

Tuesday Afternoon Poster Sessions

Surface Science

Room: Central Hall - Session SS-TuP

Surface Science Poster Session

SS-TuP1 MORTON S. TRAUM AWARD FINALIST: Quantum Tunneling Driven Assembly and Diffusion of Hydrogen and Deuterium on Cu(111). A.D. Jewell*, Tufts University, G. Peng, University of Wisconsin Madison, G. Kyriakou, Tufts University, M. Mavrikakis, University of Wisconsin Madison, C.H. Sykes, Tufts University

Hydrogenation reactions are central to the petrochemical, fine chemical, pharmaceutical, and food industries and are of increasing interest in energy production and storage technologies. The processes of molecular adsorption, dissociation, diffusion, association, and desorption are important surface phenomena in heterogeneous catalysis. Typical heterogeneous catalysts often employ alloys based on platinum, palladium, rhodium and ruthenium. While these metals are active at modest temperature and pressure, they are not always 100% selective and are expensive. Given that molecular hydrogen (H₂) dissociation is often the rate limiting step, one strategy is to engineer the minimal catalytic ensemble that will activate H₂ but leave the other reactants untouched. We describe a system which offers low dissociation barriers at one location on the surface and weaker binding in other regions. The Pd/Cu surface alloy was prepared in the dilute limit in which 1% Pd resides as individual, isolated substitutional atoms in a 99% Cu(111) surface. In terms of adsorption, these Pd atoms significantly lower the barrier to H₂ dissociation and allow the spillover of H atoms onto the Cu surface.[1] This system also offers the opportunity to study the diffusion, association, and assembly of large quantities of H and D on the Cu(111) surface. Through careful low-temperature scanning tunneling microscopy (STM) tracking experiments we show that quantum tunneling effects dominate the diffusion properties of H and D on the Cu surface.[2] With this direct visualization and quantification of quantum tunneling effects in adatom diffusion, we reveal two types of weak interactions between H adatoms, which lead to assembly into small clusters and larger assemblies of small clusters. We show that the self-assembly of H into large islands is, in fact, a tunneling effect resulting from inter-atom energy being much smaller than the diffusion barrier. We further demonstrate that these latter effects are not at play for D. Density Functional Theory (DFT) calculations provide estimates for both diffusion and interaction energies. Theory also provides quantum tunneling probabilities that agree well with experiment.[2] References: [1] G. Kyriakou, M.B. Boucher, A.D. Jewell, E.A. Lewis, T.J. Lawton, A.E. Baber, H.L. Tierney, M. Flytzani-Stephanopoulos, and E.C.H. Sykes, *Science* **335**, 1209 (2012). [2] A.D. Jewell, G. Peng, G. Kyriakou, M. Mavrikakis, E.C.H. Sykes, in preparation.

SS-TuP2 MORTON S. TRAUM AWARD FINALIST: Coverage-Dependent Interfacial Electronic Structures of Thiophenol and p-Fluorothiophenol on Cu(111). S.-Y. Hong*, P.-C. Yeh, J. Dadap, R.M. Osgood, Columbia University

Femtosecond two-photon photoemission spectroscopy is used to investigate and compare the interfacial electronic structures of thiophenol and p-fluorothiophenol films on Cu(111) as a function of molecular coverage. A new state is found to emerge as the coverage is increased; simultaneously, the Cu(111) Shockley surface state disappears for both molecular species. This similarity in behavior is shown to originate from spatial lateral confinement of the surface electron. In addition, the change in the workfunction vs. coverage shows that the two thiophenols exhibit almost identical behavior until an inflection point at ~1/3 ML coverage but then subsequently diverge. This divergent behavior is attributed to the changing orientation of the phenyl group with coverage. At a full monolayer, the net change in the workfunction for the two molecules have opposite signs, which can be explained using a quantitative model based on a surface and molecular dipole moments.

SS-TuP3 MORTON S. TRAUM AWARD FINALIST: Understanding Molecular Adsorption on Graphene-based Hybrid Nanostructures by In Situ Infrared Microspectroscopy. E. Mattson*, S. Cui, K. Pande, H. Pu, M. Schofield, G. Lu, M. Weinert, M. Gajdardziska-Josifovska, J. Chen, C. Hirschmugl, University of Wisconsin Milwaukee

Graphene is an emerging platform for many applications, and being a strictly two-dimensional material, is particularly sensitive to atomic and molecular adsorption. These characteristics have made graphene-based materials a rising candidate for sensing applications targeting harmful

chemicals which pollute our living environment. While under ideal ultra high vacuum (UHV) conditions, graphene monolayers have demonstrated single molecule detection sensitivity, such performance is not feasible under realistic operating conditions. To further improve sensitivity of graphene towards gas detection, we have performed controlled functionalization of graphene with oxygen and decoration with nanoparticles (NPs), where the graphene films act as a sensitive conduction channel, while oxygen functional groups, defects and NPs provide active adsorption sites. While these materials yield impressive performance, little is known about the chemical nature of the substrate/adsorbate interactions. To this end, we have performed *in situ* synchrotron-based infrared microspectroscopy (IRMS) on these atomically thin, micrometer-scale hybrid graphene materials during exposure to the environmentally significant gases NO₂ and NH₃ under normal working conditions (e.g., atmospheric pressure at low concentrations of target gases). Under such conditions, native functional groups are naturally present on the hybrid surfaces and may in fact contribute to the sensing processes. We have investigated hybrid sensing materials consisting of both chemically and thermally reduced graphene oxide (RGO) and chemically RGO decorated with tin dioxide NPs using transmission electron microscopy (TEM) and synchrotron-based IRMS. Experiments were performed at the synchrotron radiation center (SRC) in Stoughton, WI using the recently commissioned infrared environmental imaging (IRENI) beamline. Our studies of the as-produced materials have identified the native functional groups at the hybrid surfaces which are present under normal working conditions. As-produced chemically reduced GO contains functional groups due to residual carbonyl and epoxide species, while SnO₂-decorated RGO contains surface hydroxyl groups, adsorbed water and surface carbonyl groups. We then performed *in situ* IRMS upon exposure to gases to identify the chemical nature of the adsorbates and the resulting changes in the surface composition and electronic properties of the substrate materials. *In situ* IRMS results for NH₃ and NO₂ adsorption on RGO and SnO₂-decorated RGO will be presented.

SS-TuP4 MORTON S. TRAUM AWARD FINALIST: Layer-by-Layer Assembly of Organic Molecular Donor-Acceptor Heterojunctions on Vicinal Gold Surfaces. J. Wang*, J.-M. Tang, G.P. Miller, K. Pohl, University of New Hampshire

Molecular co-self-assembly of technological-relevant organic electron-donor and electron-acceptor molecules into ordered heterostructures on surfaces provides a fundamental molecular-level insight into how these two kinds of molecules would interact in a model organic photovoltaic cell with appropriate electrodes. I will present a study of the self-assembly of functionalized pentacenes (electron donors) and fullerenes (electron acceptors) into a layer-by-layer heterojunction on stepped gold surfaces by scanning tunneling microscopy (STM) characterization and density functional theory (DFT) calculations. The pentacene derivative -- 6,13-dichloropentacene (DCP) -- forms a striking long-range ordered brick-wall self-assembled monolayer (SAM) on a stepped Au(788) vicinal surface, with the long-axis parallel to the step edges [1]. Subsequently deposited fullerene (C₆₀) molecules form parallel triple, double, and single long molecular chains on top of the intact DCP SAM on Au(788) [2]. The novel organic-metal and organic-organic interfacial interactions, as well as the adsorption geometry, have been explored by DFT. The adsorbed C₆₀'s form parallel commensurable (3:2) molecular chains on top of the DCP lattice -- three fullerenes line up with two DCP molecules along the long axis. The initial C₆₀ chains grow along the upper step edges of the DCP/gold terraces. The observed adsorption position for the second C₆₀ chain is the trough between two DCP molecular rows in accordance with the DFT calculations. The calculated C₆₀-chain spacing of 1.1 nm agrees well with the experimental result. This subtle chain formation is attributed to the delicate balance of intermolecular interactions, interfacial dipolar interactions, and stepped-substrate interactions. The electronic properties for this model 3-component organic/metallic system, such as charge transfer between donors and acceptors, between the gold substrate and the molecular layers, will be discussed.

[1] J. Wang, I. Kaur, B. Diaconescu, J.-M. Tang, G. P. Miller, and K. Pohl, *ACS Nano* **5** (2011) 1792.

[2] J. Wang, J.-M. Tang, G. P. Miller, and K. Pohl, in preparation, (2012).

