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14. ABSTRACT To understand chemistry is to be able to control it. The fulfillment of this long sought after goal ultimately hinges on a detailed knowledge at the atomic and molecular level. Control of chemistry not only provides insights into known materials and phenomena but also leads to chemicals with novel compositions, structures, and functions. The primary objective of this project is to use a homemade, variable low temperature scanning tunneling microscope (STM) to carry out atomic and molecular manipulation of chemical interactions for the discovery of novel nanostructures and properties. In effect, the goal is to carry out chemical changes by manipulating individual atoms and molecules to induce different bonding geometry and to create new interactions with their environment. These studies provide the scientific basis for the advancement of technology in catalysis, molecular electronics, optics, chemical and biological sensing, and magnetic storage.					
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FINAL PROGRESS REPORT

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Program Manager: Michael R. Berman

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Status of Effort:

The main objective of this project is to control the chemical interactions by manipulating individual atoms and molecules on a solid surface. This control is demonstrated through spatial dependence of reversible electron transfer to a single molecule and manipulating the properties of individual C₆₀ molecules. The particular approach used in this project for probing the properties of single molecules consists of measuring the transport of electrons through a chosen point within a selected molecule. By manipulating the environment in which the molecule is in, changes in its properties are reflected in the electron transport as revealed by measuring the current as a function of the voltage (I-V) and its first (dI/dV) and second derivatives (d²I/dV²). As a scientific model system, and also of technological interest related to energy and electron transfer, catalysis and molecular electronics, a series of experiments were carried out on C₆₀ and phthalocyanine molecules in a variety of environments, such as the double barrier tunnel junction (DBTJ), nanoscale thin films and crystals, and proximity to alkali metal atoms.

Accomplishments/New Findings:

We have fabricated a nanoscale system that enabled the observation of atomic scale transistor action gated by field effect from the charging of a single impurity. The fabricated geometry consists of a Ag tip, a vacuum barrier, an alkali doped C₆₀ monolayer, an Al₂O₃ insulating layer, and a NiAl(110) substrate. A reproducible procedure was found for fabricating such a structure, involving alkali (Li, Na, K, Rb, and Cs) and C₆₀ evaporators as well as the creation of a thin (5.2 Å) and smooth oxide layer. In this double-barrier tunneling junction (DBTJ), a step-wise change in the current is observed and correlated with the ionization of the alkali impurity when the tip is located at different distances from the impurity. Thus nonlocal ionization has been achieved. In addition to knowing the positions of the impurities through imaging, spatially resolved electronic properties were measured. The experiments also demonstrated the interconnection between chemical bonding and charge transport.

These studies demonstrate gating of current at the smallest scale and provide fundamental understanding of a general class of charge transport controlled by field effects associated with the ionization of impurities in systems with larger than atomic dimensions. In previous studies, it was difficult to know the locations and the bonding characteristics of the impurities. In addition, these experiments extend the use of the STM as a two-terminal (tip and sample) to a three-terminal (tip, sample, and impurity gate) device. The involvement of a C₆₀ monolayer in our system sheds new light in the role of organic molecules and atomic dopants in charge transport at the nanoscale. Our results contribute to the fundamental understanding of the system's properties that underpin the performance in molecular electronics, a futuristic technology that is likely to have potential AF and civilian applications, and thus directly relevant to the AF's mission.

In a series of experiments, vibronic states of adsorbed molecules were resolved by controlling the bonding environment of the molecules. The resolution of the vibronic states has implications for understanding and manipulating molecular conductance and chemical dynamics. These results were obtained for single molecules and monolayer of C₆₀ adsorbed on metal and thin alumina surfaces. To further the objective, in another series of related experiments, the charge state of single copper phthalocyanine molecules adsorbed on an ultrathin alumina surface was manipulated with sub-molecular spatial resolution. These experiments add an extra

dimension to the manipulation of chemical interactions by controlling and reversibly changing the charge state of single molecules with nanoscale spatial resolution.

The scanning tunneling microscope (STM) was also used to study the differential conductance (dI/dV) of single C_{60} molecules in isolation and in monolayers adsorbed on NiAl(110) and on an ultrathin alumina film grown on the NiAl(110) surface. On the oxide layer, the electronic bands in the dI/dV spectra display a series of equally spaced features, attributed to the vibronic states of the molecules, which are absent when the molecules are adsorbed on the metal. A comparison between the molecular spectra measured on the oxide film reveals the effect of adsorption temperature and geometry, as well as intermolecular interactions on the vibronic features. Thus by manipulating the adsorption properties of the molecule, the width (lifetime) of the vibronic states is changed, which is expected to influence its chemical interactions.

