

# Tuesday Evening Poster Sessions

## Surface Science

Room: Hall D - Session SS-TuP

### Surface Science Poster Session

**SS-TuP1 Visible Light Photocatalytic Degradation of Methylene Blue using Ag<sub>2</sub>O Nanostructures**, Z.-H. Yang, Szetsen Lee, Chung Yuan Christian University, Taiwan, Republic of China

Various kinds of Ag<sub>2</sub>O nanostructures were prepared by a precipitation reaction of silver nitrate, ammonium nitrate, and sodium hydroxide with different mixing ratios and temperatures. The band gap values of Ag<sub>2</sub>O nanostructures were measured using diffuse uv-visible reflectance spectroscopy. The photocatalytic activity of Ag<sub>2</sub>O nanostructures was tested with the degradation reaction of methylene blue (MB) in aqueous solutions. A halogen lamp with a cut-off filter (> 400 nm) was used as the visible light source. The intensity variation of the 664 nm absorption peak of MB was monitored. The photocatalytic degradation rate of MB varies with the shapes of Ag<sub>2</sub>O nanocrystals. The degradation rates of MB were correlated with the measured band gap values of Ag<sub>2</sub>O. The efficiency of visible-light photocatalytic performance of Ag<sub>2</sub>O nanostructures is discussed.

**SS-TuP3 Formation of Copper Nanoparticles on a Surface of OH-terminated ZnO Powder Material**, Hsuan Kung, A.V. Teplyakov, University of Delaware

Cu/ZnO catalyst is one of promising catalysts commonly used in industry for methanol synthesis, methanol steam reforming, and hydrogen production reactions. Two typical methods to prepare this catalyst are wet chemistry or vacuum-based techniques. In this study, we grew Cu nanoparticles on zinc oxide (ZnO) powder at room temperature using common chemical vapor deposition precursors, such as hexafluoroacetylacetonate copper(I) vinyltrimethylsilane, (Cu(hfac)(VTMS)) under high vacuum conditions. Before deposition, exposing ZnO powder to the gas-phase water to form a hydroxyl-terminated monolayer was able to enhance the growth of copper nanoparticles. In-situ FTIR studies showed that the intensity of the infrared signatures of hydroxyl groups decreased following exposure to copper precursor and confirmed copper deposition. X-ray photoelectron spectroscopy and Auger electron spectroscopy studies determined that Cu(I) species are the dominant products present on the surface. Cu nanoparticles grown on ZnO(000-1), ZnO (10-10) and defect sites were visualized by Scanning electron microscopy. This Cu/ZnO surface covered with strongly bound hfac ligands was then annealed to different temperature to remove surface contamination. The thermal chemistry involved in this process and the chemical stability of the surface-bound ligands will be discussed.

**SS-TuP4 Radical Reactions with Organic Surfaces**, Robert Chapleski, D. Troya, Virginia Tech

Motivated by recent ultra-high-vacuum surface experiments, we have used electronic structure methods, quantum mechanical/molecular mechanical calculations, and molecular dynamics simulations to investigate the structure and reactions of radicals with organic surfaces.

For the first reaction being studied, that of ozone with C60 fullerene, we have characterized stationary points in the potential energy surface for the reactions of O<sub>3</sub> with C60 that include both the formation of primary ozonide and subsequent dissociation reactions of this intermediate that lead to C-C bond cleavage. We have also investigated the addition of multiple O<sub>3</sub> molecules to the C60 cage to explore potential reaction pathways under the high ozone flux conditions used in recent experiments. The lowest-energy product of the reaction of a single ozone molecule with C60 that results in C-C bond breakage corresponds to an open-cage C60O<sub>3</sub> structure that contains ester and ketone moieties at the seam. This open-cage product is of much lower energy than the C60O + O<sub>2</sub> products identified in prior work, and it is consistent with IR experimental spectra. Subsequent reaction of the open-cage C60O<sub>3</sub> product with a second ozone molecule opens a low-energy reaction pathway that results in cage degradation via the loss of a CO<sub>2</sub> molecule. Our calculations also reveal that, while full ozonation of all bonds between hexagons in C60 is unlikely even under high ozone concentration, the addition of a few ozone molecules to the C60 cage is favorable at room temperature.

