

Modification of the electronic transport in Au by prototypical impurities and interlayers

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Abstract – Electronic transport calculations for metallic interfaces based on density functional theory and a scattering theory on the Landauer-Büttiker level are presented. We study the modifications of the transport through Au due to prototypical impurities and interlayers. Our results show that the influence of S and Si impurities is well described in terms of simple vacancies. Metallic impurities and interlayers, on the other hand, have even more drastic effects, in particular when the Au *s-d* hybrid states at the Fermi energy are perturbed. The effects of a possible interface alloy formation are discussed in detail.

Introduction. – In recent years, interfaces have been investigated intensively because they can modify the transport properties drastically compared to the corresponding bulk compound. For example, the charge redistribution at metal-superconductor interfaces imposes severe restrictions on the critical current in wire and tape applications of high-temperature superconductors [1,2]. Interfaces are likewise highly important in semiconductor physics. A review on recent developments has been given by Ahn *et al.* [3]; these include the creation of a highly conductive two-dimensional electron gas at the interfaces between insulators [4–6] and the induced charge density in organic-inorganic devices [7–9].

The electron transport across metallic multilayers is of particular importance for understanding the giant magnetoresistance in ferromagnetic heterostructures, like Fe/Cr multilayers [10,11]. Also, hot-electron scattering in Au/Fe/Au trilayers is affected by the metal-metal interfaces [12]. In particular, the attenuation of the electrons strongly depends on the thickness of the Fe interlayer. Regarding non-magnetic systems, the properties of metal-metal interfaces, for instance, are of interest in many metallurgical applications [13]. For Co/Cu, Fe/Cr, and Au/Ag multilayers the resistance can be increased or decreased by interface disorder, depending on the specific system [14]. The orientation-dependent transparency of

simple metals, like Al and Ag, has been investigated in ref. [15]. In addition, simple metal interfaces have recently been studied within transport calculations [16].

In this context, the present study develops a comprehensive picture of the modifications of the charge transport in Au due to the incorporation of prototypical impurities and interlayers. We start our considerations by giving details on the applied computational method and the underlying structural setup in the next section. The results of transport calculations for metallic and non-metallic impurities as well as metallic interlayers are presented in the third section. The thickness dependence of the conductance in multilayer systems as well as the effects of alloy-like interfaces and two-component interlayers on the transmission coefficient are discussed in the fourth section. The conclusions are summarized in the last section.

Computational method and structural setup. –

In our calculations we apply the SMEAGOL transport code [17], which makes use of the SIESTA program package [18]. SIESTA is an efficient implementation of density functional theory and provides the SMEAGOL code with a self-consistent solution of the equilibrium electronic structure (using periodic boundary conditions). SMEAGOL then calculates the transport properties using a scattering theory on the Landauer-Büttiker level. The valence electrons are described by a single-zeta basis set of linear combinations of numerically adjusted

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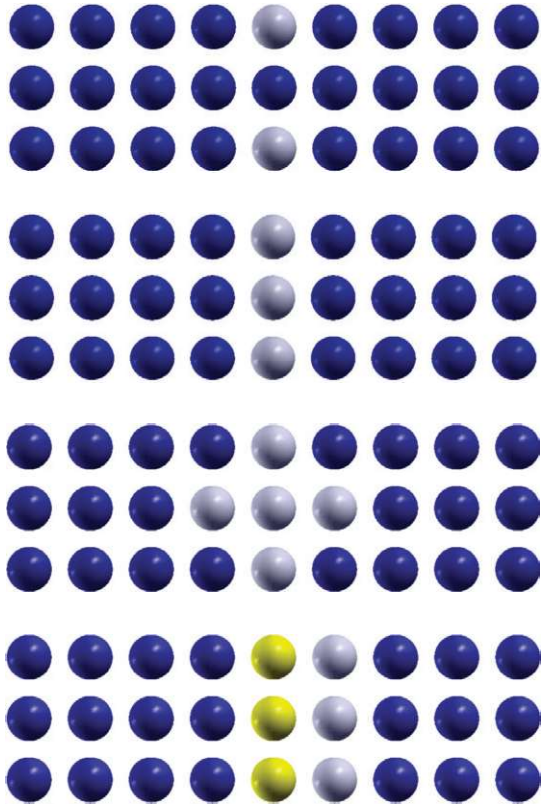


