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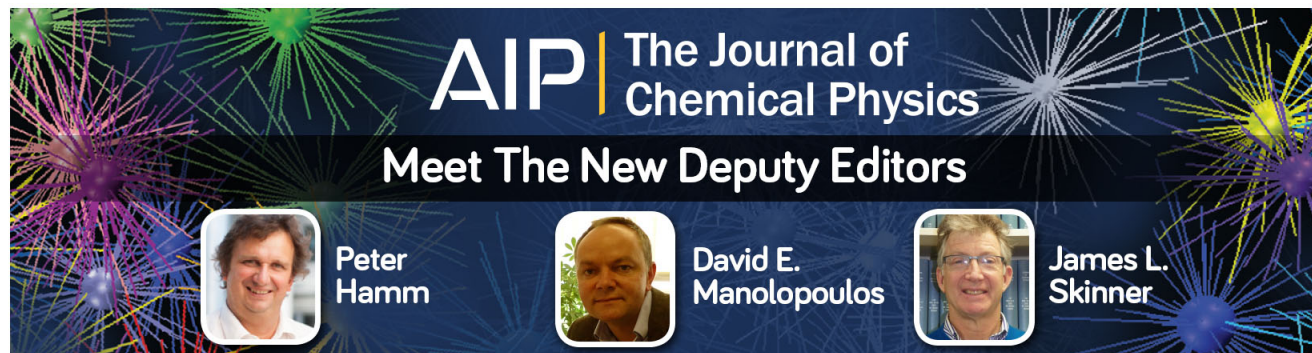Appl. Phys. Lett. **101**, 102401 (2012); 10.1063/1.4749817

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Microscopic origin of the 1.3 G_0 conductance observed in oxygen-doped silver quantum point contacts

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Besides the peak at one conductance quantum, G_0, two additional features at ~0.4 G_0 and ~1.3 G_0 have been observed in the conductance histograms of silver quantum point contacts at room temperature in ambient conditions. In order to understand such feature, here we investigate the electronic transport and mechanical properties of clean and oxygen-doped silver atomic contacts by employing the non-equilibrium Green's function formalism combined with density functional theory. Our calculations show that, unlike clean Ag single-atom contacts showing a conductance of 1 G_0, the low-bias conductance of oxygen-doped Ag atomic contacts depends on the number of oxygen impurities and their binding configuration. When one oxygen atom binds to an Ag monatomic chain sandwiched between two Ag electrodes, the low-bias conductance of the junction always decreases. In contrast, when the number of oxygen impurities is two and the O-O axis is perpendicular to the Ag-Ag axis, the transmission coefficients at the Fermi level are, respectively, calculated to be 1.44 for the junction with Ag(111) electrodes and 1.24 for that with Ag(100) electrodes, both in good agreement with the measured value of ~1.3 G_0. The calculated rupture force (1.60 nN for the junction with Ag(111) electrodes) is also consistent with the experimental value (1.66 ± 0.09 nN), confirming that the measured ~1.3 G_0 conductance should originate from Ag single-atom contacts doped with two oxygen atoms in a perpendicular configuration. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4901945]

I. INTRODUCTION

Since 1998, when Ohnishi *et al.* fabricated gold atomic contacts and measured their conductance,[1] the electronic transport properties of metallic atomic-size contacts have been investigated extensively.[2] On the one hand, many basic quantum transport concepts can be tested in these metallic atomic contacts. On the other hand, understanding the electrical conduction through metallic atomic contacts is the starting point for the design of molecular electronic and spintronic devices with the same electrode material.[3,4] It is well established that the number of conducting channels in one-atom-thick junctions is determined by the number of valence orbitals of the contact atom. Although this is only an upper limit, since some of the channels may be closed or partially closed for symmetry reasons or hybridization, the valence orbital rule is often respected. For this reason the low-bias conductance of clean monovalent metals, including alkali and noble metals, is expected to be 1 G_0, where $G_0 = 2e^2/h^2$ is the conductance quantum.