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SS-TuP5 MORTON S. TRAUM AWARD FINALIST: Synthesis and Characterization of Yttrium Aluminum Garnet and Lanthanum Zirconate Particles, R.R. Harl*, S.L. Gollub, G. Walker, B.R. Rogers, Vanderbilt University

Rare-earth doped yttrium aluminum garnet (YAG) and lanthanum zirconate (LZO) are luminescent ceramics that have been used in TV's, LED's, metal oxide transistors, and as laser sources. These materials are thermally and chemically stable. Recent work at Vanderbilt by the Walker and Rogers research groups has shown that the emitted spectrum of proton irradiated LZO particles differs from that of non-irradiated particles, suggesting these materials may be used as passive radiation exposure indicators.

We will discuss the combustion synthesis and characterization of YAG and LZO particles. Combustion synthesis involves heating a mixture of metal nitrates and a fuel until the mixture ignites. If the proper conditions are used, the energy released by the combustion is sufficient to form polycrystalline material. The type and amount of fuel used in the synthesis affect the amount of gaseous by-products produced and flame temperature achieved during a reaction, both of which affect the crystallite size formed. The organic fuels included in this study are urea and glycine with adiabatic flame temperatures 1780°C and 1210°C, respectively. Urea's higher flame temperature makes this fuel attractive for combustion syntheses. However, urea shows signs of degradation beginning around 120 °C, well below its ignition temperature. Glycine does not appear to degrade until approximately 230°C much closer to its ignition temperature. The trade-off between degradation and adiabatic flame temperature suggests the temperature ramp rate used will significantly affect the performance of combustion syntheses carried out with these fuels.

We will present results of detailed thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) experiments used to study the effects of heating rate on the combustion process and on the characteristics of the material formed. TGA/DSC-determined heats of combustion and heat capacities of the reactants and products will also be presented.

Characterization results of powders made using conditions determined by the TGA/DSC experiments will also be presented. X-ray photoelectron spectroscopy (XPS) was used to determine chemical bonding information. Rutherford backscattering spectroscopy (RBS) was used to provide quantitative elemental composition of the material. X-ray diffraction (XRD) was used to determine the crystallinity of the material and to estimate crystallite sizes. Photoluminescence spectroscopy (PL) was used to characterize the materials' emission spectra.

SS-TuP6 The Influence of the Magnetic Field on the Photo-Functional Property of TiO₂/Ni/TiO₂ Thin Films Prepared by Sputtering, A. Toyoda, I. Takano, Kogakuin University, Japan

Since the photoinduced decomposition of water on TiO₂ electrodes was discovered, various characteristics based on photocatalyst have attracted extensive interest. TiO₂ is anticipated as one of materials which are alternative for an existing solar cell based on silicon. TiO₂ shows relatively high reactivity and chemical stability under UV light whose energy exceeds a band gap of 3.2 eV in the anatase crystalline phase. The sun can provide an abundant source of photons, however, UV light accounts for the only small fraction (5 %) of the sun's energy compared to the visible region (45 %). Many techniques have been examined to achieve this purpose.

In this study, the glass (Corning#1737) was used as the substrate. After the TiO₂ layer was prepared by reactive magnetron sputtering using a Ti target in an Ar/O₂ gas mixture, the Ni layer was deposited by using DC sputtering. Finally the TiO₂ layer was coated on the Ni layer. The TiO₂/Ni/TiO₂ multi-layer films were constituted with the first TiO₂ layer of 100 - 200 nm, second Ni layer of 25 nm and the third TiO₂ surface layer of 0 - 100 nm. Composition and microstructure of these films were investigated by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. Chromatic change of a methylene blue solution was applied to photocatalytic evaluation. Light irradiation to TiO₂ films in a methylene blue solution was carried out using a commercial sterilizing lamp as ultraviolet light and an artificial sun lamp as visible light. Transmittance of a methylene blue solution was measured by a spectrophotometer. In this experiment the relationship between the photocatalytic effect and the magnetic field was investigated. Magnets with magnetic field intensity of 0.15 - 0.23 T were placed on the outside of a methylene blue cell. We anticipated that the magnetic field affected separation of an electron and a hole.

The XRD patterns of TiO₂ prepared by reactive magnetron sputtering showed anatase (101) and rutile (110) of TiO₂. The anatase content for the crystal structure of the TiO₂ was 82 %. When the magnetic field was applied in the parallel direction to the substrate surface, the TiO₂/Ni/TiO₂ thin film with the thinner TiO₂ surface layer, i.e. the third layer of 50 nm,

showed the higher photocatalytic property. It was clear that the magnetic field affected a photocatalytic property.

SS-TuP7 Photo-function Property of TiO₂/Cu₂O Thin Films by Reactive Magnetron Sputtering, T. Nakajima, I. Takano, S. Arahara, Kogakuin University, Japan

Characteristics based on photo-inducement of TiO₂ have attracted various interests in many fields. One of those characteristics is a photocatalytic effect. The photocatalytic effect shows antifouling or antimicrobial activity and also has the ability to decompose environmental pollutants. The most important characteristic as a photocatalyst of TiO₂ is well known that photo-excited state is very stable and does not cause self-decomposition. Therefore, the electrolysis of water is performed under ultraviolet irradiation to TiO₂. However the light reaction region of TiO₂ is limited at ultraviolet region corresponded with only about 3 % of sunlight.

In this study, to improve the photo-function property of TiO₂ the double layer films were fabricated by the constitution of the TiO₂ layer with 3.0 - 3.2 eV and the Cu₂O layer with 2.2 eV in a band gap energy. Each constitution of the film with TiO₂/Cu₂O and Cu₂O/TiO₂ was also investigated about optical permeability. Furthermore, to prevent diffusion of Cu from the Cu₂O layer to the TiO₂ layer, the TiN layer was inserted between the TiO₂ layer and the Cu₂O layer. TiN has a high melting point, stability and the suitable electric property as a barrier layer. Those TiO₂/Cu₂O and TiN were fabricated by reactive magnetron sputtering. Composition and microstructure of these films were investigated by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. Chromatic change of a methylene blue solution was applied for the photocatalytic evaluation. Light irradiation to the sample in a methylene blue solution was carried out using a commercial sterilizing lamp as ultraviolet light and an artificial sun lamp as visible light. Transmittance of a methylene blue solution was measured by a spectrophotometer after irradiation for 6 hours by each lamp.

The XRD pattern of the TiO₂/Cu₂O thin film showed the strong peak of the anatase-rutile TiO from an upper layer and the weak peak of Cu₂O from lower layer. The suitable photocatalytic effect was obtained by the constitution of TiO₂ with 300 nm and Cu₂O with 200 nm in thickness, when the photocatalytic effect showed about 31 % under an artificial sun lamp and about 90 % under a sterilization lamp. In the case of the TiO₂/TiN/Cu₂O film it was estimated that the diffusion of Cu was prevented by inserting TiN from the XRD pattern, however, the high photocatalytic effect was not obtained. It was considered that the photocatalytic effect depended on thickness of the TiN layer.

SS-TuP8 Atomic Arrangements and Structural Stability of the Mn Adsorbed GaAs(001) Surfaces, A. Hagiwara, The University of Electro-Communications (UEC-Tokyo), Japan, A. Ohtake, National Institute for Materials Science (NIMS), Japan, Y. Kanno, S. Yasumura, J. Nakamura, The University of Electro-Communications (UEC-Tokyo), Japan

Epitaxial growth of MnAs on the zinc-blende (ZB) GaAs substrate has been extensively studied, because MnAs with ZB has been predicted to be half-metallic. In order to understand the growth mechanism of MnAs on GaAs, it is necessary to clarify the initial adsorption sites of Mn and to determine the well-defined structure of the Mn-adsorbed surface. It has been reported that a variety of (2x2) structures on the GaAs(001) surface appears depending on the coverage of Mn and on the pressure of incident As molecular beams [1]. The local structures which appear with the Mn coverage of 0.25 monolayer under the As-rich condition have been analyzed using electron diffraction and scanning tunneling microscopy (STM); this surface consists of the buckled Ga-As dimer and one Mn adatom in a (2x2) unit cell. However, the initial adsorption site for Mn has not been clarified yet. On the other hand, STM experiments have also shown that the configuration of buckled dimers is not well-ordered anywhere between neighboring unit cells: Local (4x2) or (2x4) arrangement is observed. In this study, first, we determine the position of the Mn atom in the (2x2) unit cell using first-principles calculations based on the spin density-functional theory. Next, in order to explore the onset of the local disordering of dimers, we employ (4x2), (2x4), and c(2x4) models as well as (2x2) and evaluate interactions between the Ga-As dimers.

