Surface Science Division
Room Hall B - Session SS-TuP
Surface Science Division Poster Session

SS-TuP-1 Encapsulation of Metallic Nanoparticles near the Surface of Graphite*, **Ann Lii-Rosales**[1,2], P Thiel,* Iowa State University and Ames Laboratory

Graphite, in the bulk, is known to form graphite intercalation compounds (GICs) with certain elemental metals, for example, rare earths, alkali metals, and alkaline earths. These metals can insert between graphene sheets and alter the magnetic or transport properties of graphite. While intercalation in the bulk of graphite has received much attention, considerably less has been paid to intercalation near the *surface* of graphite, underneath only one (or a few) graphene layers. First of all, can one trap metals just beneath the graphite surface? Do the surface-intercalated metals adopt different structures compared to their bulk counterparts? What is the driving force for such surface intercalation? These questions motivate our work.

The presentation will encompass strategies for achieving *surface* intercalation of metals in graphite. In short, we find that trapping metal atoms just beneath the graphite surface requires two specific conditions: (1) ion-induced defects on the graphite surface, and (2) elevated temperature during metal deposition. We find that this strategy works for a variety of metals, and the growth temperature is metal-specific. Results on dysprosium, copper and ruthenium will be presented. We use scanning tunneling microscopy to probe and characterize the surface intercalation. Based on experimental results and density functional theory, we find that the intercalated metal atoms at the graphite surface adopt *much different* structures compared to those in bulk GICs – "encapsulated" may be a better descriptor than "intercalated". Furthermore, metals that are not known to form bulk GICs *can* be encapsulated at the graphite surface. Finally, we find that some of the metals are well protected from atmospheric oxidation by the graphene overlayer. Our synthetic strategy opens up a new avenue for metals to interact with the graphite surface, and to create novel surface nano-structures.

SS-TuP-2 Uncovering the Mechanism of Thermal Dry Etching of Cobalt Thin Films Using Hexafluoroacetylacetone (hfacH)*, **Mahsa Konh**, J Zhao, A Teplyakov,* University of Delaware

The initial steps of thermal dry etching of cobalt thin films with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone, hfacH) as the organic precursor were studied with in situ temperature-programmed desorption (TPD) and with X-ray photoelectron spectroscopy (XPS) supplemented with microscopic investigations. Comparison of the reaction of hfacH with oxidized and clean (sputtered) cobalt thin films suggested that partial surface oxidation is essential in designing dry etching schemes of this metal. On a clean surface, decomposition of the organic precursor molecule was the primary surface process. The oxidized cobalt surface can be reduced by a reaction with hfacH, releasing $Co(hfac)_2$ and water (as a side product). However, the thermal chemistry occurred at temperatures significantly higher than those required for industrial applications. The kinetic contribution to the overall etching process was investigated by exposing the oxidized cobalt films to hfacH at several temperatures and following the chemical and morphological changes of a surface. It was determined that exposure to hfacH affected the nanostructuring of the surface even at room temperature (making the surface rougher). Annealing this surface to 800 K produced a much smoother film following $Co(hfac)_2$ and water removal; however, at that point the films also started to produce microscopic level defects (pits). The optimization of surface temperature placed the upper limit of the process, before substantial surface decomposition of the hfacH precursor molecule and significant morphological changes took place, at 650 K. Further studies are required to explain the experimentally observed possibility of cobalt surface etching at temperatures as low as 440 K.

SS-TuP-3 Revealing the Atomic Scale Insights for CO_2 Dissociation on the Rh(111) Surfaces at Ambient Pressure*, **Won Hui Doh**,* Institute for Basic Science (IBS), Republic of Korea*; J Kim,* Institute for Basic Science (IBS), Republic of Korea*; J Park,* Institute for Basic Science (IBS), Republic of Korea

Carbon dioxide (CO_2) in the atmosphere is one of the main cause of the greenhouse effect due to CO_2 molecules absorb the infrared radiation emitted by the Earth's surface. Since the Industrial Revolution in 1750's, the concentration of CO_2 in the atmosphere is continuously increased owing to increase of its emission in the economic sector such as electricity and heat production, industry, transport, and etc. Therefore, the utilization of CO_2 has received great attention from many researchers because of the challenging issue to use CO_2 as an energy resource.