Notably the incorporation of atomic or molecular impurities in a junction may change dramatically its conductance. For example, Aradhya *et al.* measured the conductance of Ag quantum point contacts under ambient conditions at room temperature and found two additional features at ~0.4 G_0 and ~1.3 G_0.[5] Since oxygen molecules can dissociate into oxygen

atoms on undercoordinated silver atoms even at temperatures as low as 105 K,[6] they assigned the ~0.4 G_0 conductance to an Ag-O-Ag contact (AgO-S) in which one oxygen atom is assumed to bridge the Ag-Ag contact in series. In contrast, the ~1.3 G_0 conductance was assigned to an Ag-Ag single-atom contact with one oxygen atom connected in a parallel arrangement (AgO-P). Similar experimental results and interpretations were also reported by den Boer *et al.*[7] In order to explain the ~1.3 G_0 conductance feature, one must assume that the Ag-O bonds are in parallel to the Ag-Ag bond in the AgO-P contact and thus the total conductance of the AgO-P contact is the sum of the Ag single-atom conductance and the oxygen atom conductance.[5,7] However, this assumption is questionable because the Ag-O bond is a strong ionic bond that will perturb significantly the electronic states of the Ag-Ag contact around the Fermi level. Although many theoretical studies on the effects of oxygen atoms or molecules on the electronic transport properties of silver atomic contacts have been reported,[8–13] the microscopic origin of the ~1.3 G_0 conductance feature is still unclear.

Here we investigate the low-bias conductance and the rupture force of silver atomic contacts incorporating oxygen impurities by employing the non-equilibrium Green's function formalism combined with density functional theory (i.e., the NEGF + DFT approach).[14–23] Our calculations show that the electronic transport properties of Ag atomic contacts are modified significantly by oxygen doping, and that the magnitude of such modification depends on the number of O atoms in the junction. In details, when one oxygen atom bridges the

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Ag-Ag contact in series, the transmission coefficients at the Fermi level are calculated to be 0.38 for Ag atomic contacts with the Ag(111) electrodes, in good agreement with the measured ∼0.4 G$_0$ conductance.[5] Due to the strong Ag-O ionic bond, the transmission peaks dominated by the oxygen 2*p* atomic orbitals are all below the Fermi level. When the number of the oxygen impurities is increased to two and the O-O axis is perpendicular to the Ag-Ag axis, two oxygen 2*p* atomic orbitals contribute to the transmission at the Fermi level; one forms a fully open conducting channel, the other forms a partially open conducting channel with a transmission coefficient of 0.44. The total transmission is thus 1.44. The calculated rupture force (1.60 nN) for this oxygen-doped Ag atomic contact is also consistent with the measured value (1.66 ± 0.09 nN), providing further evidence that the measured ∼1.3 G$_0$ conductance can be attributed to Ag single-atom contacts doped with two oxygen atoms in a perpendicular configuration.

II. CALCULATION METHOD

In this work we use the SIESTA code[24] to compute the atomic structure of silver atomic contacts and the quantum transport code SMEAGOL[21–23] to study their electronic transport properties. SIESTA is an efficient DFT package, which makes use of improved Troullier–Martins pseudopotentials for describing the atomic cores and adopts a finite-range numerical orbital basis set to expand the wave functions of the valence electrons.[24,25] While a double-zeta plus polarization (DZP) basis set is used for O, two different types of basis functions are used for Ag, respectively, in the bulk and at the surface. In more detail, a double-zeta basis set augmented with polarization and diffuse functions (DZP + diffuse) is used for the surface Ag atoms, while a single-zeta plus polarization (SZP) basis is used for the bulk. This allows us to keep a balance between the efficiency and the required accuracy of the simulations.[26–28] The exchange-correlation functional is at the level of the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) formulation.[29] Geometry optimization is performed by standard conjugate gradient relaxation until the atomic forces are smaller than 0.02 eV Å^{-1}.