We have revealed that the Mn atom prefers to adsorb at the site between Ga-As dimers along the dimer row of the (2x2) surface and the simulated STM images agree well with the experimental ones. Next, we have calculated the structure models which represent the different configurations of the dimers on the surface. It has been found that the (4x2) configuration, in which the Ga-As dimer and the As-Ga one align alternately along the dimer row, is most stable. In order to test what contributes to the stabilization of this configuration, we decompose the total energy into each constituent energy term. The Hartree and core-electron terms for (4x2) are lower than those for (2x2). The electronic charges transfer from Ga to As in

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the dimer structure, which results in the dipole formation at the dimer site. From this point of view, the (4x2) configuration, in which the adjacent dipoles are antiparallel with each other, has the energy gain because of the preferable dipole-dipole interactions. Therefore, the disordered configuration observed locally at the (2x2) surface can be attributed to the stabilization of the local (4x2) unit. This work was partially supported by Grant-in-Aid for Scientific Research (B) (No.22360020).

[1] A.Ohtake *et al.*, submitted.

SS-TuP9 Facets and Surfaces Observed on Si(5 5 12) Studied by using Ultra-High-Vacuum Scanning Tunneling Microscopy. *S.-G. Zhao, Y. Li, Y.-B. Song, Y.-Z. Zhu*, Yanbian University, China, *J.M. Seo*, Chonbuk National University, Republic of Korea, *S. Zhang, Z.-P. Guo*, Yanbian University, China

Si(5 5 12)-2×1 surface, which attracts much attention for one-dimensional (1-D) metal nanowire growth on the surface, usually appears wider area single domain with well ordered 1-D structure. In this work, phenomenon of the facets observed on the Si(5 5 12) surface is studied systematically by using ultra high vacuum scanning tunneling microscopy. On the well defined Si(5 5 12) surface, in addition to (1 1 3) facet and (6 9 17) facet, some components (and/or facets) can be observed on the surface as well, such as (7 7 17), (3 3 7), (1 1 2), (1 1 1)-5×5, (1 1 1)-7×7. It is considered that the surface orientations from Si(7 7 17) to (5 5 12), are stable and have almost the same surface free energy, i.e. it is weak anisotropic on the γ -plot. But the (3 3 7), (1 1 2), (1 1 1)-5×5, and (1 1 1)-7×7 facets are appeared to be confined delicately by the surface tensions and the driving force of the single domain growth of the stable surface and facet, which is accompanied by the process of the reconstruction of the surface. Acknowledgement: This work was supported by the National Natural Science Foundation of China (10964014 and 10864008).

References:

- [1] A. A. Baski, S. C. Erwin, L. J. Whitman, *Surf. Sci.*, 392, 69 (1997).
- [2] S. Jeong, H. Jeong, S. Cho, *et al. Surf. Sci.*, 557, 183 (2004).
- [3] H. Kim, H. Li, Y.-Z. Zhu, J. R. Hahn and J. M. Seo, *Surf. Sci.* 601, 1831 (2007).
- [4] C. Herring, *Phys. Rev.* 82, 87–93 (1951).
- [5] V. A. Shchukin and D. Bimberg, *Rev. Mod. Phys.* 71, 1125 (1999).
- [6] R. J. Phanuef, N. C. Bartelt, and E. D. Williams, *et al.*, *Phys. Rev. Lett.* 67, 2986–2989 (1991).
- [7] Y.-Z. Zhu, H. Kim, J.-M. Seo, *Phys. Rev. B.*, 73, 245319 (2006).

SS-TuP10 Photoelectron Spectroscopy and Valence Band Studies of Non-Stoichiometric Superconducting FeSe_{1-x}Te_x. *L. Huerta, V. Ortiz*, Universidad Nacional Autonoma de Mexico, *M. Flores*, Universidad de Guadalajara, Mexico, *R. Escamilla*, Universidad Nacional Autonoma de Mexico

Polycrystalline samples of Fe(Se_{1-x}Te_x), with x = 0.0, 0.25, 0.50, 0.75 and 1.0, were synthesized by solid state reaction. The samples were characterized by x-ray diffraction (XRD), measurements magnetization vs. temperature and photoelectron spectroscopy (XPS). Results of x-ray diffraction shows that the effect of the substitution of Se by Te is increase the lattice parameters. Curves of magnetization vs. temperature shows superconductivity for x = 0.25, 0.5 and 0.75. Whereas, x-ray Photoelectron spectroscopy (XPS) identified the oxidation states of Fe 2p, Se 3d and Te 3d core levels associated with the chemical states Fe(Se_{1-x}Te_x). Finally we compared the Valence Band obtained by XPS for each concentration of tellurium with the density of states electronic (DOS) reported.

SS-TuP11 Photovoltaic Property of Cu₂O/Cu/TiO₂ Thin Films Prepared by Reactive Magnetron Sputtering. *Y. Suzuki, I. Takano*, Kogakuin University, Japan

Recently, TiO₂ is considered as one of attractive materials. Since the photoinduced decomposition of water on the TiO₂ electrode was discovered, the photocatalysis based on semiconductor property has attracted extensive interest. TiO₂ is an n-type semiconductor with a band gap energy of 3.0 - 3.2 eV and is well known as a versatile material. From the view of solar cells TiO₂ is applied in development of dye-sensitized solar cells (DSSCs) or quasi-one-dimensional TiO₂ nanotube structure. On the other hand Cu₂O is a p-type semiconductor with a direct band gap of 2.0 eV and is a promising material on solar cell applications because of its nontoxicity, low cost and high absorption coefficient in the visible region. In this study, the photovoltaic property of p-Cu₂O/n-TiO₂ solar cells which was prepared by magnetron sputtering was investigated. Furthermore Cu buffer layer between TiO₂ and Cu₂O was used to obtain high efficiency.

Cu₂O/Cu/TiO₂ thin films with p-n heterojunction were fabricated by reactive magnetron sputtering. Firstly, glasses (Corning#1737) and ITO-film coated glasses as a substrate were ultrasonically cleaned by an acetone rinse. The TiO₂ thin film was deposited on glass substrates using pure metallic titanium (99.99%) as a sputtering target material in an oxygen gas atmosphere. The flow rates of a sputtering argon gas and an oxygen gas were 20 sccm and 1.5 sccm, respectively. Secondly, the Cu thin film was deposited on the TiO₂ thin film using pure metallic copper (99.99%) as a sputtering target material. Thirdly, the Cu₂O thin film was deposited on the Cu/TiO₂ thin film. The flow rates of a sputtering argon gas and an oxygen gas were 15 sccm and 10 sccm, respectively. Each thickness of the TiO₂ and Cu₂O layer was about 100 nm and 200 nm. Composition and microstructure of these films were investigated by the X-ray photoelectron spectroscopy and the X-ray diffraction. Transmittance of the TiO₂ and Cu₂O thin film was measured by a spectrophotometer. The photovoltaic property was evaluated by measuring the current-voltage curve.

The Cu₂O/Cu/TiO₂ thin films with p-n heterojunction were successfully fabricated by reactive magnetron sputtering. The XRD diffraction pattern of TiO₂ layers deposited at an oxygen flow rate of 1.5 sccm showed a mixture structure. The open voltage of Cu₂O/Cu/TiO₂ thin films showed a higher value under artificial sun light than Cu₂O/TiO₂ thin films. It was confirmed that the buffer layer of Cu improved the photovoltaic property of Cu₂O/TiO₂ thin films.

SS-TuP12 Measurement of pH Induced Transition in Redox Potential for Cerium Oxidation States in Nanoceria. *S. Saraf*, University of Central Florida, *A.S. Karakoti*, Pacific Northwest National Laboratory, *S. Barkam, S.S. Seal*, University of Central Florida

Cerium oxide is an important technological materials and widely used in catalytic converters in automobiles, solid oxide fuel cells, and fuel additives, etc. Recently, it has been discovered that Nanoceria has the ability to kill cancer cells. In addition, it is found that nanoceria can mimic superoxide dismutase (SOD) and catalase activities both of which are essentially the enzymes in the body that are responsible for disproportion of superoxide and peroxide respectively. All of the previously stated applications use the dynamic nature of valence states transition in Nanoceria and makes it electrochemically active. This study is specifically designed to measure nanoceria's redox potential associated with its transition in biological media to fine-tune its further applications. In biological media, the pH also affects the transition characteristics in nanoceria. It is imperative to measure potential-pH diagram for nanoceria as well. In this study we propose to find redox potential of cerium oxide exposed to various pH by the use electrodes made up of nanoceria embedded onto platinum and nickel mesh substrates. Redox reactions are monitored by using cyclic voltammetry experiments. The redox potential of different ceria synthesis is compared at various pHs. Surfaces of Nanoceria are characterized using SEM, XPS and TEM. A complete picture of potential-pH diagram of Nanoceria is presented.