We have also investigated the reaction of nitrate radicals with functionalized self-assembled monolayer surfaces. Specifically, using quantum mechanical/molecular mechanical calculations, we have calculated vibrational modes of nitrate-SAM products that are consistent with IR experimental spectra. Also, using molecular dynamics simulations, we are able to describe the orientation of the alkanethiol chains that form the

surface in order to provide insight into reaction mechanisms under further experimental study.

**SS-TuP5 Degenerate Phases of Iodine on Pt(110) at Half-Monolayer Coverage**, N. Oberkalmsteiner, M. Cordin, Stefan Duerrbeck, E. Bertel, University of Innsbruck, Austria, J. Redinger, Vienna University of Technology, Austria, C. Franchini, University of Vienna, Austria

Iodine-surface interactions are of considerable interest in sustainable-energy research. For instance, Iodine is used as redox shuttle in dye-sensitized solar cells and serves as a promoter in photocatalytic water splitting. In most of these applications, Pt is involved either as an electrode or as co-catalyst or both. As part of a general study of Pt-halogen interaction we discuss here the adsorption of Iodine on Pt(110) at a coverage ( $\Theta$ ) of 0.5 monolayers (ML). The I/Pt(110) adsorbate system was investigated by scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) and by density functional theory (DFT) calculations using both, the LDA and the GGA approximation. Remarkably, three different phases involving occupation of two different binding sites were found to coexist at  $\Theta = 0.5$  ML. While the observed phases are similar to the ones reported for Br on Pt(110)<sup>1,2</sup>, the preferred binding sites are different. The structure of defects in the adsorbate layer as well as the dynamics at the transition between the nearly degenerate phases is not the same as the one in a Br layer indicating a shifted balance of adsorbate-substrate binding and inter-adsorbate repulsion. The  $c(2 \times 2) \rightarrow (3 \times 2)$  phase transition shows evidence for a long-range interaction. The latter phase also involves a surprisingly strong buckling in the Pt surface amounting to 15% of the interlayer distance. While the DFT calculations reflect the energetic details of the  $c(2 \times 2)$  phase with stunning precision, they only partially reproduce the experimental results from the  $(3 \times 2)$  phase. Comparison with literature data shows that the iodine adlayer is almost floating on Au(110) and uniaxially compressible on Pd(110), while on Pt(110) Iodine adsorption is tied to specific adsorption sites, precluding the formation of compression structures.

<sup>1</sup> E. Doná, T. Loerting, S. Penner, et al., *Physical Review Letters* **98**, 186101 (2007).

<sup>2</sup> M. Cordin, B. A. J. Lechner, S. Duerrbeck, et al., *Sci. Rep.* **4** (2014).

**SS-TuP6 Reaction of Hydrazine with Cl-terminated Si(111) Surface**, Fei Gao, A.V. Teplyakov, University of Delaware

This work focuses on obtaining well-defined surface of silicon functionalized with hydrazine to produce an oxygen-free platform for further functionalization. Single crystalline Si(111) surface has been prepared using modified RCA procedure to produce a well-defined H-terminated Si(111) surface. Next, Cl-terminated Si(111) surface is prepared from H-terminated Si(111) surface using PCl<sub>5</sub> in chlorobenzene solvent with trace amount of benzoyl peroxide as a reaction initiator under nitrogen atmosphere following previously established procedures. Hydrazine-functionalized Si(111) sample is obtained from Cl-Si(111) surface with anhydrous hydrazine at 35°C under Ar atmosphere. To confirm the presence of Si-N bonds following this procedure and to establish the structures of surface species produced, we followed the reaction by Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry. To study the configuration of Si-NH<sub>x</sub> groups on the surface, result was compared with the results of phenylhydrazine reactions on Cl-terminated silicon surface by wet chemistry method and also on clean silicon surface under ultrahigh vacuum (UHV) condition. Density functional theory (DFT) calculations were performed to infer the mechanisms of surface reactions and to compare the predicted vibrational spectra and core-level energies with the results of experimental studies.

