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Interface Engineering for Nanoelectronics

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Abstract

Innovation in the electronics industry is tied to interface engineering as devices increasingly incorporate new materials and shrink. Molecular layers offer a versatile means of tuning interfacial electronic, chemical, physical, and magnetic properties enabled by a wide variety of molecules available. This paper will describe three instances where we manipulate molecular interfaces with a specific focus on the nanometer scale characterization and the impact on the resulting performance. The three primary themes include, 1-designer interfaces, 2-electronic junction formation, and 3-advancing metrology for nanoelectronics. We show the ability to engineer interfaces through a variety of techniques and demonstrate the impact on technologies such as molecular memory and spin injection for organic electronics. Underpinning the successful modification of interfaces is the ability to accurately characterize the chemical and electronic properties and we will highlight some measurement advances key to our understanding of the interface engineering for nanoelectronics.

Introduction

The pace of innovation within the electronics industry is rapid in response to critical challenges as conventional silicon technology matures and electrical components become ubiquitous and interconnected. Increasingly, new semiconductor-based systems consist of nanoscale heterogeneous materials where the interface dominates the electronic performance. As these materials are used for applications ranging from small sensors to high performance computers, there is a drive to maximize performance while minimizing energy use and providing security and assurance. A fundamental understanding of electronic processes at interfaces is necessary since the interface increasingly dominates electronic performance. In fact, Dr. Kar was intimately aware of this and highlighted many successes in interface engineering that made high-k dielectrics a technological reality (1).

A natural means to engineer interfaces is to use organic monolayers since an organic molecule is one of the smallest readily designed and fabricated components. The versatility of chemical synthesis enables a wide variety of molecules to be used to engineer interfaces. Molecular layers can be formed on surfaces to change the electronic, chemical, physical, and magnetic properties. This paper will describe three instances where we manipulate organic and molecular interfaces with a specific focus on the nanometer scale characterization and the impact on the resulting performance. The three primary themes include, 1-designer interfaces, 2-electronic junction formation, and 3-advancing metrology for nanoelectronics. The foremost step of interface engineering is the ability to create designer surfaces where

monolayers can be tailored for specific electronic properties. This can be achieved by controlling the tunnel barrier thickness on a ferromagnetic electrode or by using click chemistry to create dense, high-quality electrically active molecular layers. Understanding the electrical response on the nanoscale is non-trivial as often creating the test structure creates artifacts that dominate the electronic response. In particular, focus will be on the measurement advances highlighting our understanding of the interface science and characterization.

Designer Interfaces

Nobel Laureate Herbert Kroemer realized early on that the “interface is the device,” (2) and this is even more true today as critical feature sizes of electrical components shrink and even become 2D, 1D, and 0D materials such as graphene, nanowires, and quantum dots. This creates an immense opportunity to use chemistry to impart the properties that one desires by creating molecular layers. For example, strong covalent bonding at the silicon surface can be used to modify the electronic properties of the semiconductor by changing the atomic linker from O, C, or S (3). Dr. Kar developed an admittance spectroscopy technique to further characterize the nature of this interface (4). The reactivity of silicon enables strong covalent interfacial bonds which can lead to charge transport and trapping across the interface but makes formation of a densely packed molecular layer a challenge. For this reason, many studies take advantage of organic-metal interfaces where the interaction is weaker and self-assembly of monolayers is favored, particularly at the Au-S interface (5). In fact, the gold substrate is often used as a model system to compare chemical, physical, and electrical aspects of different molecular layers such as molecular organization, surface free energy, friction, conductivity, and others. The foundation of knowledge amassed from gold-based studies forms the basis to investigate more complex molecular species and more complex surface chemistries, where competing reactions must be considered. Two interface engineering opportunities highlighted here include the ability of a self-assembled monolayer to tailor “spinterfaces” for spin-based organic devices and the ability to use “click” chemistry to build molecular functionality at the surface in a piecewise fashion.

