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Structure and electronic states in Cu nanocontacts

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Abstract

We study structure and electronic states of Cu nanocontacts. The Korringa–Kohn–Rostoker (KKR) Green's function method for low-dimensional systems and the density functional theory in the local density approximation are used in our calculations. Atomic relaxations of nanocontacts and electrodes are performed using ab initio based many body potentials constructed by means of the KKR Green's function method and the tight-binding approach. We demonstrate that nanocontacts exhibit stress oscillations during stretching caused by changes in their structure. Performing ab initio calculations of electronic states in nanocontacts in a fully relaxed geometry, we reveal a strong enhancement in the density of electronic states at the Fermi level before breaking.

Keywords: Contact; Copper; Green's function methods; Ab initio quantum chemical methods and calculations; Surface electronic phenomena (work function, surface potential, surface states, etc.)

1. Introduction

Atomic-sized contacts are of great interest for development of nanoelectronics [1]. Recent experiments have demonstrated that it is possible to shrink the contact to just a few atoms [1,2]. Electronic, magnetic and transport properties of nanocontacts are governed by size and quantum effects [1,3] which become very important as the size of the contact approaches atomic dimensions. The correlation between the structure of contacts and their electronic and transport properties was predicted [4] and found in experiments [5]. It has been shown that abrupt structural changes in nanocontacts lead to abrupt changes in the conductance [1].

There are many theoretical studies of structural and transport properties of nanocontacts. Important results in this field have been obtained using semi-empirical potentials [6], the effective-medium theory [7] and the jellium model in the framework of the density functional theory [8].

In this paper we present a new approach based on the KKR Green's function method and the density functional theory for calculations of electronic states in nanocontacts. We take into account the structure of nanocontacts and electrodes. Our method can be used for self-consistent calculations of electronic and magnetic properties of large systems with d-electrons.

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It has been found [1] that bonds in nanocontacts are considerably stronger than bonds in the bulk. Therefore, we have developed new potentials which can correctly describe strong bonding in nanocontacts. Atomic relaxations of nanocontacts and electrodes are performed with many-body potentials fitted to ab initio results for low-dimensional systems.

2. Method of calculation

We create the two uncoupled electrodes by removing the atomic potentials of several crystal layers in the bulk. The Green's function of the bulk is calculated using the Korringa–Kohn–Rostoker (KKR) Green's function method [9]. Electrodes are considered as two-dimensional

Quantity	Ab initio data	Fitted values
$E_{Surface\ energy}$ (J/m^2)	1.42	1.41
E_c (eV)	-4.310	-4.391
E_{dimer} (eV)	-0.490	-0.442
E_{trimer} (eV)	-1.010	-0.861
$E_{2x2island}$ (eV)	-1.640	-1.801
$E_{3x3island}$ (eV)	-5.320	-5.301
a_0 (Å)	3.563	3.539
B (Mbar)	1.780	1.933
C_{11} (Mbar)	2.256	2.413
C_{12} (Mbar)	1.537	1.694
C_{44} (Mbar)	1.156	1.126

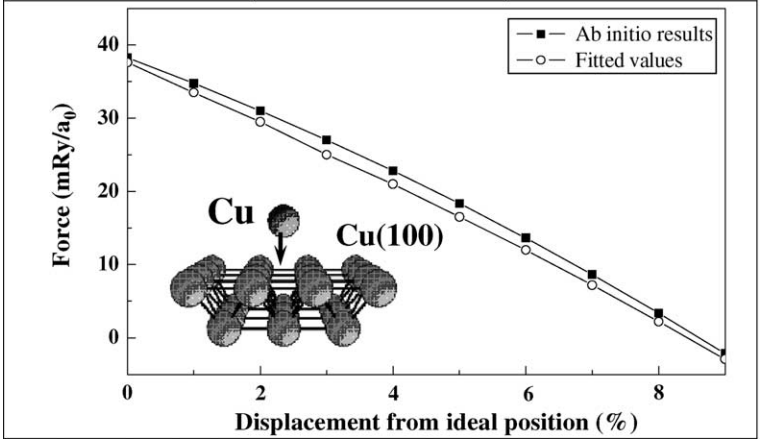

Fig. 1. Data used for fitting of the potential for Cu–Cu interaction. Binding energies of Cu clusters on Cu(0 0 1), surface energy of Cu(0 0 1), cohesive energy, bulk modulus B, elastic constants, forces acting on the Cu adatom near Cu(0 0 1) calculated by means of the KKR Green's function method and the optimized many-body potential.