**SS-TuP8 Synthesis of Formate Species on Cu Surface using CO<sub>2</sub> Molecular Beam**, Tetsuya Ogawa, Q. Jiamei, T. Kondo, J. Nakamura, University of Tsukuba, Japan

The methanol synthesis by hydrogenation of CO<sub>2</sub> attracts a great deal of attention because this process can realize the direct conversion of CO<sub>2</sub> into a useful chemical feedstock. In a present industrial process using Cu/ZnO-based catalyst, however, the reaction requires high pressure (50-100 bar) and high temperature (200-300°C). If this reaction proceeds at a mild reaction condition, it would be a very attractive process to convert CO<sub>2</sub>. But the detailed process of the reaction is not well understood. We focus on the formate synthesis on Cu surfaces, which is the first step of the methanol synthesis reaction. Our previous studies suggest that this process proceeds by the translational and vibrational energy of CO<sub>2</sub> molecules. The kinetic analysis of formate synthesis suggests that the mechanism of the reaction can be an Eley-Rideal type, in which gaseous CO<sub>2</sub> directly reacts with hydrogen atoms on Cu surfaces [1]. DFT calculation also suggests that the

activation barrier can be overcome by supplying energy to CO<sub>2</sub> molecules [2]. In this work, we conduct formate synthesis with translationally and vibrationally hot CO<sub>2</sub> molecules to prove the mechanism of formate synthesis on Cu surfaces.

The translational and vibrational energy of CO<sub>2</sub> molecules is controlled by the supersonic molecular beam technic. Firstly hydrogen atoms are pre-adsorbed on Cu single crystal with hot tungsten filament. Then CO<sub>2</sub> molecular beam is irradiated to H/Cu surface. The relation between the energy of incident CO<sub>2</sub> molecules and the formation of formate are investigated using temperature programmed desorption and infrared reflection absorption spectroscopy.

[1] H. Nakano, I. Nakamura, T. Fujitani, and J. Nakamura, *J. Phys. Chem. B* **2001**, 105, 1355

[2] G. Wang, Y. Morikawa, T. Matsumoto, and J. Nakamura, *J. Phys. Chem. B* **2006**, 110, 9

**SS-TuP9 Chemical and Electronic Structure of (Y<sub>1-x</sub>Ca<sub>x</sub>)CrO<sub>3</sub>, (0.00 ≤ x ≤ 0.15) in Core Levels and Valence Band by XPS and DOS, Lazaro Huerta, R. Escamilla, M. Cruz, A. Duran, Universidad Nacional Autónoma de México**

Polycrystalline samples of (Y<sub>1-x</sub>Ca<sub>x</sub>)CrO<sub>3</sub> with 0.00 ≤ x ≤ 0.15 were synthesized by combustion method. The samples were studied by X-ray diffraction (XRD) and photoelectron spectroscopy (XPS). Results of refinement of Rietveld shows that the cell volume decrease occurs through the change from Cr(III) to Cr(IV) as a result of the charge compensation of the Ca doping. XPS was used to investigate the binding energies of the Y 3d, Cr 2p, Ca 2p, and O 1s core level and Y 4d, Cr, 3d Ca 3d and O 2s contributions of valence band. The valence band measurement is consistent with the calculations of the band structure calculated near the Fermi level.

**SS-TuP10 Wettability of MgO-P<sub>2</sub>O<sub>5</sub> Glasses: Relation between Bulk and Surface Properties, Naoya Yoshida, N. Masuda, M. Yamada, T. Okura, Kogakuin University, Japan**

MgO-P<sub>2</sub>O<sub>5</sub> glass system shows anomalous changes in bulk properties, such as density, with changing in its composition; density does not simply

increase with increase of MgO composition, and significantly decreases at around meta composition (50MgO-50P<sub>2</sub>O<sub>5</sub>). This phosphorus oxide anomalies derive from local structural changes between tetrametaphosphate and pyrophosphate structures. Wettability, one of the important surface properties, depends on surface energy and surface roughness, therefore, with samples of constant surface roughness, wettability simply reflects surface energy, which relates with chemical composition and structure of the surface.

Here, we prepared MgO-P<sub>2</sub>O<sub>5</sub> glasses with changing composition from 35MgO-65P<sub>2</sub>O<sub>5</sub> to 55MgO-45P<sub>2</sub>O<sub>5</sub>, and studied the relation between their bulk properties (density and solubility in water) and wettability. As a result, simple relation was found among wettability, density, and

solubility in water. Of course, wettability is only a surface phenomenon, however, the results suggested that bulk properties are possibly estimated by measurements of wettability. We will discuss the results of other glass systems such as Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>.

