# Work Function Modulation with Self-assembled Monolayers: Effect of Dipole Moment on Packing Density

Nia Nurfitria[1], Yu-Tai Tao[2], Ding-Chi Huang[3]

***Abstract – A series of benzylmercaptans carrying different para-substituents were used to form self-assembled monolayers on gold in order to modulate the work funtion of the metal electrode. Ellipsometry, Reflection Absorption Infrared Spectroscopy (RAIRS), and cyclic voltametry were used to chracterized the structure of the monolayer. The results show that as the dipole moment increases in the molecule, the surface coverage decreases. This can be the reason that a more polar molecule does not necessarily generate work function change proportionally.***

***Index Terms – Work function, Self-assembled monolayer, Dipole moment.***

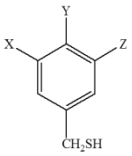
## INTRODUCTION

Organic electronics are attracting much attention in recent years. For example, flat panel displays based on Organic Light-Emitting Diodes (OLEDs) have a tremendous market, almost $50 billion in value in portable electronic devices based on OLEDs, like mobile phone, camera, laptop, etc [1]. So, improving the efficiency and performance of the OLEDs become a continued research effort and focus. In an OLED device, charge injection that occurs at the interface between the electrode and the organic layer is the first factor that needs to be addressed while study efficiency and performance of the device. Charge injection will influence the driving voltage and also the luminesence from the device [2]. A Schottky barrier present at the metal/organic interface has a big effect on the charge injection process. This barrier results from the different alignment of the electrode work function and the Highest Occupied Molecular Orbital (HOMO) for hole injection, or the Lowest Unoccupied Molecular Orbital (LUMO) for electron injection into the organic semiconductor [3]. To reduce the barrier, one can use molecule with different HOMO (LUMO) levels or metals with different work function.

Surface modification of the metal electrode with Self-Assembled Monolayer (SAM) of organic molecule has been a popular way to modulate the work function and thus change the energy barrier. The extent of work function change ($\Delta\Phi$) depends on the size and direction of dipole moment the molecule carries, as well as the number of the molecules adsorbed on the surface, as shown in equation 1.

$$\Delta\Phi = \frac{e\mu_{\perp}}{\varepsilon_0 A} \quad (1)$$

With $\varepsilon_0$ is the vacuum permitivity, $\mu_{\perp}$ is molecular dipole along surface normal and A for surface area per absorbed molecule [4]. To effect a large change of work function, molecule with larger dipole moment is favored. Nevertheless, the molecular dipole moment may also affect the assembling of the monolayer because of electrostatic repulsion between dipoles oriented in the same direction in a monolayer on substrate.




| Molecule | X | Y | Z |
|---|---|---|---|
| 1 | H | H | H |
| 2 | F | F | F |
| 3 | H | $CF_3$ | H |
| 4 | H | $SCF_3$ | H |
| 5 | H | $SO_2CF_3$ | H |

**Figure 1.** Structure of benzyl mercaptan series

In this work, benzylmercaptans carrying different para-substituents (Figure 1) were used to form self-assembled monolayers on gold. Ellipsometry, Reflection Absorption Infrared Spectroscopy (RAIRS), and cyclic voltammetry were used to characterized the structure of the monolayer. The results show that as the dipole moment increases in the molecule, the surface coverage decreases. This can be the reason that a more polar molecule does not generate work function proportionally.

## MATERIAL AND METHOD

The thiol compounds were synthesized and fully characterized in the laboratory. Reflection-absorption IR spectra were taken with a Bio-Rad FTS-60 infrared spectrometer equipped with a MCT detector. The 86° incidence angle and p-polarized were used for the measurement. Work function of the self-assembled monolayer modified gold was measured with a photoelectron spectrometer (AC-2, Riken Keiki, Japan) with an UV source.

The gold substrates were prepared by a vapour deposition of 100 nm gold (99.99%) onto freshly cleaned 1-in silicon wafer. A 10 nm chromium (99.99%) were deposited as adhesion layer before gold deposition. The thiolate monolayer was prepared by immersing the gold substrates in the ethanolic solution for 24h and then rinsing with pure ethanol before characterization.

## RESULT AND DISCUSSION

RAIRS spectra (Figure 2) and the experimental thickness (Table 1) from ellipsometry measurements proved that self-assembled monolayer succesfully adsorbed on gold surface. According to equation 1, the

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work function change should be proportional to the fraction of dipole along the surface normal. The calculation from Spartan program shows that the dipole moment for all molecules (except benzyl mercaptan) are pointing away from the anchoring sulfur group due to the electron-withdrawing nature of the substituents. The dipole moment increases in going from **2** to **5**. But, the measured work function for the monolayer-covered surface does not increase in the same order. This may have to do with number of molecules adsorbed on each sample or the size of the dipole along the surface normal.

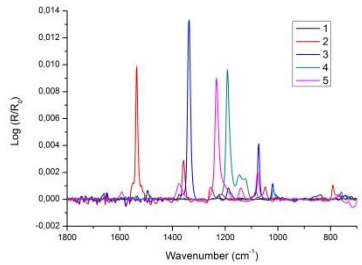


**Figure 2.** Reflection Absorption IR spectra of SAM-modified gold surfaces.

The cyclic voltammetry was used to estimate the surface coverage by integration of the areas under the reductive desorption wave in each sample (Figure 3). As can be seen from Table 2 that molecule **5** , which has highest dipole moment, has the lowest surface coverage, nearly 60% of that of the nonpolar compound **1**. Compound **3** also has low coverage. The loose coverage, presumably due to the repulsion between the neighboring dipoles, also make the adsorbed molecule more tilted away from the surface normal, making the component along the surface normal small.

**Table 1.** Thickness of various monolayers by ellipsometry.

| Molecule | Thickness Å (theoretical) | Thickness Å (experimental) |
|---|---|---|
| 1 | 8.399 | 9.17 |
| 2 | 8.651 | 9.48 |
| 3 | 9.288 | 10.73 |
| 4 | 11.132 | 11.6 |
| 5 | 11.219 | 9.82 |

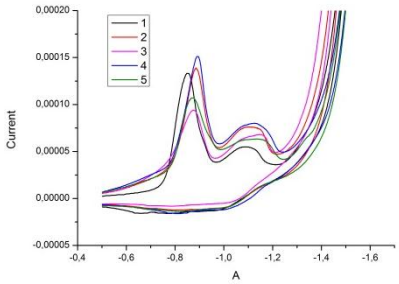


**Figure 3.** Cyclic voltammogram of SAM-modified gold samples.

**Table 2.** Dipole moment, work function and surface coverage of SAM-covered Au substrates.

| Molecule | Dipole (D) | Work Function (eV) | Surface Coverage ($mol.cm^{-2}$) |
|---|---|---|---|
| 1 | 1.705 | 4.48 | $7.80 \times 10^{-10}$ |
| 2 | 3.985 | 5.46 | $6.13 \times 10^{-10}$ |
| 3 | 4.162 | 5.44 | $5.04 \times 10^{-10}$ |
| 4 | 4.246 | 5.51 | $6.66 \times 10^{-10}$ |
| 5 | 8.129 | 5.28 | $5.07 \times 10^{-10}$ |

## CONCLUSION

In this study, hydrophilicity of CA/PEG membrane increases with the increasing of silica content as shown by the increasing of contact angle and Si-OH bond's intensity. Permeate flux, salt rejection, and permeability increase by the increasing amount of silica in membrane.

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