Absorption geometry and interfacial properties for CH_3SH self assembled on Cu(110)

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Introduction

With the aim to characterize the real nature of the S-Cu bond and to shed light on the interfacial electrostatics for a copper surface, an *ab initio* study has been carried out for CH_3SH self-assembled on a Cu(110) substrate. Theoretical results suggest that the binding of the adsorbate to the substrate is rather weak and that the molecular structure is correspondingly almost unaffected by the adsorption on metal. Otherwise, when CH_3SH decomposes by deprotonation producing methanethiolate, stronger chemical bonds appear between sulfur of CH_3S-radical and the outer Cu atoms. Therefore for a p(2x2) and a c(2x2) CH_3S coverage, a detailed analysis on the relaxed geometries has been necessary to elucidate the electronic properties at the interface. By studying the partial density of states (PDOS) and the electrons dislocations in the real space, a strong hybridization among *p*-orbitals of sulfur and *d*-states from the metal substrate was deduced. Work function variations of CH_3S/Cu(110) were also monitored when the coverage changes between 0 ML and 0.5 ML.

Theory and Computational Details

Calculations were executed in the framework of Density Functional Theory using the Generalized Gradient Approximation (GGA) in the Perdew-Burke-Ernzerhof parametrization[1]. Atoms were described by Ultrasoft Pseudopotentials[2] with a kinetic energy cutoff of 35 Ryd. The Fermi energy was calculated using the Gaussian Broadening technique[3], with a smearing parameter of 0.05 Ryd. To study the molecule-substrate interaction, the cubic lattice constant (3.67 Å) was optimized by minimizing the total energy of the bulk Cu and the Cu(110) surface was modeled by a 7 Cu-layers and 10 vacuum layers (13 Å) supercell with a 2x2 surface unit cell (Fig. 1). The Brillouin-zone (BZ) integration was executed with a 8x8x1 Monkhorst-Pack[4] mesh, corrisponding to 16 k-points in the irreducible SBZ. All calculations were performed with the PWSCF code[5] and all the figures were realized by the XCRYSDEN graphical package[6].

Relaxed Geometries

Section I: Dissociation of the molecule

It is experimental known[7-9] that the adsorption of methanethiol on the clean Cu(110) surface is characterized by the formation, through the S-H bond cleavage, of an adsorbed mercaptide.

TOP VIEW   **LATERAL VIEW**

(Eb=0.96 eV)

Fig. 1
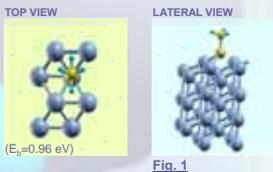
The same result has been obtained by relaxing the CH_3SH-surface system[10]. What we noticed was that if for methanethiol the binding to surface is rather weak (physisorption), larger adsorption enegies and smaller bond lengths appear (chemisorption) when the molecule dissociates (as in Fig. 1), yielding H and CH_3S.

Section II: Adsorption geometries for methanethiolate

For the methanethiolate a wide study of adsorption configurations has been performed[10]. For the CH_3S/Cu(110) system, both p(2x2) and c(2x2) geometries have been analyzed: energies and structural parameters obtained for the most stable configurations ("shortbridge" site in Fig. 2-3) for the two coverages (with an initial S-surface distance of 1.2 Å) are here reported in Tables I and II.

p(2x2)

$$E_b = \left(E_{Cu(110)} + E_{(CH_3S)_2}/2\right) - E_{CH_3S/Cu(110)}$$

Fig. 2

Initial Geometry	E_b(eV)	d_{Cu-S}(Å)	h(Å)	α	β	δ(Å)	Δd_x	Δd_y	Δd_z
S/0˚	1.064	2.29	1.69	41˚	270˚	1.01	+1%	+8%	+8%

Tab. I

c(2x2)

$$E_b = \left[\left(E_{Cu(110)} + E_{(CH_3S)_2}\right) - E_{CH_3S/Cu(110)}\right]/2$$

Fig. 3

Initial Geometry	E_b(eV)	d_{Cu-S}(Å)	h(Å)	α	β	δ(Å)	Δd_x	Δd_y	Δd_z
S/0˚	1.144	2.26	1.76	56˚	270˚	0.53	+1%	+1%	+9%

Tab. II

Electronical properties

For the analysis of the electronical properties of the most stable configurations found for both chemisorption and physisorption, we used the electronic charge density difference[10].
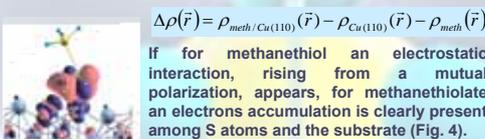

$$\Delta\rho(\vec{r}) = \rho_{meth/Cu(110)}(\vec{r}) - \rho_{Cu(110)}(\vec{r}) - \rho_{meth}(\vec{r})$$

If for methanethiol an electrostatic interaction, rising from a mutual polarization, appears, for methanethiolate an electrons accumulation is clearly present among S atoms and the substrate (Fig. 4).

Fig. 4

To highlight the real nature of the bond, then, we studied the modification induced on the *d*-PDOS of the Cu surface atoms (black line) by the CH_3S adsorption. Results show that, respect to the clean Cu(110) (red dashed line in Fig. 5), new states appear at the upper edge of the *d*-Cu band, at -1 eV, and the density of states increases at -3÷-4 eV and decreases around -2 eV.