An important property of molecules is their charge state. The removal and addition of an electron can have important effects on the structure and reactivity of the molecule. Our work demonstrates the ability of the scanning tunneling microscope to control the charging of a single molecule. Furthermore, the control is spatially dependent inside the molecule. The molecule is divided into two regions; the location of the boundary between them can be controlled by changing the voltage bias across the tunnel junction. With the tip positioned within the outer region, the molecule is charged. Electron transfer does not occur with the tip over the inner region, and the molecule remains neutral. This spatial dependence of charge transfer in a single molecule enables a deeper understanding of molecular properties and control of its chemical interactions with atomic scale resolution.

A new conduction mechanism has been discovered and given the name - bipolar conduction. This phenomenon is revealed by studying C_{60} and ring-like molecules such as phthalocyanines and porphyrins. The same molecular electronic state is found to be involved in electron transport at positive and negative sample biases. This observation is counterintuitive since unoccupied states, such as the lowest unoccupied molecular orbital (LUMO) and higher lying excited states, are involved at positive bias, while occupied states, such as the highest occupied molecular orbital (HOMO) and lower lying filled states, are involved at negative bias. We have found that when the molecule is in a double barrier tunnel junction (DBTJ), formed by adsorbing the molecule on an ultrathin oxide film evaporated on a metallic substrate and in a vacuum tunnel barrier, bipolar conduction becomes a novel mechanism of electron transport.

Ultrathin insulating films, of the order of $5 \text{ \AA}$, form an important component of electronic circuits. The electrical isolation provided by the thin insulating film usually serves to prevent electrical shorts. However, we have discovered that the isolation gives rise to new transport phenomena and properties of molecules that are not observable when they are directly adsorbed on the metallic substrate. In addition to the novel phenomenon of bipolar conduction, vibronic states are resolved. The observation of these vibrational states provides direct evidence for the coupling of electrons to the nuclear motions during the transport. Furthermore, the selective coupling to particular vibrational modes has implications for the understanding of superconductivity, such as organic superconductors as in alkali doped C_{60} .

It is therefore critical to explore other types of insulating films beside oxides. We have learned how to grow ultra thin alkali halide films, such as NaCl and NaBr. In a series of experiments, the adsorption of C_{60} and ring-like molecules on NaBr thin films has been compared to that on Al_2O_3 films. Surprisingly, NaBr film is found to be more leaky, i.e. there is more interaction between the molecule and the underlying metallic substrate, through the intermediate insulating film. The NaBr film, however, forms a more perfect crystallographic lattice compared to the Al_2O_3 film. Bipolar transport is also observed. Wetting of C_{60} is less on NaBr compared to the Al_2O_3 film. Thus three-dimensional nanocrystalline structures are formed on NaBr while two-dimensional monolayer islands are formed on Al_2O_3 film. This difference provides a new opportunity to study the adsorption and electron transport of single C_{60} molecules on top of NaBr with different thicknesses, with the thickness increased one by one up to 5 layers. Strikingly different STM images and transport properties of the molecule are obtained when the molecule is adsorbed on the fourth layer compared to the first three layers of a nanocrystalline C_{60} . For example, negative resistance is observed for single molecules but the phenomenon is dependent on the number of underlying C_{60} layers.

In experiments on $TiO_2(110)$ at 10 K, a single Zn-etio porphyrin molecule was manipulated toward another molecule with a different conformation. The electronic levels of both molecules are shifted as the distance between the two molecules is decreased, revealing the change in interactions between them and illustrating manipulation of chemical interactions at the single molecule level. These experiments also represent studies at the lowest temperature on $TiO_2(110)$.

Personnel Supported:

Two graduate students (Ning Liu and Nilay Pradhan) were supported by the AF grant. In addition, a supplementary support was provided to Christophe Silien, a postdoctoral associate who holds a fellowship from the Belgian National Fund for Scientific Research (FNRS). Partial support was also provided to Gary Mikaelian and Xiuwen Tu to perform the experiments on altering the charge state of individual copper phthalocyanine molecules on Al_2O_3 and C_{60} molecules adsorbed on NaBr thin films and C_{60} nanocrystals. In addition, Naoki Ogawa was involved in some of the experiments while holding a fellowship from the Japanese government. These five researchers benefited from interactions with 7 other researchers in the group since all our research projects involved the STM. The sharing of laboratory skills and knowledge as well as scientific results among the researchers creates a positive environment for obtaining new findings as well as innovations in instrumentation.