Fig. 1: (Color online) Structures under investigation (from top to bottom): Interface with impurity, metallic interlayer, interface alloy, and two-component interlayer. Blue, gray, and yellow spheres indicate Au, Ag, and Cu atoms, respectively.

atom-centered orbitals. We have checked for bulk Au and for the Cu impurities and interlayers in Au that deviations between a single- and a double-zeta basis are subordinate. Furthermore, the core electrons are represented by norm-conserving pseudopotentials in the fully non-local form [19] and the exchange-correlation functional is treated in the local density approximation (LDA). The principal layer of the leads comprises two Au unit cells and the scattering region consists of six fcc unit cells in each case. We apply periodic boundary conditions perpendicular to the [100] transport direction, where the periodic unit is one fcc unit cell. For the leads, we employ a $15 \times 15 \times 100$ Monkhorst-Pack k -grid for sampling the Brillouin zone, while the k -grid is $10 \times 10 \times 1$ for the device region. We study the electronic transport through interfaces oriented perpendicular to the transport direction.

Impurity systems are generated by replacing each second interface atom by an impurity atom (Mg, Si, S, Ni, and Ag), see the top structure in fig. 1. The interlayer systems, on the contrary, consist of impurity monolayers (Cu and Ag) in the center of the Au host. In addition, we consider the formation of an interface alloy [20] and heterostructures with two-component interlayers. The interface alloy is modeled as an impurity monolayer with additional impurities on both sides. The different setups

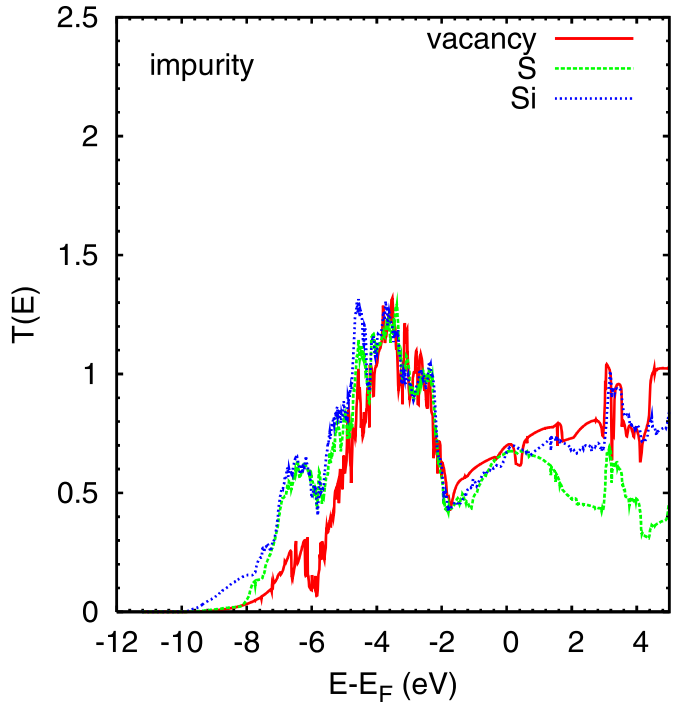


Fig. 2: (Color online) Transmission coefficient of the interfaces with S and Si impurities, as compared to the interface with a vacancy.

are illustrated in fig. 1. We also address the dependence of the conductance on the interlayer thickness. In order to highlight the principal effects induced by our prototypical interface modifications, we do not take into account any additional structure relaxation.