SMEAGOL is a practical implementation of the NEGF + DFT approach, which employs SIESTA as the DFT platform.[21–23] We use an equivalent cutoff of 200 Ryd for the real space grid. The charge density is integrated over 36 energy points along the semi-circle, 36 along the line in the complex plane, while 36 poles are used for the Fermi function (the electronic temperature is 25 meV). We always consider periodic boundary conditions in the plane transverse to the transport. The unit cell of the extended molecule comprises the oxygen atoms, some silver atoms with lower coordination and either ten Ag(111) or 13 Ag(100) atomic layers with a (3 × 3) in plane supercell. The total transmission coefficient *T(E)* of the junction is evaluated as

$$T(E) = \frac{1}{\Omega_{2DBZ}} \int_{2DBZ} T(\vec{k}; E) d\vec{k}, \qquad (1)$$

where Ω_{2DBZ} is the area of the two-dimensional Brillouin zone (2DBZ) in the transverse directions. The *k*-dependent transmission coefficient is obtained as

$$T(\vec{k}, E) = Tr[\Gamma_L G_M^R \Gamma_R G_M^{R+}], \qquad (2)$$

where G_M^R is the retarded Green's function matrix of the extended molecule and Γ_L (Γ_R) is the broadening function matrix describing the interaction of the extended molecule with the left-hand (right-hand) side electrode. Here, we calculate the transmission coefficient by sampling 4 × 4 k-points in the transverse 2DBZ.

III. RESULTS AND DISCUSSION

We first investigate the atomic structure and the electronic transport properties of a clean Ag quantum point contact, which can provide an important reference for the oxygen-doped case. Considering that when the conductance is measured around 1 G$_0$ in clean Ag atomic contacts it is likely that a two-atom-long monatomic chain is formed,[30,31] we construct a symmetric Ag atomic contact model in which one Ag cluster with four atoms arranged in a pyramid configuration is attached to the Ag(111) surface of each electrode [see Fig. 1(a)]. In order to find the equilibrium structure, we systematically adjust the separation between the two silver electrodes and optimize the positions of silver atoms with lower coordination and those at the electrode surfaces until the total energy reaches a local minimum. The Ag-Ag bond length in the constriction is optimized to be 2.695 Å, about 0.26 Å shorter than the calculated bulk value (2.951 Å). The equilibrium transmission spectrum is shown in Fig. 1(b). As we can see, the transmission starts to increase from 2.8 eV below the Fermi level and shows some small oscillations around the Fermi level, E$_F$. The transmission coefficient at E$_F$ is calculated to be 0.94, in good agreement with the low-bias conductance of 1 G$_0$ measured for clean Ag quantum point contact.[5,7,30,31] By correlating the transmission function with the local density states (LDOS) of the Ag atom at the apex of
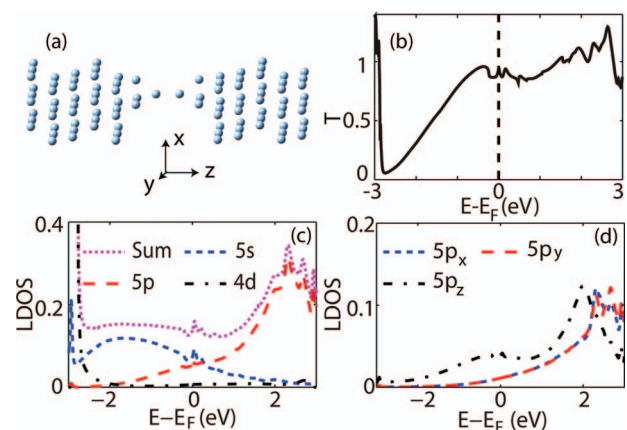