A fully oxidized form of carbon e.g. CO_2, however, is a very stable compound which has two double bonds between carbon (C) and oxygen (O) in opposite direction. To facilitate the CO_2 utilization, as the first step of the reaction, the bond between C and O need to weaken or broken for further reactions. Rhodium is well known reducing material which can offer its electrons to the reactants. Previous research on CO_2 reduction reaction showing that CO_2 molecules have a bent structure or CO_3^{2-} after they adsorbed on a catalyst surface by using vibrational and spectroscopies such as IRARS and XPS. However, there is no direct observation for the bent structure of CO_2 on the catalyst surface. Here, we will show the first atomic-scale observation of bent CO_2 adsorption on Rh(111) surface as an intermediate by using near ambient pressure scanning tunneling microscope (NAP-STM). Furthermore, we will discuss the possible mechanism of CO_2 dissociation on Rh(111) based on the NAP-STM images of CO and O_2 adsorption structures on Rh(111) at NAP conditions.

SS-TuP-4 Study of Spin Dependent Electrochemical Charge Transfer Across the Ferromagnetic Electrode/Solution Interface*, **Mika Tamski**, F Blumenschein, C Roussel, J Ansermet,* Ecole Polytechnique Fédérale de Lausanne, Switzerland

The Pauli Exclusion principle is known to result in spin dependent charge transfer, where the current is rectified for spins of the same orientation compared to the spins of opposite orientation.[1,2]

Similar spin selectivity has been observed for Ferromagnetic electrodes such as Nickel and Cobalt in electrochemical systems, where chiral molecules have been used as spin filters for selecting one spin orientation over the other. [3,4]

Here we report the progress concerning our studies of spin dependent charge transfer across a ferromagnetic-electrode/solution interface, using the following methodology (Fig.1, online at organiser's website):

1. Saturating the magnetization of the electrode and polarising the spins of radicals in the solution phase by applying a magnetic field $\boldsymbol{B_0}$.

2. Applying a negative potential to the electrode to induce a charge transfer from the electrode to the paramagnetic species in the solution.

3. Introducing spin-flips of the radical spins with resonant microwave irradiation $\boldsymbol{B_1}$.

4. Detecting the modulation of the reduction current as a function of modulation of the $\boldsymbol{B_0}$ or $\boldsymbol{B_1}$ amplitude, i.e. an electrically detected magnetic resonance (EDMR) experiment.

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SS-TuP-5 Two-faced Steps: How Molecular Alignment does and does not Impacts O_2 Sticking Dynamics on Pt.*, K Cao,* Leiden University, Nederland*; M Kurahashi,* National Institute for Materials Science, Japan*; **Ludo Juurlink**,* Leiden University, Nederland, Netherlands

Adsorption and dissociation of O_2 on Pt are intensely studied reactions. In heterogeneous catalysis, it is claimed to be of high importance to automotive air pollution control. In electrochemistry, the oxygen reduction reaction limits the efficiency of hydrogen fuel cells. From previous dynamical and spectroscopic studies, it is well-established that O_2 does not dissociate as an elementary reaction on Pt(111). It requires trapping in a

[1] **Morton S. Traum Award Finalist**

[2] **National Student Award Finalist**

chemisorbed molecular state prior to dissociating. Surface corrugation enhances the sticking probability for O_2 at low incident energy, whereas at higher incident energy the influence depends on the step type causing corrugation. In this contribution, we study the origins of these findings combining two recently developed techniques. First, we apply a curved single crystal approach in combination with supersonic molecular beam techniques with high spatial resolution. At low incident energy, the enhanced reactivity is linear with step density and nearly identical for two different step types over a step density range covering approximately two orders of magnitude. At high incident energy, the enhancement mostly disappears. These result suggest energy-dependent dominance of parallel mechanisms causing sticking and dissociation. Second, we use spin-rotation state-selected and aligned O_2 to determined how rotation parallel and perpendicular to the (111) plane and the step direction affect dissociation on 'flat' Pt(533), Pt(553) and Pt(111) single crystals. At lower incident energy, activated molecular chemisorption on the (111) plane strongly favors helicoptering O_2 molecules. This effect diminishes with increasing kinetic energy. The A- and B-stepped surfaces show, on the contrary, at low incident energy no dependence on the orientation of the molecular axis upon impact. This is ascribed to the dominance of initial scattering into a physisorbed state preceding molecular chemisorption and dissociation. At higher incident energy, this mechanism loses its dominance and steps become stereodynamically selective. We observe a clear preference for O_2 molecules impacting with the molecular axis parallel to the step facet.