**SS-TuP11 Preparation and Characterization of Photocatalytic Thin Films of Zn-doped Calcium Phosphate, Yuji Nakamura, N. Yoshida, T. Okura, Kogakuin University, Japan**

Ti-doped hydroxyapatite (TiHAP), partially substituted Ca<sup>2+</sup> with Ti<sup>4+</sup>, exhibits photocatalytic activities such as decomposition of organic compounds similar to that of TiO<sub>2</sub>, as our group has reported. Oxidation power of TiHAP seems to be weaker than that of TiO<sub>2</sub>, and, it shows excellent adsorption ability derived from hydroxyapatite structure. The mechanism of photocatalytic activities of TiHAP is still unknown, however, Ti-doping and/or defects derived from Ti-doping are thought to play an important role in photocatalytic reactions. Here, we tried to fabricate thin films of Zn-doped calcium phosphate, and to evaluate those photocatalytic activities.

Transparent and homogeneous thin films of Zn-doped calcium phosphate were successfully fabricated from a solution of zinc nitrate, calcium nitrate, and phosphorus oxide by spin-coating on glass substrates and following calcination. Several characterizations, such as UV-vis transmission and reflection spectroscopy, X-ray diffraction analysis, and surface structural analysis by atomic force microscope, were carried out. Methylene blue decomposition tests under irradiation of UV light suggested that photocatalytic activity was improved by Zn-doping.

**SS-TuP12 Critical Review and Recommended Values of Work Functions for Low Index Faces of Clean Metal Surfaces, Gregory Derry, Loyola University Maryland**

Despite the fundamental interest and technological importance of the work function, the standard reference tables of this quantity used by the surface science community are outdated, incomplete, and include flawed experimental information. In this work, a thorough critical review of the entire literature is undertaken, with both the cleanliness and characterization of the surfaces and the reliability of the experimental techniques examined. Unreliable data is rejected and realistic uncertainty estimates are made for all of the comparatively reliable data. Based on this information, recommended values of the work functions and their uncertainties are presented for all clean metal surfaces with low index crystal faces for which good data exists, along with updated tables that include all of the primary references and relevant information needed to evaluate each surface and generate such recommended values. Details of the evaluation protocols employed are also presented. It is anticipated that the information presented here will be useful both in technological applications (such as electrochemistry and microelectronics) and in the testing of theoretical models for electrons at metal surfaces.

**SS-TuP13 Unveiling Hidden Information in Temperature-Programmed Desorption-Reaction Data: Identification of Desorbing Compounds by Their Desorption and Fragmentation Patterns, JuanCarlos Rodriguez-Reyes, Universidad de Ingeniería y Tecnología, UTEC, Peru, J.-M. Lin, J. Zhao, A.V. Teplyakov, University of Delaware**

Temperature-programmed desorption/reaction (TPD/R) experiments are very powerful for providing information in several fields related to surface science, including heterogeneous catalysis, thin film precursor analysis and thermal treatments. Data can be, however, very complex and difficult to extract, especially when competing reaction pathways yield products with similar spectrometric features. We present a mathematical method for analyzing TPD/R data, which is able to extract, for each desorbing compound, its desorption pattern and its fragmentation pattern. This method is called multivariate curve resolution (MCR) and, briefly, requires the organization of data (e.g. "n" m/z traces followed over "t" temperature points) as a (n x t) matrix, which can be seen as the product of two matrices, (n x k) and (k x t), where k is calculated by considering variations and correlations between m/z traces. Interestingly, k turns out to be the number of components (compounds desorbing from a surface), and its value is limited not only by correlations between data points, but also by the fact that intensities in the two matrices cannot be negative. Therefore the two matrices correspond to the fragmentation pattern, (n x k) matrix, and to the desorption pattern, (k x t) matrix. Since it is a mathematical method, MCR is applicable even when no previous knowledge of the system under investigation is available. However, any available information can be used as constraints that guide the outcome, increasing the accuracy of the resolution. The usefulness of this method is demonstrated using datasets from a variety of surface reactions, including the reaction of ethyl halides with a Si(100) surface and the thermal decomposition of the TiN precursor tetrakisdimethylamido titanium, TDMAT.

**SS-TuP14 Dependence on an O<sub>2</sub> Gas Flow Rate of NiO Thin Films Prepared by Reactive Magnetron Sputtering, Tomokazu Tsuchiya, I. Takano, Kogakuin University, Japan**

As one solution to the power shortage and global warming, a renewable energy such as solar cells is desired. Silicon-based solar cells having over 30% in the theoretical efficiency are the present mainstream, however the single crystal-silicon has a problem on the manufacturing cost. Further more the high purity silicon that is the main raw material for solar cells is insufficient worldwide, and so a new solar cell without silicon that is replaced silicon-based solar cells has been required. Practical application of oxide-based thin film solar cells is expected in reduction of energy costs or environmental loads.

