University of Nebraska - Lincoln
DigitalCommons@University of Nebraska - Lincoln

Peter Dowben Publications | Research Papers in Physics and Astronomy

5-1-2003

Substrate Dependent Bonding of Chemisorbed 1,1'-Biphenyl-4,4'-Dimethanethiol

A.N. Caruso
University of Nebraska - Lincoln

R. Rajesekaran
University of Nebraska - Lincoln

Jody Redepenning
University of Nebraska-Lincoln, jredepenning1@unl.edu

Ya.B. Losovyj
University of Nebraska - Lincoln

Peter A. Dowben
University of Nebraska-Lincoln, pdowben@unl.edu

Follow this and additional works at: http://digitalcommons.unl.edu/physicsdowben

Part of the Physics Commons

Caruso, A.N.; Rajesekaran, R.; Redepenning, Jody; Losovyj, Ya.B. ; and Dowben, Peter A., "Substrate Dependent Bonding of Chemisorbed 1,1'-Biphenyl-4,4'-Dimethanethiol" (2003). *Peter Dowben Publications.* Paper 170.
http://digitalcommons.unl.edu/physicsdowben/170

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Peter Dowben Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Substrate Dependent Bonding of Chemisorbed 1,1'-Biphenyl-4,4'-Dimethanethiol

A.N. Caruso,[1] R. Rajesekaran,[2] J. Redepenning,[2] Ya.B. Losovyj,[1,3] and P. A. Dowben*[1]

[1]Department of Physics and Astronomy and the Center for Materials Research and Analysis, Behlen Laboratory of Physics, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0111
[2]Department of Chemistry, Hamilton Hall, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0304
[3] Center for Advanced Microstructures and Devices, Louisiana State University, 6980 Jefferson Highway, Baton Rouge, LA 70806

ABSTRACT

We compare the adsorption of 1,1'-biphenyl-4,4'-dimethanethiol (BPDMT) on gold and cobalt surfaces. The molecular orbitals, identified from combined photoemission and inverse photoemission studies, exhibit shifts in binding energies with different deposition methods and substrates. These shifts indicate that this potential molecular dielectric exhibits stronger bonding to cobalt surfaces than gold surfaces.

INTRODUCTION

In particular, the molecular orientation of thiols and bonding of "self-assembled" layers of alkanethiols has attracted much attention over the last two decades [1-9], and have been thought to be effective dielectric barrier layers [10,11]. Unfortunately, a bonding configuration with the molecular axis tilted 20-30° off the surface normal has be commonly identified for many alkanethiols [1,4,12], though a planar orientation is observed for films formed from the vapor [9]. Bibenzyl and biphenyl like thiols have been similarly investigated for device applications [12-14] but with some uncertainty concerning molecular orientation [4,15].

Most studies that have addressed the orientation and bonding have not actually exploited valence band photoemission and conduction band inverse photoemission, so that the influence of the substrate electron structure on the orientation and bonding has not been directly investigated [4]. If organic barriers are to be used to replace Al_2O_3 as a dielectric barrier in junction magneto-resistive devices, the interactions of the molecular dielectrics must be undertaken with ferromagnetic substrates and compared to the number of studies have been carried out on noble metal substrates (copper, gold and silver). To address this deficiency, we compare the adsorption of 1,1'-biphenyl-4,4'-dimethanethiol (BPDMT) on gold with the adsorption of 1,1'-biphenyl-4,4'-dimethanethiol (BPDMT) on cobalt from the vapor, as well.

EXPERIMENTAL DETAILS

All valence band photoemission were taken at the Center for Advanced Microstructure and Devices synchrotron in Baton Rouge, LA from light dispersed by a 3-meter Toroidal Grating Monochromator with electrons collected by a hemispherical analyzer. The electronic structure of the unoccupied states or conduction bands were determined by inverse photoemission. Electron collection (or incidence in inverse photoemission) was always normal to the surface ($\overline{\Gamma}$) to preserve the highest possible symmetry and the binding energies are referenced to the substrate Fermi level. The inverse photoemission studies were completed by variable incident electron

energy method, measuring photon emission by Geiger-Müller detector with a SrF_2 window, with a pass energy of 9.5 eV.

The synthesis of [1,1'-biphenyl]-4,4'-dimethanethiol was performed at atmospheric pressure under nitrogen. A 1.0 g (2.9 mmol) sample of 4,4'-bis(bromomethyl) biphenyl (TCI America) and 0.5 g (6.6 mmol) of thiourea (Aldrich) were added to 100 mL of anhydrous ethanol in a 250 mL round bottom flask fitted with a reflux condenser. The mixture was allowed to reflux under nitrogen for approximately 19 hours. A 1 mL aliquot of a 10 mol KOH solution was then added to the flask and the reaction mixture was refluxed for an additional 5 hours. At the end of this time, the reaction mixture was acidified with 1.5 mol HCl and then evaporated to dryness. After being extracted from the inorganic salts with methylene chloride, the crude product was recrystallized from hot ethanol.