SS-TuP-6 Secondary Electron Emission from Borosilicate Glass Under Electron Impact, *C Li,* University of Science and Technology of China, China*; L Repetto,* Università di Genova, Italy*; Z Ding,* University of Science and Technology of China, China*; **Karoly Tokesi**,* Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI), Hungary

Under charged particles impact, insulator surfaces can be charged up. If the incident beam is positive the insulator can charge up only positively partly because the incident positive charge can accumulate on the surface and partly due to the electron emission from the surface thereby increasing the positive charge on the surface. But what happen if the incident beam is negative? In this case the insulator either charges up positively or negatively depending on the secondary emission yield. If one impact electron generates in average less than one secondary electron the surface will charge up negatively and if generates more than one secondary electron than will charge up positively.

Along this line we performed extended Monte Carlo simulation by including charging dynamics, based on the classical transport theory, when both the elastic and inelastic collision are taken into account, to determine the secondary electron emission yield from borosilicate glass by electron impact. The incident electron energies were chosen between 200 eV and 15 keV. We found strong energy dependence for the secondary electron emission yield. Our calculations show that while at low electron impact energies the insulator charges up positively at high electron impact it charges up negatively.

The work was support by the National Research, Development and Innovation Office (NKFIH) Grant KH126886 and by the National Natural Science Foundation of China (No. 11574289) and Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (2nd phase).

SS-TuP-7 Crystallinity-Transport Investigations of Nanoscale Ru Conductors at Al_2O_3 and/or SiO_2 Interfaces, ***Asim Khaniya**, S Ezzat, W Kaden, K Coffey,* University of Central Florida

Enhanced scattering of charge-carriers at sufficiently small dimensions[1] (on the order of the mean free path of electrons), also known as the resistivity size-effect, leads to non-scalable increases in resistivity in conductors. As the trend of miniaturization continues in microelectronic fabrication, this size effect becomes a major challenge to current CMOS technology (Cu based) due to the loss of the majority of power at the interconnects due to their larger abundance. By using single-crystalline sub-nanometer metallic interconnects, room temperature ballistic conduction may be achieved. Within this general area of research, Ru has emerged as a promising candidate to replace Cu due to its weaker resistivity-thickness interdependence.[2] In practical applications, interconnects are necessarily in contact with isolating dielectric materials, and this work includes studies of Ru (0001) films epitaxially grown on c-axis sapphire, both with and without various silica capping layers in various states of crystallinity and chemical interaction with the underlying metal. The overall goal of the project is to measure the transport properties of the controllably different samples, while providing sufficient materials characterization to unequivocally establish correlations between changes in resistivity and changes in bulk/interface conductor properties.

To-date, efforts within our group have centered on physical characterization of films produced by collaborators from the Coffey Group in MSE at UCF, and early-stage efforts at reproduction of established SiO_2 thin-films via physical vapor deposition (PVD) within UHV. X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) have been used to demonstrate a high degree of both surface cleanliness and long-range crystal order following large-scale growth recipes carried out by the Coffey group. Further investigation has shown clear correlation between the extent of Ru oxidation and sheet resistivity following different annealing procedures during the film growth recipes. XPS, LEED, and low energy He^+ ion scattering spectroscopy (ISS) have been used to characterize our in situ SiO_2 film growth, which is highly dependent upon both coverage and oxidative crystallization temperature. Further, in-situ measurement of resistivity of Ru(0001) and SiO_2/Ru(0001) films will be made and additional atomically localized information will be collected using scanning tunneling microscopy (STM).

SS-TuP-8 Iron Oxide Surface Transformations Revealed by AP-XPS for Ammonia Synthesis, ***Mikhail Trought*,** Michigan Technological University*; E Crumlin, S Nemsak,* Advanced Light Source, Lawrence Berkeley National Laboratory*; K Perrine,* Michigan Technological University

The industrial synthesis of ammonia, known as the Haber-Bosch process[1, 2], occurs at high temperatures and pressures where hydrogen (H_2) and nitrogen (N_2) react to produce ammonia (NH_3). The dissociation of nitrogen is known as the rate-limiting step on the surface of an iron oxide catalyst.[3-6] At equilibrium conditions, this reaction is well-known, however the surface transformations of the iron oxide single crystal surfaces have not been explored in the near-ambient pressure (intermediate) regime, which may allow for a better understanding of the role of the surface sites and transformations under pressure regimes between traditional surface science (in ultra-high vacuum) and reaction conditions (high pressures).