Generally a typical oxide-based thin film solar cell is a wet dye-sensitized solar cell composed of an electrolyte, an electrode of titanium oxide and a sensitizing dye. Recently a solid-state dye-sensitized solar cell which uses metal oxides instead of an electrolyte has been studied.

In our previous study on TiO<sub>2</sub>/Cu<sub>2</sub>O solid-state dye-sensitized solar cells, the problem was Cu diffusion from underlayer Cu<sub>2</sub>O. The diffusion of Cu induced collapse of p-n junction. In this study, we used NiO as a next p-type oxide semiconductor instead of Cu<sub>2</sub>O. The NiO thin film is used as the transparent oxide semiconductor. Most of the transparent oxide semiconductors are an n-type semiconductor, while NiO is a p-type semiconductor. The NiO thin films prepared by changing an oxygen gas flow rate were evaluated by crystallinity, optical properties, semiconductor properties, surface morphology in comparison with Cu<sub>2</sub>O thin films.

NiO thin films were fabricated by reactive magnetron sputtering. As substrates, the glass (Corning#1737) and ITO-film coated glass were

ultrasonically cleaned. The NiO thin film was deposited on those substrates using pure metallic nickel (99.99%) as a sputtering target material in an oxygen gas atmosphere. The flow rate of an argon gas for sputtering was 20 sccm. The flow rate of an oxygen gas was changed at 2.0 sccm, 2.7 sccm, 3.2 sccm, 3.7 sccm and 4.4 sccm. A thickness of the NiO thin films was kept at about 200 nm.

The NiO thin films were successfully fabricated by reactive magnetron sputtering. The XRD pattern of the NiO thin film showed the stronger peak at the (012) crystal plane of NiO, when the flow rate of an oxygen gas was lower. The resistivity of NiO thin films showed a higher value than that of Cu<sub>2</sub>O thin film and the mobility of NiO thin films showed a lower value than Cu<sub>2</sub>O.

#### **SS-TuP15 Properties of Cu/Ti Thin Films on the Biodegradable Resin Irradiated by an Ar<sup>+</sup> Ion Beam, Ryosuke Tan, I. Takano, Kogakuin University, Japan**

Recently, biodegradable resin attracts attention as one of the effective use of resources on environmental measures. PGA (Polyglycolic acid) used in this study is categorized to a kind of polyester resin and is composed of hydrogen, carbon and oxygen. PGA shows a high gas barrier property, a high hydrolysis property and high mechanical strength. These characteristics are applied for sutures of surgery or multi-layer PET bottles, while there is hardly application in an electronic field. The usage of PGA in electronic parts such as a printed circuit board has the important role in environmental measures, however there are some problems that have to be overcome.

In this study, the surface of PGA was modified by using an ion beam so that the durability of the PGA coated with metal films was improved. The ion beam cut off the bonding of molecules and as a result the surface of PGA turned to a carbon layer which was stable against heating or humidity. Double layer films of Cu/Ti were deposited on the modified PGA by vacuum evaporation. The Ti layer between the Cu film and the modified PGA (carbon layer) improved adhesion and electrical conductivity. The ion beam irradiation and vacuum evaporation were performed using the high current ion implanter with an electron beam evaporator. The ion beam was extracted from the bucket-type ion source with multi-aperture electrodes of 100 mm in diameter.

The Ar<sup>+</sup> ion irradiation conditions were controlled at a current density of 20  $\mu\text{A}/\text{cm}^2$ , an acceleration voltage of 1 kV and irradiation time of 50 s. The deposition conditions of Ti were kept at a deposition rate of 0.3 nm/s and were changed a film thickness of 0-200 nm. The deposition conditions of Cu were kept at a deposition rate of 0.3 nm/s and a film thickness of 200 nm. The kind of prepared samples was the metal coated PGA sample, the ion irradiated PGA sample and the metal coated sample on the irradiated PGA. The sample hardness was measured by a load-unloading method using a micro-hardness tester with a Knoop indenter. Electrical conductivity of metal films was calculated from V-I characteristics measured using the four probe method. A surface chemical-bonding state was investigated by X-ray photoelectron spectroscopy.

