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Work functions of self-assembled monolayers on metal surfaces by first-principles calculations

Paul C. Rusu and Geert Brocks
Computational Materials Science, Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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Using first-principles calculations we show that the work function of noble metals can be decreased or increased by up to 2 eV upon the adsorption of self-assembled monolayers of organic molecules. We identify the contributions to these changes for several (fluorinated) thiolate molecules adsorbed on Ag(111), Au(111), and Pt(111) surfaces. The work function of the clean metal surfaces increases in this order, but adsorption of the monolayers reverses the order completely. Bonds between the thiolate molecules and the metal surfaces generate an interface dipole, whose size is a function of the metal, but it is relatively independent of the molecules. The molecular and bond dipoles can then be added to determine the overall work function.

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Recent advances in molecular electronics, where organic molecules constitute active materials in electronic devices, have created a large interest in metal organic interfaces.[1] Transport of charge carriers across the interfaces between metal electrodes and the organic material often determines the performance of a device.[2] Organic semiconductors differ from inorganic ones as they are composed of molecules, and intermolecular forces are relatively weak. In a bulk material this increases the importance of electron–phonon and electron–electron interactions.[3] At a metal organic interface the energy barrier for charge carrier injection into the organic material is often determined by the formation of an interface dipole localized at the first molecular layer. The interface dipole can be extracted by monitoring the change in the metal surface work function after deposition of an organic layer.[1,4]

Atoms and molecules that are physisorbed on a metal surface usually decrease the work function, as the Pauli repulsion between the molecular and surface electrons decreases the surface dipole.[5,6] Chemisorption can give an increase or a decrease of the work function, and can even lead to counterintuitive results.[7,8] Self-assembled monolayers (SAMs) are exemplary systems to study the effect of chemisorbed organic molecules upon metal work functions.[9] More specifically, alkyl thiolate ($C_nH_{2n+1}S$) SAMs on the gold (111) surface are among the most extensively studied systems.[10–14] The sulfur atoms of the thiolate molecules form stable bonds to the gold surface and their alkyl tails are close packed, which results in a well-ordered monolayer. SAMs with similar structures are formed by alkyl thiolates on a range of other (noble) metal surfaces.[10,14,15]

Often the change in work function upon adsorption of a SAM is interpreted mainly in terms of the dipole moments of the individual thiolate molecules, whereas only a minor role is attributed to the change induced by chemisorption.[9,11,12,16] This assumption turns out to be reasonable for adsorption of methyl thiolate (CH_3S) on Au(111),[13] but for CH_3S on Cu(111) it is not.[14] In this paper we apply first-principles calculations to study the interface dipoles and the work function change induced by adsorption of thiolate SAMs.

In particular, we analyze the contributions of chemisorption and of the molecular dipoles to uncover the effects of charge reordering at the interface. The chemical bonds between the thiolate molecules and the metal surfaces generate an interface dipole. We find that this dipole strongly depends upon the metal, but it is nearly independent of the electronegativity of the molecules. The size and direction of the interface dipole are such that it overcompensates for the difference between the clean metal work functions. This results in the SAM adsorbed on the highest work function metal having the lowest work function and vice versa. Modifying the molecular tails allows one to vary the absolute size of the work function over a range of more than 2 eV.

Since alkyl thiolate molecules form SAMs with a similar structure on (111) surfaces of several noble metals, they are ideal model systems for studying metal organic interfaces. By varying the relative electronegativity of surface and molecules one can induce electron transfer and create an interface dipole, without completely rearranging the interface structure. The electronegativity of a metal substrate is given by its work function. We consider the (111) surfaces of three metals that have a substantially different work function, but the same crystal structure and a similar lattice parameter: Ag (4.5 eV, 2.89 Å), Au (5.3 eV, 2.88 Å) and Pt (6.1 eV, 2.77 Å).

