacts represent, barriers can be strategically used to favor the design of specific devices; however, this requires the precise evaluation of such an interface.

Methods of quantum chemistry have been probed to successfully determine the characteristics of organometallic systems for molecular electronics.[1,2] We use these methods to study the molecule and the atomistic nature of the metallic contacts extending them with a Green function approach that considers the "infinite" nature of the contacts.[3] The successfully tested[1,2] B3PW91/LANL2DZ level of theory as implemented in the Gaussian-98 program[4] is used to obtain the discrete nature of the molecule attached to metal atoms and its electronic characteristics are obtained under the presence of an external electrical field representing the external bias potential applied to the molecule.[5] We compare the $I-V$ characteristics of thio and isonitril *alligator clips* (defined as the molecular groups attached to the metal atoms) with metals of groups 10 (Ni, Pd, and Pt) and 11 (Cu, Ag, and Au). The systems are treated as in the "break junction" experiment[6] where a single molecule is addressed by two metallic tips that end up practically in one atom on the molecule side as shown in Figure 1. A typical problem computing metal−molecule interfaces is that the exact boundary between molecule and metal is not well defined. As shown in Figure 1, the number of Au atoms that can be considered as part of the molecule cannot be established.

Table 1 shows the corresponding density of states ρ at the Fermi energy[7] (E_F) for all metals used for this study. The E_F corresponds to the negative of the experimental work function for a (111) surface.[8] There is a strong s contribution on the elements of group 11, roughly three times bigger than that on group 10; group 11 elements also present stronger p and d contributions. This is a direct consequence of their atomic nature.[9] The geometries of the molecular systems are shown in Scheme 1. An important factor for the transport properties is the angle made by the metal atom, alligator clip, and the molecule. It is considered that angles of 180° favor conduction because it implies the presence of π character, which we find yields higher conductance than systems with nonlinear angles. Thus, S as the alligator clip might not be as effective as CN, which favors linear angles. However, the type of metal used at the interface and the nature of the bond are the main factors for determining the transport properties of the junction.

Figure 2 shows the $I-V$ curves for all cases reported in this communication. The highest conductance is obtained for Pd. The S−Pd interface provides the best combination followed by CN−Pd. These results are in full agreement with the experimental

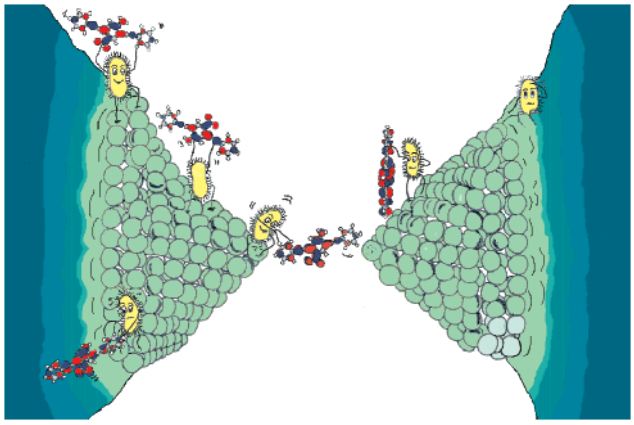

Figure 1. Molecules positioned between two metallic ends. Atoms connecting the molecule can be considered part of the molecule.

Scheme 1. Metal−Molecule Systems

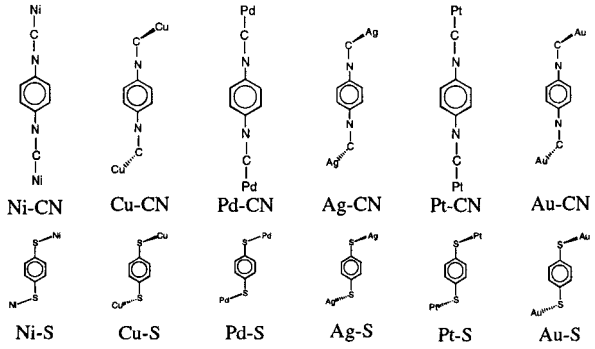

Table 1. Density of States ρ (1/eV-atom) for the Metals[7] at Their Fermi Energy E_F (eV) [8] Used To Represent the Bulk Metal

metal	s	p	$d_{t_{2g}}$	d_{e_g}	E_F
Ni	0.0206	0.0176	0.0918	0.0544	−5.35
Cu	0.0647	0.0852	0.1014	0.0450	−4.94
Pd	0.0242	0.0331	1.8979	0.4078	−5.60
Ag	0.0779	0.1257	0.0471	0.0132	−4.79
Pt	0.0169	0.0265	1.6466	0.5077	−5.93
Au	0.0720	0.0426	0.1286	0.0492	−5.31