FIG. 1. Transport properties and electronic structure of a clean Ag atomic contact in which one Ag cluster with four atoms arranged in a pyramid configuration is attached to the Ag(111) surface of each electrode. The optimized atomic structure (a), the equilibrium transmission spectrum (b), the LDOS (c), and the LDOS projected onto the 5*p* atomic orbitals (d) of the Ag apex atoms.
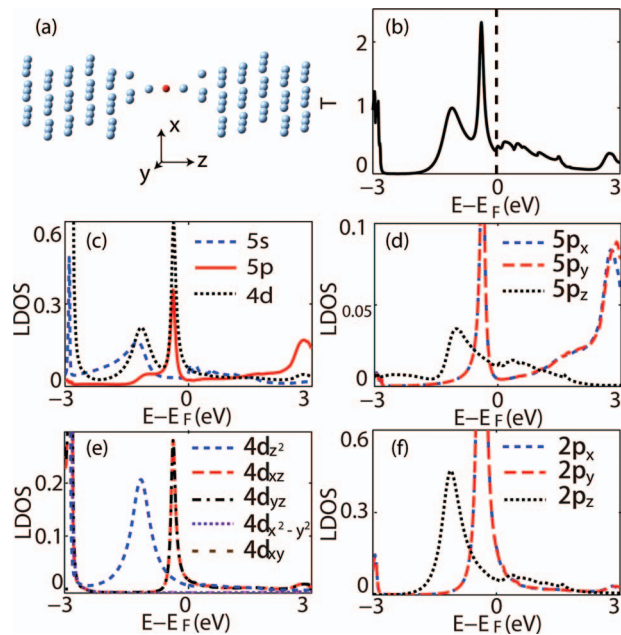
FIG. 2. Transport properties and electronic structure of the AgO-S junction. The optimized atomic structure (a), the equilibrium transmission spectrum (b), the LDOS of the Ag apex atom (c) and projected onto its $5p$ orbitals (d) and $4d$ orbitals (e), the LDOS of the oxygen atom projected onto its $2p$ orbitals (f).

FIG. 3. The optimized atomic structure (a) and the equilibrium transmission spectrum (b) of the Ag2O-S junction.

the pyramid [Figures 1(c) and 1(d)], we can conclude that the transmission around the Fermi level originates mainly from the $5s$ and $5p$ atomic orbitals of the Ag apex atom, especially the Ag $5p_z$ atomic orbital. In contrast, the $4d$ atomic orbitals of the Ag apex atom only contribute to the transmission far below E_F.

Next we insert one oxygen atom in between the two Ag apex atoms and investigate its effects on the electronic transport properties of the Ag atomic contact. The optimized atomic structure of the AgO-S junction is given in Fig. 2(a), in which the Ag-O bond length is determined to be 1.996 Å. As one can see in Fig. 2(b) the presence of oxygen drastically modifies the transmission spectrum of the contact. The transmission coefficient at the Fermi level is now decreased to 0.38, illustrating that the measured ~0.4 G_0 conductance can indeed originate from the incorporated oxygen atom bridging the Ag-Ag contact in series. Two noticeable transmission peaks appear in the spectrum at −1.08 eV and −0.36 eV, respectively. The LDOS of the oxygen and Ag apex atoms reveal that the transmission peak centered at −1.08 eV is mainly contributed by the oxygen $2p_z$ atomic orbital and both the $4d_{z^2}$ and $5p_z$ orbitals of the Ag apex atoms, while that the transmission peak at −0.36 eV is dominated by the $2p_x$ and $2p_y$ orbitals of O and the $4d_{xz}$, $4d_{yz}$, $5p_x$, and $5p_y$ orbitals of the apical Ag. Thus, in the AgO-S contact the $4d$ atomic orbitals of the Ag apex atoms also contribute to the transmission around E_F due to the strong interactions between O and the Ag apex atoms.

It has been verified experimentally and theoretically that the presence of oxygen impurities can enhance the probability of chain elongation.[11,30,31] Therefore it is natural to lengthen the AgO-S junction by adding one more silver atom into the chain. We name such configuration Ag2O-S. The optimized
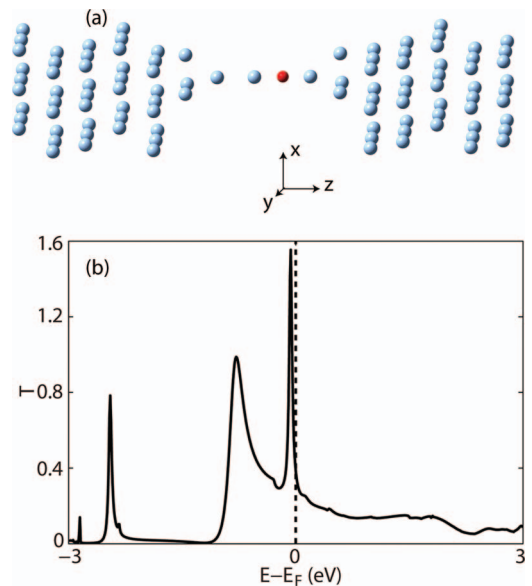
atomic structure and the corresponding equilibrium transmission spectrum are presented in Fig. 3. The transmission coefficient at the Fermi level is found to be 0.37, which is almost the same as that of the AgO-S junction. This reinforces further the idea that the ~0.4 G_0 conductance originates from the oxygen atom bridging the Ag contacts in series, because the low-bias conductance of these junctions does not depend on the specific length of the Ag monatomic chain bridging the two Ag electrodes. When one compares the Ag2O-S junction with the AgO-S one, the interaction between O and the Ag electrodes becomes weaker so that the two transmission peaks dominated by the O $2p$ atomic orbitals not only become sharper but also move to higher energies.