The Ti layer between the Cu film and the carbon layer improved adhesion and electrical conductivity of samples. Those properties showed the maximum value at 50 nm in a Ti thickness, while the excess Ti-layer thickness decreased those properties. The measurement results of electrical conductivity suggested the possibility of PGA used as a printed circuit board.

#### **SS-TuP17 Understanding the Growth and Activity of Monometallic and Bimetallic Clusters on TiO<sub>2</sub>(110), Randima Galhenage\*, University of South Carolina, H. Yan, Brookhaven National Laboratory, D.A. Chen, University of South Carolina**

The study of metal clusters on single-crystal oxide supports has garnered much attention as model systems for fundamental investigations of surface activity that can guide the rational design of new catalyst. We have studied the growth and activity of monometallic and bimetallic clusters on TiO<sub>2</sub>(110) for metals such as Au, Co, Pt and Re, since these metals are known to have desirable properties for alcohol reforming and oxidation reactions. Scanning tunneling microscopy studies show that the cluster size and number of nucleation sites for these metals depend on the mobility of each metal on the titania surface. In general, the diffusion length decreases with increasing metal-titania bond strengths, and DFT studies show that the metal-titania bond strengths can be predicted directly from metal-oxygen bond strengths. Bimetallic clusters (Au-Co, Pt-Co, Pt-Re) were prepared from sequential deposition by growing the metal with the lower mobility first, followed by the more mobile metal. In general, exclusively bimetallic clusters are formed when the number of seed clusters generated from the deposition of the first metal provides a sufficient number of nucleation sites

for the second metal. Surface compositions for the clusters were investigated by low energy ion scattering spectroscopy; for metals that do not alloy in the bulk, like Co and Au, core-shell structures are formed, and the surface composition is determined by the relative surface free energies. For metals that are bulk miscible, like Co-Pt and Pt-Re, both metals exist at the surface, regardless of the relative surface free energies. The chemical activity of the bimetallic clusters for CO adsorption and methanol reaction were investigated by temperature programmed desorption experiments. The addition of Au and Pt to Co clusters increased the thermal stability of the surface intermediate by inhibiting C-H bond scission and resulted in H<sub>2</sub> and CO desorption at higher temperatures.

#### **SS-TuP18 Conductivity of Graphene as a Function of its Lattice Orientation Relative to Substrate Layers, Hyunsoo Lee\*, KAIST, Republic of Korea, Y. Qi, Okinawa Institute of Science and Technology Graduate University, Japan, S. Kwon, KAIST, Republic of Korea, M.B. Salmeron, Lawrence Berkeley National Laboratory, J.Y. Park, KAIST, Republic of Korea**

We report strongly varying electrical transport properties of graphene layers on graphite that depend on the relative lattice orientation of the surface and subsurface layers. Employing the pressure dependence of conductance on the surface of highly ordered pyrolytic graphite (HOPG) using the conductive tip of an atomic force microscope as an electrode, we found that the electrical conductivity of graphite terraces separated by steps can vary by large factors of up to 100. This effect can be attributed to interlayer interactions when stacked commensurately in a Bernal sequence (ABAB...), which opens a band gap, while rotational misaligned layers behave as graphene. Small angular misorientations of a few degrees were found to give rise to large increases in the conductivity of the top layer, with the maximum occurring at around 30°. In addition, two types of steps were encountered on HOPG surface: external steps where the edge C atoms have dangling or broken bonds, and internal steps where the bonds are only broken in the second layer or deeper. Accordingly, graphite layers covering several underlying terraces and steps retain the same conductivity across the terraces. Top layer terraces have higher friction on the edges, making it easy to distinguish them from subsurface steps where no friction changes occur. These results suggest new applications for graphene multilayers using stacked layers at various angles to control the resistance of connected graphene ribbons in devices.