Synchrotron radiation ambient pressure-X-ray photoelectron spectroscopy (AP-XPS) was used to measure changes in the surface structure and oxidation states of single crystal Fe_3O_4(001) (magnetite) and α-Fe_2O_3(0001) (hematite) surfaces near-ambient pressure conditions. Adsorption of N_2, H_2, and O_2 on single crystal Fe_3O_4(001) and α-Fe_2O_3(0001) surfaces was measured as a function of temperature and pressure to gain a better understanding of the fundamental surface reactions associated with ammonia formation. In particular, the shape and states in the valence band photoemission spectra were examined to measure the affect of oxidation and reduction of the surfaces.[7] The valence band region helped to identify the states associated with the Fe^{2+} and Fe^{3+} cations in each compound highlighting the differences in structure between magnetite, hematite and the transformations that occurred due to the oxidative and reductive environments. The states present in the N1s, Fe2p and O1s regions complemented the changes in the valence band region observed on the iron oxide surfaces. The results reveal N_2 adsorbs on Fe_3O_4(001) but not α-Fe_2O_3(0001). These studies give insight into the complexity of adsorption processes and surface transformations during heterogeneous catalysis that merge surface science experiments with reaction conditions.

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SS-TuP-9 Surface Energies of Thin Oxides of Si(100) as Function of Thickness, Composition and Surface Processing, ***Saaketh Narayan**, J Day, N Herbots, A Brimhall, A Mascareno,* Arizona State University*; A Krishnan,* Harvard University*; S Whaley,* Arizona State University*; R Bennett-Kennett,* Stanford University*; K Kavanagh,* Simon Fraser University, Canada

Processing modifies hydroaffinity, reactivity, and total surface energy, γ^T, of semiconductor oxides. Si(100) and its oxides are studied, including native oxides, conventional thermal SiO_2, Rapid Thermal Oxides (RTO), Rapid Thermal Annealed (RTA) oxides, RCA processed Si, Herbots-Atluri (HA) passivated [1] Si, alpha-quartz SiO_2, and oxides after HF-based etching.

Correlating surface energies of Si(100) and SiO_2 to composition and processing can reproducibly establish the metrology needed for wafer bonding. Cross-bonding is key in bonding conducted at T < 220°C, or NanoBonding™, [2,3] for Si(100) to SiO_2, GaAs(100), and $LiTaO_3$. Si(100) and Si(111) samples investigated include B-doped p- and p+ wafers, and P-doped n- and n+ wafers.

The surface energy of 50 wafers is measured via Three Liquid Contact Angle Analysis (3LCAA) using the van Oss-Chaudhury-Good (vOCG) model for semiconductors and insulators. The γ^T includes Lifshitz-van der Waals interaction, γ^{LW}, interaction with electron donors, γ^+, and with acceptors, γ^-. Reproducibility of contact angle measurements to extract γ^T, γ^{LW}, γ^+, and γ^- is achieved by metering µL droplets of 18 MΩ deionized H_2O, glycerin, and α-bromonaphthalene in a class 100/ISO 4 laminar flow hood. 4 contact angles are extracted from each droplet and its reflection through 18 MP images analyzed automatically via the Drop and Reflection Operative Program (DROP) which removes subjectivity and speeds up analysis. 30 droplets yield 120 angles, with an accuracy of 3%.