Impurities and interlayers. – In the first step we compare the effects of non-metallic and metallic impurities. As non-metallic impurities we consider Si (electronic configuration $3s^23p^2$, chemically inert) and the chalcogen S (electronic configuration $3s^23p^4$) which are typical impurities found in Au. Crystalline Si and S are insulators. In fig. 2 we compare the effects of Si and S impurities on the transmission coefficient $T(E)$ and also show the corresponding data for a vacancy system taken from ref. [16]. Here and in all following figures, $T(E)$ is normalized with respect to the number of points in the k -mesh. The (zero-bias) conductance $G = G_0 \cdot T(E_F)$ obtained for the three systems shows rather similar values close to $G = 0.6 \cdot G_0$, where $G_0 = 2e^2/h$. Just below the Fermi energy E_F the transmission coefficient grows almost linearly with the energy, reflecting a delocalized nature of the related states. In addition, the reduction of the transmission due to the impurities in the energy range from -6 eV to -2 eV, where the Au $5d$ states dominate, is similar in all three cases. Since the d bands are more sensitive to local disorder [21], the reduction here is much stronger than near E_F . Minor differences between the three systems in fig. 2 concern the lower band edge. Below -8 eV (s -like Au) $T(E)$ is suppressed for both the S impurity and the vacancy but not for the Si impurity, because Si states are present in this

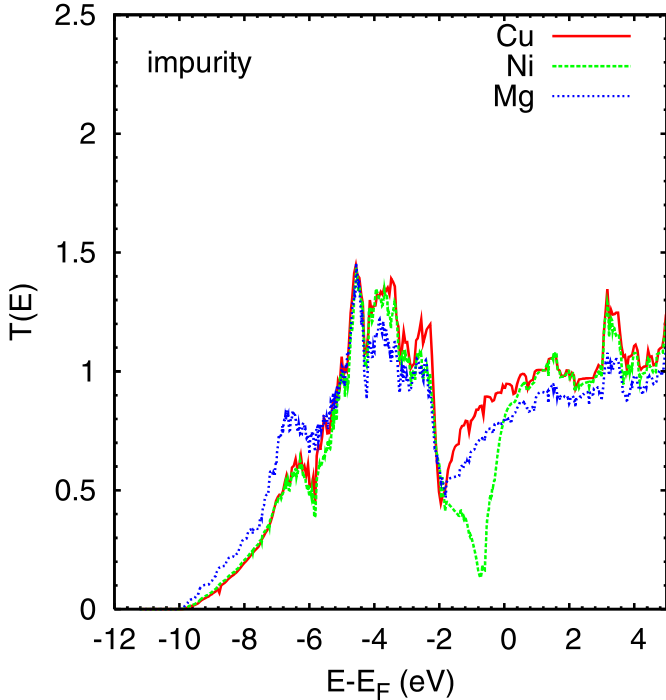


Fig. 3: (Color online) Transmission coefficient of the interfaces with Cu, Ni, and Mg impurities.

energy range and hybridize with the Au. Between -8 eV and -6 eV (s - and d -like Au) the impurities do not reproduce the reduction of $T(E)$ as found for vacancies. Apart from that, non-metallic impurities resemble the effects of vacancies even quantitatively.

Turning to the metallic impurities Mg and Ni, a comparison to previous findings for a Cu impurity [16] is helpful. Mg is a metal which can be described by a nearly free electron model. Ni and Cu, on the other hand, are transition metals with narrow d -bands. Despite this different physical nature of the three metals, they behave rather similar when acting as impurities in Au, see fig. 3. The onset of $T(E)$ is found at -9.5 eV and the conductance is $\sim 0.8 \cdot G_0$. Also, the reduction of $T(E)$ in the Au $5d$ dominated energy range is comparable. However, a pronounced reduction of $T(E)$ near -0.5 eV is obtained for the Ni impurity. We may conjecture that Au-Ni bonding, in contrast to Au-Cu bonding, affects the Au s - d hybrid states. In fact, the Ni $3d$ states are located around -1 eV [22], *i.e.* in the region of the Au s - d hybrid states, whereas the Cu $3d$ states are located around -2 eV, *i.e.* in the Au $5d$ dominated energy range. Hence, only the Ni $3d$ states can interact with the Au s - d hybrid states and form a d - d hybrid. The Au $6s$ states, in turn, hybridize with the Ni $4s$ states and both shift to much lower energy. Since the Ni $4s$ states therefore are missing in the vicinity of the Fermi energy, the transmission is strongly reduced. We find the highest conductivity for the Cu impurity system, $T(E_F) = 0.93$, since in this case the electronic structure of the impurity is closely related to that of the Au host. For the Mg system the states deviate more while the impurity is still