SS-TuP13 XPS and STM Studies of Metal Dopant-Ceria Mixed Oxide Interfaces. *J. Zhou, E. Ginting*, University of Wyoming, *Y.H. Zhou*, Xiamen University, China

Ceria has attracted great attentions in catalysis due to its unique redox properties and oxygen storage capacity. To improve the properties of ceria, suitable metal dopants such as Ti and Mn can be incorporated into it and form dopant-ceria mixed oxides. The additional metal component can modify the physical/chemical properties of ceria. To understand the intriguing chemistry at the metal dopant-ceria interfaces, we examined their structures at the nano-scale using X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) techniques. Dopants including Ti and Mn were vapor-deposited onto well-ordered reducible CeO₂(111) thin films grown on Ru(0001) under ultrahigh vacuum conditions. Both Mn and Ti are oxidized at the cost of ceria reduction upon deposition at 300 K. Ti is in the +4 formal oxidation state. However, +2 state of Mn is the predominate species on ceria. STM studies show the formation of two-dimensional structures on ceria which can further develop into chain structures or triangular domains upon heating. Our studies suggest a strong interaction between metal dopants and ceria. The nature of dopant-ceria interfaces greatly depends on the dopant type. The research is sponsored by the School of Energy Resources at University of Wyoming.

SS-TuP14 Phosphonic Acids for Surface Initiated Polymerization from Oxide Nanoparticles and Flat Surfaces: Towards Applications in Organic Electronics. *S.A. Paniagua, Y. Kim, N. Doubina*, Georgia Institute of Technology, *C.K. Luscombe*, University of Washington, *J.W. Perry, S.R. Marder*, Georgia Institute of Technology

In this work, tailor-made phosphonic acids are used as surface initiators for the growth of both dielectric and semiconductor polymers from barium titanate nanoparticles and transparent conductive electrodes respectively.

For capacitor applications, grafting the polymer from the barium titanate surface gives a composite with high permittivity due to the inorganic inclusions as well as high breakdown strength, mechanical flexibility, and ease in processability due to the organic polymer. The polymer is grown using an atom transfer radical polymerization with catalyst in the ppm level and can be done with limited presence of air. The amount of polymer grown can be controlled in order to fabricate devices with varying polymer content to study its influence in device performance. Devices are created by simple blade casting without the need for any ball milling.

For transparent electrodes in solar cells, the growth of the donor phase directly from the substrate could lead to new morphologies, long term stability, and increased charge collection. We recently published a paper describing the growth of polymethylthiophene from ITO and some of its electrochemical properties.[1] Currently we are working on the optimization of the procedure to obtain smooth, thick polymer brushes that can be used to fabricate devices. Ongoing work involves X-ray photoelectron spectroscopy characterization of the starting monolayers and intermediate metallated species.

[1] Doubina, N.; Jenkins, J. L.; Paniagua, S. A.; Mazzio, K. A.; MacDonald, G. A.; Jen, A. K. Y.; Armstrong, N. R.; Marder, S. R.; Luscombe, C. K. *Langmuir* **2011**, *28*, 1900-1908.

SS-TuP15 Determination of Active Surface Region in Pure and Modified TiO₂ Photocatalysts, *T. Luttrell, J. Tao, M. Batzill*, University of South Florida

A novel approach for determining the photo catalytically active surface region is presented. In this method the photo activity of well-defined epitaxial anatase and rutile TiO₂ thin films is measured by methyl orange decomposition. The photo activity as a function of film thickness then enables to extract the active surface region, which is closely related to the bulk charge carrier diffusion length. Using this methodology we are able to compare differences in the photoactive region of anatase and rutile polymorphs of TiO₂ as well as to investigate the effect of dopants (nitrogen and tungsten) on the depth of the active surface layer. The latter highlights the trade-off between enhanced (visible light) absorption and reduction of active volume of the photocatalyst. These studies are the first that quantifies the differences in rutile and anatase and the influence of dopants on charge carrier diffusion and thus photocatalytic activity.

SS-TuP16 Basic Regimes and Reaction Mechanisms of Chemicurrent Generation during H₂ Oxidation on Catalytic MIM Nanostructures with Porous TiO₂ Support, *M. Hashemian, S. Dasari, E. Karpov*, University of Illinois at Chicago

Fundamental charge transfer processes and chemical reaction mechanisms at gas-solid interfaces require better understanding for catalysis, advanced sensing, and energy conversion and storage applications. Here, we report on distinct regimes of hydrogen oxidation reaction on catalytic Pt/TiO₂/Ti porous nanostructures with a potential barrier, identified via analysis of long term chemicurrent kinetics recorded in the course of the surface reactions. Three regimes in total have been observed, where the reaction turnover rate, thermal effect and chemicurrent production efficiency vary by orders of the magnitude. One the regimes is characterized with a nearly negligible thermal effect, but a surprisingly high yield of 0.1-0.4 electrons per water molecule produced, being highly encouraging for novel energy conversion applications of the present system. Correlations between occurrence of the distinct regimes and conditions in the gas phase are also established.

SS-TuP17 Photo-patternable Superhydrophobic Porous TiO₂ Films Prepared by Hydrothermal Treatment, *S. Nishimoto, M. Becchaku, Y. Kameshima, M. Miyake*, Okayama University, Japan

In recent years, highly porous TiO₂ surfaces prepared by hydrothermal treatment using aqueous alkaline solutions have attracted great interest due to their unique architectures, which include TiO₂ nanotubes and nanowires. These nanostructured surfaces can potentially be used as filtration membranes, high-surface-area electrodes, and photocatalysts for environmental purification. In addition to these applications, porous TiO₂ surfaces are considered to be suitable for use as functional surfaces that undergo photostimulated wettability conversion that changes them from being superhydrophobic to being superhydrophilic. However, to the best of our knowledge, no studies have been conducted on potential applications of such superhydrophobic-superhydrophilic surfaces. In this paper, we report the preparation of superhydrophobic TiO₂ surfaces by hydrothermally treating Ti plates with concentrated NaOH solution and then washing them in deionized water and HCl and subjecting them to heat treatment and surface modification with octadecylphosphonic acid (ODP). Rough nanostructured anatase TiO₂ surfaces with many pores were prepared by the

hydrothermal treatment. Surface modification with self-assembled monolayers (SAMs) of ODP made the surface superhydrophobic with a static water contact angle (CA) of about 174°. This superhydrophobic surface could be converted into a superhydrophilic surface with a water CA of nearly 0° by irradiating it with ultraviolet light as the result of photocatalytic decomposition of the ODP SAM. Thus, the large wettability contrast of the surface, with a water CA difference of over 170°, would allow this photostimulated wettability conversion porous films to be used in many applications including offset printing, cell growth, spotting of biomolecules fluidic microchips, site-selective immobilization of functional materials, and so on.

SS-TuP18 High Hydrophobic Surface with Metabolic System using Organic Monolithic Structure, *M. Sakai*, Kanagawa Academy of Science and Technology, Japan, *T. Kato, A. Nakajima*, Tokyo Institute of Technology, Japan, *A. Fujishima*, Science University of Tokyo, Japan

Recently, the importance of controlling the wettability on the solid surface is recognized in various industries. Superhydrophobic surfaces with water contact angles exceeding 150° are currently the subject of great interest and intensive study. Superhydrophobic coatings that produce rough surfaces at the micro- and nanoscale level with low surface energies have been prepared by several methods. However, the practical applications have been limited, because the superhydrophobic coatings suffered from physical/chemical durability. In the current paper, the super hydrophobic coating with the high physical/chemical durability was designed using organic monolithic structure with TiO₂ photocatalyst and polytetrafluoroethylene particles. The structure was formed by nanoscale frames with 3-dimensional co-continuous, which was composed of epoxy resin. Therefore, the surface with micro structures newly appeared when the top surface was scratched by physical force. Moreover, the organic frame of top surface was slowly decomposed by TiO₂ photocatalyst. Then, the grimy surface could be removed by water fluid (ex. rain). The appearance of fresh micro structure might be similar to metabolic system in a plant. We evaluated the durability performance of the superhydrophobic coating in accelerated weathering test and wear resistance test. In these results, the superhydrophobic coating has kept outdoor durability for 6 years.

SS-TuP19 Adsorption of Water on a Hydrophobic Sb(111) Surface, *A. Chakradhar, J. Shan, Z. Yu, U. Burghaus*, North Dakota State University

The adsorption of water is studied on Sb(111) single crystals by using temperature programmed desorption (TPD) and molecular beam scattering. The surface of Sb(111) is characterized by Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and x-ray photoelectron spectroscopy (XPS). Interestingly, water TPD shows only a single peak at ~155 K while recording the parent mass of water obeying zeroth-order kinetics. The fact that the water monolayer peak is missing, suggests that the Sb(111) surface is hydrophobic. In addition, the results show that the antimony surface is inert towards the adsorption of small molecules such as CO, CO₂, and NO. Moreover, the co-adsorption of n-butane and water shows site blocking effects for n-butane adsorption only at very large pre-exposures of water, indicating the formation of a porous water film, as expected for a hydrophobic surface.