MeV Ion Beam Analysis (IBA) combining <111> channeling with nuclear resonance yields ^{16}O coverage, which is then correlated to γ^T, γ^{LW}, γ^+, and γ^-. Native oxides on p- Si are always hydrophilic, with a γ^T of 53 ± 2 mJ/m^2. RCA wafers have a lower γ^T of 47.3 ± 0.5 mJ/m^2, as RCA removes impurities, but are still relatively hydrophilic. Next, RTA oxides exhibit a lower γ^T than RCA oxides, as thicker oxides are more hydrophobic, corroborated by higher ^{16}O coverage. H-A wafers have a lower ^{16}O coverage but also a more hydrophobic γ^T of 37.3 ± 1 mJ/m^2, being terminated with ordered $Si_2O_4H_4$. RTO on H-A wafers yields the most hydrophobic surfaces with γ^T = 34.5 ± 0.5 mJ/m^2. IBA on native oxides of p- Si detects 13.3 ± 0.3 ^{16}O ML, while IBA on H-A and HF etched Si detects 11.8 ± 0.4 ^{16}O ML. IBA on RTA and RTO oxides show that thicker oxides yield more hydrophobic surfaces. In summary, 3LCAA in conjunction with IBA yields new insights in the relationship between γ^T, oxygen coverage, and processing.

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SS-TuP-10 Space Weathering Effects at the Surface of Thin-Film Aluminosilicate Model Regolith, ***Bijoya Dhar**, W Kaden,* University of Central Florida

Space weathering effects on volatile-rich airless bodies have been studied far less extensively, than those anhydrous interfaces. Although the presence of volatile resources has been established by recent space exploration missions, the fundamental physics and chemistry behind volatile formation and sequestration, associated with radiation processing of regolith, is yet to be thoroughly explored. Therefore a systematic and integrated study of the effect of radiation processes on regolith is needed to better understand the fundamental driving forces governing the volatile transformation at the interface of such bodies. Accordingly, the overall goal of the project is an in situ study of regolith, irradiated with laboratory-based sources within a UHV system, mimicking solar wind processes on airless bodies in space.

To carry out this work, our group is leveraging established thin-film recipes to generate and characterize a well-ordered regolith simulant within our multi-purpose UHV system. Herein we use aluminosilicate ($Al_xSi_yO_z$) sheets as model regolith. The $Al_xSi_yO_z$ film will be grown on a ruthenium (Ru) substrate via sequential PVD of Al and Si in the presence on O_2. The Ru is cleaned with repeated Ar^+-sputtering/annealing. XPS and He^+ ISS have been used for cleaned Ru to ensure surface cleanliness (no detectable contaminants) and LEED for long-range crystal order (sharp 1x1 hexagonal pattern). Initial silica (SiO_2) thin-film growth has been employed to establish both coverage and oxidative crystallization temperature. Using the calibrated Si flux and relative XPS sensitivity factors, Al flux will be calibrated, and both will be used to create bilayer $Al_xSi_yO_z$ film. In addition to the XPS, ISS and LEED, atomic scale confirmation of planar/crystalline silicate layers will be provided by STM analysis.

To simulate solar wind processing of model regolith, we will use irradiation facilities available in our lab, such as an electron gun, an ion gun, and an X-ray source. The physical and chemical characterization of radiation-induced defects to the fabricated $Al_xSi_yO_z$ sheet (like those previously reported by others for SiO_2 film) will be investigated with the in-house equipment. Previously established experiments used to investigate SiO_2 will be helpful to study the electron-stimulated desorption of volatiles. In addition, $Al_xSi_yO_z$ film transference to other supports will be attempted in support of collaborative efforts with others.

Our methods encompass surface science methodologies for radiation investigation on regolith samples, which will help to minimize the gaps in knowledge related to space weathering effects on the airless bodies.

SS-TuP-11 Identification of Surface Processes in Individual Minerals of a Complex Ore through the Analysis of Polished Sections using Polarization Microscopy and X-ray Photoelectron Spectroscopy (XPS), ***Dhamelyz Silva Quiñones**,* UTEC, Perú; *C He,* University of Delaware; *J Rodriguez,* UTEC, Perú; *A Teplyakov,* University of Delaware; *C Benndorf,* UTEC, Perú

The changes at the surface level of a mineral during ore processing is of fundamental

importance for the improvement of strategies aimed at increasing the efficiency of metal

extraction. This task is often difficult due to the refractory behavior of minerals and the

deficiency of valuable metals within them. Specifically, surface processes such as metal

readsorption (preg-robbing) on specific minerals are difficult to evaluate, this process can block

or encapsulate the valuable mineral and affect negatively the extraction process. In this study,

we show a powerful approach, through which surface processes in individual minerals are

identified by combining polarization microscopy (MP) and X-ray photoelectron spectroscopy