One would also like to vary the molecule's electronegativity without changing the structure of the SAM. This can be achieved by fluorinating the alkyl tails of thiolate molecules, which increases their electronegativity.[10] However, fluorinating the alkyl tails also reverses the polarity of the thiolate molecules and one has to separate this electrostatic effect from the charge reordering caused by chemisorption. In this paper we study the short chain thiolates CH_3S, C_2H_5S, CF_3S, and CF_3CH_2S.

Density functional theory (DFT) calculations are carried out using the projector augmented wave (PAW) method,[17,18] a plane wave basis set, and the PW91 generalized gradient approximation (GGA) functional, as implemented in the VASP program.[19,20] We use supercells containing a slab of at least five layers of metal atoms with a SAM adsorbed on one side of the slab and a vacuum region of ∼12 Å. The Brillouin zone of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface unit cell is sampled by a 11×11 **k**-point grid. The plane wave kinetic energy cutoff is 450 eV. To avoid interactions between periodic im-

TABLE I. Calculated work functions W (eV) of clean (111) surfaces and of surfaces covered by SAMs in a $(\sqrt{3}\times\sqrt{3})\mathrm{R}30°$ structure.

	Clean	CH_3S	C_2H_5S	CF_3S	CF_3CH_2S
Ag	4.50	3.95	4.13	6.14	6.30
Au	5.25	3.81	3.93	5.97	6.27
Pt	5.84 (6.14[a])	3.45	3.47	5.68	5.87

[a] LDA value.

ages of the slab we apply a dipole correction.[21] The geometry of the SAM is optimized, as well as the positions of the top two layers of metal atoms. The atoms in the remaining metal layers are fixed at their bulk positions. The optimized bulk lattice parameters are 2.93, 2.94, and 2.79 Å for Ag, Au, and Pt, respectively.

The work function is given by $W=V(\infty)-E_F$, where $V(\infty)$ is the asymptotic electrostatic potential in vacuum, and E_F is the Fermi energy of the bulk metal. $V(\infty)$ is extracted from the plane-averaged potential $\bar{V}(z)=A^{-1}\int\int_A V(x,y,z)dxdy$, with A the area of the surface unit cell. In practice, $\bar{V}(z)$ reaches an asymptotic value within a distance of 5 Å from the surface. Accurate values of the Fermi energy are obtained following the procedure outlined in Ref. 22. By varying the computational parameters discussed above we estimate that the work functions are converged to within 0.05 eV. Typically DFT calculations give work functions that are within ~0.1 to 0.2 eV of the experimental values, although occasionally somewhat larger deviations are found.

The $(\sqrt{3}\times\sqrt{3})\mathrm{R}30°$ structure of CH_3S on Au(111) has been studied in several first-principles calculations.[13,14,23–25] We find basically the same optimized geometry as obtained in those calculations. Several structures exist that have a slightly different geometry, but are very close in energy, such as a $c(4\times2)$ superstructure.[24] We find that the work functions of these structures are within 0.1 eV of that of the simpler structure, so we will not discuss these superstructures here.

The $(\sqrt{3}\times\sqrt{3})\mathrm{R}30°$ structure is also a good starting point for studying other systems. Thiolates with longer alkyl tails on Au(111) adopt this structure, as does CH_3S on Pt(111), as well as alkyl thiolates on Au(111) whose end groups are fluorinated.[10,15] Thiolates with long alkyl tails on Ag(111) form a somewhat denser packing, whereas long fluorinated alkyl thiolates form a somewhat less dense packing.[10] To analyze the work function we use optimized $(\sqrt{3}\times\sqrt{3})\mathrm{R}30°$ structures for all our SAMs. We find that varying the packing density only introduces a scaling factor to the work function change.[13]

Table I lists the calculated work functions. The work functions of the clean Au and Ag surfaces agree with the experimental values,[26,27] but that of Pt is ~0.3 eV too low.[28] The latter can be attributed to the GGA functional. Using the local density approximation (LDA) the calculated work function of Pt(111) is 6.14 eV, which agrees with experiment. In other cases the difference between the work functions calculated with GGA and LDA functionals is much smaller. For instance, the GGA and LDA work functions of the SAMs on Pt are within 0.02 eV of one another. We will use the GGA values throughout this paper. The trend in the work functions of the SAM covered surfaces agrees well with experimental observations.[9,11,12] The experimental work function shifts with respect to the clean surface are sometimes somewhat smaller than the calculated ones.[29]