SS-TuP20 Insulating Si(111) Surfaces by Organic Fluorine Compound Molecular Monolayer, *F.Y. Tian, A.V. Tephlyakov*, University of Delaware

Both trifluoroethylamine (TFEA) and p-fluoroaniline (pFA) were modified on Si(111) surfaces as insulators by forming Si-N bond through wet-chemistry. Fluorine functional groups are good chemical building block and tracking label for X-ray photon spectroscopy (XPS). Infrared spectroscopy (IR) was also employed to identify the surface Si-N bonding information. The experiment strategy is starting from native oxidized silicon (111) wafers, hydrogen-terminated Si(111) samples were obtained through modified RCA cleaning method and HF/NH₄F etching. Then, the H-Si(111) wafers were treated with PCl₅ to get Cl-terminated Si(111) surfaces. Finally, the samples were reacted in TFEA and pFA/THF solution, respectively, at inert atmosphere at room temperature for a variety reaction period. The formation of molecular monolayer of TFEA and pFA was confirmed by both XPS and IR. Density functional theory (DFT) was also applied to mimic both TFEA and pFA's behavior on Si(111) surfaces. In addition, due to various basicity and electron drawing capabilities, TFEA and pFA presented different reactivity towards Cl-terminated Si(111) surfaces.

SS-TuP21 Methanol Induced Nanopatterning of Si(111):H – Insights from Density Functional Calculations, *P. Thissen, T. Peixoto, K. Roodenko*, University of Texas at Dallas, *E. Fuchs*, Zyvex Labs LLC, *W.G. Schmidt*, University of Paderborn, Germany, *Y.J. Chabal*, University of Texas at Dallas

The reaction of methanol with hydrogen terminated Si(111) surfaces has been studied using density functional theory (DFT). Depending on the

chemical potentials of hydrogen and methanol several surface configurations with various coverage are found to be stable. The temperature dependence of the chemical potentials as well as the entropy contributions to the surface free energy are found to result in only minor changes of the calculated surface phase diagram. In contrast, the calculated reaction barriers are found to be strongly dependent on the methoxy coverage of the surface. They strongly increase with increasing methoxy coverage. Our calculations thus suggest that the formation of a nanopatterned Si(111) surface, featuring 1/3 methoxy and 2/3 hydrogen termination as observed experimentally is related to the reaction kinetics rather than the surface thermodynamics. Consequently, we show that higher temperatures are the key parameter to prepare Si(111) surfaces with higher methoxy-group coverage than 1/3. Finally, a Kinetic Monte Carlo algorithm is applied to investigate the adsorption and the desorption rates until the surfaces reaction reaches the temperature-dependent equilibrium state. We find the reaction of methanol with hydrogen terminated Si(111) to be self-limited at temperatures over 400 K, since the methanol starts to react with itself.

SS-TuP22 Reactivity of Propane on Pd Oxide Phases Prepared by Surface Oxidation vs. Reduction, C. Hakanoglu, J.F. Weaver, University of Florida

We used temperature-programmed reaction spectroscopy (TPRS) to study the reactivity of propane on oxidized Pd(111) surfaces that were prepared by partially oxidizing Pd(111) as well as partially reducing a PdO(101) thin film in ultrahigh vacuum. These experiments were motivated in large part by recent observations of multiple phases co-existing during the autocatalytic thermal decomposition of a PdO(101) thin film, and the possibility that such phases exhibit distinct reactive properties. We find that the surface reactivity toward propane oxidation increases monotonically with increasing surface oxygen concentration, but that the reactivity exhibits a slight hysteresis as a function of oxygen coverage for surfaces prepared by Pd(111) oxidation vs. PdO(101) reduction. Based on the observation that propane desorbs in distinct features from different Pd-oxide phases, we determined that the hysteresis in reactivity arises from differences in the amount of PdO(101) domains present on partially oxidized vs. reduced surfaces and present evidence that propane reacts exclusively on PdO(101) domains even when a mixture of surface phases is present. We show that deconvolution of the propane desorption traces also allows us to estimate the relative fractions of surface phases which develop during both oxide growth and reduction, and thus provides a means to quantify the phase evolution as a function of oxygen coverage. The analysis demonstrates that metallic domains as well as phases characteristic of monolayer oxides, so-called surface oxides, develop during the early stages of reduction of a multilayer PdO(101) film and appear to form on top of the multilayer oxide. This finding clarifies the nature of new structures that were observed in prior STM studies of PdO(101) film decomposition, and provides key insights for understanding the processes governing oxide decomposition.

SS-TuP23 Structural Properties of TbO_x Thin Films Grown on Cu(111), W.S. Cartas, University of Florida, T.E. Milstrey, J.F. Weaver, University of Florida

The oxides of the rare earth metals Tb, Pr and Ce are desirable for several catalytic applications due to their ability to store and release oxygen atoms. In contrast to ceria, terbia surfaces have not been widely investigated, and may exhibit interesting structural behavior since several bulk Tb oxide phases are known to exist. In this study, we investigated the growth of terbium oxide (TbO_x) thin films on Cu(111) in ultrahigh vacuum, using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) to characterize the surface structures. We used a stepwise procedure to prepare the TbO_x films, with each step involving Tb deposition onto Cu(111) held at 300 K in an O₂ background to produce an ~1 monolayer (ML) film, followed by annealing in O₂ at 750 K. The TbO_x films grow epitaxially on the Cu(111) substrate to generate TbO_x(111) with unit cell dimensions of about (1.4 x 1.4) relative to the Cu(111) lattice. STM images show that the TbO_x films (~2 - 5 ML) are comprised of large, flat terraces and reveal an atomic-structure consisting of hexagonal, close-packed arrangements of atoms that are separated by rows of oxygen vacancies at a spacing of about 2.2 nm. Estimates of the vacancy concentrations suggest that the oxide stoichiometry corresponds to an O:Tb ratio between 1.67 and 1.71, which agrees well with the composition of the stable iota phase of bulk terbia. The capability of preparing TbO_{1.7}(111) films with well-defined arrangements of vacancies may provide new opportunities for preparing model catalyst surfaces and studying the interactions of molecular reactants with ensembles of vacancies. Such studies are currently in progress.

SS-TuP24 Modeling of Chemical Reaction – Induced Thermal Currents in Metal Nanofilm – Semiconductor Schottky Diodes, I. Nedrygailov, University of Duisburg-Essen, Germany, E. Karpov, University of Illinois at Chicago, E. Hasselbrink, D. Dising, University of Duisburg-Essen, Germany

Chemically induced currents (chemicurrents) in metal nanofilm – semiconductor contacts attracted considerable attention of the surface physics and chemistry community since McFarland, Nienhaus *et al.* reported a direct detection of hot electrons and holes, excited by a surface chemical reaction, using Schottky diodes under zero-bias voltage conditions. This phenomenon is highly promising for studying the dynamics of elementary chemical processes on the interface between the gas phase and a solid surface. The use of the chemicurrents for ultrafast chemical sensing and direct conversion of energy of surface chemical reactions into electricity is also currently discussed. As a matter of fact, the mechanism underlying the chemicurrent generation and detection is a subject of ongoing discussions due to the presence of unavoidable thermal effects, accompanying surface chemical reactions, which hamper an unambiguous identification of the experimental data. In this contribution we report on a simple theoretical model for estimating the

magnitude of the chemical reaction - induced thermal currents in metal nanofilm – semiconductor Schottky diodes. As well, we present a comparison of our calculations with the experimental values of the chemicurrents reported earlier.

SS-TuP25 Synthesis, Characterization and Catalytic Activity of Pt Nanoparticles Supported on γ -Al₂O₃ and WC: Size and Support Effects, M. Ahmadi, L. Merte, B. Roldan Cuenya, University of Central Florida

Direct-methanol fuel cells (DMFC) are one of the promising candidates for alternative clean energy generation. Extensive efforts are going on to improve the efficiency of these cells using different Pt-based catalyst. Although tungsten carbide (WC) shows similar electronic structure as Pt and has promising catalytic properties, it is not extensively used due to its instability. However, it has been observed that one monolayer of Pt on the surface of WC displays a similar performance as bulk Pt and furthermore, it stabilizes the WC, which makes it a very cost-effective alternative for Pt electrodes. In this work we have synthesized size- and shape-selected Pt nanoparticles (NPs) via inverse micelle encapsulation methods. The NPs were then supported on WC and γ -Al₂O₃ nanocrystalline powders as well as on WC/W thin films. We have investigated the size and morphology of our NPs by atomic force microscopy (AFM) and by transmission electron microscopy (TEM) and their chemical composition by X-ray photoelectron spectroscopy (XPS). Methanol oxidation was carried out in a packed-bed mass flow reactor and mass spectrometry was employed to quantify the catalyst's activity as a function of the NP size. The evolution of the structure of the Pt NPs during the oxidation of methanol was investigated under operando conditions using extended X-ray absorption fine-structure spectroscopy (EXAFS).