Next we look at whether or not the particular O binding configuration determines sensitively the low-bias conductance of AgO-P junctions. In particular we investigate the effect of the O atom moving away from a co-axial position with the two apical Ag atoms. Fig. 4(a) shows the optimized atomic structure of the AgO-P junction, in which the Ag-O bond length and the distance between the two Ag apex atoms are, respectively, calculated to be 2.032 Å and 3.187 Å. In this case O is placed at an angle of 38.35° with respect to the bond axis between the two Ag atoms. The corresponding transmission spectrum is given in Fig. 4(b). As we can see, the transmission at E_F decreases further to 0.16, in contrast to the expectation that an AgO-P junction can bear a low-bias conductance in the region of 1.3 G_0.[5,7] Because of symmetry lowering the degeneracy between the O $2p_x$ and $2p_y$ orbitals gets lifted. Thus, the sharp transmission peak located at −0.48 eV is now dominated by the O $2p_y$ atomic orbital together with the $5p_y$, $4d_{yz}$, and $4d_{xy}$ of the Ag apex. The O $2p_x$ and $2p_z$ orbitals make contributions to the broad transmission peak centered at −0.88 eV, whose amplitude is also shared by the $5s$, $5p_x$, $5p_z$, $4d_{xz}$, $4d_{x^2-y^2}$, and $4d_{z^2}$ of the Ag apex. Although all the $4d$, $5s$, and $5p$ orbitals of the Ag apex atoms contribute to the transmission around E_F, the peaks attributed
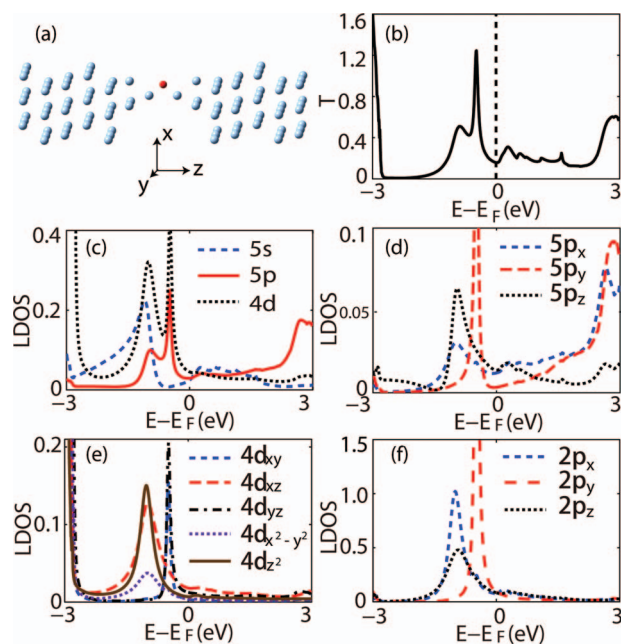
FIG. 4. Transport properties and electronic structure of the AgO-P junction. The optimized atomic structure (a), the equilibrium transmission spectrum (b), the LDOS of the Ag apex atom (c), and projected onto its $5p$ orbitals (d), and $4d$ orbitals (e), the LDOS of the oxygen atom projected onto its $2p$ orbitals (f).

