

# Reactivity indexes for different geometries of palladium leads

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**Abstract.** Electronic transport through metallic break junctions or molecules is clearly dependent not only on the electronic structure of the central nanodevice connecting the leads, but also the shape and crystalline orientation of the contacts which can define the possible conduction channels. In this work we examine different geometries of contacts of palladium characterizing them through global and local reactivity indexes as electrophilicity, chemical hardness and Fukui functions. In molecules, these indicators are essentially defined by the energies of the frontier molecular orbitals and in solids they are related with the local and partial density of states. We use for this purpose an *ab-initio* based code (FIREBALL), applied to plane contacts with (001) fcc faces and also pyramidal tips grown following a (001) and (111) packaging. The results allow us to have an insight about the chemical features of this type of nanojunctions.

## 1. Introduction

Controllable metallic break junctions connected by molecules are good candidates to realize electronic transport at the nanoscale. Many of this molecular junctions are made with molecules with terminal functional groups as it is the case of thiols or amine [1; 2]. Conductance measurements for these systems show an ample range of values for transport properties, and this diversity of values is mainly attributed to different chemical arrangement between functional groups and metallic leads. Besides, the fabrication method of break junctions not always guarantees that the leads have the same crystalline structure [3]. Thus, it becomes interesting to have tools which allow to give quick insights about the feasibility of different geometrical configuration for leads to react chemically with radicals connecting them. In this work we progress in this sense by calculating reactivity indexes as electrophilicity, chemical hardness and softness and Fukui functions. From the chemical point of view, these indicators are essentially defined by the energies of the frontier molecular orbitals but in solids they are related with the local and partial density of states (DOS). We calculate DOS from an *ab-initio* based code (FIREBALL) using Density Functional Theory. The selected systems are contacts of palladium with different geometries. One of the attractive on this metal resides on it can be form nanowires at the last stage of the breaking [4] with transport measurements presenting a peak at  $0.5G_0$  (being  $G_0$  the quantum of conductance) whose interpretation is controversial. Some authors

attributes this peak to a spontaneous polarized current [4; 5] and others to a effect of an hydrogen atmosphere [6]. The results allow us to have an insight about the chemical features of this type of nanojunctions.

## 2. Reactivity indexes

The density functional theory (DFT) is a description of many-body systems with the electronic density  $\rho$  as a functional parameter.  $\rho$  is related with the number of electrons,  $N$ , by  $\int \rho(\mathbf{r})d\mathbf{r} = N$  and the value which minimizes the total energy depends on the external potential  $v(\mathbf{r})$ . Thus, the ground state energy of a system  $E$  can be expressed as a functional of  $N$  and  $v$ ,  $E[N, v]$  and then a differential change in the ground state energy is:

$$dE = \left( \frac{\partial E}{\partial N} \right)_v dN + \int \left[ \frac{\delta E}{\delta v(\mathbf{r})} \right]_N dv(\mathbf{r})d\mathbf{r} = \mu dN + \int \rho(\mathbf{r})dv(\mathbf{r})d\mathbf{r}, \quad (1)$$

where it was defined the chemical potential as  $\mu = \left( \frac{\partial E}{\partial N} \right)_v$ , and  $\rho(\mathbf{r}) = \left[ \frac{\delta E}{\delta v(\mathbf{r})} \right]_N$  in a first order of perturbation [7]. From the chemical point of view,  $\mu$  is identified as the negative of the electronegativity and in solids, for 0 K, is the Fermi energy,  $E_f$ .

Equivalently, a differential change in the chemical potential is:

$$d\mu = \left( \frac{\partial \mu}{\partial N} \right)_v dN + \int \left[ \frac{\delta \mu}{\delta v(\mathbf{r})} \right]_N dv(\mathbf{r})d\mathbf{r} = 2\eta dN + \int f(\mathbf{r})dv(\mathbf{r})d\mathbf{r}, \quad (2)$$

where  $\eta$  and  $f$  are defined by

$$\eta = \frac{1}{2} \left( \frac{\partial \mu}{\partial N} \right)_v = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_v, \quad f(\mathbf{r}) = \left[ \frac{\delta \mu}{\delta v(\mathbf{r})} \right]_N = \left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_v. \quad (3)$$

$\eta$  is the (chemical) hardness, which is basically a half of the difference between ionization and affinity levels in atoms and molecules, and it is a half of the band gap in insulators and semiconductors [8].  $f(\mathbf{r})$  is the so-called Fukui function. This is a local indicator which account for how much of the frontier orbitals are localized at  $\mathbf{r}$  position. In this sense, Fukui function measures the reactivity towards a radical reagent and it is normalized as  $\int f(\mathbf{r})d\mathbf{r} = 1$  [9].