(XPS). A silver-containing polymetallic sulfide ore from the Peruvian central Andes (pyrite-

based with small amounts of galena and covellite) is evaluated, and we track the gradual

changes in the sample during the course of leaching with cyanide. The polarization microscopy

technique identifies mineralogical species such as pyrite, galena, and covellite, while XPS

provides evidence of readsorption of lead on the surfaces of pyrite and covellite after leaching,

possibly as lead oxide or thiosulfate. The surface of pyrite does not show significant changes

after leaching process according to the microscopic result, although species of oxidized iron

are detected together with the readsorption of lead by XPS. The methodology shown here is a

tool of significant importance for understanding complex surface processes affecting various

minerals during metal extraction and highlights the importance of using surface analytical

techniques for the development of novel strategies in the mining industry.

SS-TuP-12 Effect of Surface Roughness, Etch Pits, and Adsorbates on the Surface Phonon Density of States of Graphite, ***Krishnan Swaminathan-Gopalan**, K Stephani,* University of Illinois at Urbana-Champaign

Gas-surface interactions are encountered in a wide variety of disciplines and a detailed understanding of the underlying physics is critical. When a gas-phase particle strikes a surface, it can undergo adsorption, direct impact reactions, or inelastic scattering. These processes are coupled with the phonon bath at the material interface. During the interaction, energy transfer occurs both between and within the sub-systems (substrate and gas particle). A number of mechanisms including multi-phonon processes, translational and internal mode excitations may be captured by the evaluation of the detailed scattering kernels and transition matrix of the gas-phonon interaction. Such a framework provides a powerful alternative to full molecular dynamics (MD) for computing various surface interaction quantities such as accommodation coefficients, adsorption and reaction probabilities, etc. Further, since this framework captures the underlying microscopic details, and can be extended to describe the system in the state of extreme non-equilibrium. These theoretical models have been shown to provide excellent agreement with experiments.

In this work, we will focus on understanding the effect of (i) random surface roughness, (ii) etch pits, and (iii) adsorbates on the phonon density of states of carbon using Molecular dynamics (MD). The phonons at the surface are qualitatively and quantitatively different from the bulk due to the broken symmetry. In addition, the roughness of engineering material surfaces affects the phonon distributions. Furthermore, the gas-surface interactions also alter the PDOS due to the presence of adsorbates on the surface and removal of surface atoms due to surface participation reactions. This results in a highly coupled and dynamic system. Random surface roughness in MD will be obtained via irradiation with low energy particles. The effect of varying height and density of the defective region on the PDOS of this system will be investigated. The etch pits produced as a result of removal of surface atoms resembles a semi-ellipsoid with larger diameters and shorter depth. Here, the phonon distribution will be characterized as a function of both diameter and depth of the etch pits. Finally, the effect of adsorbates on the PDOS will be studied in terms of bond strength (physisorbed vs chemisorbed) and surface coverage.

SS-TuP-13 Variation of Structure Colors of Copper with LIPSS(Laser-Induced Periodic Surface Structure) by Femtosecond Laser Irradiation*, **TaeHoon Park**, J Kim, T Hwang, J Kang,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; K Kim,* Sejong University, Republic of Korea*; H Lee,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

The Laser-Induced Periodic Surface Structure (LIPSS) formed under femtosecond laser irradiation has been a way to change optical, tactile, hydrophobic properties, etc. without chemical reaction. Specially, the LIPSS can be applied to enhance the visual perception of skin materials in order to meet the user's aesthetic choice of mobiles, auto vehicles, electronics, etc. It has been reported through many studies that the structure color by LIPPS is due to the refraction of the light by periodically nano-scaled structure, however, its variation of structure colors has not been studied generally on the microstructures such as pitch and depth of nano-scaled microstructure. In this study, the metal substrates consisting of pure copper were processed with the condition of femtosecond laser irradiation with the scan rate from 4 mm/s to 20 mm/s and the scan space of 40 μm. The color difference (ΔE) of periodically nano-scaled structure obtained by femtosecond laser irradiation was measured by a multi angle spectrophotometer and quantified by the value of L*a*b* chromaticity diagram. The periodically nano-scaled structures of pure copper showed the roughness (R_a) from 29 nm to 50 nm at the pitch of approximately 280 nm. The brightness was decreased as 15% with an increase of roughness due to a diffused refraction from the surface. The value of L* was ranging from 4 to 81, a* was from 4 to 19 and also b* was from 2 to 24 in the chromaticity diagram of pure copper as detected with tilt angles of 15° to 110°. The calculated ΔE from these results were widely shown from 1.5 to 77, which means that distinctive colors can be realized although the composition of material is not different. It could be expected that the structure color was sufficiently controlled by the periodically nano-scaled structures from femtosecond laser process, and was to be applied at various skin materials.