The first observation one can make by comparing the numbers in Table I within columns is that on SAM covered surfaces the work function *decreases* in the order Ag, Au, Pt. This is striking, since the work function of the clean metal surfaces clearly *increases* in this order. Second, comparing the numbers within rows one finds that the work functions of the fluorinated alkyl thiolate covered surfaces are 2–2.5 eV higher than of the nonfluorinated ones. We will argue that the first observation can be ascribed to the interface dipole formed upon chemisorption. This interface dipole is independent of the molecular tails. The second observation will be interpreted in terms of the individual molecular dipoles.

In order to visualize the charge reordering at the surface upon adsorption of the SAM, we calculate the difference electron density Δn. It is obtained by subtracting from the total electron density n_{tot} of the SAM on the surface, the electron density n_{surf} of the clean surface, and that of the free standing SAM n_{SAM}. n_{surf} and n_{SAM} are obtained in two separate calculations of a clean surface and a free standing SAM, respectively, with their structures frozen in the adsorbed geometry. As an example, Fig. 1 shows Δn for SAMs of CF_3S and CH_3S on Ag(111).

Figure 1 illustrates that Δn is localized mainly at the metal-SAM interface, i.e., near the sulfur atoms and the metal atoms in the first surface layers. In case of adsorption on Ag, electrons are transferred from the metal to the molecule, which results in an increase of the electron density on the sulfur atoms and a decrease on the surface metal atoms. The charge transfer does not depend strongly on the molecule, compare Figs. 1(a)–1(d). This is somewhat surprising since the electronegativity of CF_3S is much higher than that of CH_3S.

Very often a charge transfer between two systems is interpreted in terms of their relative electronegativity. For a metal surface the latter is simply the work function W_{clean}. For a molecule the Mulliken electronegativity χ_M is defined as the average of the ionization potential and the electron affinity and considered to be the molecular equivalent of a chemical potential.[30] We find $\chi_M=5.4$ eV for the CH_3S and CH_3CH_2S molecules. Since χ_M is close to W_{clean} for Au(111), this would explain the lack of electron transfer upon adsorption of these molecules.[13,14] However, the calculated χ_M for CF_3S and CF_3CH_2S are much higher, i.e., 6.9 and 6.1 eV, respectively. Yet this does not result in a markedly increased electron transfer to these molecules, as Fig. 1 indicates. It means that χ_M is not a generally suitable parameter to predict the amount of charge transfer between surface and molecules. χ_M reflects the relative stability of charged molecular states. In particular, for the thiolates χ_M reflects the ability of the (fluorinated) alkyl chains to stabilize or screen charge that resides on the sulfur atom. We suggest that this is not important in case of adsorbed molecules, as the metal surface takes over this role.