Interfaces for Spin Injection

Spin-based electronics made from organic materials are promising for non-volatile devices, optoelectronic, and ultra-low power applications. In addition, the synthetic design of organic materials can lead to low cost production, light-weight and mechanically flexible electronics. However, these technologies rely on the non-trivial, efficient coupling between an organic material and a ferromagnetic electrode, such as Fe or Co. Common ferromagnetic metals are d-block elements that have multiple oxidation states and many stable oxide structures. Controlling the interface to realize new spin effects in organic materials remains an opportunity for molecular monolayers (6) (7). Self-assembled monolayers offer a means to not only passivate the ferromagnetic surface but can also be used to control the oxide thickness (8), tune the electronic band alignment, and impart interfacial spin polarization (9). For example, Figure 1 shows the impact of a self-assembled monolayer of 16-mercaptohexadecanoic acid ($\text{HO}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ denoted here as $\text{HOOCH}_{15}\text{SH}$) on the cobalt oxidation state measured by X-ray photoelectron spectroscopy (XPS). The surface of the

cobalt substrate was initially oxidized as CoO (Figure 1, top red curve). After soaking the substrate in an ethanol solution of HOOCH_2SH overnight, the XPS spectral shape changes substantially (Figure 1, middle blue curve) and resembles that of metallic cobalt (Figure 1, bottom black curve). The proposed mechanism for this reaction is that the HOOCH_2SH -ethanol solution reacts with and removes the cobalt oxide and thus the metallic cobalt feature can now be detected at the surface by XPS(8). This process can likely be optimized to control the cobalt oxide thickness which may be useful for fabricating cobalt-based magnetic tunnel junctions. Recent results have observed that carboxylate anchoring is more stable for connecting aromatic molecules to ferromagnetic substrates than thiol-based linkers (10) further supporting the promise of selective use of organic monolayers to engineer spintronic interfaces.

Click Chemistry

Self-assembled monolayers rely on solution dynamics to form high-quality monolayers. This means that high-quality monolayers can only be made from molecules that are readily soluble. Synthetic routes to add side chains to increase solubility can have unintended consequences of disrupting monolayer packing structure or adding unwanted functionality such as making the molecular layer more resistive. Click chemistry provides a modular approach to build functionality into molecular layers in a piecewise approach (11) (12). The most common approach is to use a copper catalyst to react alkyne and azide functional groups resulting in a heterocyclic ring in high yield. In this way, a high-quality dense monolayer can first be formed from an aliphatic chain with a tail azide group and a larger, bulkier alkyne containing molecule can be linked to the surface in higher density than possible using only a one-step self-assembly approach. We have demonstrated high-quality molecular layers of a redox active diruthenium organometallic molecule on both gold and silicon surfaces with similar packing densities using click chemistry (13). Shown in Figure 2 are the C1s XPS spectra of a similar diruthenium compound where the ligands to the Ru atoms are at equatorial positions rather than axial as in (13). The initial silicon surface shows a small amount of adventitious carbon in the bottom of Figure 2. The spectrum obtained from the self-assembled 11-azidoundecyltrimethoxysilane ($\text{N}_3(\text{CH}_2)_{11}\text{Si}(\text{OCH}_3)_3$) surface is shown in the middle of Figure 2 and is consistent with an aliphatic monolayer. Finally, shown in the top of Figure 2, the C1s spectrum obtained after the click reaction confirms the presence of the Ru species validating the redox active portion are attached to the surface.

Electrical measurements of the azide terminated and Ru2 terminated monolayers indicate a thicker tunneling layer is created after the click reaction (13). The Ru based molecules are attractive for molecular memory devices since they can store charge and potentially store multiple charge states because the Ru molecule has multiple accessible redox states. The Ru based molecules were used as molecular memory devices on silicon micrometer-sized wells and nanowires where the charge retention was directly related to the presence of the Ru molecules(14) (15). Such multi-bit molecular memory is very attractive for high-endurance and high-density on-chip applications in future portable electronics.

Electronic Junction Formation

Interface engineering for nanoelectronics requires a means to test and validate the electrical properties of the molecular layer. This is a non-trivial task because many methods used to make a top electrode on the molecular layer often change the interface leading to uncertainty in whether the resulting electrical properties are truly representative of the starting molecular interface. Careful chemical and physical characterization needs to accompany electrical measurements in order to understand what the device structure is at every step of the fabrication process. Vibrational measurements of silicon based devices are a particularly effective means of probing the molecular layer under a top metal electrode because silicon is transparent in the infrared and p-polarized backside reflection absorption infrared spectroscopy (pb-RAIRS) can be used (16, 17). This technique was instrumental in showing the impact of metallization conditions on self-assembled monolayers. Gold metallization of nitro-benzene on silicon resulted in very different junctions when the samples were metallized using a “soft landing” technique when compared with traditional metallization which resulted in significant molecular degradation (18). Moreover, the junction must be considered holistically since not all metals react with the monolayers in the same fashion. For instance, metallization of aliphatic monolayers on silicon yielded very different junctions when comparing gold and silver top contacts (19). Ultimately, it became clear that the softest, most benign means of forming the top contact will result in the most reliable electrical characterization of the molecular layer. We have used two “soft” contact, bottom-up methods: flip-chip lamination and eutectic gallium indium.

