

Surface Science

Room: 21 - Session SS-MoM

Nonequilibrium and Nonlinear Processes

Moderator: D. Diesing, University of Duisburg-Essen, Germany, E. Karpov, University of Illinois at Chicago

8:20am **SS-MoM1 Hot Electron Flow Generated by Photon Absorption Probed with Metal-Semiconductor Nanodiodes**, *J.Y. Park, Y.K. Lee*, KAIST, Republic of Korea

A continuous flow of hot electrons that are not at thermal equilibrium with the surrounding metal atoms is generated by the deposit of energy from the external source to the surface through nonadiabatic electronic excitation. Here we show that hot electron flow generated on a gold thin film by photon absorption (or internal photoemission) is amplified by localized surface plasmon resonance. This was achieved by direct measurement of photocurrent on a chemically modified gold thin film of metal-semiconductor (TiO₂) Schottky diodes. Photons coupled into the modified gold thin film excite surface plasmon resonance, which enhances hot electron flows going over Schottky barrier between the gold film and TiO₂. The short-circuit photocurrent obtained with low-energy photons is consistent with Fowler's law, confirming the presence of hot electron flows. The morphology of the metal thin film was modified to a connected gold island structure after heating such that it exhibits surface plasmon. Photocurrent and optical measurements on the connected island structures revealed the presence of a localized surface plasmon at 550 ± 20 nm. The results indicate an intrinsic correlation between the hot electron flows generated by internal photoemission and localized surface plasmon resonance. We discuss the effect of dye molecules or metal nanowires on gold film in the efficiency of internal photoemission.

8:40am **SS-MoM2 The Nature of Charge Transfer at Metal-Liquid Interface: Equilibrium vs. Non Equilibrium Processes**, *D. Bürstel, M. Scheele, I. Nedrygailov, D. Diesing*, University of Duisburg-Essen, Germany

The hydrogen evolution reaction is one of the key reactions in catalysis whereby protons from a liquid phase discharge at a metal surface and form atomic hydrogen. A correlation between the reaction rate and the chemisorption energy of the metal-hydride species (so called Volcano plot) was motivated for decades by an exponentially increasing reaction rate originated from a stronger chemisorption energy by arguments from the equilibrium thermochemistry. Progress in the study of metal-gas phase interactions points to electronically excited states, when atoms adsorb on a metal or chemical reactions with molecules occur. Up to now metal-liquid interfaces are not in the focus of research activities considering non equilibrium processes in the course of interfacial chemical reactions. We show experimental concepts how reactions on metal-liquid interfaces can be reviewed with respect to the existence of chemically induced electronic excitations. In a theoretical model we show that even small deviations from the electronic equilibrium may change the rate of the discharge reaction of protons on metal surfaces.

9:00am **SS-MoM3 Probing Surface Chemical Reactions with Metal Nanofilm - Semiconductor Schottky Diodes**, *I. Nedrygailov, E. Hasselbrink, D. Diesing*, University of Duisburg-Essen, Germany

Most catalytic chemical reactions are complex processes, which include a variety of steps such as molecular and dissociative adsorption on a solid surface, interactions between intermediates, and desorption of products from the surface to the gas phase. Considerable effort has been made to achieve a detailed microscopic understanding of the dynamics of these processes using different experimental and theoretical methods, nevertheless still little is known about the routes of energy transfer accompanying the gas-surface interactions. As shown by McFarland, Nienhaus and coworkers, dissipation of chemical energy, released in catalytic reactions on metals, may proceed non-adiabatically by transferring a part of the energy into electronic degrees of freedom. This process is caused by a nonequilibrium state of the adsorbate surface complex and leads to the excitation of highly energetic (hot) electrons and holes in the metal surface. Detection of the excited charge carriers in metals is rather challenging because they relax within some 10 fs due to scattering processes (including electron and phonon pathways). A loophole is the use of metal nanofilm - semiconductor Schottky diodes. A ballistic transport of the excited charge carriers from the metal surface, where the excitation takes place, into the underlying semiconductor is possible in such diodes allowing for the direct detection of the hot electrons and holes as a

chemicurrent. Detailed studies of chemicurrents can further our knowledge about the role of electronic and nuclear degrees of freedom in the dissipation of the chemical energy and thereby can give us a key for understanding of surface dynamics. In this contribution, we report on our methodology of nanofilm Pt-SiO₂-Si Schottky diodes manufacturing and their application as detectors for chemically induced currents. We show experimental results with currents of up to several μ A detected in the Pt-SiO₂-Si diodes while the Pt top electrode is exposed to molecular hydrogen, oxygen or their mixtures with different molar ratios and a pressure in the range of 1 – 10 mbar. Thermal effects and electronic excitations in the Pt top electrode of Pt-SiO₂-Si diodes, caused by the water formation reaction, are considered as possible sources of the observed currents.

9:20am **SS-MoM4 Non-adiabatic Electronic Effects in Multiquanta Energy Transfer and Reactions at Metal Surfaces: Do We Need to Go Beyond the Electronic Friction Picture?**, *D.J. Auerbach*, University of California, Santa Barbara, *K. Golibrzuch*, University of Göttingen, Germany, *A. Kandratsenka*, Max Planck Institute for Biophysical Chemistry, Germany, *R. Cooper, C. Bartels*, University of Göttingen, Germany, *I. Rahinov*, The Open University of Israel, *A.M. Wodtke*, University of Göttingen, Germany

Interactions of molecules at metal surfaces can result in nonadiabatic electronic energy exchange with the metal. This complicates theoretical strategies designed to simulate surface reactivity, most of which today are based on the assumption that the electronic motion can be treated adiabatically, i.e. within the Born-Oppenheimer approximation. One widely applied electronically nonadiabatic theory that makes the leap beyond the Born-Oppenheimer approximation is "electronic friction". In this method coupling of adsorbate motion to metal electrons is treated as a weak perturbation involving frictional forces modifying the molecular dynamics in a systematic and simple way.

