

Molecular/Semiconductor Heterostructure Devices

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This program seeks to develop molecular heterostructures, including metal/molecule/semiconductor structures, to develop novel electronic devices based on these structures, and to characterize and model the properties of the devices. The term “heterostructure” implies well-controlled and well-understood interfaces between the various layers in the structure. As has been demonstrated by the participants, the use of both molecular and semiconductor states can provide interesting electronic characteristics, and raises possibilities for integrated sensing or memory elements. The approach is novel in terms of both the electronic properties and structural stability that can be achieved via covalent bonds to semiconductor surfaces. Toward the overall goals, the interdisciplinary team includes synthetic organic chemistry, structural characterization of molecular layers in device structures, device fabrication at scales from nanometers to microns, scanning probe microscopy-based characterization, electrical characterization, and theoretical modeling.

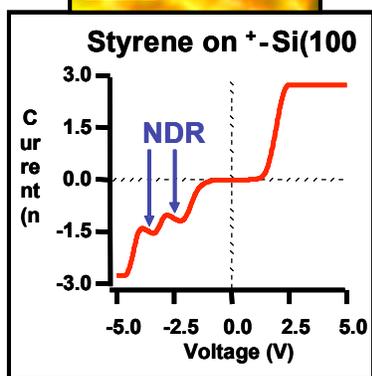
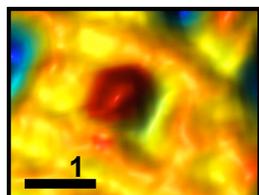
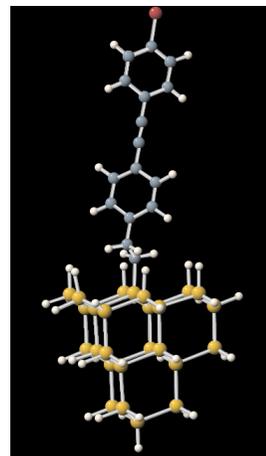
The program includes development of molecular heterostructures on Si, including well-ordered monolayers of various molecular species and 1-D heteromolecular nanostructures, structural and chemical characterization of the interfaces between the molecular layers and the contacts, device structures at size scales from the single molecule level to the micron scale, measurements of the current-voltage characteristics of the devices and development of experimentally verified models for electronic conduction through molecular heterostructures. As a result of this collaborative program, we will develop an inventory of molecular layers on silicon with known chemical and electronic properties and investigate potential device and sensing applications. We will explore device structures which can provide negative differential resistance, memory/switching effects, sensor elements and interconnect structures.

In conjunction with the collaborative research program, we are pursuing several initiatives in formal and experiential informal education and professional development. We are developing and disseminate course modules, including Nano-101 modules suitable for high school and undergraduate students and high school teachers. The integrated educational and professional development initiatives expose undergraduate and graduate students at the participating universities to new interdisciplinary approaches, provide opportunities for students and faculty from partner universities, and enrich the educational experiences for students at other universities through web-based initiatives. We will disseminate the research and educational results through a number of avenues, including the Nanohub, a central point of dissemination for nanoscience and engineering computational tools.

Key Results

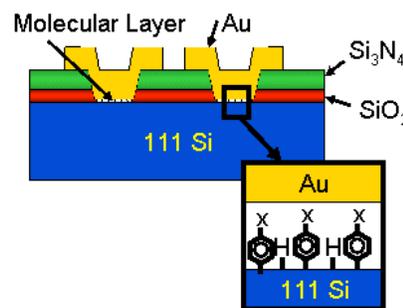
The Northwestern University team of **Hersam** and **Nguyen** has been focusing on the fabrication and characterization of organic monolayers on silicon surfaces that are relevant for silicon-based molecular electronics. We have synthesized a series of highly conjugated alkenes and alkynes [e.g., 4-bromo-4'-vinylbiphenyl, 4-((*p*-bromophenyl)ethynyl)styrene (shown in Fig.), 4-bromo-1-ethynylbenzene, 4-bromo-4'-ethynylbiphenyl, and ((*p*-bromophenylethynyl)phenyl)ethyne] and explored their subsequent organic monolayer formation