(1) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 411−416.
(2) Seminario, J. M.; Zacarias, A. G.; Derosa, P. A. *J. Phys. Chem. A* **2001**, *105*, 791−795.
(3) Derosa, P. A.; Seminario, J. M. *J. Phys. Chem. B* **2001**, *105*, 471−481.
(4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; G. E. Scuseria; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian Inc.: Pittsburgh, PA, 1998.
(5) Seminario, J. M.; Zacarias, A. G.; Derosa, P. A. *J. Chem. Phys.* **2001**, submitted for publication.
(6) Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. *Science* **1997**, *278*, 252−254.
(7) Papaconstantopoulos, D. A. *Handbook of the Band Structure of Elemental Solids*; Plenum Press: New York, 1986.
(8) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, 1998.
(9) Derosa, P. A.; Seminario, J. M.; Balbuena, P. B. *J. Phys. Chem. A* **2001**, submitted for publication.

10.1021/ja015661q CCC: $20.00
Published on Web 05/18/2001

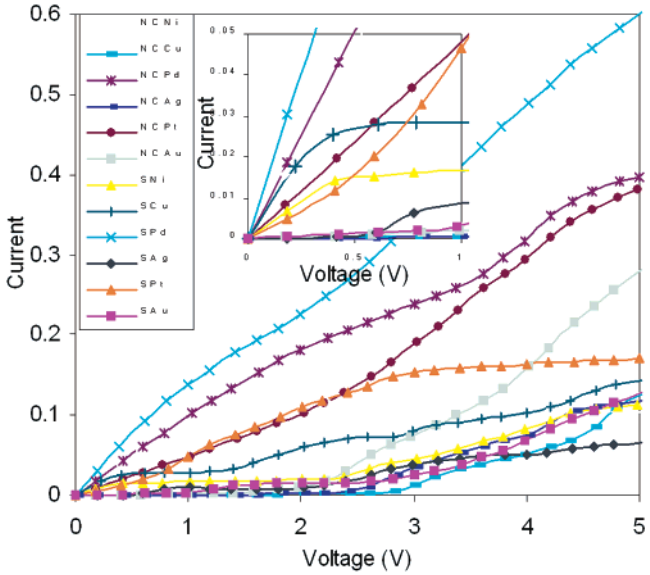

Figure 2. Current−voltage curves for all systems Y−X−C_6H_4−X−Y (indicated in the Figure by XY), where X is the alligator clip (S or CN) and Y is the metal (Ni, Cu, Pd, Ag, Pt, or Au).

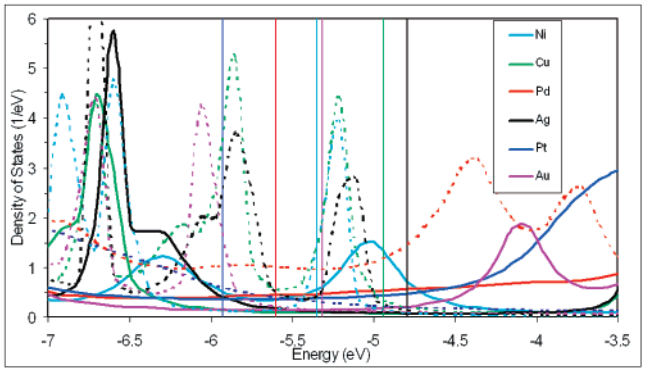

Figure 3. Density of states for S (dotted line) and CN (solid line) systems. Vertical lines indicate the position of the E_F.

results showing that NC−Pd yields higher conductance than CN−Au.[10] The second best metals correspond to the other two in group 10, Ni and Pt. This leaves group 11 metals as the worst in making interfaces with S and CN alligator clips. Actually Au, one of the most used contacts, seems to provide one of the worst characteristics. Apparently, Pd, Ni, and Pt appear to yield barrierless contacts. An explanation of this behavior follows from the DOS and TF curves in Figures 3 and 4.