FIG. 5. Transport properties and electronic structure of the AgO2-P junction. The optimized atomic structure (a), the equilibrium transmission spectrum (b), the LDOS of the Ag apex atom (c) and projected onto its $5p$ orbitals (d) and $4d$ orbitals (e), the LDOS of the oxygen atom projected onto its $2p$ orbitals (f).

to the O $2p$ orbitals are much lower than the Fermi level and thus the transmission coefficient at E_F is still very small.

It should be noted that the distance between the two Ag apex atoms in the AgO-P junction is much larger than that of a clean Ag point contact [Fig. 1(a)], and one may wonder whether the small value of $T(E_F)$ in the AgO-P junction is caused by this large Ag-Ag distance. In order to test this assumption, we add one oxygen atom to the Ag-Ag bond in the clean Ag constriction shown in Fig. 1(a), and then relax the structure while keeping the positions of the Ag atoms fixed. For this constrained AgO-P junction model, the transmission coefficient at the Fermi level remains 0.16, suggesting that it is not the large distance of the two Ag apex atoms but the adsorption of O to suppress $T(E_F)$ in the AgO-P junction. Consequently, junctions like AgO-P are not at the microscopic origin of the ~ 1.3 G_0 conductance observed in the oxygen-doped silver quantum point contacts.

Considering that oxygen molecules can dissociate at under-coordinated Ag sites, it is highly possible for two oxygen atoms to bind to the Ag atomic contact simultaneously. Thus, we investigate the electronic transport properties of an Ag atomic contact with two oxygen atoms adsorbed at the Ag-Ag bond in the constriction [Fig. 5(a)]. This configuration is called AgO2-P. This time the O-O axis is perpendicular to the Ag-Ag one, the Ag-O bond length is optimized to 2.095Å, while the distance between the two Ag apex atoms and that between the two oxygen atoms are, respectively, 2.761 Å and 3.150 Å. As it can be seen from the calculated transmission spectrum [Fig. 5(b)], a transmission peak appears at E_F, along with three other transmission peaks centered, respectively, at -1.84 eV, -1.07 eV, and -0.75 eV. At the Fermi level T reaches a value of 1.44, in good agreement with the $\sim 1.3 G_0$
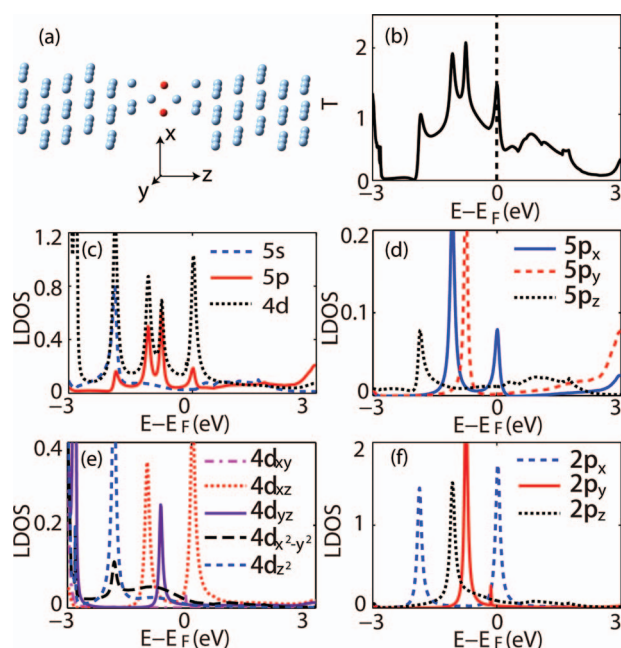
conductance observed experimentally. When we look at the LDOS of the two oxygen atoms, we find that these four transmission peaks correspond closely to the O $2p$ orbitals. To be more specific, the $2p_z$ orbitals of O (oriented along the junction axis), together with the $5p_x$ and $4d_{xz}$ orbitals of the Ag apex, dominate the transmission peak located at -1.07 eV, while the O $2p_y$ orbitals mainly contribute to T at -0.75 eV with smaller contributions of the $5p_y$ and $4d_{yz}$ orbitals of the Ag apex. In contrast, due to the strong coupling the O $2p_x$ orbitals split and dominate the two transmission peaks centered at -1.84 eV and at the Fermi level. Such last point in the analysis is further verified by employing the concept of transmission eigenchannel.[32,33] We find that there are two eigenchannels contributing to the transmission at E_F (the isosurface plots of these two eigenchannels are displayed in Fig. S1 of the supplementary material).[34] As we can see, in the central region the first eigenchannel consists of the oxygen $2p_x$ orbitals, which couple strongly with the electronic states of the Ag electrodes through the $4d_{xz}$ orbitals of the apex and thus form a fully open conducting channel. In contrast, the second eigenchannel consists of the oxygen $2p_z$ orbitals and the $5p_z$, $4d_{z^2}$ orbitals of the Ag apex. This channel is only partially open. Thus, a transmission coefficient larger than unity is achieved at the Fermi level.