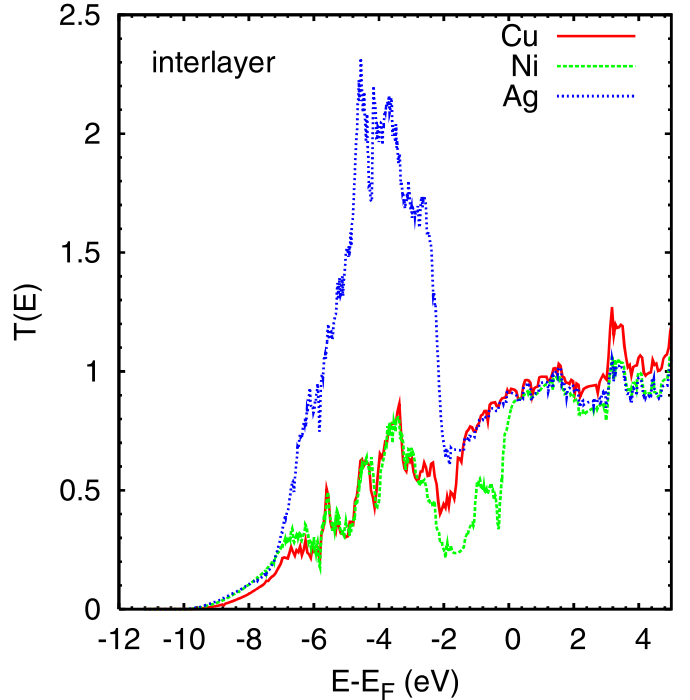


Fig. 4: (Color online) Transmission coefficient of the Cu, Ni, and Ag interlayer systems.

metallic, which results in a reduction of the conductivity, $T(E_F) = 0.78$. A further reduction is expected in the case of a non-metallic impurity. An example is the S system for which we obtain $T(E_F) = 0.63$.

Going beyond the impurity systems, we next study full impurity interlayers of Cu, Ni, and Ag, which all crystallize in a fcc structure. In addition, the lattice constant and valence electronic structure of Ag are rather similar to Au. As discussed in detail in ref. [16], the transmission mediated by the Au $5d$ states usually is smaller in interlayer than in impurity systems, while both the onset of $T(E)$ and the conductance agree very well. The transmission coefficients of Cu, Ni, and Ag interlayer systems are depicted in fig. 4. In order to understand the high values of $T(E)$ in the Ag case, as compared to Cu and Ni, we address the related densities of states (DOS): Since the Cu and Ni $3d$ bands are very narrow, they do not hybridize with the Au states and the Au $5d$ transmission consequently is significantly reduced. In contrast, Ag has $4d$ states in the whole energy range between -8 eV and -2 eV and therefore strongly hybridizes with the Au host. Furthermore, the reduced transmission between -2 eV and the Fermi level in the case of the Ni interlayer system has the same origin as discussed before for the Ni impurity.

Multilayers and interface alloys. – In this section we deal with modifications of the interlayer system. First, we discuss the influence of an increasing interlayer thickness. Second, we consider interlayers which are not