SS-TuP26 Ligand Functionalized Cerium Oxide Nanoparticles - Investigating the Mode and Energetics of Binding, A.S. Karakoti, Z. Lu, W. Wang, P. Nachimuthu, H. Wang, P. Yang, S. Thevuthasan, Pacific Northwest National Laboratory

Despite the significant amount of work done on functionalization of nanoparticles for various applications, studies on the determining the fundamental molecular level interaction between the various ligands and nanoparticle surfaces have been limited due to the inherent challenges associated with the characterization of highly reactive and dynamic nature of these particles. In order to obtain a fundamental understanding of nanoparticle-ligand interaction, cerium oxide nanoparticles (ceria) functionalized with simple ligands such as carboxylic acids were studied to characterize the nature of bonding, configuration of ligands and the energetics of the ligand-nanoparticle interactions. Mono-disperse ceria nanoparticles were synthesized by thermal hydrolysis process and functionalized with carboxylic acid groups from various organic ligands. The size distribution and morphology of the nanoparticles prior to and following functionalization were characterized by various imaging and spectroscopy tools to ascertain the integrity of nanoparticles. In-situ x-ray photoelectron spectroscopy (XPS) from aqueous solution of functionalized ceria nanoparticles frozen at liquid nitrogen temperature was performed to avoid any surface contamination and preserve the chemistry of the functionalized nanoparticles. XPS data suggests that the following functionalization the ceria nanoparticles predominantly exist in Ce⁴⁺ oxidation state. From XPS elemental quantification it was found that the oxygen from carboxylate molecules becomes a part of the ceria lattice to maintain the stoichiometry and bind to the ceria surface in bidentate orientation. Sum frequency generation vibration spectra (SFG-VS) showed the presence of OCO modes of vibration on the surface of cerium oxide confirming the bidentate mode of bonding between carboxylate and ceria

nanoparticle surface. In addition isothermal titration calorimetry was used to determine energetics of ligand binding on the surface of nanoparticles. Results from these characterizations were combined with the periodic density functional theory (DFT) calculations to develop a complete visualization of the interaction of organic ligands with nanoparticle surfaces.

SS-TuP27 *In Situ* Coarsening Study of Micellar Pt Nanoparticles Supported on γ -Al₂O₃: Pretreatment and Environmental Effects, J. Matos, L.K. Ono, F. Behafarid, J.R. Croy, S. Mostafa, University of Central Florida, A.T. DeLaRiva, A. Datye, University of New Mexico, A.I. Frenkel, Yeshiva University, B. Roldan Cuenya, University of Central Florida

The thermal stability of micellar Pt nanoparticles (NPs) supported on nanocrystalline γ -Al₂O₃ was monitored in situ under different chemical environments (H₂, O₂, H₂O) via extended x-ray absorption fine-structure spectroscopy (EXAFS) and ex situ via scanning transmission electron microscopy (STEM). Drastic differences in the stability of identically synthesized NP samples were observed upon exposure to two different pre-treatments. In particular, exposure to O₂ at 400°C before high temperature annealing in H₂ (800°C) was found to result in the stabilization of the micellar Pt NPs, reaching a maximum overall size after coarsening of ~1 nm. Interestingly, when an analogous sample was pre-treated in H₂ at ~400°C, a final size of ~5 nm was reached at 800°C. The beneficial role of oxygen for the stabilization of small Pt NPs was also observed in situ during annealing treatments in O₂ at 450°C for several hours. In particular, while NPs of 0.5 ± 0.1 nm initial average size did not display any significant sintering (0.6 ± 0.2 nm final size), an analogous thermal treatment in hydrogen lead to NP coarsening (1.2 ± 0.3 nm). The same sample pre-dosed and annealed in an atmosphere containing water only displayed moderate sintering (0.8 ± 0.3 nm). Our data suggest that PtOx species, possibly modifying the NP/support interface, play a role in the stabilization of small Pt NPs. Our study reveals the enhanced thermal stability of micellar Pt NPs and the importance of the sample pre-treatment and annealing environment in the minimization of undesired sintering processes affecting the performance of nanosized catalysts.

SS-TuP28 Synthesis, Characterization and Reactivity of Cu-Zn and Cu-Pd Bimetallic Nanoparticles, H. Mistry, L. Merte, B. Roldan Cuenya, University of Central Florida

Bimetallic nanoparticles have become an important area of study because of their unique catalytic properties. We describe the synthesis and characterization of bimetallic copper-zinc and copper-palladium nanoparticles. The Cu-Zn and Cu-Pd bimetallics are synthesized using inverse micelle encapsulation in PS-P2VP diblock copolymers. The size and morphology of these nanoparticles supported on SiO₂/Si(111) and TiO₂(110) are characterized using atomic force microscopy (AFM), as well as scanning tunneling microscopy (STM) under ultra high vacuum. Characterization of electronic and chemical properties is carried out using x-ray photoelectron spectroscopy (XPS). Applications of these nanoparticles supported on γ -Al₂O₃ for the catalytic synthesis of methanol will be shown.

SS-TuP29 CO Oxidation over Au/TiO₂ Model Catalyst, T. Fujitani, I. Nakamura, AIST, Japan

In this work we have investigated the reaction mechanism and active sites for CO oxidation over the Au/TiO₂ model surface and Au single crystal surfaces, along with the role of moisture CO.

We examined the effect of moisture on the CO₂ formation rate at the reaction temperature of 300 and 400 K. The CO₂ formation rate at 300 K was increased significantly with increasing H₂O partial pressure up to 0.1 Torr, and then gradually decreased with H₂O pressure. In contrast, no promotional effect of H₂O was observed at the reaction temperature of 400 K. The moisture has an essential role to promote the CO oxidation reaction over Au/TiO₂ catalyst at low temperature, whereas the CO oxidation reaction proceeded without moisture with high reaction temperature. This important observation indicates that the CO oxidation mechanism over Au/TiO₂ is different between 300 and 400 K, considering that the activation process of oxygen molecules strongly depended on a reaction temperature. That is, molecular oxygen has been activated directly over the Au surface at the high temperature while the moisture takes part in the activation of the oxygen molecule at low reaction temperature.

Next, we examined the turnover frequencies (TOFs) for CO₂ formation at the two reaction temperatures as a function of mean gold particle diameter. To determine whether the active sites for CO oxidation were exposed gold atoms on the gold particles or perimeter sites at the interface between the gold particles and the TiO₂ support, we calculated the TOFs in two ways: (i) by normalizing the total number of exposed Au atoms at the gold particles (TOF-S) and (ii) by normalizing the the total number of gold atoms at the perimeter interfaces (TOF-P). The results clearly showed that the

relationship between TOF and mean gold particle diameter depended strongly on reaction temperature. At 300 K, TOF-S decreased with increasing mean gold particle diameter, whereas TOF-P remained nearly constant regardless of particle diameter, suggesting that the active sites for CO oxidation were the gold atoms located at the periphery of the gold particles attached to TiO₂. In contrast, TOF-S at 400 K remained nearly constant regardless of the mean gold particle diameter, indicating that the active sites for CO oxidation were newly created on the gold metal surface at the high temperature. Thus, we can conclude that both the reaction mechanisms and the active sites differed between the low temperature region and the high temperature region.

SS-TuP30 Active Sites for H₂ Dissociation on Gold Model Catalyst, I. Nakamura, T. Fujitani, AIST, Japan

Au nanoparticles supported on metal oxides are highly active for various hydrogenation reactions. The dissociation of H₂ molecules is one of the most important elementary steps in hydrogenation reactions, and the nature of H₂ dissociation sites has been the subject of various studies. Recently, we demonstrated using Au/TiO₂(110) that the perimeter interface between Au and TiO₂ was the active sites for H₂ dissociation. However, the oxidation state of Ti and the structure of Ti oxide at the perimeter interface are not entirely clear. Here, we performed H₂-D₂ exchange reaction using TiO_x/Au(111) and TiO_x/Au(100) (x = 0–2), and clarified the influence of the oxidation state of Ti and the Au and TiO₂ structures on the creation of active sites for H₂ dissociation. We found that the presence of stoichiometric TiO₂ was essential for the creation of H₂ dissociation sites over the Au surfaces. The activation energies (E_a) for HD formation over TiO₂/Au(111) and TiO₂/Au(100) were consistent with each other, and these E_a agreed well with that for Au/TiO₂(110). This result shows that the active sites for H₂ dissociation created on TiO₂/Au(111) and TiO₂/Au(100) were identical to those formed on Au/TiO₂(110). Furthermore, we demonstrated that turnover frequencies (TOFs) for HD formation were close among these three surfaces, where TOFs were calculated by normalizing the number of HD molecules formed per second to the total number of Au atoms at the perimeter interfaces. These results clearly indicate that the active sites for H₂ dissociation over TiO₂/Au(111) and TiO₂/Au(100) were the perimeter interface between TiO₂ and Au. Concerning the structure of TiO₂ on Au surfaces, LEED observations showed that the TiO₂ produced on Au(111) was the ordered structure, in contrast to disordered TiO₂ structure on Au(100). Thus, the creation of active sites for H₂ dissociation was independent of the Au and TiO₂ structures consisting perimeter interface. We concluded that local bonds between Au and O atoms of stoichiometric TiO₂ (Au–O–Ti) create the active sites for H₂ dissociation.

