

# Tuesday Evening Poster Sessions

## Surface Science

Room: Hall 3 - Session SS-TuP

### Surface Science Poster Session

**SS-TuP1 Self-assembly and Thermally induced Conformational Changes of Ni(II)-*meso*-tetrakis (4-*tert*-butylphenyl) benzoporphyrin on Cu(111) Studied by STM.** Michael Lepper, M. Stark, L. Zhang, FAU Erlangen-Nürnberg, H.-P. Steinrück, FAU Erlangen-Nürnberg, Germany, H. Marbach, FAU Erlangen-Nürnberg

A detailed scanning tunneling microscopy study of the self-assembly and thermally induced conformational changes of Ni(II)-*meso*-tetrakis (4-*tert*-butylphenyl) benzoporphyrin (Ni-TTBPP) on Cu(111) will be presented. The coverage-dependent adsorption behavior at room temperature reveals that Ni-TTBPP molecules can easily diffuse on the surface and self-assemble into islands with square order and a certain registry to the substrate.<sup>1</sup> The role of molecule-molecule and molecule-substrate interactions for the formation of the well-ordered supramolecular structure will be discussed. Interestingly, upon moderate heating two successive, irreversible intramolecular conformational changes are observed. This is explained comprehensively by a thermally induced dehydrogenative, intramolecular aryl-aryl coupling reaction. In addition this intramolecular structural change is coverage dependent, exhibiting a lower rate at higher initial coverage. This modification and the overall adsorption behavior of Ni-TTBPP on Cu(111) will be discussed and compared to the very different behavior of the similar Ni(II)-tetraphenylbenzoporphyrin on the same substrate.

1. L. Zhang, M. Lepper, M. Stark, D. Lungerich, N. Jux, W. Hieringer, H.-P. Steinrück and H. Marbach, Phys. Chem. Chem. Phys., 2015, DOI: 10.1039/C5CP01490E.

**SS-TuP3 Characterization of Pt-Re Bimetallic Clusters on TiO<sub>2</sub>(110).** Randima Galhenage, K. Xie, University of South Carolina, H. Yan, Brookhaven National Laboratory, G. Seuser, D.A. Chen, University of South Carolina

The study of metal clusters on single-crystal oxide supports as model systems has garnered much attention for fundamental investigations of catalytically active surfaces that can guide the rational design of new catalysts. For instance, Pt-based catalysts have been recently proposed for the aqueous phase reforming of alcohols but suffer from a lack of stability due to poisoning by CO and other carbonaceous species. The addition of a second metal, such as Re, to Pt has been shown to increase the stability and the activity of the catalyst, but the exact reason behind this enhanced activity is not well understood. To better understand this bimetallic system, we have prepared model catalysts consisting of bimetallic Pt-Re clusters on TiO<sub>2</sub> to investigate the growth of metals, metal-metal interactions, metal-support interactions and activity using Scanning Tunneling Microscopy (STM), X-ray Photoelectron Spectroscopy (XPS), Low Energy Ion Scattering Spectroscopy (LEIS) and Temperature Programmed Desorption (TPD). Re shows strong metal support interactions (SMSI) even at room temperature, resulting in highly dispersed 2D clusters. Encapsulation of Re by TiO<sub>x</sub> was observed due to SMSI effects. Pt-Re bimetallic clusters were prepared by depositing the less mobile Re first followed by deposition of Pt for submonolayer coverages. The surface composition of the bimetallic clusters was Pt-rich due to the lower surface free energy of Pt and the oxophilic nature of Re. CO adsorption behavior of the bimetallic clusters resembled the activity of pure Pt. At higher coverages (3.7 ML total metal coverage) bimetallic clusters were formed by both orders of deposition, Re on Pt and Pt on Re. When Re was deposited first, it resulted in a higher nucleation density for the bimetallic clusters with 100% Pt at the surface, and the activity resembled that of pure Pt. When Pt was deposited first, the initial seed cluster density was low, resulting in a lower density of bimetallic clusters, which led to a smaller number of active sites. In this order of deposition, the surface composition was a mixture of Pt and Re, and the activity studies suggest that both Pt and Re are active sites for the adsorption of CO. Pt-Re interactions were observed when Pt was deposited on titania followed by the deposition of Re.