Comparing this analysis with the density of states associated to sulfur and carbon atoms (respectively the red line and the blue dashed line in Fig. 6) we can attribuite the observed variations in the copper properties to the presence of sulfur *p*-states (both at -1 eV and also at -3÷-4 eV).
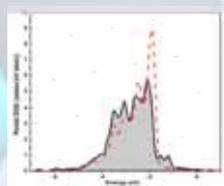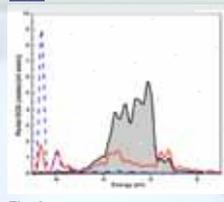
Fig. 5

Fig. 6

Work function behaviour

This adsorption of sub-monolayers of covalently bound molecules on Cu(110) has been further analyzed to understand the energetics of such kind of systems at the surface. Within the DFT-GGA approximation, the electrostatic potentials and then the work function values, obtained as the difference between the electrostatic potential in the vacuum region V_{ES} and the Fermi energy for the bulk material E_F,

$$\Phi = V_{ES} - E_F$$

have been calculated for the most stable configurations obtained of the p(2x2) and the c(2x2) coverages, corrisponding respectively to 0.25 Monolayer (ML) and 0.5 ML. Reported results, which are also visualized in Fig. 7, are:

- clean Cu(110):   4.42 eV
- CH_3S/Cu(110), p(2x2): 3.06 eV
- CH_3S/Cu(110), c(2x2): 3.19 eV

Trend of Φ with coverage θ
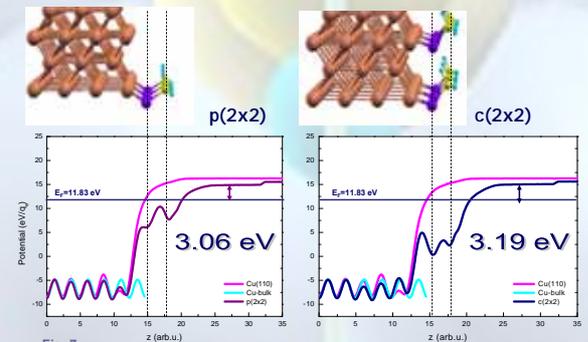

p(2x2)   c(2x2)

3.06 eV   3.19 eV

Fig. 7

By reporting these results in a graph we can observe an evident Φ non-linear decrease at increasing coverage (Fig. 8). This effect can be explained by applying the *Topping Model*[11] according to which the change in the work function is given by the formula

$$e\Delta\Phi = \pm\frac{e}{\varepsilon\varepsilon_0}Pn_{dip}\left(1+\frac{9\alpha}{4\pi}n_{dip}^{3/2}\right)^{-1}$$

where n_{dip} is the dipole density, *P* is the electric dipole moment, ε_0 is the vacuum permittivity and α is the molecule polarizability. In the low-coverage regime ($ndip \ll 1$) the most im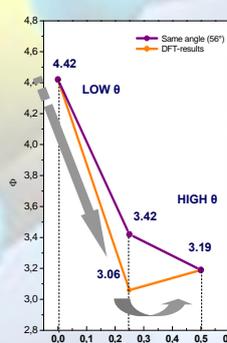portant contribution is due to the intrinsic molecular dipole which in this case is negative ($\mu_{mol} < 0$) so the variation can be reproduced through the simple Helmholtz equation.

On the contrary for higher coverages the depolarization effects due to the dipole-dipole electrostatic interaction (strongly dependent from the adsorption geometry, Fig. 8) become to appear and to reduce the entity of the work function variation $\Delta\Phi$.

56˚   41˚

LOW θ   HIGH θ

4.42   3.42   3.19   3.06

Fig. 8

Conclusions

In this work the structural and the electronic properties of methanethiolate chemisorbed on Cu(110) have been analyzed for two coverages. We have identified the shortbridge site, with an angle from the normal to surface, respectively of 41˚ and 56˚ for the p(2x2) and c(2x2) phase, as the most stable adsorption geometries (excluding the lying-down configuration proposed by Lee et all[9]). Moreover we have found that the 0.5 ML coverage gives the highest methanethiolate binding energy, confirming the observed stability of the c(2x2) phase. The electronic analysis has revealed that the main molecule-surface interactions can be considered due to a strong hybridization among *p*-orbitals of sulfur and *d*-states from the substrate, confirming the importance of S in the chemisorption of such kind of organic adsorbates on the (110) copper surface. A study on work function (Φ) variations proves an evident Φ non-linear decrease at increasing coverage and this can be explained by the negative molecular dipole together with the mutual depolarization effects.

References

[1] P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[2] M. C. Payne, M. P. Teter, D. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. 64, 1045 (1992).
[3] M. Methfessel and A. T. Paxton, Phys. Rev. B 40, 3616 (1989).
[4] C. J. Fall, N. Binggeli, and A. Baldereschi, Phys. Rev. B 61, 8489 (2000).
[5] S. Baroni, A. Dal Corso, S. De Gironcoli and P. Giannozzi, http://www.pwscf.org/, (2001).
[6] A. Kokalj, Comput. Mater. Sci. 28, 155 (2003). Code available from http://www.xcrysden.org/.

[7] A. F. Carley, P. R. Davies, R. V. Jones, K. R. Harikumar, M. Wyn Roberts, and C. J. Welsby, Top. Catal. 22, 161 (2003).
[8] A. F. Carley, P. R. Davies, R. V. Jones, K. R. Harikumar, G. U. Kulkarni, and M. W. Roberts, Surf. Sci. 447, 39 (2000).
[9] J. G. Lee and J. T. Yates, J. Phys. Chem. B 107, 10540 (2003).
[10] S. D'Agostino, L. Chiodo, F. Della Sala, R. Cingolani, R. Rinaldi, Phys. Rev. B 75, 195444 (2007).
[11] J. Topping, Proc. R. Soc. London, Ser A 144, 67 (1927).

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