#### **SS-TuP19 Electron Percolation via In-Gap States in Semiconductor Quantum Dot Arrays, Yingjie Zhang\*, University of California, Berkeley and Lawrence Berkeley National Laboratory (LBNL), D. Zherebetsky, S. Barja, L. Lichtenstein, LBNL, N.D. Bronstein, University of California, Berkeley, P. Alivisatos, University of California, Berkeley and LBNL, L.-W. Wang, LBNL, M.B. Salmeron, University of California, Berkeley and LBNL**

Charge hopping and percolation in disordered semiconductors has been widely studied, but the microscopic nature of the percolation process is not understood and has never been determined. Here we directly image the charge percolation pathways in 2-D PbS quantum dot (QD) arrays using Kelvin probe force microscopy. We showed that the electrons percolate via in-gap states (IGS) instead of the conduction band, while holes percolate via valence band states. This exotic transport behavior is explained by the electronic structure and energy level alignment of the individual QDs, which was measured by scanning tunneling spectroscopy. Density functional theory and spectroscopic analysis show that the IGS are induced by oxygen molecules adsorbed on the QDs' surface. These states are partially hybridized with the valence band states, enabling inter-IGS coupling and electron transport via IGS. Surface chemical treatments open the way of defect engineering, achieving tunable electronic structure and transport properties by controlling the IGS.

#### **SS-TuP20 Mechanisms of CO Oxidation on Well-defined Pd Oxide Films on Pd(111), Feng Zhang\*, T. Li, University of Florida, L. Pan, A. Asthagiri, The Ohio State University, J.F. Weaver, University of Florida**

The surface chemistry of late transition-metal oxides has attracted significant attention due largely to observations that the formation of metal oxide layers can drastically alter the catalytic performance of parent metals in applications of oxidation catalysis. For example, previous *in situ* studies have shown that CO oxidation over palladium undergoes a significant rate increase when the palladium surface becomes oxygen rich. This observation has been attributed to the formation of various types of palladium oxide layers or surface oxygen phases, though the reaction mechanisms have not been determined in detail. In this presentation, I will show results of recent experiments and density functional theory (DFT) calculations in which we studied CO oxidation on well-defined Pd oxide surfaces. In the experiments, we utilized mass spectrometry to investigate the CO oxidation kinetics on both surface and bulk Pd oxides during TPRS and under isothermal conditions and used reflection absorption infrared spectroscopy

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(RAIRS) to monitor the evolution of CO binding states and hence the formation of new surface phases as the oxides undergo reduction.

In direct rate measurements under isothermal condition, we find that the initial reaction rates are nearly ten times larger on PdO(101) compared with the Pd<sub>3</sub>O<sub>4</sub> surface oxide, demonstrating that PdO(101) has a much higher intrinsic activity toward CO oxidation compared with the surface oxide. The measurements also show that the reactions occur on both oxide surfaces in an autocatalytic fashion, where the CO<sub>2</sub> generation rate increases as oxygen on the surface is consumed. The RAIRS data shows that the reduction of PdO(101) by CO initially creates oxygen vacancies and that CO preferentially binds to atop-Pd sites located next to the O-vacancies. This atop CO-species yields a characteristic IR peak between 2090 cm<sup>-1</sup> and 2060 cm<sup>-1</sup>. DFT results agree very well with the measured C-O stretching frequencies, and further show that CO achieves significantly stronger binding on an atop-Pd site located next to an oxygen vacancy vs. on the pristine PdO(101) surface. In addition to oxygen vacancies, we also find that surface metal domains develop during the early stages of isothermal reaction of CO on PdO(101) and the Pd<sub>3</sub>O<sub>4</sub> surface oxide, except that on the Pd<sub>3</sub>O<sub>4</sub> surface CO reaction only leads to the creation of metallic domains without producing oxygen vacancies. Thus, the autocatalytic kinetic behavior observed for both oxides arises from a similar mechanism wherein surface reduction during CO oxidation continually creates sites that bind CO strongly and thus facilitate the adsorption and subsequent reaction of CO.

**SS-TuP21 Surface Structure and Chemistry of Rh(110) Model Catalyst under Reaction Condition and during CO Oxidation, Luan Nguyen\*, L. Liu, S. Zeng, F. Tao, University of Notre Dame**

Heterogeneous catalysis is a chemical process performed at a solid/gas or solid/liquid interface. An elevated pressure of a reactive environment could cause materials surface likely to restructure geometrically and electronically to adapt to the surroundings. Since catalytic performance (activity, selectivity, promotion effect, deactivation, etc.) depends on the surface structure of a catalyst during the reaction, it is necessary to study the surface under reaction condition (a reactant) and during catalysis (a mixture of all reactants).