Flip-chip lamination (FCL) takes advantage of nano-transfer printing and the robust Au-thiol self-assembly to make silicon-molecule-gold electrical junctions(20). First, we start with a template stripped gold substrate on plastic. The ultrasMOOTH gold surface is important to minimize shorts and defects in the nanoscale molecular junction. Next, a bifunctional molecule is self-assembled onto the gold surface utilizing the gold-thiol chemistry to produce a high-quality, dense monolayer with a second functional group exposed at the surface. Finally, the junction is created by using nano-transfer printing to bring the functional group into contact with a hydrogen-terminated silicon substrate under mild heating and pressure. FCL is very versatile and has been applied to a variety of molecular backbones (aliphatic, aromatic), functional groups (acids, alkenes, thiols) and metals (Au, Co) (8, 20–23). Flip chip lamination does have some constraints however, necessitating bifunctional molecules and a significant amount of processing.

A method of quickly screening the electrical properties of monolayers with little processing is to use a liquid metal, such as a eutectic of gallium indium (EGaIn). EGaIn is a non-Newtonian liquid which allows for a soft, non-destructive electrical contact to molecular layers. The electrical “tips” are formed by dispensing a drop from a syringe, bringing the drop into contact with a substrate, and pulling the syringe back so the EGaIn cleaves in a conical shape which then can be used to interrogate the electrical properties of monolayers. We have previously used an EGaIn-based electrical measurement platform to measure molecular layers through the click chemistry reaction steps and the associated conductivity changes (13).

The electrical properties of similar molecular layers were measured using both the FCL and EGaIn techniques and representative data are shown in Figure 3. FCL junctions of $\text{HOOCH}_{10}\text{SH}$ (11-mercaptoundecanoic acid, $\text{HO}_2\text{C}(\text{CH}_2)_{10}\text{SH}$ in black dash) and $\text{HOOCH}_{15}\text{SH}$ (in blue dash) were measured using DC current-voltage (I - V) measurements. EGaIn-based measurements of H_{16}SH (hexadecanethiol, $\text{H}_3\text{C}(\text{CH}_2)_{15}\text{SH}$ in blue solid line) and H_{18}SH (octadecanethiol, $\text{H}_3\text{C}(\text{CH}_2)_{17}\text{SH}$ in red solid line) are shown in figure 3 where the junction area was defined by wet etching wells in SiO_2 with a bottom Au contact. Comparing the data obtained from a similar length aliphatic chain consisting of 16 carbons (Figure 3, solid and dashed blue line) show good agreement between the two measurement platforms with some deviation occurring as the bias increases. This deviation could be due to the different electrode or different chemistries at the electrode-molecule interface. It should be noted that contact area of the EGaIn tip may be up to 4 orders of magnitude smaller than the optical area due to oxidation of the gallium and interfacial roughness (24). Data obtained from both FCL and EGaIn show the expected molecular length dependent trend. Both FCL and EGaIn provide reliable approaches to making systematic electrical contact to molecular monolayers.

Advancing Metrology for Nanoelectronics

Having established a reliable means of characterizing molecular layers, we now apply this approach to observe transport properties in monolayers with differing dipolar properties. The use of dipolar organic monolayers to tune interfaces introduces two competing effects, changing of the surface free energy (i.e. surface wetting (25)) or changing the interfacial conductivity (i.e. charge-based effects such as detrapping or hybridization). Early work using organic molecules as electrode-modifiers for organic electronic applications observed the surface wetting was the dominate mechanism responsible for transistor results (26). EGaIn can be used in conjunction with other characterization methods to separate the electronic dipolar effects from the surface wetting effects.

