

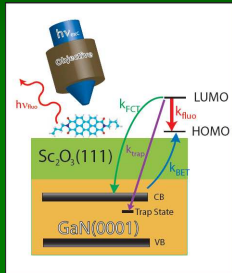
Charge Transfer in Excitonic Solar Cells

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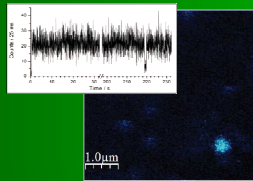


Approach

- Single molecule fluorescence spectroscopy on single crystalline surface under UHV conditions
- Fluorescence fluctuations encode heterogeneous charge transfer kinetics
- Observe both forward and reverse charge transfer
- Control molecule / semiconductor distance, dopant and defect density
- Model system: Perylene bisimide (PTCDI) on GaN (0001) with epitaxially grown Sc_2O_3 (111) layer



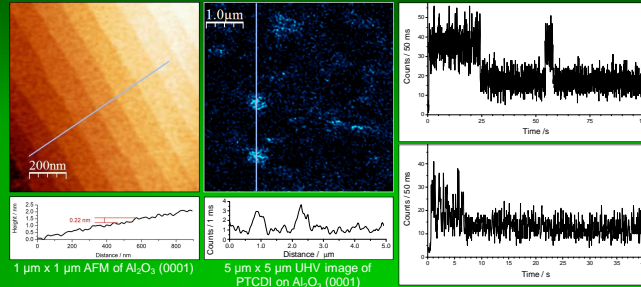
Single Molecule Microscopy



- Base pressure: 10^{-10} mbar
- CW multimode Ar⁺ laser,
- PTCDI onto glass cover slip
- Extraordinary long survival times
- Fast intersystem crossing, few transitions to dark states

Single Molecule Fluorescence Microscopy

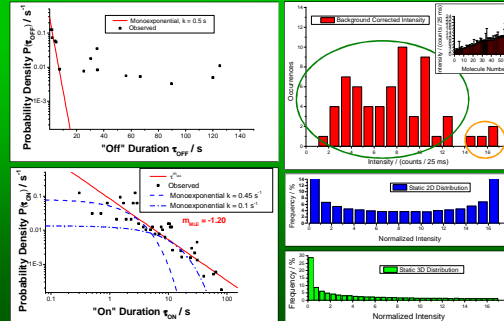
Single Molecule Spectroscopy on Al_2O_3 (0001)



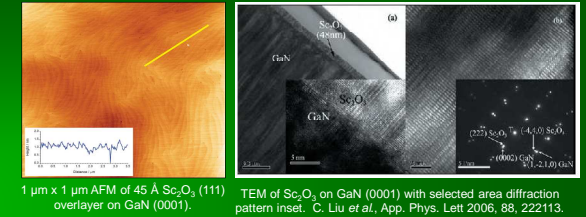
- Single crystal oxide with large, flat terraces (0.2 nm step-height)
- UHV preparable insulator without charge transfer
- Fluorescence quenched in comparison to glass or $\text{Sc}_2\text{O}_3/\text{GaN}$ origin?
- Test of PTCDI as a fluorophore in UHV
- Distinct long-lived "off" periods, not triplet excursions

Fluorescence Trajectory Analysis

- Analysis with Change Point Detection algorithm
- Nonexponential "off"-period distribution
 - Distribution of dark states
- Power-law distributed "on"-period
 - Dynamic fluctuations
- Fluorescence intensities indicative of two classes of adsorption sites
- Broad, continuous distribution of fluorescence intensities
 - Not due to the random orientation of molecules

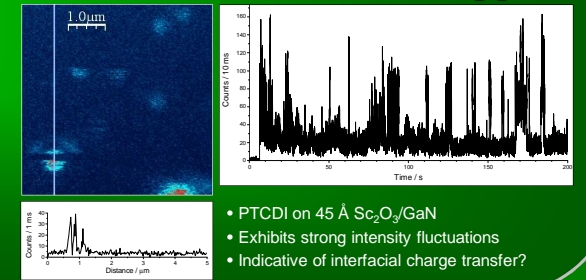


Characterization of Model Structure



- Sc_2O_3 (111) heteroepitaxial insulator layer with thicknesses 5-1000 Å
- GaN/ Sc_2O_3 interface exhibits <10% lattice mismatch
- Atomically flat step-flow patterns with screw dislocations
- Mg and Si for p- n- doping

Single Molecule Spectroscopy on $\text{GaN}/\text{Sc}_2\text{O}_3$

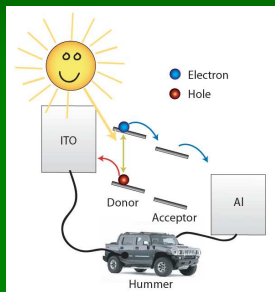


- PTCDI on 45 Å $\text{Sc}_2\text{O}_3/\text{GaN}$
- Exhibits strong intensity fluctuations
- Indicative of interfacial charge transfer?