Depositions of BPDMT, for reference, were undertaken by a deposition from solution method on Au/Si (111) and by adsorption, from the vapor, on both Co/Au/Si (111) and Au/Si(111) substrates. Vapor deposition was undertaken on substrates cooled to –180 C° (93 K).

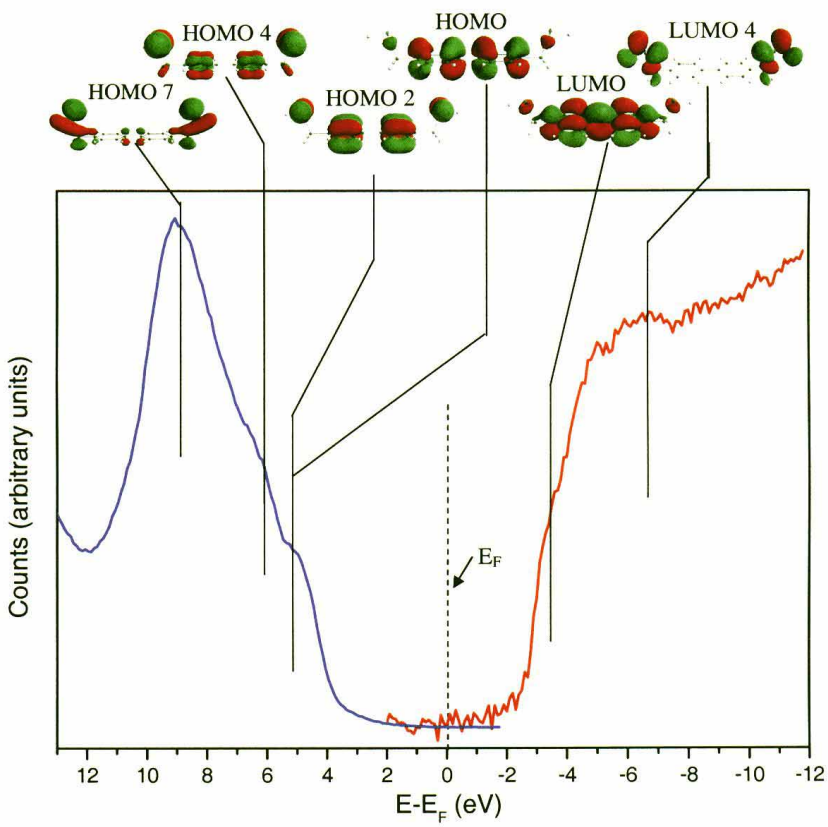

Figure 1. Occupied (blue) and unoccupied (red) molecular orbitals of [1,1'-biphenyl]-4,4'-dimethanethiol are indicated in the photoemission (left) and inverse photoemission (right) spectra. The BPDMT thin films were deposited from solution on Au(111) thin films and the molecular film thickness is more than three molecules in thickness.

The deposition from solution was based on the Gölzhäuser method [16] through which the 'self-assembled monolayers" are produced by immersing the Au coated Si(111) in a degassed solution of 15 mmol 4,4` bibenzyldithiol in N,N-dimethylformamide (DMF) for 72 hours. After this

period the samples were soaked for 10 minutes in DMF and for two minutes in ethanol. This new approach to depositing BPDMT from solution is a less caustic method of deposition than prior methods.

DISCUSSION

A number of the molecular orbitals of BPDMT can be identified in both photoemission and inverse photoemission, as indicated in Figure 1. For the thicker films, deposited from solution, the gold substrate photoemission and inverse photoemission features are completely

