

Injection Barriers of Molecular Wires

The drive to produce molecular-scale electronic device applications is motivated by a number of potentially attractive features, such as ease of fabrication and the wide extent to which organic materials can be functionalized via organic synthetic methods. A range of applications is foreseen for switches and memory devices. In addition to replacing inorganic semiconductors in conventional device architectures, organic systems are also of interest in the more revolutionary area of “molecular electronics”. Here, it is envisioned that the nonlinear characteristics of individual molecules, or small ensembles, will provide the required device functionality, allowing low cost chemical synthetic methods to replace, at least partially, multi-billion dollar semiconductor fabrication lines in the production of nanoscale device structures.

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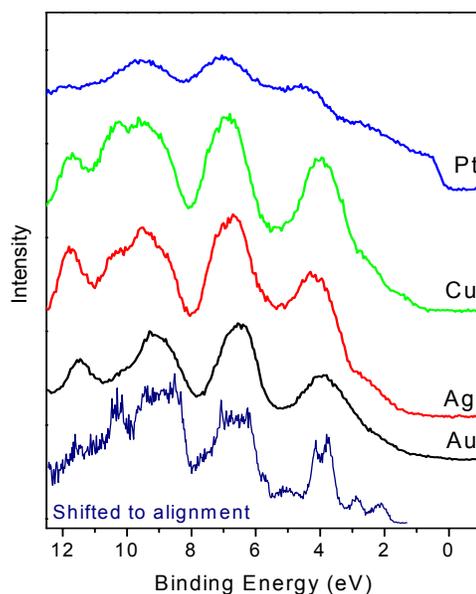
One of the most important properties of a heterostructure device is the mismatch between the energy levels of the materials. This mismatch is commonly referred to as the charge injection barrier. In molecular electronic devices, the injection barriers are heavily influenced by the interfacial chemistry of the metal-molecule contact. Information relating to charge injection barriers is difficult to obtain for molecular electronic devices using the conventional techniques of electrical engineering. We have employed a combination of one-photon (He I) and two-photon photoelectron spectroscopy, using sub-picosecond Ti:sapphire laser-based excitation, to determine the electronic structure, including injection barriers to both occupied and unoccupied levels, of oligio(*p*-phenyleneethynylene)thiol (OPE) self-assembled monolayers, a system that has become a benchmark for theoretical and experimental studies in the area of molecular electronics.

Most previous studies of covalently bound monolayers on metallic surfaces involve thiol-coupling (R-SH) chemistry on gold surfaces. Self-assembly of monolayers utilizing thiol chemistry is known to form densely-packed and reproducible monolayers on gold. Gold is ideal for these general characterization studies because it is robust, inert, and easily prepared. Gold, however, is not an ideal contact from a manufacturing standpoint because of its high surface mobility and tendency to form eutectics with inorganic semiconductors. Moreover, our previous studies have shown the transport gap for thiol-gold interfaces to be at least 3.5 eV. We have studied how this gap changes with metal substrate, with a special interest on refractory metals compatible with conventional semiconductor manufacturing processes.

The energy-level alignment of chemisorbed OPE-SH was studied on a variety of several metallic surfaces (Ag, Cu, Au, Pt, Pd). These metal systems were chosen for two rea-

sons; 1) several are often processed for industrial applications, and 2) their work functions span a wide range; therefore, comparisons will determine if the charge injection barrier is aligned or correlated with the metal vacuum level. In this investigation we found that chemisorption forms an interfacial dipole that reduces the work function, and that higher metal work functions are correlated with lower charge injection barriers. Thus, Pt (highest work function) is the best metal system for reduction of the charge injection barrier and Cu (lowest work function) has the highest charge injection barrier.

The figure shows one photon photoemission spectra of OPE-SH chemisorbed to single crystal surfaces of Pt, Cu, Ag, and Au. The gas-phase spectrum of OPE-SH (blue) is shown for reference.



Beyond the inherent challenges of fabricating sub-nanometer scale electronic devices, there has been a growing concern that the switching and rectification observed in molecular-based devices is not correlated to molecular properties; instead, it is related to charge traps or other interface defects. These reference data will provide a point of comparison for evaluation of the performance of device prototypes.

Future Plans: It is important to link the inherently molecular properties that we measure with the current-voltage behavior of device prototypes. We are working with industrial and academic partners to apply the measurement infrastructure and methods perfected in studying these model compounds to the more complex molecular structures of interest in switches and rectifiers. Specifically, we are working with scientists and engineers at Hewlett-Packard Research Labs, the University of Virginia, and NIST's Electronics and Electrical Engineering Laboratory to carry out a round-robin comparison of current-voltage characteristics of multiple device platforms built using molecular monolayers fully characterized by photoemission studies described in this investigation.

Publication:

L.B. Picraux, C.D. Zangmeister, and J.D. Batteas, "**Preparation and Structure of Low-Density, Flat-lying Decanethiol Monolayer for the Densely-packed, Upright Monolayer on Gold**", Langmuir, ASAP release Nov. 23, 2005.

Patent:

C.D Zangmeister and R.D. van Zee, Granted May 26, 2005. "**Method for Selective Electroless Attachment of Contacts to Electrochemically-Active Molecules**" United State Patent #6828581.