It has been shown that the electrode orientation significantly affects the calculated transport properties of molecular junctions.[35] Therefore, we have also investigated the low-bias conductance of clean and oxygen-doped Ag atomic contacts made from (100)-oriented Ag electrodes (see Fig. S2 in the supplementary material). Similarly to the cases of the Ag(111) electrodes, the transmission coefficients at the Fermi level are, respectively, calculated to be 0.52 (AgO-S),
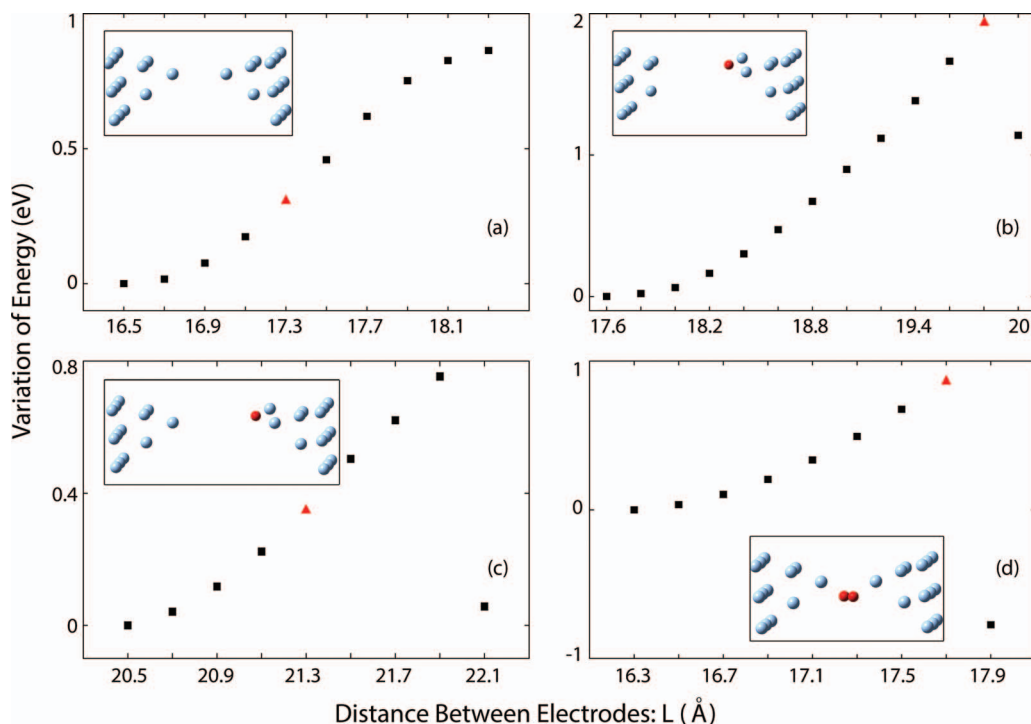
FIG. 6. Variation in the calculated total energy of the contact relative to its equilibrium structure as a function of L for the clean Ag (a), AgO-S (b), Ag2O-S (c), and AgO2-P (d) junctions with the Ag(111) electrodes. The symbol Δ (red) in each panel indicates the position at which the rupture force is calculated, and the inset in each panel shows the contact structure after rupture.