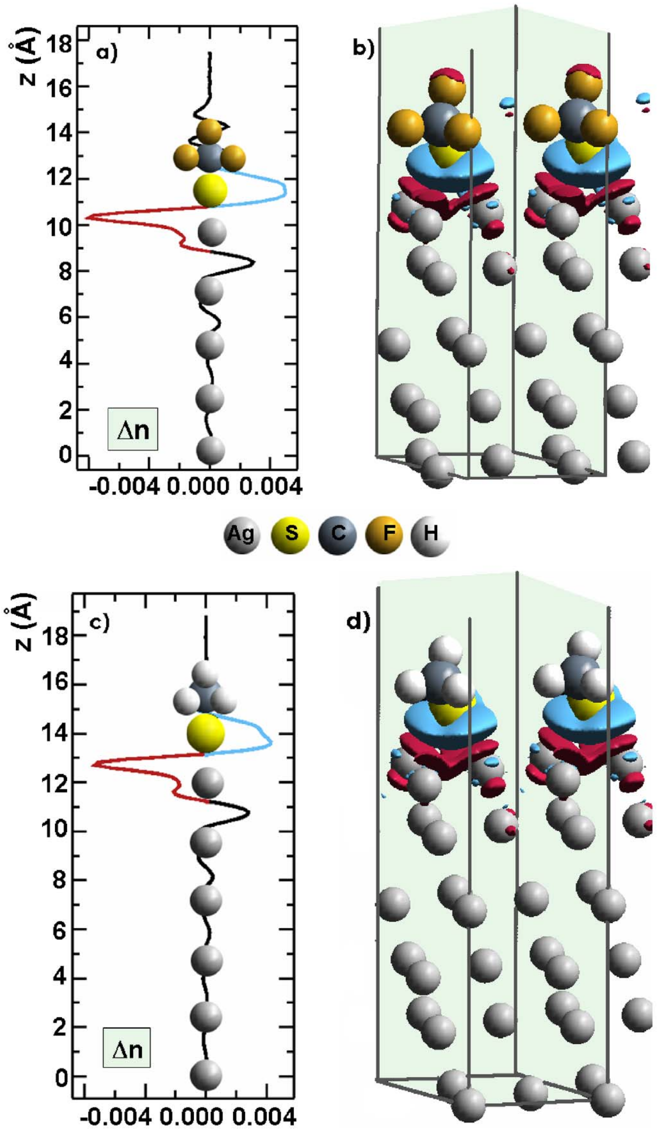

FIG. 1. (Color online) Difference electron density $\Delta n = n_{\mathrm{tot}} - n_{\mathrm{surf}} - n_{\mathrm{SAM}}$ for CF_3S on Ag(111), (a) as a function of z, averaged over the xy plane, in units of $\AA^{-3}$; (b) as an isodensity surface; and (c), and (d) the same for CH_3S on Ag(111).

Meanwhile, Fig. 1 suggests the following analysis. From the change in the work function upon adsorption of the SAM, $\Delta W = W - W_{\mathrm{clean}}$, see Table I, one can obtain the change of the surface dipole upon adsorption, $\Delta\mu = \varepsilon_0 A \Delta W / e$ (with ε_0 the permittivity of vacuum and A the area of the surface unit cell). Since the unit cell contains one molecule, $\Delta\mu$ is the change in the surface dipole per adsorbed molecule. The results are shown in Table II. $\Delta\mu$ contains contributions from the charge reordering at the interface due to chemisorption, as well as from the dipole moments of the individual molecules.

The latter can be accounted for by calculating the dipole moment μ_{SAM} per molecule of free standing SAMs, i.e., without the presence of a metal surface. We focus upon the component of the dipole that is perpendicular to the surface, since the other components do not contribute to the work function. As the calculation uses a full monolayer of molecules, it incorporates the effect on each molecule of the depolarizing field caused by the dipoles of all surrounding molecules. The calculated μ_{SAM} are given in Table II. The structure of a SAM is fixed in its adsorption geometry, which is similar for the three metal surfaces. Therefore the μ_{SAM} values for adsorption on Ag, Au, and Pt in Table II differ only slightly. Of course μ_{SAM} depends upon the molecule. In CH_3S and CH_3CH_2S the dipole points from the sulfur atom to the alkyl group. The large electronegativity of fluor causes a reversal of the dipole in CF_3S and CF_3CH_2S.

We define the contribution to the interface dipole resulting from chemisorption as $\mu_{\mathrm{chem}} = \Delta\mu - \mu_{\mathrm{SAM}}$. The results shown in Table II clearly demonstrate that μ_{chem} is nearly independent of the molecule and strongly dependent on the metal substrate. As an independent check we have also calculated the dipole on the basis of the electron density redistribution, see Fig. 1, $\mu_{\Delta n} = -e \int\int\int_{\mathrm{cell}} z \Delta n(\mathbf{r}) dx dy dz$. We find that $\mu_{\Delta n} \approx \mu_{\mathrm{chem}}$, which indicates the consistency of this analysis.