Interfacial Electronic Structure in Organic Photovoltaics

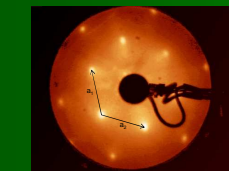
Growth of Organic layers on Well-Defined Surfaces

- Organic semiconductor devices have the potential to revolutionize solar power generation - reducing production costs and expanding viable applications.
- Bulk heterojunction organic photovoltaics are dominated by interfaces.
- Charge transfer at interfaces controls device function and depends on local environment.

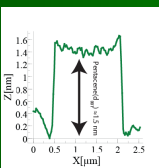


Conceptual diagram of a Donor-Acceptor blended bulk heterojunction solar cell.

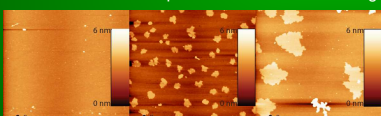
- Low Energy Electron Diffraction verifies the integrity of the substrate surface prior to deposition.
- Atomic force microscopy (AFM) can determine coverage of some molecules (i.e. pentacene).
- Growth of organic layers can then provide in a highly controlled fashion to produce the desired coverage.



Low energy electron diffractogram of the prepared surface of a Cu(111) single crystal.



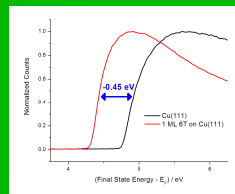
AFM lineout demonstrating single monolayer coverage of pentacene on Si(111)/ SiO_2 .



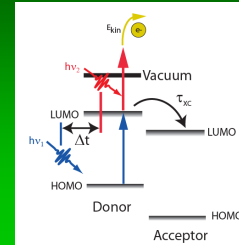
Growth dynamics of sub-monolayer pentacene films on Si(111)/ SiO_2 as measured by Atomic Force Microscopy.

Two-Photon and Ultraviolet Photoemission Spectroscopy of Interfacial States

- The electronic environment is sensitive to both chemical and physical modification.
- Two-photon photoemission (2PPE) and ultraviolet photoelectron spectroscopy (UPS) provide detailed information about the surface electronic environment and its interactions.
- High peak powers in 2PPE can be used to drive both coherent and sequential photoemission.

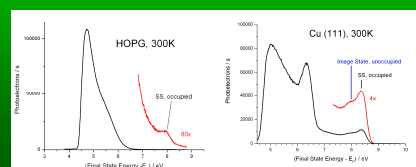


Work function shift by UPS due to an adsorbed 6T monolayer on Cu(111).

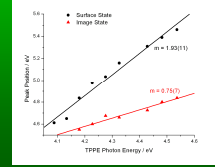


Two-photon photoemission scheme showing factors affecting photoelectron generation.

- Deposition of sexithiophene (6T) monolayer on pristine Cu(111) lowers the work function by 0.45eV – implying the formation of a strong surface dipole.
- Using 2PPE, occupied surface states obscured in UPS can be detected in addition to unoccupied states such as the n=1 image state of Cu(111).

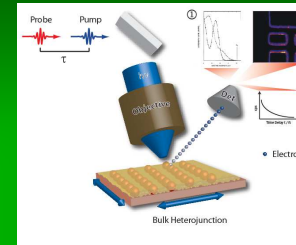


2PPE spectra of highly ordered pyrolytic graphite (HOPG) (left) and Cu(111) (right).



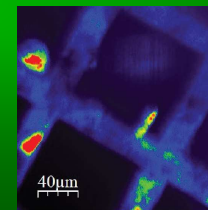
State occupancy in Cu(111) can be determined by varying photon energy.

Novel Imaging of Electronic Heterogeneity by Scanning Photoionization Microscopy (SPIM)



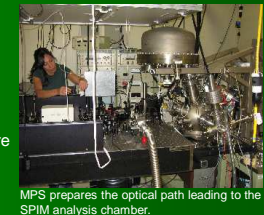
Cartoon depicting the concept of scanning photoionization microscopy.

- Images up to 200x200 micron are generated by rastering the sample and integrating over the desired photoelectron KE range.
- "Hot-spots" or morphological areas of interest are selected for acquisition of full spectral content.



SPIM image of a Cu TEM grid showing total photoelectron current.

- Diffraction limited spatial resolution suited to probe nanoscale variations of the electronic environment in organic photovoltaic devices.
- Pump-probe photoionization provides exquisite chemical contrast of occupied and vacant states with femtosecond temporal resolution.
- Ultra-high vacuum environment ensures a well defined surface



MPS prepares the optical path leading to the SPIM analysis chamber.

Acknowledgments

We would like to thank Stefan Kreitmeyer, David Bartz, Michelle Sois, Jason Tyler and the UofA Chemistry Department Laboratory for Electron Spectroscopy and Surface Analysis, Machine Shop and Electronics Facility for valuable contributions to this work. We gratefully acknowledge financial support from the Arizona Research Institute for Solar Energy, a 3M Nontenured Faculty Grant, The National Science Foundation (CHE-0618477), The American Chemical Society's Petroleum Research Fund (40516-G6) a National Science Foundation Graduate Research Fellowship for MLB and the University of Arizona.