Dipolar molecules are known to change the work function of gold electrodes by as much as 1 eV. Shown in Figure 4 are the ultraviolet photoelectron spectra (UPS) of a hexadecanethiol monolayer and two fluorine-containing monolayers (F-SAMs), a fluorine capped monolayer ($\text{CF}_3[\text{CH}_2]_{19}\text{SH}$, abbreviated “ FH_{19}SH ”) was compared against a monolayer with fluorine along the backbone ($\text{CH}_3[\text{CF}_2]_6[\text{CH}_2]_{13}\text{SH}$, abbreviated “ $\text{HF}_6\text{H}_{13}\text{SH}$ ”) (27). The UPS data clearly show the monolayer has a large impact on the work function with the hexadecanethiol changing the work function by nearly 1 eV, the $\text{HF}_6\text{H}_{13}\text{SH}$ having a moderate impact ~ 0.4 eV and the FH_{19}SH causing very little change in the work function.

Representative charge transport data obtained from 20-carbon long aliphatic molecular layers by using the EGaIn method are presented in Figure 5. The devices were ~ 20 μm in diameter and the current was normalized by contact area to remove size artifacts. There is little variation in the current density (J) obtained from these three molecular layers, despite the large difference in work function. There is a subtle variation with the current largest for $\text{HF}_6\text{H}_{13}\text{SH}$ and smallest for the FH_{19}SH layer. Previous literature has estimated the tunneling barrier across an alkanethiol to be ~ 5 eV or higher (28) and the effect of the

dipoles will not completely overcome this barrier. A full understanding of the electrical properties of the F-SAM monolayers is underway (29).

Impedance Spectroscopy (FSAMS)

Interrogating molecular layers with AC and DC electrical bias makes it possible to understand the molecular junctions in greater detail. In particular, the impact of contact resistance, molecular resistance and capacitance can be understood by looking at the frequency dependent data obtained with impedance spectroscopy(30, 31). We used the same EGaIn measurement setup for the AC-impedance measurements of the C₂₀ monolayers to better understand the difference that fluorine functionalization imparts on the molecular junction. Measurements were taken from 20 Hz to 2 MHz at room temperature in ambient conditions with an AC amplitude of 100mV at a DC bias of +0.1 V. Figure 6 presents representative impedance modulus and phase data for the three SAMs. At low frequencies, the modulus $|Z|$ is flat since the data are dominated by the resistance of the molecular layer. It can be seen that the HF₆H₁₃SH data are slightly lower than the H₂₀SH and FH₁₉SH in agreement with the current density data in Figure 5. As the frequency increases, the $|Z|$ decreases at a transition frequency where the AC bias frequency is too large for the molecular layer to respond. This is related to the thickness of the molecular layer assuming this is the separation of the parallel plates of a capacitor(31). Again, HF₆H₁₃SH appears different with a transition frequency at a higher value which could be caused by either a slightly thinner monolayer or a slightly less resistive molecular layer. The phase of the complex impedance data shown in figure 6B is near zero in the low frequency region and approaches 90° in the high frequency region for all monolayers. The phase is 90° for an ideal capacitor and at high frequencies, the phase measured from these monolayers approaches 90°. Further work is underway to fully understand the differences between these molecular layers(29).

Plotting the complex impedance data as a Nyquist plot, shown in Figure 7, with the real portion of the impedance (Z') against the imaginary portion (Z''), shows the impedance data for all three molecular layers appears as a single semicircle. This is consistent with only one capacitor in the equivalent circuit, making the molecular layers easily modeled as a R[CR] circuit. In this RCR circuit (Figure 7, inset), the molecular portion consists of one capacitor and one resistor (R_{SAM} , C_{SAM} , respectively) and the resistances (molecule-EGaIn, Au-S, wires, probes, etc.) associated with the contact can be modeled as one resistance ($R_{contact}$). The data in Figure 7 were fit and the RCR values were extracted and presented in Table 1. First, the resistance of the monolayers (R_{SAM}) are somewhat consistent with the HF₆H₁₃SH noticeably smaller in agreement with the DC current density data. It should be mentioned that the preliminary resistance of these molecules is consistent with aliphatic monolayers that are much thinner(30, 32) and further experiments are underway to understand this difference. The capacitance of the monolayer is understood as $\epsilon A/d$ where ϵ is the dielectric constant, A is the area of the contact/device and d is the distance between electrodes in a parallel plate capacitor. The capacitance from all of these molecular layers are similar and nearly an order of magnitude lower than previous aliphatic monolayers(30, 32). Prior work has shown the capacitance is dominated by the area of the contact and the actual area may be the reason for this discrepancy(24). The contact resistance for the three molecular layers

exhibits a large variation. The largest contact resistance was obtained from the FH₁₉SH molecular layer. This could be related to the terminal fluorine group and is consistent with previous reports showing that the fluorine-EGaIn interface is more resistive (33). Further work is underway to understand the full details of these molecular layers and the impact of the dipoles, fluorine, and interfacial electronic properties (29).