With the chemical potential and the hardness we can define two more indexes which give us information about as the system could react chemically with an adsorbate or molecule. These are the softness  $S$  and the electrophilicity  $\omega$ :

$$S = \frac{1}{2\eta} = \left( \frac{\partial N}{\partial \mu} \right)_v, \quad \omega = \frac{\mu^2}{2\eta}. \quad (4)$$

$S$  and  $\omega$  are global indexes and by using the Fukui function it is possible to define local softness and electrophilicity as  $s(\mathbf{r}) = f(\mathbf{r})S$ , and  $\omega(\mathbf{r}) = f(\mathbf{r})\omega$  [7].

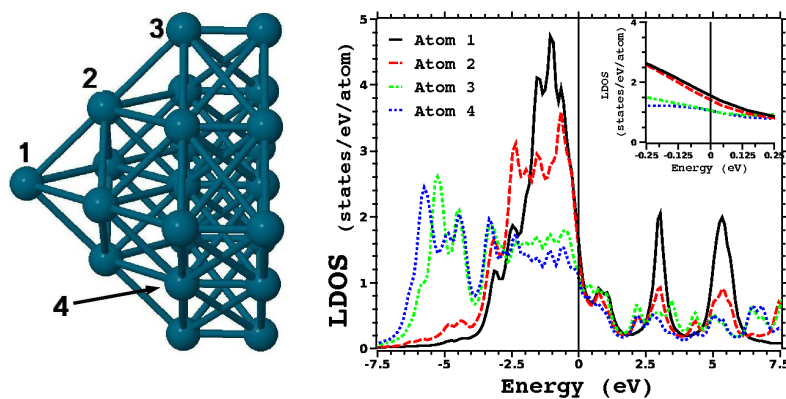
Finally, to complete the prescription of calculation we give the relationship between these quantities and the microscopic electronic properties of the material forming the contacts. If  $g(E, \mathbf{r})$  and  $g(E)$  are the local and total density of states respectively, it can be demonstrated that for 0 K [7; 9]:

$$s(\mathbf{r}) = g(\mathbf{r}, E_f), \quad S = g(E_f), \quad f(\mathbf{r}) = \frac{g(\mathbf{r}, E_f)}{g(E_f)}. \quad (5)$$

### 3. Results and discussion

For the calculation of the DOS we use an *ab-initio* DFT-based code (FIREBALL)[10; 11]. We use the Local Density Approximation for the exchange-correlation functional. The basis set is composed by numerically generated pseudo-atomic *fireball* wavefunctions and the core effective potentials were calculated following Ref. [12]. We have studied two pyramidal contacts grown following (001) and (111) packaging and a plane contact with a (001) fcc crystalline surface. Figure 1-3 show these geometries and the corresponding DOS. The energy scale was changed so that the Fermi level is fixed to 0 eV and the insets show a detail of DOS around  $E_f$ . The reactivity indexes are summarized in Tables 1-3.

In the (001) pyramidal contact, the atom with higher  $f$  function is the number 1, although atom 2 has a value quite close to atom 1 [Table (1)]. Atoms 3 and 4 are practically equivalent but they have lower  $f$  values. Thus, in this configuration it is expected that an adsorbate is located either near the apex atom or in a bridge place between atoms 1 and 2.



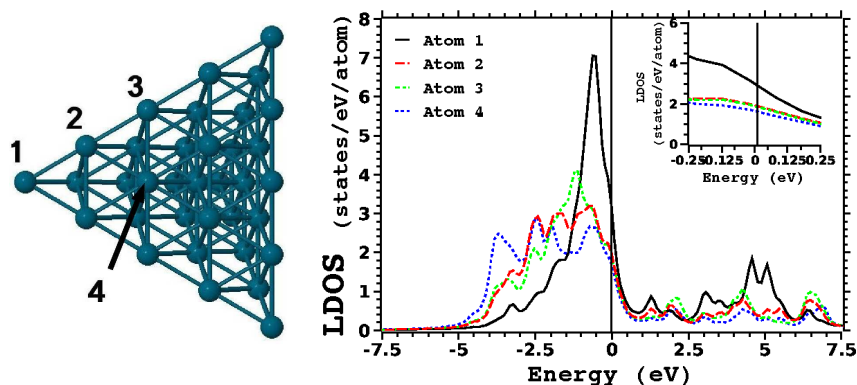
**Figure 1.** Pyramidal lead grown following (001) packaging and LDOS for labelled atoms.

**Table 1.** Reactivity indexes for (001) pyramidal tip.  $\eta$ ,  $\omega$  and  $\omega(\mathbf{r})$  are given in eV,  $S$  in  $\text{eV}^{-1}$ ,  $s(\mathbf{r})$  in  $1/\text{eV}/\text{atom}$  and  $f(\mathbf{r})$  is dimensionless.