Ph.D. Theses Completed with AFOSR Support:

1. Nilay A. Pradhan, "Vibronic Spectroscopy and Atomic Scale Transistor Action Observed with a Scanning Tunneling Microscope", 2004; he is currently on the technical staff at Intel.
2. Ning Liu, "Atomic Scale Understanding of Nanostructures in a Double Barrier Tunneling Junction: Scanning Tunneling Microscopy of Alkali Doped Buckminsterfullerenes on Partially Oxidized $NiAl(110)$ ", 2005; she is holding a Canadian Postdoctoral Fellowship at the University of Alberta.

3. Gareguin R. Mikaelian, "Scanning Tunneling Microscopy and Spectroscopy of Single Molecules and Nanocrystals in Double-Barrier Tunnel Junctions"; he is a staff scientist at Opto-Knowledge Systems, Inc. in Torrance, CA.

Publications:

1. "Atomic Scale Conductance Induced by Single Impurity Charging", N.A. Pradhan, N. Liu, C. Silien, and W. Ho, Phys. Rev. Lett. **94**, 076801-1-4 (2005).
2. "Tuning the Bipolar Conductance of an Alkali-Doped C₆₀ Layer Sandwiched Between Two Tunneling Barriers", N.A. Pradhan, N. Liu, C. Silien, and W. Ho, Nano Letters **5**, 55-59 (2005).
3. "Vibronic Spectroscopy of Single C₆₀ Molecules and Monolayers with the STM", N.A. Pradhan, N. Liu, and W. Ho, J. Phys. Chem. B **109**, 8513-8518 (2005).
4. "Atomic Scale Control of Single Molecule Charging", G. Mikaelian, N. Ogawa, X.W. Tu, and W. Ho, J. Chem. Phys., Communication **124**, 131101-1-4 (2006).
5. "Distance Dependence of C₆₀ Mediated Interaction Between Alkali Atoms", N. Liu, N.A. Pradhan, and W. Ho, to be published (2007).
6. "Electronic Properties of Low-Level Alkali-Doped C₆₀ in DBTJ Probed by STM", N. Liu, N.A. Pradhan, and W. Ho, to be published (2007).
7. "STM Study of Cs Adatoms Adsorbed on Double C₆₀ Layers Formed on NiAl(110) and Oxidized NiAl(110)", N. Liu, C. Silien, and W. Ho, to be published (2007).
8. "Bipolar Conductance in a Single C₆₀ Molecule in DBTJ Observed by STM", N. Liu and W. Ho, to be published (2007).
9. "Electron Transport Through Fullerene Nanocrystals Grown on Thin NaBr Overlayers", G. Mikaelian, X.W. Tu, N. Ogawa, and W. Ho, to be published (2007).
10. "Electron Transport in a Single Molecule Adsorbed on Thin Films with Large Polarizability", G. Mikaelian, X.W. Tu, N. Ogawa, and W. Ho, to be published (2007).

Interactions/Transitions:

Gary Mikaelian presented a Physics Colloquium at California State University, Fullerton in September 2005. The PI has not acted in consultative function to other laboratories and agencies during this period. The PI has served on a few advisory boards, including the International Academic Advisory Committee for the Hefei National Laboratory for Physical Sciences at the Microscale, Hefei, China, 2005-2009, the International Advisory Board of the National Center for Nanoscience and Technology, Beijing, China, 2006 – present, and the Fritz-Haber Institute of the Max Planck Society in Berlin, 1999-2009. No transitions have been made during this period.

New Discoveries, Inventions, or Patent Disclosures:

A new mechanism of electron flow through a molecule has been discovered and coined “bipolar conduction”, the same electronic state is involved in electron conduction at both positive and negative sample bias voltage. It was also discovered that the charge in a molecule can be manipulated with sub-molecular spatial resolution. The ionization of an impurity was found to influence nonlocally the conduction of electrons – a phenomenon similar to transistor gating. In addition, such charge manipulation in a molecule is expected to lead to changes in its chemical interactions. A different type of insulating layer was successfully grown and its influence on the physical, chemical, and electrical properties of singly adsorbed molecules was measured.

Honors/Awards:

Xiuwen Tu received the Best Paper Award at the 2006 Southern California Chapter of the American Vacuum Society. Lifetime achievement honors for the P.I. include American Physical Society Fellow, Bonn Chemistry Prize, and the Alexander von Humboldt Research Award.