Conclusions

Innovation in the electronics industry is underpinned by the ability to engineer the interface for the desired device properties. We have demonstrated that making designer interfaces are useful for technologies such as molecular memory or organic spintronics. For example, adjusting the surface chemistry with monolayer formation can be used to control the oxide thickness for spin injection from cobalt into an organic molecule (8, 9). Using click chemistry, we fabricated successful molecular charge storage devices (14, 15). These device demonstrations are possible only after a detailed understanding of the molecular layers. Thorough spectroscopy is necessary to understand the chemical and physical properties at the interface. Understanding the electrical properties is more challenging, because a top electrical contact is needed and this fabrication step could change the molecule and interface. We have presented two methods that are effective for characterizing molecular layers, FCL and EGaIn. Adding AC measurement capabilities by using impedance spectroscopy is a promising means of further understanding molecular interfaces by differentiating effects from contacts, molecular resistance, and capacitance.

After a dedicated effort, the focus on understanding the fundamentals of molecular interfaces is beginning to bear fruit. A unique molecular junction forms the basis of a commercial guitar amplifier (34). There is recent excitement to surrounding a molecular rectifier, first theorized in 1974 (35) and realized in 1997 (36). In 2015, break junction devices observed a rectification ratio of more than 200 (37) and recently a rectification ratio exceeding 10⁵ has been reported (38). The continued understanding of using molecular layers to engineer interfaces holds great promise for the future high-speed, low-power consumption electronics (7, 39).

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Figure 1.

XPS spectra of Co 2p_{3/2} obtained from the initial native oxidized cobalt surface (top, in red), and after formation of a HOOCH₁₅SH monolayer (middle, in blue). A metallic cobalt surface is shown for reference (bottom, in black).

Figure 2.

XPS spectra of the C 1s and Ru 3d region obtained from a bare Si(100) (bottom most, in black), after azide functionalization ("before click," middle, in red), and after functionalization by click chemistry (top most, in blue).

Figure 3. DC I-V measurement of molecular electronic junctions of different molecular lengths formed by FCL (Au-SAM-Si) (dash lines) and EGaIn (Au-SAM-EGaIn) (solid lines).

Figure 4.

UPS data for F-SAMs and H₁₆SH compared to a gold reference, showing high and low binding energy regions for work function determination.

Figure 5.
Representative EGaIn top contact measurements of F-SAMs and H20SH on gold surfaces.

Figure 6. Representative impedance data for F-SAMs. Red circles- H_{20}SH ; Blue squares- FH_{19}SH ; Green triangles- $\text{HF}_6\text{H}_{13}\text{SH}$. A) Complex impedance $|Z|$ vs frequency; B) Phase ϕ versus frequency

Figure 7. Representative Nyquist plots of the impedance data obtained from F-SAMs. Red circles- H_{20}SH ; Blue squares- FH_{19}SH ; Green triangles- $\text{HF}_6\text{H}_{13}\text{SH}$. Inset shows the idealized molecular junction under measurement and the corresponding model circuit.

TABLE 1

R[CR] Fits for F-SAM Impedance Measurements

Molecule	R_{contact} [$\Omega \cdot \text{cm}^2$]	C_{SAM} [$\mu\text{F}/\text{cm}^2$]	R_{SAM} [$\Omega \cdot \text{cm}^2$]
H_{20}SH	0.024 ± 0.010	0.114 ± 0.002	5.986 ± 0.409
FH_{19}SH	0.072 ± 0.016	0.153 ± 0.010	5.634 ± 0.445
$\text{HF}_6\text{H}_{13}\text{SH}$	0.011 ± 0.003	0.126 ± 0.004	4.838 ± 0.329