**SS-TuP4 Growth of Polymer Nanoparticles by Vapor Phase Polymerization onto Liquid Substrates.** Robert Frank-Finney, P. Haller, M. Gupta, University of Southern California

The vapor phase deposition of polymers onto liquid substrates can result in the formation of polymer films or particles at the liquid-vapor interface. The initial polymer morphology at the interface is determined by the surface tension interaction between the liquid and polymer. Polymer particles form

when it is energetically favorable for the polymer to aggregate rather than spread over the surface of the liquid as characterized by a spreading coefficient. The particles that are formed on the surface either remain partially protruding from the surface or submerge below the surface based on the engulfment energy of the polymer-liquid interaction. We systematically study the effects of deposition time, molecular weight, polymer accumulation, and liquid viscosity on the particle size and distribution to determine the mechanism of growth. Our results provide a fundamental understanding about polymer growth at the liquid-vapor interface that can be used to tailor the reaction conditions to produce particles of a desired size and improve upon the size distribution and can even offer insight into the growth of other materials on liquid surfaces. Vapor phase deposition onto liquid substrates is a rapid, one-step synthetic approach for fabricating functional polymer nanoparticles without the use of surfactants or volatile solvents.

**SS-TuP6 Efficiency Improvement of Cu<sub>2</sub>O/NiO/TiO<sub>2</sub> Solar Cells 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. Furthermore the high purity silicon that is the main raw material for solar cells is insufficient worldwide, and so new solar cells without silicon that are able to be replaced to silicon-based solar cells have been required. Practical application of oxide-based thin film solar cells is expected in reduction of the energy cost or the environmental load.

Generally a typical oxide-based thin film solar cell is a wet dye-sensitized solar cell composed of an electrolyte, an electrode of a 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 main problem was Cu diffusion from the under layer Cu<sub>2</sub>O. The diffusion of Cu to a titanium oxide layer induced the collapse of p-n junction.

The NiO thin film is used as a transparent oxide semiconductor. Most of the transparent oxide semiconductors are an n-type semiconductor, while NiO is a p-type semiconductor. In this study, we used NiO as a barrier layer between TiO<sub>2</sub> and Cu<sub>2</sub>O for preventing the diffusion of Cu, and we investigated the characteristics of Cu<sub>2</sub>O/NiO/TiO<sub>2</sub> solar cells.

Cu<sub>2</sub>O/NiO/TiO<sub>2</sub> solar cells were fabricated by reactive magnetron sputtering. As substrates, the glass (Corning#1737) and an ITO-film coated glass were ultrasonically cleaned by acetone. The NiO thin film was deposited on those substrates by 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 2.7 sccm. A thickness of the NiO layer was changed from 2 nm to 50 nm. On the other hand the fundamental preparations of the Cu<sub>2</sub>O layer and the TiO<sub>2</sub> layer were performed by 200 nm in a thickness through 15 sccm and 20 sccm in an argon gas, and 10 sccm and 2.3 sccm in an oxygen gas, respectively.

Cu<sub>2</sub>O/NiO/TiO<sub>2</sub> solar cells were successfully fabricated by reactive magnetron sputtering. The solar cell with the NiO layer of 4 nm thickness showed the maximum conversion efficiency of 5.6×10<sup>-3</sup> % which was 9 times compared with the sample without the NiO layer.