perturbations of the bulk. We apply the multiple-scattering theory and solve self-consistently a Dyson equation for the structural Green's function of electrodes using the bulk as the reference system. Atomic structure of electrodes is fully taken into account in our method.

The nanocontact suspended between electrodes is treated as the perturbation of electrodes. The Green's function of ideal electrodes is then used as the reference Green's function for calculations of the Green's function of the nanocontact-electrodes system in a real space formulation. In self-consistent calculations we allow the potentials of all atoms of the nanocontact, adjacent vacuum sites and the potentials of electrodes in the area of contacts to be perturbed. Exchange and correlation effects are included in the local density approximation. The full charge density and the full potential approximation can be used in the calculations. Our approach allows us to calculate the Green's function for ideal and relaxed atomic positions of the contact and electrodes fully self-consistently. Using the Green's function, the charge density and the local density of electronic states (LDOS) can be calculated. For large systems of several hundred atoms we can use the screened KKR Green's function method [10]. Details of the KKR Green's function method for low-dimensional systems can be found elsewhere [9].

The equilibrium structure of the contact and electrodes is determined by computing the forces at each atomic site and relaxing the geometry of the contact and electrodes. We use the quasi-ab initio molecular static method [11], which is based on the second-moment tight-binding approximation for many-body potentials [12]. In this approximation the cohesive energy is the sum of band energy and repulsive part.

$$E_{\mathrm{coh}} = \sum_i (E^i_{\mathrm{R}} + E^i_{\mathrm{B}}), \tag{1}$$

$$E^i_{\mathrm{B}} = -\left\{ \sum_j \xi^2_{\alpha\beta} \exp\left[-2q_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) \right] \right\}^{1/2}, \tag{2}$$

Parameter	Cu-Cu
A^1 (eV)	0.0000
A^0 (eV)	0.0702
ξ (eV)	1.3962
p	11.601
q	2.3849
r_0 (Å)	2.5908

Fig. 2. Parameters of interatomic interaction.

$$E^i_{\mathrm{R}} = \sum_j \left[A^1_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) + A^0_{\alpha\beta} \right] \exp\left[-p_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) \right], \tag{3}$$

r_{ij} is the distance between the atoms, all parameters of interactions are determined as described below.

Accurate first principle calculations of cluster-substrate properties, ab initio forces acting on adatoms and surface energy are performed to fit the parameters of interactions. The ab initio forces are determined by means of an ionic version of the Hellmann–Feynman theorem [13] in the full potential approximation. Thus, only ab initio data for low-dimensional systems are used to construct potentials. Fig. 1 shows forces acting on a Cu adatom near the Cu(0 0 1) surface calculated fully ab initio and fitted with optimized potentials. To link the interaction between atoms in the low-dimensional systems to that in the bulk the set of data used for fitting includes such bulk properties as bulk modulus, lattice constant, cohesive energy and elastic constants calculated in the LDA approximation. Data used for the fitting of the potential together with values calculated with the potential are presented in Fig. 1. One can see that the bulk and surface properties are well reproduced. The parameters of interatomic interactions are presented in Fig. 2.