Comparing results for CN first and then for S and in each case comparing between metals of the same row, we find that for NiCN and CuCN, the linear character of the N−C−Ni angle yields conducting channels around Ni E_F, thus Ni yields much better conductance than Cu. The TF at E_F is ∼1 for Ni but ∼0.002 for Cu. The N−C−Cu angle is 139.6, eliminating the possibility of having conducting channels around the E_F energy. However, as the bias potential increases, both metals present complementary behavior: the TF for Ni decreases while the TF for Cu increases, thus both yield similar currents when the bias voltage approaches 5 V. A voltage bigger than 4 V is impractical from an experimental point of view.

Similar behavior is found when comparing Pd and Ag. Pd is much more conductive than Ag. TF for Pd is ∼0.8 and only 0.002

(10) Chen, J.; Calvet, L. C.; Reed, M. A.; Carr, D. W.; Grubisha, D. S.; Bennett, D. W. *Chem. Phys. Lett.* **1999**, *313*, 741−748.

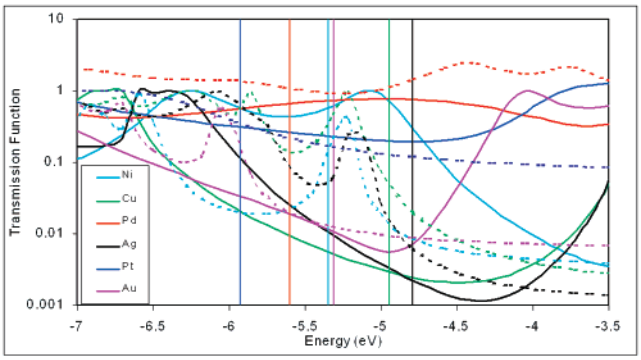

Figure 4. Transmission functions (TF) for NC (solid lines) and for S (dashed lines) clips. Vertical lines indicate the position of the E_F.

for Ag at their respective E_F due to the very poor density of states around the E_F. Contributing to this is the geometry of the contact, which is linear for Pd but not for Ag. The TF for Pd is ∼1 in a large range of energies around the E_F. There is a threshold for the conductance through Ag at about 2.8 V, which can be predicted observing the TF. Pd does not present such a threshold.

A similar behavior is predicted for Pt and Au. The TF is ∼0.3 for Pt and ∼0.01 for Au. The angle is nonlinear for Au. As the bias voltage increases, both metals tend to the same characteristics. Roughly, as we go down in group 10, the conductance decreases; however, the reverse takes place with the metals in group 11. Precisely speaking, Pd is the best of group 10 and Cu of group 11 when attached to S.

When S is the alligator clip, all cases present nonlinear angles, which are always smaller for group 11. This makes the characteristics for both metals in each row more similar than the case when CN is the alligator clip. The TF is larger for Ni than for Cu at their respective E_F values. However, for Cu the TF increases as the bias voltage increases. Since both interfaces have similar geometries, their molecular orbitals are practically identical, resembling similar DOS and TF curves, thus, in this case, the $I-V$ differences are due to the exact location of the E_F. The E_F for Cu is in a region of smaller density of states, thus of low TF; however, the Ni E_F value is in a region where more occupied states are accessible for conduction.

A different trend is observed for the next row. Pd has roughly a constant DOS with high TF on both sides of the E_F but Ag has negligible DOS around E_F, and it increases only on the occupied side. This yields a TF of ∼1 for Pd on a large interval of input energies. However, the TF for Ag is ∼0.007 at the E_F, increasing on the occupied side but decreasing on the unoccupied side. The comparison with Pt and Au is similar but more pronounced than the last one. Although the TF for Pt decreases for the unoccupied states, it remains above 0.1 for the range of practical input energies and increases on the occupied side. The TF for Au is ∼0.01 and remains around the same value with a slight increase on the occupied energies.

We present a straightforward method to compare metal−molecule interfaces. This method can be used for any metal and any molecule. It is predicted that the best metal for the metal−molecule interface corresponds to Pd, followed by Ni and Pt. Cu can be considered intermediate, and the worst correspond to Au and Ag. The best alligator clip corresponds to S but it is not much better than CN.

Acknowledgment. We thank the support of ARO under grant DAAD19-00-1-0154, DARPA/ONR under grant N00014-99-1-0406, and ARO under grant DAAD19-99-1-0085, as well as the supercomputer support of NASA, and Gaussian Inc.

JA015661Q