Recent experiments on multiquantum vibrational excitation at metal surfaces suggest that at least for certain systems, multi quantum transitions involve energy transfer between the molecule and a single electron hole pair of the solid. These processes might better be described as an electron transfer reaction than as friction. These results suggest that theoretical approaches that go beyond electron weak coupling and electronic friction will be needed to properly treat electronically nonadiabatic effects in surface chemistry.

9:40am **SS-MoM5 Experimental Evidence of Non-adiabatic Effects in Gas-Surface Interactions**, *H. Nienhaus*, University of Duisburg-Essen, Germany

INVITED

The perturbation of the electronic system during gas-metal interactions can cause significant electronic excitations with lifetimes on the femtosecond timescale [1]. Such non-adiabatic processes occur when electronic states are injected below the Fermi level such rapidly that the occupation of the states by resonant charge transfer is delayed. According to Zener's criterion [2] this happens more likely in cases of fast nuclear motion and of low coupling between gas particle and metal states. Experimental evidence of chemically induced electronic excitations is gained by detecting exoelectron emission into the vacuum, surface chemiluminescence and internal hot hole or hot electron chemicurrents. The latter method uses thin-film electronic devices with internal potential barriers as high-pass energy filters. Metal-semiconductor (Schottky) diodes are the most prominent examples for sensitive detectors of both, hot charge carriers and chemiluminescence photons. Independent measurements of the phenomena uncover the various excitation mechanisms. An empty state below the Fermi level may inject a hot hole into the band of occupied electronic metal states or can be filled after Auger relaxation leading to an excited electron in the metal surface. For the oxidation of metals these two fundamental processes can be experimentally distinguished. In addition, it is shown that rapid state injection does not necessarily imply the dissociation of the oxygen molecule as peroxide formation also leads to a significant excitation of the electronic system. The non-adiabatic energy transfer can be associated with a rapid intermolecular motion of the oxygen atoms during the reactive collision. The interaction of chlorine with potassium will be discussed as an example for a strong chemiluminescence reaction. By use of K/Ag/Si-multilayer Schottky diodes the coupling between emitted photons and Ag surface plasmons leads to an enhanced photocurrent in the device at a typical Ag film thickness of around 50 nm. Competing effects in the devices due to adiabatic energy dissipation, e.g., local heating of the system, are discussed. In the experiments such can be either certainly excluded or clearly separated from the non-adiabatic signatures.

[1] B.I. Lundqvist et al. in : Handbook of Surface Science, Vol. 3, Eds.: E. Hasselbrink and B.I. Lundqvist (North-Holland, Amsterdam, 2008), pp. 430-524.

11:20am **SS-MoM10 Analysis of Chemicurrent Components Induced by Hydrogen Oxidation on Pt/n-GaP and Pt/n-SiC Planar Schottky Nanostructures**, *S. Dasari, M. Hashemian, E. Karpov*, University of Illinois at Chicago

Studies of chemically induced hot electron flow over Schottky barriers in planar metal-semiconductor nanostructures provides interesting possibilities for electrolyte-free conversion of chemical energy into electricity in solid-state devices and ultra-fast sensor applications. A method is described here to separate the hot electron current contribution to the total generated current based on in-situ resistive heating of cathode nanolayer of the Schottky structure. The total current is comprised of the hot electron and thermal components. The method preserves usability under application-relevant conditions requiring lower sample temperatures and higher pressures of a reactive gas mixture. Analysis of the current induced during oxidation to water of molecular hydrogen in 60-150 Torr mixtures on Pt/n-GaP nanostructure surface at 341-433 K is performed. Hot electron contribution to the total current has a nonmonotonic dependence on temperature, and its fraction reaches 25% at 341 K and 32% at 433 K. We also found that adsorption of molecular hydrogen and nitrogen gases on Pt/SiC planar nanostructure at normal atmospheric conditions leads to generation of a detectable chemicurrent only in the case of hydrogen. Nitrogen admission conditions were tuned to imitative an equal or greater thermal effect of adsorption as observed during admission of hydrogen gas; therefore the recorded chemicurrent cannot be thermally driven. Adsorptive chemicurrents can occur from admission of hydrogen to samples not only at pre-vacuum conditions, as in earlier studies, but also in reactive and inert gas mixtures at normal atmospheric pressure.

11:40am **SS-MoM11 Enhanced Chemicurrent Effect of H₂ Oxidation on Porous MIM Nanostructures**, *E. Karpov, M. Hashemian, S. Dasari*, University of Illinois at Chicago

Understanding of the basic charge transfer processes at solid interfaces with reactive gas mixtures is a pathway toward advanced sensing, novel catalyst and energy conversion applications. In particular, currents induced in surface reactions on catalytic nanofilms forming Schottky or MOS type contact with a semiconductor substrate have received considerable attention during the last decade. Physical nature of these currents is intriguing, since the Schottky nanofilm device contains no explicit ion conductive layer, and it resembles a photovoltaic cell much closer than an electrochemical device. In this presentation we report on observation stationary chemicurrents in the 0.1 mA/cm² range induced by molecular hydrogen oxidation on surface of porous Pt/TiO₂/Ti nanostructures with a potential barrier at room temperature conditions. Possible physical and chemical mechanisms of the current production are discussed.

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