SS-TuP31 Image Potential State Mediated Excitation of Rubrene on Graphite, J. Park, Seoul National University, Republic of Korea, T. Ueba, L. Terawaki, T. Yamada, H. Kato, T. Munakata, Osaka University, Japan

Electronic excitation at the interface between an organic molecular film and a substrate is of general importance for the area of organic electronics and light conversion processes. We demonstrate rubrene/HOPG as a model system for an organic film/substrate interface. Many efforts have been devoted to improve the performance of a rubrene thin film transistor after high carrier mobility was achieved for rubrene single crystals. The reasons for the poor efficiency of the thin films are attributed to the molecular geometry on the surface. To understand the mechanisms of charge transportation for organic molecular devices, it is the primary step to unravel the molecular electronic structures of both occupied and unoccupied states at interfaces between the film and the substrate.

We have performed two-photon photoemission (2PPE) spectroscopy for rubrene films formed on HOPG substrate. It is revealed a prominently enhanced unoccupied molecular peak, which is resonantly excited from the highest occupied molecular orbital (HOMO). Interestingly, the enhancement of the peak becomes less significant at the coverage higher than 1 monolayer, where the image potential state (IPS) peak on the substrate disappears. The resonance enhancement is moderate with s-polarization, by which the transition to IPS is completely suppressed. We ascribe that the excitation of the the level is mediated by the IPS on HOPG. Though the IPS wave function extends outside the molecules, it interacts with the unoccupied molecular orbital at the edges of molecular islands, causing the strong resonance enhancement of the unoccupied molecular level.

By clarifying the mechanism, the excitation process is expected to be useful to highly enhance the efficiency of organic molecular devices and light conversion processes. The energy of IPS is generally governed by the work function. It may be possible to tune the IPS level nearly resonant to an unoccupied level of organic films. This provides a way to tailor the electronic excitation efficiency.

SS-TuP32 Tribological Properties in a Vacuum of DLC Thin Films Prepared by N_2^+ Ion Beam Assisted Deposition, H. Nishi, K. Harada, I. Takano, Kogakuin University, Japan

DLC (Diamond-like carbon) classified in new materials is amorphous carbon including hydrogen and has the similar property to diamond. DLC films were formed by the ion beam evaporation method in the early 1970's and after that have been manufactured by various methods. Because the representative property of DLC shows the high hardness and low friction coefficient, DLC is applied in various fields such as motor parts or tools. The ion beam assisted deposition method has many parameters on the film formation condition in comparison with other dry process methods. Therefore this method was anticipated in production of new characteristics such as a high adhesion film.

From the result of our research, DLC thin films prepared by the ion beam assist method using an N_2 gas showed the excellent low friction coefficient in the atmosphere. In this study, the behavior on friction in a vacuum of those DLC films was investigated. The DLC films were formed using N_2^+ ion beam assisted deposition in a toluene (C_7H_8) atmosphere. The formation conditions of DLC films were changed with an ion beam current density and an accelerating voltage. Stainless steels (304SS) were used for the sample substrate. The mechanical properties of hardness and friction coefficient were measured using the dynamic micro knoop hardness tester and the ball-on-disk tribotester respectively. Atomic concentration and structure of the films were investigated by X-ray photoelectron spectroscopy and Raman spectroscopy. The friction coefficient in a vacuum was measured under 5×10^{-4} Pa. The conditions of the ball-on-disk test were 0.98 N in a weight and 135 rpm in a sliding speed.

The suitable friction property of DLC films was obtained by the condition with an accelerating voltage of 5 kV at a current density of $10 \mu A/cm^2$. The minimum friction coefficient in a vacuum was 0.016 for an SUJ2 ball of the counter material, however, the DLC thin film started to cause partial peeling-off in a sliding distance of 52 m. It is anticipated that the property in a vacuum of these DLC films is applied in space technology.

SS-TuP34 Atomic Structure of the Bi-induced (1×3) Surface Reconstruction on GaAs(001), A. Duzik, J.C. Thomas, A. Van der Ven, University of Michigan, N.A. Modine, Sandia National Laboratories, J.M. Millunchick, University of Michigan

Bismuth (Bi) is a nearly ideal surfactant on GaAs owing to its large size relative to Ga and As, smoothing the surface morphology of the GaAs(001) surface. Surface modification in this manner is potentially useful in high-quality device growth, but corresponding atomic structure and its effects on subsequent device growth are unknown. Reflection high-energy electron diffraction indicates that the Bi surfactant induces a (1×3) surface reconstruction. Experimental scanning tunneling microscopy clearly shows a nm-length-scale step structure with a high density of alternating up/down steps and reconstruction rows of $\times 3$ periodicity. From these observations, we propose a mechanism for the Bi surfactant surface smoothing. The alternating step heights on the nm length scale are likely a result of a Bi-induced surface energy change. However, compositional disorder obscures the atomic structure within the rows. Thus, the atomic structure of the (1×3) reconstruction cannot be revealed through experiment, but must be determined from simulation.

Ab-initio density functional theory and cluster expansion calculations were carried out to determine the relative stability of reconstruction in the Bi/GaAs(001) system. Differences in stability originate from two sources: structure, determined by surface bonding topology, and configuration, arising from the arrangement of Ga, As, and Bi species over the surface dimer sites. For the Bi/GaAs system, the (2×1), $\alpha 2(2 \times 4)$, $\beta 2(2 \times 4)$, (4 ×3), and c(4 ×4) reconstructions and their species configurations were considered. Calculations show the observed (1×3) reconstruction explained by the (4×3) structure first proposed for AlSb and GaSb, which has a large number of stable configurations at 0K. At typical growth temperatures, the calculated Monte Carlo entropy approaches that of ideal mixing, indicating thermal excitations of these configurations produce the experimentally observed disorder.

SS-TuP35 Spectroscopic Study of the Chemical Reaction at the Ca/PMMA Interface, H.X. Ju, J.F. Zhu, University of Science and Technology of China

PMMA is an important thermoplastic material which has been utilized in a variety of engineering areas ranging from aeronautical applications to electronics industries, due to its attractive physical and optical properties. The physical and chemical interactions have been observed at the interfaces between metals and PMMA, which can play a crucial role in the device performance. As a result, significant attention has been paid to the interfaces in order to promote devices performance and stability.

In this work, we investigate in detail the chemical reaction during deposition of Ca on the PMMA surface by applying X-ray photoemission

spectroscopy (XPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS), which provide detailed information concerning surface chemical reaction. The changes of the O 1s and C 1s core level XPS spectra indicate a strong interaction between the Ca and the PMMA. The O K-edge NEXAFS spectra give a comprehensive insight into reaction sites. In this way, the pronounced decrease of the π^* (C=O) resonance intensities with deposition of Ca clearly demonstrates that Ca atoms attack carbonyl groups in PMMA. The experimental results confirm the previous work regarding the adsorption microcalorimetry measurements of metal particles adsorption on polymer surfaces, which provide a powerful approach for determining the adsorption energy and understanding interfacial interactions. There is a high heat of Ca adsorption on PMMA surfaces of 780 kJ/mol, attributed to the reaction of each Ca reacts with 2 esters to form the Ca carboxylate. Furthermore, we provide addition information regarding the details of specific chemical interactions at the interface. These will greatly contribute toward further understanding of the interfaces between metals and polymers.

SS-TuP36 Mass Ratio Effects in Hyperthermal Surface Scattering, D. Kulkarni, C.E. Sosolik, Clemson University

The forward scattering of heavy ionic projectiles from oriented crystal surfaces gives evidence of collective effects that are far more pronounced than those seen in scattering of light ionic projectiles. For example, molecules containing heavy atoms such as XeF_2 are known to initiate novel surface chemistry effects. To study these kinematic trends, MD and trajectory simulations were performed for hyperthermal energy ions. By sequentially increasing the mass of the projectile across the periodic table, we have observed energy and angle resolved trends that show a clear deviation from standard scattering events, which are typically interpreted as sequential binary collisions. The simulation results were compared to experimental data for alkali ions on metal surfaces, specifically for the cases of K^+ and Cs^+ scattered from Cu(001).