SS-TuP-14 Bio-synthesis of Finely Distributed Ag Nanoparticle-decorated TiO_2 Nanorods for Sunlight-induced Photoelectrochemical Water Splitting*, **Moo Hwan Cho**, S Sawant, M Sayed, T Han, J Shim,* Yeungnam University, Republic of Korea

Metal-semiconductor heterostructures have attracted considerable attention for applications in photoelectrochemical (PEC) water splitting. In this study, Ag nanoparticles (NPs) grafted on to the surface of TiO_2 nanorods (NRs) via the simple biological reduction of $AgNO_3$ using electroactive biofilms (EABs) composed of *Shewanella oneidensis* were assessed as a photoanode for PEC water splitting under solar light irradiance. Transmission electron microscopy showed that EABs-assisted bio-reduction leads to the uniform decoration of spherical Ag NPs with 10-40 nm diameters and stronger attachment to the Ag-TiO_2 NRs interface due to the prior adsorption of Ag^+ ions. In addition, the plasmonic interaction of Ag NPs with TiO_2 NRs was reflected in their optical properties, showing stronger absorption in the visible range and a reduced band gap due to surface plasmon resonance, which are crucial factors for charge carrier generation. Compared to TiO_2 NRs, Ag-TiO_2 NRs/FTO containing 11.17 at.% Ag, as confirmed by X-ray photoelectron spectroscopy exhibited a 8 times higher current density (0.08 mA/cm^2 at 1.2 V vs. RHE) under solar light irradiation (1.5 G illumination; 100 mW/cm^2) due to enhanced visible light absorption, surface plasmon resonance effect, and efficient electron-hole separation. A mechanism was also proposed to elucidate the PEC water splitting activity of Ag-TiO_2 NRs photoanode under solar illumination. The exceptional photostability of the Ag-TiO_2 NRs photoanode is expected to pave the way for efficient visible-light-driven PEC water splitting.

SS-TuP-15 Oxidation of Nb(100) and Kinetics of Surface to Bulk Transport and Extension to Nb_3Sn*, **Rachael Farber**, D Veit, S Sibener,* The University of Chicago

Niobium (Nb) is commonly used in superconducting radio frequency (SRF) accelerator cavities due to its ultra-low surface resistance (R_s) and high cavity quality factor (Q) at ~ 2 K. Nb cavities are, however, highly susceptible to localized surface heating, resulting in quenching of the superconducting properties. To minimize quenching, much work has been done to understand factors influencing SRF cavity performance for the clean and oxidized Nb surface. In this work, we have investigated the structural evolution of oxidized Nb(100) under ultra-high vacuum (UHV) conditions to elucidate the structural evolution of the (3×1)-O ladder structure following exposure to O_2. Auger electron spectroscopy (AES) was used to determine oxygen coverage and surface structure was determined using scanning tunneling microscopy (STM). The (3×1)-O Nb(100) surface was exposed to O_2 at 300 K and annealed to various substrate temperatures to facilitate oxygen dissolution. Dissolution kinetics elucidated the surface to bulk oxygen transport mechanism. STM showed the decomposition of the ordered (3×1)-O ladder structure during oxygen dissolution, indicating the importance of oxygen concentration on surface structure. As the fundamental limits of Nb SRF cavities are being realized, it is crucial that alternative SRF materials be studied. Nb_3Sn has been identified as a most promising next generation SRF material with higher Q as well as the ability to operate at much higher temperatures, greatly reducing cryogenic infrastructure costs. Ongoing work is focusing on developing preparation methods leading to more homogeneous Nb_3Sn films. *In situ* Sn doping on (3×1)-O Nb(100) combined with surface sensitive techniques such as AES, XPS, and LT-STM will hopefully allow for the diffusion mechanism for Sn on Nb to elucidated, leading to improved procedures for Sn infusion and materials growth.

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