

SPECTROSCOPY OF SURFACE ADSORBED MOLECULES

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I. Research Scope and Objectives

Under this contract we have been developing applications of inelastic electron tunneling spectroscopy (IETS) and elastic tunneling to the study of surfaces and interfaces. These techniques are very sensitive to the presence of adsorbed molecules at the tunnel junction interface and the resulting charge transfer and barrier modification. Correlated studies on the same adsorbed molecules have been carried out using x-ray photoelectron spectroscopy (ESCA).

We have detected changes in both the absolute and relative intensity of vibrational modes as well as large shifts in the tunnel barrier characteristics as a function of molecular dopant and substrate preparation. We are developing models in terms of charge transfer, molecular reactivity, electron delocalization and surface electronic structure.

In order to gain more information on the electronic structure of the adsorbed molecules we have also been developing x-ray photoelectron spectroscopy to measure the chemical shifts in the core electronic levels of atoms in the adsorbed molecules. So far, we have successfully used the N 1s level as a marker for surface adsorption changes in the electron density on the N atom in NO₂ substitutional groups of aromatic ring compounds. An upshift of ~6 eV in the binding energy has been observed for specific adsorbed compounds on AlO_x corresponding to a charge transfer of nearly one electron.

For doped tunnel junctions we have also discovered a new and unusual electric field induced barrier shift at 77 K and below. This is induced above certain threshold voltages and must result from a net change in the electron affinity of the doped barrier. The change lasts indefinitely at low temperature but can be completely annealed out by heating the junction to 300 K for a short time. The effect is strongest for molecules with highly delocalized π -electrons and is greatly enhanced by Ag electrodes. We are developing a more detailed model in terms of charge polarization and bond rearrangement as well as collecting more data on the correlation of this effect with the systematics of molecular charge structure and surface interaction.

All of these related experiments exhibit aspects of the molecular structure at the interface in contact with an oxide substrate and a metal electrode. We hope to develop a theory of IETS intensities and to understand the interactions with the barrier substrates and the effects of metal electrodes. Experimentally we wish to develop a wider range of substrates for IETS work and in the process learn more about the detailed adsorption mechanisms and their influence on electron tunneling.

II. Description of Research Effort

Inelastic electron tunneling spectroscopy (IETS) has been used to obtain the vibrational spectra of molecules adsorbed on oxide substrates. A series of aromatic carboxylic acids have been studied with a variety of substituent groups, including compounds with both single and multiple rings. Carboxylic acids form a strong bond to the surface with the formation of a bidentate CO₂⁻ group which is easily identified by the characteristic vibrational modes and the absence of the C=O stretching mode characteristic of an unreacted COOH group.

We have found that both the absolute and relative mode intensities are extremely sensitive to the electronic structure of the molecule and to its subsequent interaction at the oxide-electrode interface. Type of substituent group, position of the substituent on the ring, number of substituent groups, as well as the number and arrangement of the aromatic rings all affect the IETS intensity.

The detailed electronic structure of the barrier can also be studied by IETS. We have shown that the inelastic tunneling modes associated with OH groups on an alumina substrate can be used to monitor detailed changes in the OH density and structure

such as hydrogen bonding. This in turn affects both the barrier parameters and the IET spectrum of the adsorbed molecules. The elastic tunneling current versus voltage is also extremely sensitive to these changes in electronic structure and we have developed successful models for computer analysis of the barrier parameters.

Various adsorbed molecules in the carboxylic acid series produce extreme changes in the effective tunnel barrier heights. Preliminary analysis shows a strong correlation with π -electron delocalization and the charge interaction with the substrate.

For any given molecule, the substitution of a silver electrode for a lead electrode produces an additional lowering of the effective tunnel barrier. For barriers below some critical value (usually in the range 1-2 eV) application of a bias voltage above a threshold in the range 1 to 2 volts at 4.2 K produces a permanent shift to a lower barrier as long as the junction remains at low temperature. The magnitude of this shift is largest for molecules producing the lowest effective barrier heights. This change requires 10 to 100 milliseconds for completion and represents some type of bond rearrangement which lowers the electron affinity of the barrier. This also affects the IETS intensity (lowering the intensity of the higher frequency modes). These electric field induced changes can be completely annealed at room temperature and the barrier parameters return to those of the original junction at 4.2 K.

Mixed silica-alumina barriers have been compared to pure alumina barriers and we find changes in the relative molecular IETS mode intensity for a given molecule adsorbed on the two types of barrier as well as specific changes in the elastic barrier parameters. Correlation with differences in OH surface structure are underway.

These results all demonstrate the extreme sensitivity of both the IETS intensity and the elastic tunneling as governed by the effective barrier characteristics to the subtle changes in charge arrangement, charge transfer or electron sharing and weak bond formation at the interface. None of these perturbations are sufficient to change the vibrational frequencies and are hard to detect in other types of spectroscopy.

X-ray photoemission spectroscopy is one possibility where core level shifts can be interpreted in terms of charge transfer at the surface. Promising initial results have been obtained with NO_2 groups substituted in a series of aromatic carboxylic acids where chemical shifts up to 6 eV in the N 1s level have been observed on AlO_x substrates. This is due to weak surface bonding and preliminary correlation with tunneling barrier heights has been established. Doped substrates prepared with small metal particles have been used to simulate electrode effects. Additional charge modifications due to Ag versus Pb particles have been detected. Experiments are underway on a wider range of nitrogen substituted compounds and preliminary experiments using sulfur as a marker atom have been successful.

III. Future Research

Experiments are planned using a wider range of selected molecules in order to more thoroughly establish the correlation with the molecular charge structure and modifications produced by different types of substitutional groups. The electric field induced barrier shifts and associated bond rearrangements need to be understood in more detail. Planned experiments include studies of systems forming metal ion complexes as well as doping procedures that change the electronic structure of the barrier. New barrier substrates with different chemical properties from alumina and silica are being developed. These include carbon and other types of oxides where charged OH groups do not dominate the behavior. Chemical shift data on a wider range of adsorbed molecules will be obtained using x-ray photoemission. X-ray photoemission will also be used for characterizing modified tunneling barriers where metallic ions or mixed oxides have been used to modify the chemical properties.