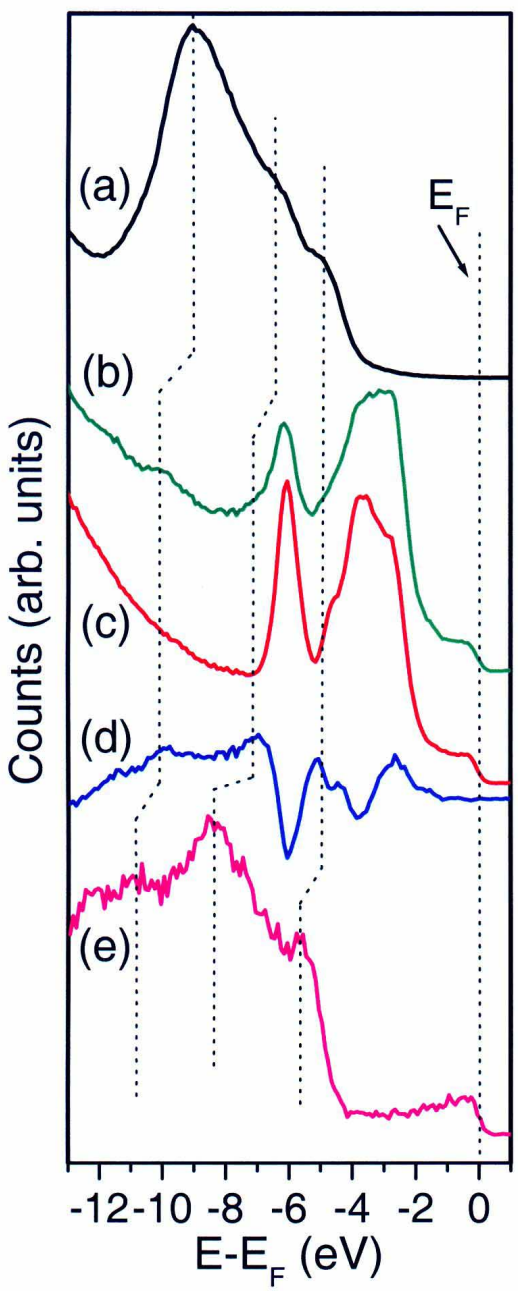

Figure 2. Spectra of 1,1'-biphenyl-4,4'-dimethanethiol deposited from the vapor on thin film gold (e) and cobalt (b) substrates compared with the thicker 1,1'-biphenyl-4,4'-dimethanethiol films deposited from solution on gold thin films (a). The spectra were taken at a photon energy of 32 eV with s+p polarized light. The photoemission spectra of clean gold (c) is shown for comparison with the film after 1,1'-biphenyl-4,4'-dimethanethiol adsorption. The 1,1'-biphenyl-4,4'-dimethanethiol molecular orbitals can be identified in the difference spectrum (adsorbate minus clean gold substrate photoemission spectra) shown in (d). Lines to indicate the Fermi level and the principal 1,1'-biphenyl-4,4'-dimethanethiol molecular orbital photoemission feature shifts have been drawn to guide the eye.

suppressed. The expected molecular orbitals of 1,1'-biphenyl-4,4'-dimethanethiol can be observed in the combined photoemission/inverse photoemission spectra. The chemical potential adjusts to place the Fermi level, approximately, in the middle of the highest occupied molecular orbital (HOMO) to lowest molecular orbital (LUMO) gap. As seen in Figure 1, one can directly observe an insulator-like band gap of ~5.5 eV.

With adsorption from the vapor, the substrate gold photoemission features are only weakly suppressed, indicating that the BPMDT film is much thinner than that formed by deposition from solution. For BPMDT deposited on cobalt, there is more suppression of the substrate cobalt features, with only the Co 3d bands evident near the Fermi level.

By comparing spectra for 1,1'-biphenyl-4,4'-dimethanethiol, differences in the molecular orbitals can be observed. In some cases, the molecular orbitals of very thin films are better identified in difference spectra (spectra taken after adsorption, with the photoemission spectra of the clean metal substrate subtracted). As can be seen in Figure 2, thin molecular films of 1,1'-biphenyl-4,4'-dimethanethiol (about 1 molecule thick), formed by vapor deposition, exhibit molecular orbitals binding energies that strongly depend upon substrate.

Table 1.

Orbital	Symmetry[a]	Thick BPMDT[b]	BPMDT on gold	BPMDT on cobalt
LUMO+4 LUMO+3 LUMO+2	a_1 b_1 a_2	6.6	-	-
LUMO+1 LUMO	b_2 a_1	3.4	-	-
HOMO	b_1	-4.4	-4.7	-5.6
HOMO+1 HOMO+2	a_2 b_2	-5.1	-5.3	-
HOMO+3 HOMO+4 HOMO+5	a_2 b_2 a_1	-6.4	-7.1	-8.4
HOMO+6 HOMO+7	b_1 a_1	-9.0	-10	-10.8

Table 1. Binding energies (in eV) of the molecular orbitals of BPMDT on gold and cobalt referenced to thicker BPMDT films (b) deposited on gold from solution. The molecular orbitals have been assigned using a molecular symmetry of C_{2v}, which is probably not applicable to the adsorbed molecule. Occupied molecular orbitals (negative values of binding energy ($E-E_F$) or below the Fermi level) were abstracted from photoemission spectra at several different photon energies, and difference spectra (where appropriate) while unoccupied molecular orbitals were derived from inverse photoemission spectra (positive values of binding energy ($E-E_F$) or above the Fermi level)

The molecular orbitals binding energies for vapor deposited 1,1'-biphenyl-4,4'-dimethanethiol layers on gold thin films and cobalt thin films have been abstracted from photoemission and inverse photoemission and compared to the reference (thicker) thin films of 1,1'-biphenyl-4,4'-dimethanethiol formed by deposition from solution, as described above. This is summarized in Table 1.