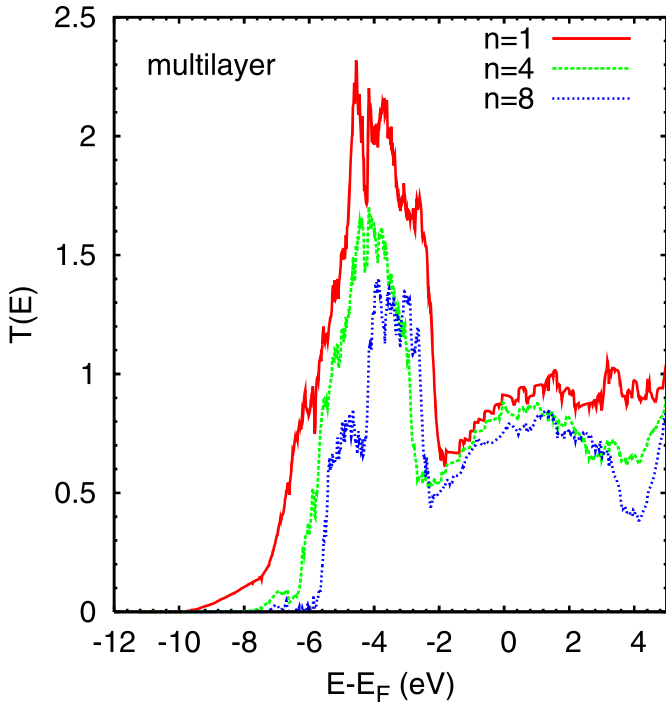


Fig. 5: (Color online) Transmission coefficient of the Ag interlayer system for interlayer thicknesses of $n = 1, 4,$ and 8 .

atomically sharp but show interface alloy formation. Third, we investigate two-component interlayers.

The influence of the interlayer thickness is studied for Au/ n Ag/Au heterostructures with n Ag monolayers. According to fig. 5, the conductance of the system decreases with growing n , where no saturation is found up to $n = 8$. In addition, the shape of $T(E)$ is closely related to the shape of the bulk DOS of the two components. In the case of a single interlayer, $T(E)$ resembles the DOS of the Au host. Therefore, a linear increase of $T(E)$ between -10 eV and -8 eV (Au s states) and a high transmission in the energy range of the Au $5d$ states are observed. With increasing n , however, the shape of $T(E)$ is given by the bulk Ag DOS. Since the width of the bulk Ag $4d$ bands (~ 3.5 eV) is smaller than the width of the Au $5d$ bands (~ 6 eV), the broad peak in $T(E)$ narrows with growing n . In fact, for $n = 8$ the bulk Ag $4d$ band width is reached. At the transmission maximum around -4 eV the amplitude is suppressed strongly for growing n because of the localized nature of the d states. On the contrary, the reduction of the conductance is much less pronounced, amounting to 4% at $n = 4$ and 16% at $n = 8$ with respect to the $n = 1$ value. Finally, we note that these results are specific for the Au/ n Ag/Au system and may change with the electronic structures of the component materials.

It is known that alloys can be formed at metallic interfaces [20]. We address this issue by comparing the $n = 2$ interlayer system to a configuration with alloy layers next to a single Ag interlayer, see the third structure of fig. 1. Both systems comprise the same number of Ag atoms. According to fig. 6, the transmission is slightly reduced as compared to the $n = 1$ curve, which traces

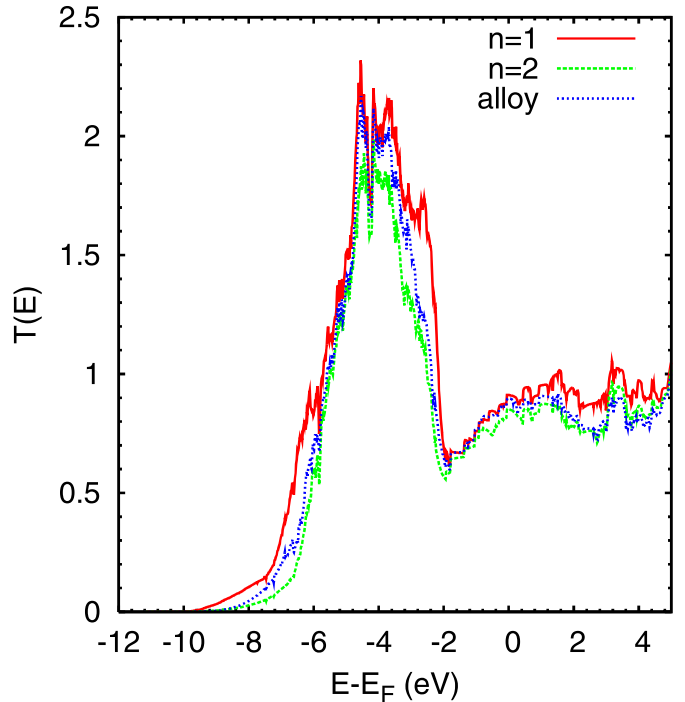


Fig. 6: (Color online) Transmission coefficient of the interface alloy, as compared to the $n = 1$ and $n = 2$ interlayer systems.