Since a high pressure of a reactant gas typically results in high adsorbate coverage, one alternative approach to mimic the gas environment of a high pressure is to increase coverage of adsorbate by lowering the catalyst temperature. However, decreasing of catalyst temperature in low pressure environment is only valid when entropy effects are negligible and the relevant adsorption structure is not kinetically hindered. In fact, the magnitudes of entropy contribution to the surface free energy in ultrahigh vacuum (UHV) and under an ambient pressure of a reactant gas are actually different by about 0.3 eV or even larger. Therefore, pressure-dependent entropy can lead to large restructuring of catalyst surfaces. It is difficult to predict how a system will respond to the change of pressures of gases and temperatures of catalysts. Here we will present an in-situ investigation of a model catalyst surface Rh(110) which revealed interesting restructuring of Rh(110) surface in pure CO and a mixture of CO and O<sub>2</sub> in the temperature range of 25°C-130°C.

In UHV environment clean Rh(110) surface exhibits a (1x1) structure. However, upon O<sub>2</sub> adsorption at elevated temperature (approximately 500 °C), the surface reconstructs to an O-covered (1x2) missing row structure, namely Rh(110) (2x2)p2mg-O. High pressure STM and ambient pressure XPS were used in in-situ studies of surface chemistry and structure of Rh(110) in the mixture of CO and O<sub>2</sub>. Initially, the Rh surface exhibits a (1x2) missing row structure. During CO (0.08 Torr) oxidation with O<sub>2</sub> (0.02 Torr) at room temperature, the (1x2) structure reconstructs to form (1x1) islands. Interestingly, no surface reconstruction was observed when Rh(110)-(2x2)p2mg-O surface was exposed to only one reactant gas, CO or O<sub>2</sub> at room temperature, or in the mixture of CO and O<sub>2</sub> at in the pressure range of 10<sup>-7</sup> Torr. The surface chemistry and structure of Rh(110) in pure CO, O<sub>2</sub> and mixture of CO and O<sub>2</sub> at different temperatures and pressures will be presented. A correlation between surface chemistry and structure of this catalyst during CO oxidation and its catalytic activity will be discussed.

**SS-TuP22 Mechanism of Formation of Zinc Oxide Nanostructures Synthesized by Photon Irradiation, Rupali Nagar, Symbiosis Institute of Technology (SIT), Symbiosis International University (SIU), India, A. Praveen, S. Ramaprabhu, Indian Institute of Technology Madras, India**

Zinc oxide (ZnO) is a wide bandgap semiconductor with strong room temperature luminescence, high electron mobility and good transparency. These properties make it an attractive transparent conducting oxide rendering it suitable for optical and photovoltaic applications. It is imperative to devise synthesis techniques that are quick, safe, economical,

and easy to implement. In this direction, ZnO nanostructures were synthesized by photon irradiation technique by using different sets of precursors and reducing agents. The synthesized nanostructures were characterized by X-ray diffraction, scanning and transmission electron microscopy, and optical properties investigated by UV-Visible and Raman spectroscopy. Various aspects of the synthesis procedure are compared to understand the mechanism of formation of nanostructures, and the effects of pH, irradiation time that impact the morphology and yield of ZnO nanostructures are discussed.

**SS-TuP23 Crystallization and Phase Separation Kinetics of Organic Molecules from Solution on Si(111) Substrates, Miriam Ceza, R.J. Phaneuf, University of Maryland, College Park**

Understanding the underlying science behind the arrangements of small organic molecules in mixtures is important for numerous technological applications, among which organic solar cells (OSCs) are especially noteworthy, given the drive toward alternative energy sources. An important process on which organic solar cells depend is the phase separation of organic small molecules. The spontaneous formation of a particular morphology during phase separation from a solvent-based, bimolecular solution onto a substrate depends on several parameters, including relative molecular concentrations, solubilities of each type of molecule in the solvent, mutual interaction between molecules of the same species, interaction of individual molecules with the substrate surface, solvent evaporation rate, and annealing conditions. In this work, we carry out a study of molecular mixtures consisting of tetranitro zinc-phthalocyanine (tn-ZnPc) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) using chloroform as a solvent, and native oxide-covered Si(111) substrates. We investigate the role that the solvent evaporation rate during deposition, followed by solvent vapor annealing (SVA), plays on the formation of phase separated mixtures and their crystallization and phase transformation. We also investigated the relative concentration of individual molecules in the mixtures. We found that the PCBM molecules alone undergo several phase transformations as the evaporation rate of the solvent decreases and upon SVA, while the tn-ZnPc molecules alone are very stable. Moreover, the concentration of the phthalocyanine molecules in the mixture with the PCBM highly affects the crystallization process of the latter.

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