While for thin films and thicker films of 1,1'-biphenyl-4,4'-dimethanethiol adsorbed on gold, the binding energies differ a little, with slightly greater binding energies observed with the thinner films, the differences of the molecular binding energies between 1,1'-biphenyl-4,4'-dimethanethiol (BPMDT) adsorbed from the vapor on Au and Co are evident. The far greater binding energies are observed with 1,1'-biphenyl-4,4'-dimethanethiol on cobalt. The increased molecular binding energies for BPDMT films on cobalt, particularly close to the Fermi level, are clear evidence that this biphenyl-dithiol forms a stronger bond on cobalt, the more reactive metal substrate, than to gold. This is an initial state effect not a final state effect.

CONCLUSIONS

We found the bond strength of 1,1'-biphenyl-4,4'-dimethanethiol on cobalt is far larger than that observed for 1,1'-biphenyl-4,4'-dimethanethiol adsorbed on gold by two different methods. The density of states, resulting from the molecular thin film, is very low in the vicinity of several eV of the Fermi level, indicating that this does have the potential to form an excellent molecular dielectric layer.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research, the NSF "QSPINS" MRSEC (DMR 0213808), Petroleum Research Fund administered by the ACS.

REFERENCES

1. A. Ulman, *Chemical Reviews* **96**, 1533-1554 (1996)
2. G.E. Poirier, *Chemical Reviews* **97**, 1117-1127 (1997)
3. L.H. Dubois, R.G. Nuzzo, *Annual Review of Physical Chemistry* **43**, 437-463 (1992)
4. P.A. Dowben, Jaewu Choi, E. Morikawa and Bo Xu, in: Handbook of Thin Films, edited by H.S. Nalwa, Volume 2: Characterization and Spectroscopy of Thin Films, Chapter 2 (Academic Press, 2002) pp. 61-114
5. N. Camillone III, T. Y. B. Leung and G. Scoles, *Surface Science* **373**, 333 (1997).
6. N. Camillone III, P. Eisenberger, T.Y.B. Leung, P. Schwartz, G. Scoles, G.E. Poirier and M. J. Tarlow, *J. Chem. Phys.* **101**, 11031 (1994).
7. N. Camillone III, B.T.Y. Leung and G. Scoles, *SPIE Proceedings*, LASE 2125(1994).
8. N. Camillone , C.E.D. Chidsey, G.Y. Liu, T.M. Putvinski, G. Scoles, *Journal Chem. Phys.* **94**, 8493-8502 (1991)
9. F. Schreiber, A. Eberhardt, T.Y.B. Leung, P. Schwartz, S.M. Wetterer, D.J. Lavrich, L. Berman, P. Fenter, P. Eisenberger and G. Scoles, *Phys. Rev. B* **57**, 12476-12481 (1998).
10. C. Boulas, J.V. Davidovits, F. Rondelez, D. Vuillaume, *Physical Review Letters* **76**, 4797-4800 (1996)

11. J. Collet, O. Tharaud, A. Chapoton, D. Vuillaume, *Applied Physics Letters* **76**, 1941-1943 (2000)
12. A. Ulman, James E. Eilers and Nolan Tillman, *Langmuir* **5**, 1147, (1989).
13. C. Zhou, M.R. Deshpande, M.A. Reed, L. Jones, J.M. Tour, *Applied Physics Letters* **71**, 611-613 (1997)
14. J. H. Schön, H. Meng and Z. Bao, *Nature* **413**, 713, (2001).
15. J. H. Schön, H. Meng and Z. Bao, *Science* **294**, 2138, (2001).
16. W. Eck, A. Gölzhäuser, V. Stadler, W. Geyer, M. Zharnikov, and M. Grunze, *Adv. Materials* **12**, 805 (2000).
17. M. T. Cygan, T.D. Dunbar, J. J. Arnold, L. A. Bumm, N. F. Shedlock, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour, and P. S. Weiss, *J. Am. Chem. Soc.* **120**, 2721 (1998)