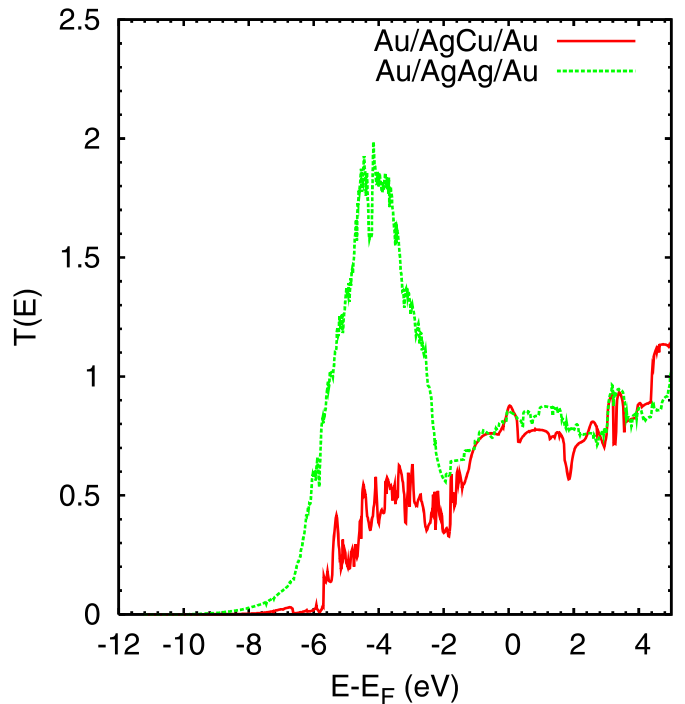


Fig. 7: (Color online) Transmission coefficient of the heterostructure, as compared to the $n = 2$ interlayer system.

back to the additional impurities, and, analogously, is higher than for a double Ag layer. Moreover, it is worth mentioning that the alloy formation affects $T(E)$ almost uniformly in the studied energy range.

As seen before, the electronic structure of the impurity/interlayer material strongly influences $T(E)$. This

becomes even more critical when multiple interlayers of different materials are considered, as we shall demonstrate for the Au/AgCu/Au heterostructure, which we compare to the Au/AgAg/Au heterostructure in fig. 7. Since the conductance is reduced neither for the Au/AgAg/Au heterostructure nor for a single Cu interlayer, see fig. 4, it is not surprising that the conductance of the two-component interlayer system also resembles the Au host. The suppression of the transmission below -2 eV is due to the narrow Cu $3d$ bands, see our earlier discussion. It is even larger than for a single Cu interlayer, since the Ag-Cu interface results in a further localization of these states. The shape of $T(E)$ of the two-component interlayer system again can be interpreted as a superposition of the component effects.

Conclusion. – In conclusion, our results demonstrate that non-metallic impurities alter the electronic transport similar to simple vacancies, since they do not contribute to the electronic states at the Fermi energy. In the case that an impurity, interlayer, or interface alloy resembles the Au electronic structure, its incorporation alters the transmission only marginally. However, when distinct bonds are formed between the contaminant and the Au host the transmission can be strongly affected. For Ni impurities, the Au s - d hybridization is suppressed in the vicinity of the Fermi energy due to the formation of d - d hybrid states. The transmission coefficient thus decreases by a factor of four. We find only a minor interdependence between multiple modifications, *i.e.* their cumulative effect is well described in terms of a superposition of the individual effects. This paves the way for tailoring the energy dependence of the transmission coefficient.

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