Global indexes			Local indexes			
$\eta$	$S$	$\omega$	$f(\mathbf{r})$	$s(\mathbf{r})$	$\omega(\mathbf{r})$	
0.44	1.13	52.98	Atom 1	1.38	1.57	73.36
			Atom 2	1.25	1.42	66.29
			Atom 3	0.94	1.06	49.71
			Atom 4	0.92	1.04	48.82

For the (111) tip the scenario changes a little from the (001) case. Here, we have again the atom 1 as the more reactive while atoms 2 and 3 have almost the same low value for Fukui function [Table (2)]. Atom 4 is the less favorable site for a bonding. Differences between atoms 3 and 4 can be understood from the fact that atom 3 form part of the edge of the pyramid and then it has a different coordination compared with the atom 4, located at the face of the tip.

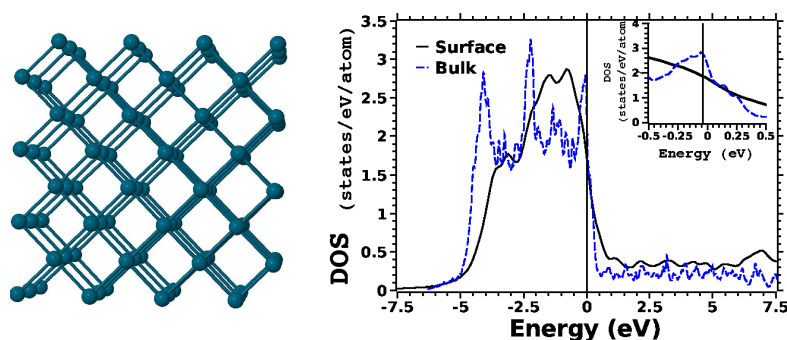
In the (001) surface all the atoms are symmetrically equivalent and then we have only one set of local indexes whose values are clearly lower than contacts with pyramidal shape [Table (3)]. In order to do a relative comparison among different geometries, the local electrophilicity is the proper index to observe. This is because  $\omega(\mathbf{r})$ , in contrast with  $f$ , contains information



**Figure 2.** Pyramidal lead grown following (111) packaging and LDOS for labelled atoms.

**Table 2.** Reactivity indexes for (111) pyramidal tip. Same conventions that in Table 1.

Global indexes			Local indexes			
$\eta$	$S$	$\omega$		$f(r)$	$s(r)$	$\omega(r)$
0.26	1.96	103.77	Atom 1	1.53	3.00	159.23
			Atom 2	0.98	1.92	101.66
			Atom 3	0.96	1.89	100.06
			Atom 4	0.84	1.64	86.98



**Figure 3.** (001) superficial plane and DOS for (001) surface and bulk.

**Table 3.** Reactivity indexes for (001) plane. Same conventions that in Table 1.

Global indexes			Local indexes			
$\eta$	$S$	$\omega$		$f(r)$	$s(r)$	$\omega(r)$
0.27	1.82	114.69	Surface	1.03	1.87	117.73

not only about the spatial distribution of the frontier states but also about the relative energetic ordering. Thus, Fukui functions are suitable to analyze reactivity in different places of a given system, while local electrophilicity becomes a better tool to compare chemical activity of regions of different systems. By comparing the maximal local electrophilicities for the three geometries

we observe that the tendency to form chemical bond follow the ordering: (111) tip  $\rightarrow$  (001) tip  $\rightarrow$  (001) surface. On the other hand, for pyramidal contacts, it is predicted in both cases that the apex atom is the more convenient site to realize the contact, although the edge region can be an alternative site to do this. These result are in qualitatively agreement with previous ones for H adsorption on a (111) Pd tip and Au nanowires [13; 14] and for dissociation of O<sub>2</sub> and O<sub>3</sub> molecules on Al pyramidal contacts oriented in the (111) direction [15]. Nevertheless, here we have calculated indexes only for the contacts and then the results offer us a first order insight about the chemical reactivity in molecular junctions composites. More conclusive statements could be extracted if these indexes were calculated for each pair of molecule/lead combination. Moreover, following the ideas of chemical reactivity, it should be necessary the definition of (solid state) Fukui functions and local electrophilicity for electrophilic (acceptor) or nucleophilic (donor) attacks. One way to progress in this direction are suggested in Ref. [16].

#### 4. Conclusions

Starting from *ab initio* based DFT calculation, we have evaluated reactivity indexes for different contacts of palladium. Local electrophilicity results indicate that (111) oriented tips are more reactive than (001) ones and these, more than the (001) surface. Besides, from Fukui function results, the preferred site for the chemical bonding is on the surroundings of an edge atom of the pyramid, being the apex atom the most convenient place for bonding. The results are in overall agreement with those obtained for similar atom/metal junctions.

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