3. Results and discussions

As an example, we calculate the atomic resolved stress in the Cu nanocontact during stretching in a

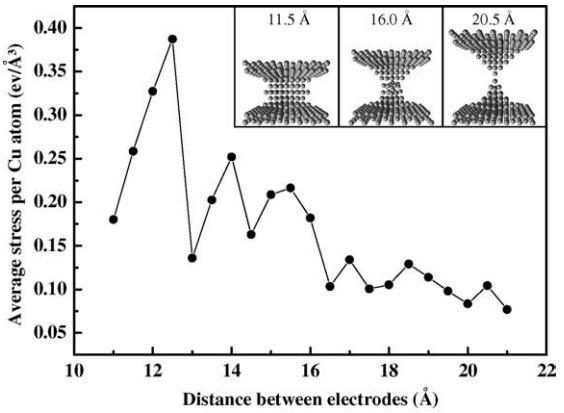

Fig. 3. Stress oscillation in the Cu nanocontact during stretching. The average hydrostatic stress per Cu atom in the nanocontact is presented.

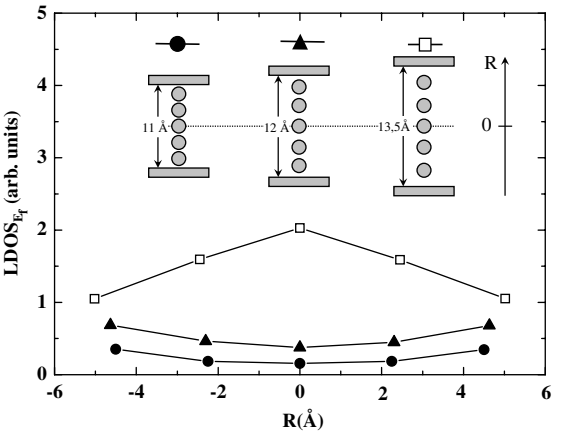

Fig. 4. s-LDOS at the Fermi level during stretching of the Cu chain calculated in the relaxed geometry for the contact and the electrodes. The breaking point is characterized by a strong enhancement of the LDOS at the Fermi level.

fully relaxed geometry. Details of stress calculations can be found in our recent work [14]. Fig. 3 shows the average hydrostatic stress in the Cu nanocontact for different distances between electrodes. The stress oscillations found in our calculations are determined by structural changes in the contact with its elongation. In the initial steps of stretch, the layered ordered structure is well seen. The increase of the stress corresponds to the elastic stage [1,15]. Upon increasing the distance between electrodes, the layers of the contact become wider and rougher and at some point the layered structure is distorted. The elongation process consists of a sequence of elastic and yielding stages. Our calculations show that the stress relief at the end of each elastic stage is connected with atomic rearrangement in the contact. We have to note that the atomic relaxations in the electrodes where the nanocontact is connected are stronger than in the contact. In other words, electrodes are softer than the nanocontact. Shortly before the break the contact consists of only a few atoms and the stress is strongly reduced.

Now, we turn to the discussion of the interplay between structure and electronic states in nanocontacts. To give clear demonstration of the impact of structural changes on electronic states, we consider an evolution of the LDOS at the Fermi level in a simple Cu contact of five atoms suspended between electrodes. We perform atomic relaxations of the contact and electrodes during stretching. Afterwards a self-consistent KKR calculation of the LDOS is performed for relaxed geometries. Our results show dramatic changes in the LDOS at the Fermi level during stretching. In Fig. 4 the s-component of the LDOS at the central atom of the contact is presented for several distances between electrodes. A strong enhancement of the LDOS at the Fermi level before the break is well seen. The standing-wave is formed due to the interference of wave back reflected from the electrodes and the resonance peaks move to lower energy with stretching. As a result of this the enhancement of the LDOS can be found only for some size of the contacts. We believe that this effect can be important for understanding of the transport properties of nanocontacts.

4. Conclusion

We have presented a new approach for calculations of structural and electronic properties of nanocontacts based on the KKR Green's function method. We have demonstrated that our method allows us to study stress variations in nanocontacts caused by atomic rearrangement during stretching. Ab initio calculations of the LDOS of the Cu

contact in a fully relaxed geometry have revealed a strong impact of the structure on electronic states at the Fermi level. Our method can be used for nonmagnetic and magnetic nanocontacts on the same footing. Calculations of magnetic nanocontacts are currently in progress.

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