**SS-TuP7 Electrical Conductivity Control of Metal Doped DLC Films Prepared by N<sub>2</sub><sup>+</sup> Ion Beam Assistance.** Tsuyoshi Inoue, I. Takano, Kogakuin University, Japan

DLC is amorphous carbon that contains a significant fraction of sp<sup>2</sup> and sp<sup>3</sup> bonds. It is known that their films show a low friction coefficient and are applied in a mechanical field such as cutting tools or frictional parts. DLC films were formed by the ion beam evaporation method in the early 1970's, and after that have been manufactured by various methods. In our experiment N<sub>2</sub><sup>+</sup> ion beam was used with metal evaporation to deposit metal doped DLC films. This deposition method has some independent parameters from the film formation condition in comparison with other dry process methods. Therefore this method is anticipated in appearance of superior characteristics such as a high adhesion. In our previous research, DLC thin films have been prepared by the N<sub>2</sub><sup>+</sup> ion beam assistance in a hydrocarbon gas. Their results showed that the films contained nitrogen of 8 % and mechanical properties were improved in hardness, friction and abrasion. On the other hand the electrical conductivity of metal doped DLC films prepared by this method is not clear.

In this study, the control of the electrical conductivity of DLC thin films was performed by the metal dope. Stainless steels (304SS) and slide glasses were used for sample substrates. The formation conditions of metal doped DLC films were changed with a metal evaporation rate from 0.01 nm/s to

0.05 nm/s and were an ultimate pressure of  $6 \times 10^{-4}$  Pa, an  $N_2$  gas pressure of  $4 \times 10^{-3}$  Pa, a  $C_7H_8+N_2$  gas pressure of  $2 \times 10^{-2}$  Pa in an ambient atmosphere. The ion beam irradiation was performed with 12 kV in an accelerating voltage and  $5 \mu A/cm^2$  in a current density, through an exposure time of 3600 s. The electrical conductivity and friction coefficient were determined by the four probe method and the tribotester of a ball-on-disk type, respectively. The tribotester was set with the conditions of an SUJ2 ball as a counter material and a constant load of 0.19 N until a sliding distance of 100 m.

The suitable electrical conductivity and mechanical property of the Ti or Cu doped DLC films were obtained by a Ti evaporation rate of 0.03 nm/s and a Cu evaporation rate of 0.05 nm/s respectively. The friction coefficient of Ti or Cu metal doped DLC films was about 0.24 - 0.23 at a distance of 100m. The electrical conductivity was  $1.4 \times 10^5$  S/m in Ti doping and  $5.17 \times 10^6$  S/m in Cu doping in comparison with the typical DLC film showing  $1.0 \times 10^{-7}$  S/m.

#### **SS-TuP8 NEXAFS Studies of $N_2O$ - $N_2$ Conversion on Reduced Ceria Surface.** Alexei Nefedov, C. Yang, F. Bebensee, C. Wöll, Karlsruhe Institute of Technology, Germany

Ceria, one of the most reducible metal oxides, has proven to be a highly active catalyst for  $NO_x$  reduction to  $N_2$ . Here, we use synchrotron based photoemission spectroscopy (PES) and near edge X-ray absorption fine structure spectroscopy (NEXAFS) to monitor the conversion of  $N_2O$  to  $N_2$  over reduced ceria surfaces ( $N_2O + CeO_{2-x} \rightarrow N_2 + CeO_2$ ) in a time-resolved fashion. This enables us to determine the kinetics of this process.

The NEXAFS and PES measurements were carried out using the HE-SGM beamline at the synchrotron facility BESSY II operated by the Helmholtz-Zentrum Berlin. The clean and stoichiometric  $CeO_2(111)$  single crystal was annealed at 800 K for 15 min in vacuum to create surface oxygen vacancies prior to exposure to  $N_2O$ , whereas ceria powders were annealed at 1000 K for 30 min. Exposure to 50 Langmuir  $N_2O$  at sample temperatures typically below 120 K was achieved by backfilling the analysis chamber up to  $10^{-9}$  mbar before NEXAFS spectra acquisition. The NEXAFS spectra were recorded in the partial electron yield mode for the  $\pi^*$  resonance region of N K absorption edge. The Ce oxidation state was judged by PES before and after  $N_2O$  exposure.