on silicon surfaces (e.g., Si(100)-2x1:H, Si(111)-1x1:H, and Si(111)-7x7) under UV exposure. Characterization techniques include scanning probe microscopy, X-ray photoelectron spectroscopy, secondary ion mass spectrometry, and Fourier-transform infrared spectroscopy. The choice of terminally brominated organic molecules is motivated by the possibility of further substitution chemistry on top of the Si-supported monolayer and the option of physically interrogating the terminal bromine atom by a variety of additional complimentary X-ray based techniques. In this vein, a close collaboration with Michael Bedzyk of Argonne National Laboratory has been established to characterize



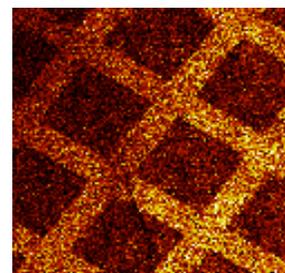
brominated organic monolayers on silicon using X-ray fluorescence, X-ray reflectivity, and X-ray standing waves at the Advance Photon Source. The unique combination of organic synthesis, surface science, and X-ray characterizations, coupled with density functional theory calculations, have enabled unprecedented atomically precise, three-dimensional mapping of the structure and chemistry of organic monolayers on silicon. At the single molecule level, ultra-high vacuum (UHV) scanning tunneling microscopy (STM) measurements have also been initiated in the Hersam laboratory. UHV STM is providing atomic-scale spatial resolution imaging of organic molecules on silicon, while scanning tunneling spectroscopy is allowing the electronic structure of individual molecules to be probed (figure at left). [1-4] **Datta** has developed modeling approaches suitable for explaining the observed characteristics.

Janes has developed microfabricated electronic devices employing metal/molecule/semiconductor structures on both GaAs and Si [5,6] (Si device structure in figure). The strong covalent bonds achievable with these structures allows the formation of stable contacts to the molecules. These studies have considered the effects of semiconductor doping type and doping density, as well as effects of molecular headgroups and developed models explaining these effects. Correlations of electrical and structural characterization (via time-of-flight secondary ion mass spectrometry (TOF-SIMS)) are being conducted in collaboration with **Walker**, and are aimed at understanding fundamental structure-property relationships in the molecular systems[6]. Future experiments will investigate the charge transport properties of organic monolayers developed by **Hersam** and **Nguyen**.



Walker has also been developing approaches optimized top contact structures to molecular devices, which utilize interactions between deposited materials and the organic monolayers. Fundamental studies include the development of chemical vapor deposition approaches (CVD),

which have not been widely employed to deposit thin films on SAMs because high thermal activation barriers ($T_{\text{substrate}} > 200\text{ }^{\circ}\text{C}$) are often required [7], making CVD incompatible with most organic materials, including SAMs. **Walker** has recently developed a room temperature CVD process using trimethyl aluminum (TMAI; $\text{Al}(\text{CH}_3)_3$), which is the most widely used aluminum precursor in metal organic CVD (MOCVD) [8]. We observe that TMAI reacts with both $-\text{OH}$ and $-\text{COOH}$ terminated SAMs to form an Al overlayer, but not $-\text{CH}_3$ terminated SAMs. We have employed this reaction to selectively deposit Al on a UV-photopatterned $-\text{COOH}/-\text{CH}_3$ SAM surface (TOF-SIMS image of patterned surface shown in image). Aluminum (Al^+) is observed only in the $-\text{COOH}$ terminated SAM areas. The study is being extended to the photooxidation and UV photopatterning of alkanethiolate SAMs on GaAs [9] using a protocol based on the methodology of McGuinness *et al* [10]. These surfaces will be employed for the selective deposition of metals on patterned SAM/GaAs surfaces so that the electrical properties of metal/SAM/GaAs devices can be studied.



$m/z = 27\ \text{Al}^+$

References

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