The results obtained allow for a simple qualitative picture. The chemisorption dipole μ_{chem} is very small for all SAMs on Au(111), indicating that the charge transfer between the Au surfaces and the molecules is small. This generalizes previous results obtained for methyl thiolate SAMs on Au(111).[13,14] Since the work function of Ag(111) is substantially lower than that of Au(111), a significant electron transfer takes place from the surface to the molecules for SAMs on Ag. This is confirmed by the values of μ_{chem} for Ag in Table II. Figure 1 shows that the electrons are transferred mainly to the sulfur atoms. Integrating the positive peak of Δn on the sulphur atom gives a charge of $(-0.24 \pm 0.02)e$. The sign of the charge transfer is such that μ_{chem} increases the work function with respect to clean Ag(111). By a similar argument, since the work function of Pt(111) is much higher than that of Au(111), an electron transfer takes place from the molecules to the surface for adsorption on Pt. The values of μ_{chem} for Pt in Table II confirm this. In this case the net

TABLE II. Dipole per molecule $\Delta\mu$, from the change in work function upon adsorption. The (perpendicular) molecular dipole moment μ_{SAM} in a free standing SAM. The chemisorption dipole moment is $\mu_{\mathrm{chem}} = \Delta\mu - \mu_{\mathrm{SAM}}$. All values are in D.

	Ag				Au				Pt			
	CH_3S	C_2H_5S	CF_3S	CF_3CH_2S	CH_3S	C_2H_5S	CF_3S	CF_3CH_2S	CH_3S	C_2H_5S	CF_3S	CF_3CH_2S
$\Delta\mu$	−0.32	−0.22	0.97	1.07	−0.86	−0.79	0.43	0.61	−1.28	−1.27	−0.08	0.02
μ_{SAM}	−0.88	−0.79	0.44	0.50	−0.88	−0.81	0.44	0.53	−0.86	−0.80	0.37	0.47
μ_{chem}	0.56	0.57	0.53	0.57	0.02	0.02	−0.01	0.08	−0.42	−0.47	−0.45	−0.45

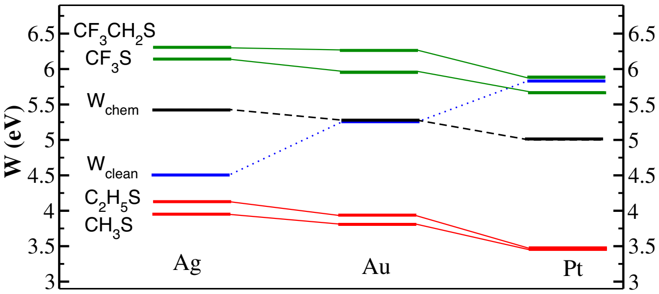

FIG. 2. (Color online) Work functions W_{clean} of the clean surfaces, W_{chem} of the surfaces including the chemisorption dipole, and of the SAM covered surfaces.

charge on the sulphur atom is positive and μ_{chem} decreases the work function with respect to clean Pt(111).

The size of the charge transfer is remarkable. Chemisorption creates an interface dipole μ_{chem} that overcompensates for the difference between the metal work functions. We define a work function that includes the contribution from the chemisorption dipoles as $W_{\text{chem}}=W_{\text{clean}}+e\mu_{\text{chem}}/(\varepsilon_0 A)$. The results shown in Fig. 2 demonstrate that W_{chem} decreases in the order Ag, Au, and Pt, whereas W_{clean} increases in that order. The work function of the SAM covered surfaces can then be expressed as $W=W_{\text{chem}}+e\mu_{\text{SAM}}/(\varepsilon_0 A)$. From the polarity of the molecules discussed above, it is clear that SAMs of CH_3S and CH_3CH_2S decrease the work function, whereas SAMs of CF_3S and CF_3CH_2S increase it.

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[29] This could be due to a number of reasons. The experiments are not performed in UHV, which might introduce impurities. Moreover, since in experiment longer molecules with a larger polarizability are used, the effect of the depolarizing field of the molecular dipoles is larger, which reduces the interface dipole.

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