In the NEXAFS spectra, two intense resonances (401.2 eV and 404.8 eV) are observed. The resonances are assigned to the transition from the 1s orbital into the lowest unoccupied molecular orbital ( $3\pi^*$ ) of the terminal and central nitrogen atom of  $N_2O$ , respectively. In agreement with previous experimental spectra for  $N_2O$  on  $CeO_2(111)$  thin films, both resonances exhibit equal intensity. Theoretical calculations for thin films indicate that  $N_2O$  is adsorbed with the oxygen-end towards a cation on the surface also on the  $CeO_2$  single crystal. Moreover, these two resonances decrease in parallel over time and one may speculate at this point that the decrease is caused by conversion of  $N_2O$  to  $N_2$  over reduced  $CeO_2(111)$ . The difference in valence band photoemission spectra measured before and after the introduction of 50 Langmuir  $N_2O$  clearly demonstrate that the initial reduced  $CeO_2(111)$  surface is re-oxidized to some extent and thus confirms the speculation above that  $N_2O$  can interact with oxygen vacancies resulting in vacancy healing.

Annealing can easily reduce ceria, while  $N_2O$  can heal the oxygen vacancies on the reduced ceria surface, giving rise to a complete catalytic cycle. The first set of data on  $N_2O$  adsorption and reaction over ceria surface suggest the feasibility of the study of the conversion of  $N_2O$  to  $N_2$  by using PES and NEXAFS, which gives us a chance to determine the kinetics of this reaction.

#### **SS-TuP9 Photocatalytic Properties of $TiO_2/NiO/Cu_2O$ Thin Films Prepared by Reactive Magnetron Sputtering.** Toshiya Souma, I. Takano, Kogakuin University, Japan

In recent years, various characteristics of  $TiO_2$  have attracted considerable attention. One of their characteristics is a photocatalytic effect. The photocatalytic effect of  $TiO_2$  shows antifouling or antimicrobial activity, and has the ability to decompose environmental pollutants. Thus  $TiO_2$  has superior characteristics in many metal oxides, because its photo-excited state is very stable and does not cause self-decomposition. Therefore,  $TiO_2$  can perform the electrolysis of water by light, however, a light reaction region of  $TiO_2$  is limited within the ultraviolet region corresponded with only about 3 % of sunlight.

In this study, to improve the photocatalytic property of  $TiO_2$  the  $TiO_2/NiO/Cu_2O$  thin films were fabricated by laminating the  $TiO_2$  layer with 3.0 - 3.2 eV and the  $Cu_2O$  layer with 2.2 eV in a band gap energy. In order to prevent the diffusion of Cu, the NiO layer was inserted between the  $TiO_2$  layer and the  $Cu_2O$  layer. NiO has a high melting point, high hardness and has been used as a barrier layer. These three layers were prepared by reactive magnetron sputtering.

The film composition and microstructure were investigated by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. Chromatic changes of a methylene blue solution were applied to the measurement of a photocatalytic property. Light irradiation to the  $TiO_2/NiO/Cu_2O$  thin 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.

On the XRD measurement for the crystal structure of  $TiO_2/NiO/Cu_2O$  thin films, the strong peaks of the anatase-rutile mixture from  $TiO_2$  of the upper layer and the weak peaks of  $Cu_2O$  or NiO from the lower layer appeared. It was estimated that the diffusion of Cu from the  $Cu_2O$  layer was prevented by inserting the NiO layer. The suitable photocatalytic effect was obtained by inserting the NiO layer of 20 nm in a thickness and then the decomposition activity of a methylene blue solution showed about 57 % under an artificial sun light and about 77 % under a sterilization light. In the case of  $TiO_2/NiO/Cu_2O$  thin films, it was considered that the role of the NiO layer was not only the protection of the diffusion but also the electric effect as a p-type semiconductor.

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