0.28 (AgO-P), and 1.24 (AgO2-P), further supporting the conclusion that the observed $\sim$0.4 G_0 conductance can be assigned to the AgO-S contacts with one oxygen atom bridging the Ag-Ag contact in series, whereas $\sim$1.3 G_0 does not originate from the AgO-P contacts but from the AgO2-P ones with two oxygen atoms adsorbed on the Ag-Ag contact.

Finally, in addition to the electronic transport properties, we have also investigated their mechanical ones, especially their rupture force. This is the maximum force sustainable by the contact just before snapping. In order to simulate the evolution of the mechanical properties of clean and oxygen-doped Ag atomic contacts during stretching, we elongate the contacts through small increments, $\Delta L = 0.2$Å, here the parameter L gives the distance between the two second outmost atomic layers of the two Ag electrodes. At each step the atoms belonging to the Ag electrodes are treated statically (they are fixed), while all the other atoms are allowed to relax. The total energy of the contact is then recalculated. In simulating the rupture, the relaxed structure of the previous step is used as input structure of the next step. This process is continued until the contact breaks. Fig. 6 presents the variation of the total energy of the clean Ag, AgO-S, Ag2O-S, and AgO2-P contacts with the Ag(111) electrodes as a function of L. For the clean Ag junction and the Ag2O-S junction, an inflection point can be found in their total energy vs distance curve and thus the rupture force is calculated at the inflection point. However, for the junctions AgO-S and AgO2-P, their structures break down before the inflection point can be reached so that the rupture force is calculated at the last step when their structure is still stable. The rupture forces are, respectively, calculated to be 1.22 nN (clean Ag atomic contact), 1.08 nN (Ag2O-S),

and 1.60 nN (AgO2-P), in good agreement with the experimental values of 0.95 $\pm$ 0.02 nN (Ag single-atom contacts), 0.83 $\pm$ 0.03 nN (oxygen-doped Ag contacts with the $\sim$0.4 G_0 conductance) and 1.66 $\pm$ 0.09 nN (oxygen-doped Ag contacts with the $\sim$1.3 G_0 conductance).[5] As expected, the clean Ag atomic contact shown in Fig. 1(a) breaks at the Ag-Ag bond in the constriction and the AgO2-P contact shown in Fig. 5(a) breaks at the Ag-O bonds. In contrast, the Ag2O-S contact (Fig. 3(a)) does not break at one of the two Ag-O bonds but at the Ag-Ag one just next to the oxygen atom, reflecting the fact that the Ag-O bond is stronger than the Ag-Ag bond.[12,30,31] This is more drastic in the AgO-S contact (Fig. 2(a)), in which the rupture occurs between one Ag apex atom and its neighboring three Ag atoms attached directly on the Ag(111) surface and thus the rupture force is increased to 2.29 nN.

IV. CONCLUSION

We have investigated the electronic transport and the mechanical properties of clean and oxygen-doped Ag atomic contacts using the NEGF + DFT approach and found that for both the Ag(111) and Ag(100) electrodes the observed $\sim$0.4 G_0 conductance can be assigned to Ag single-atom contacts with one oxygen atom bridging the Ag monatomic chain in series. Moving the oxygen atom out of the Ag monatomic chain axis does not shift the transmission peaks associated with the oxygen 2p atomic orbitals to the Fermi level and thus the junction conductance remains small. In contrast, when two oxygen atoms are adsorbed at the Ag monatomic chain with the O-O axis perpendicular to the Ag-Ag one, two conducting channels are present at the Fermi level. These are

hybrids between the O $2p$ orbital and those of the apical Ag atoms. One of them is fully open while the other is only partially open. As a results, the transmission coefficients at the Fermi level are increased to 1.44 for the junction with Ag(111) electrodes and to 1.24 for that with Ag(100) electrodes. These values are both consistent with the measured $\sim$1.3 G_0 conductance. The quantitative agreement between the calculated rupture force (1.60 nN for the junction with Ag(111) electrodes) and the experimental value (1.66 $\pm$ 0.09 nN) further confirms that the $\sim$1.3 G_0 conductance arises from Ag single-atom contacts doped with two oxygen atoms in a perpendicular configuration. These findings are helpful in facilitating the design and fabrication of molecular electronic devices made with Ag electrodes.

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