SS-TuP37 Ag Nanoparticles on Reducible CeO₂(111) Thin Films: Effect of Nanoscale Ceria, S.W. Hu, X.F. Feng, D.D. Kong, D.L. Cheng, Y.F. Ye, J.F. Zhu, University of Science and Technology of China

Ag/CeO₂ is of particular interests because of its importance in technical applications as catalysts for many chemical reactions such as CO and hydrocarbon oxidation. However, there are still some discrepancies remaining in the fundamental recognition of the Ag/CeO₂ catalysts such as the oxidation state of Ag species and the mechanism of Ag-induced the reduction of CeO₂. In order to obtain a detailed insight of the Ag/CeO₂ system, the growth and structures of Ag nanoparticles on CeO_x(111) thin films with different thicknesses, morphologies and reduction degrees have been systematically studied by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). These CeO_x(111) thin films were epitaxially grown on Cu(111). It is found that in most cases Ag exhibits the three-dimensional (3D) growth with constant particle densities on the CeO_x(111) surfaces. Ag only populates the sites at the ceria-ceria step edges, independent of the thicknesses and the reduction degree of the ceria films. Moreover, the particle density is directly proportional to the number of step edges of ceria, which is related to its thickness on Cu(111). On the reduced ceria films, Ag nanoparticles do not nucleate on point defects. Upon heating, the Ag nanoparticles undergo serious sintering before desorption at 800 K on the fully oxidized CeO₂ films. While on the reduced ceria films, the sintering and desorption process are slowed down at the same annealing temperatures as those on CeO₂. This result suggests that although the surface point defects have no influence on the growth behavior of Ag, they can enhance the thermal stability by inhibiting the diffusion of Ag on the ceria surface to form large particles during annealing.

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Cui, S.: SS-TuP3, **1**

— D —

Dadap, J.: SS-TuP2, **1**
Dasari, S.: SS-TuP16, **4**
Datye, A.: SS-TuP27, **6**
DeLaRiva, A.T.: SS-TuP27, **6**
Diesing, D.: SS-TuP24, **5**
Doubina, N.: SS-TuP14, **3**
Duzik, A.: SS-TuP34, **7**

— E —

Escamilla, R.: SS-TuP10, **3**

— F —

Feng, X.F.: SS-TuP37, **7**
Flores, M.: SS-TuP10, **3**
Frenkel, A.I.: SS-TuP27, **6**
Fuchs, E.: SS-TuP21, **4**
Fujishima, A.: SS-TuP18, **4**
Fujitani, T.: SS-TuP29, **6**; SS-TuP30, **6**

— G —

Gajdardziska-Josifovska, M.: SS-TuP3, **1**
Ginting, E.: SS-TuP13, **3**
Gollub, S.L.: SS-TuP5, **2**
Guo, Z.-P.: SS-TuP9, **3**

— H —

Hagiwara, A.: SS-TuP8, **2**
Hakanoglu, C.: SS-TuP22, **5**
Harada, K.: SS-TuP32, **7**
Harl, R.R.: SS-TuP5, **2**
Hashemian, M.: SS-TuP16, **4**
Hasselbrink, E.: SS-TuP24, **5**
Hirschmugl, C.: SS-TuP3, **1**
Hong, S.-Y.: SS-TuP2, **1**
Hu, S.W.: SS-TuP37, **7**
Huerta, L.: SS-TuP10, **3**

— J —

Jewell, A.D.: SS-TuP1, **1**
Ju, H.X.: SS-TuP35, **7**

— K —

Kameshima, Y.: SS-TuP17, **4**
Kanno, Y.: SS-TuP8, **2**
Karakoti, A.S.: SS-TuP12, **3**; SS-TuP26, **5**
Karpov, E.: SS-TuP16, **4**; SS-TuP24, **5**
Kato, H.: SS-TuP31, **6**
Kato, T.: SS-TuP18, **4**
Kim, Y.: SS-TuP14, **3**
Kong, D.D.: SS-TuP37, **7**
Kulkarni, D.: SS-TuP36, **7**
Kyriakou, G.: SS-TuP1, **1**

— L —

Li, Y.: SS-TuP9, **3**
Lu, G.: SS-TuP3, **1**
Lu, Z.: SS-TuP26, **5**
Luscombe, C.K.: SS-TuP14, **3**
Luttrell, T.: SS-TuP15, **4**

— M —

Marder, S.R.: SS-TuP14, **3**
Matos, J.: SS-TuP27, **6**
Mattson, E.: SS-TuP3, **1**
Mavrikakis, M.: SS-TuP1, **1**
Merte, L.: SS-TuP25, **5**; SS-TuP28, **6**
Miller, G.P.: SS-TuP4, **1**
Millunchick, J.M.: SS-TuP34, **7**
Milstrey, T.E.: SS-TuP23, **5**
Mistry, H.: SS-TuP28, **6**
Miyake, M.: SS-TuP17, **4**
Modine, N.A.: SS-TuP34, **7**
Mostafa, S.: SS-TuP27, **6**
Munakata, T.: SS-TuP31, **6**

— N —

Nachimuthu, P.: SS-TuP26, **5**
Nakajima, A.: SS-TuP18, **4**
Nakajima, T.: SS-TuP7, **2**
Nakamura, I.: SS-TuP29, **6**; SS-TuP30, **6**
Nakamura, J.: SS-TuP8, **2**
Nedrygailov, I.: SS-TuP24, **5**
Nishi, H.: SS-TuP32, **7**
Nishimoto, S.: SS-TuP17, **4**

— O —

Ohtake, A.: SS-TuP8, **2**
Ono, L.K.: SS-TuP27, **6**
Ortiz, V.: SS-TuP10, **3**
Osgood, R.M.: SS-TuP2, **1**

— P —

Pande, K.: SS-TuP3, **1**
Paniagua, S.A.: SS-TuP14, **3**
Park, J.: SS-TuP31, **6**
Peixoto, T.: SS-TuP21, **4**
Peng, G.: SS-TuP1, **1**
Perry, J.W.: SS-TuP14, **3**
Pohl, K.: SS-TuP4, **1**
Pu, H.: SS-TuP3, **1**

— R —

Rogers, B.R.: SS-TuP5, **2**
Roldan Cuenya, B.: SS-TuP25, **5**; SS-TuP27, **6**
Roldan Cuenya, B.: SS-TuP28, **6**
Roodenko, K.: SS-TuP21, **4**

— S —

Sakai, M.: SS-TuP18, **4**
Saraf, S.: SS-TuP12, **3**
Schmidt, W.G.: SS-TuP21, **4**
Schofield, M.: SS-TuP3, **1**
Seal, S.S.: SS-TuP12, **3**
Seo, J.M.: SS-TuP9, **3**
Shan, J.: SS-TuP19, **4**
Song, Y.-B.: SS-TuP9, **3**
Sosolik, C.E.: SS-TuP36, **7**
Suzuki, Y.: SS-TuP11, **3**
Sykes, C.H.: SS-TuP1, **1**

— T —

Takano, I.: SS-TuP11, **3**; SS-TuP32, **7**; SS-TuP6, **2**; SS-TuP7, **2**
Tang, J.-M.: SS-TuP4, **1**
Tao, J.: SS-TuP15, **4**
Teplyakov, A.V.: SS-TuP20, **4**
Terawaki, L.: SS-TuP31, **6**
Thevuthasan, S.: SS-TuP26, **5**
Thissen, P.: SS-TuP21, **4**
Thomas, J.C.: SS-TuP34, **7**
Tian, F.Y.: SS-TuP20, **4**
Toyoda, A.: SS-TuP6, **2**

— U —

Ueba, T.: SS-TuP31, **6**

— V —

Van der Ven, A.: SS-TuP34, **7**

— W —

Walker, G.: SS-TuP5, **2**
Wang, H.: SS-TuP26, **5**
Wang, J.: SS-TuP4, **1**
Wang, W.: SS-TuP26, **5**
Weaver, J.F.: SS-TuP22, **5**; SS-TuP23, **5**
Weinert, M.: SS-TuP3, **1**

— Y —

Yamada, T.: SS-TuP31, **6**
Yang, P.: SS-TuP26, **5**
Yasumura, S.: SS-TuP8, **2**
Ye, Y.F.: SS-TuP37, **7**
Yeh, P.-C.: SS-TuP2, **1**
Yu, Z.: SS-TuP19, **4**

— Z —

Zhang, S.: SS-TuP9, **3**
Zhao, S.-G.: SS-TuP9, **3**
Zhou, J.: SS-TuP13, **3**
Zhou, Y.H.: SS-TuP13, **3**
Zhu, J.F.: SS-TuP35, **7**; SS-TuP37, **7**
Zhu, Y.-Z.: SS-TuP9, **3**