Friday Morning, October 6, 2000

Surface Science Room 209 - Session SS+MC-FrM

Characterization of Oxides and Thin Films Moderator: J.A. Kelber, University of North Texas

8:20am SS+MC-FrM1 Characterisation and Microreactor Studies of Nanofabricated Model Pt/Ceria Catalysts, C. Werdinius, Chalmers University of Technology, Sweden; O. Hjortsberg, Volvo Technological Development Corporation, Sweden; L. Österlund, B. Kasemo, Chalmers University of Technology, Sweden

In modern automotive catalysts, ceria is an important component for transient storage and release, respectively, of oxygen during lean and rich conditions. In order to study the detailed kinetics of the oxygen storage, well-characterised samples are required. Model catalysts (1 cm@super 2@ sample area) of platinum particles on ceria were nano-fabricated by a novel method called "colloidal lithography".@footnote 1@ Its principal feature is the ability of fast parallel fabrication of almost mono-sized, evenly distributed nano-particles. The manufacturing consists of the following steps; (i) deposit a ceria film on a silicon wafer, (ii) deposit a Pt film of desired thickness, (iii) deposit an array of colloidal particles of desired size and spatial separation, (iv) remove all Pt not shadowed by the particles, using Ar-ion beam etching, (v) remove the particles. The final step leaves an array of Pt particles with size and separation reflecting the colloidal particle size and separation. Samples with different Pt-particle densities and particle sizes (40 and 110 nm) were made, and characterised by several surface analytical techniques, including SEM and XPS. Preliminary results of pulsed CO oxidation experiments in a specially designed microreactor are presented, along with vacuum CO TPD measurements. @FootnoteText@ @footnote 1@ P. Hanarp, D. Sutherland, J. Gold, and B. Kasemo, Nanostructured Materials 12, 429-432 (1999).

8:40am SS+MC-FrM2 Characterization of Hf and Zr Oxides, Silicides and Silicates, Formed on the (0001) Surfaces of HfB@sub 2@ and ZrB@sub 2@, by AES, XPS, LEED and STM, *R. Singh*, University of Illinois at Chicago; *Y. Paderno*, Academy of Sciences of Ukraine; *T. Tanaka*, National Institute for Research in Inorganic Materials, Japan; *M. Trenary*, University of Illinois at Chicago

Transition metal (TM) diborides have comparable and often higher degrees of hardness, chemical inertness and thermal stability than their nitride and carbide counterparts. Therefore, TM-diborides are attractive for the same type of applications as nitrides and carbides such as for hard coatings and diffusion barriers. In order to explore their usefulness as diffusion barriers and gate dielectrics, a series of experiments with silicon were performed. Silicon was deposited by the UHV-CVD of silane gas on clean and oxygen covered HfB@sub 2@ and ZrB@sub 2@(0001) surfaces. On the clean surfaces, HfSi@sub 2@ and ZrSi@sub 2@ were formed. A p(2x2)R30° LEED pattern was observed. The structure of Si on the surfaces was also investigated with STM. On the oxygen covered surfaces, silicates were formed. Oxidation of the crystals leads to the formation of HfO@sub 2@ and ZrO@sub2@, which both exhibited a (3x3) LEED pattern at a high exposure (5 L) and a p(2x2)R30 pattern at a low exposure (0.5 L). Information gained from exposure of oxygen to ZrB@sub 2@ was crucial in interpreting the O 1s region in HfB@sub2@, which partially overlaps with the Hf 4s peak.

9:00am SS+MC-FrM3 Controlled Coordination and Oxidation State of Copper and Manganese Cations in Complex Nickel-Copper-Cobalt-Manganese Oxide Thin Films, D.A. KuKuruznyak, M.-H. Lee, K.A. Omland, M.C. Gregg, F.S. Ohuchi, University of Washington

lonic configuration and cation distribution of the nickel-copper manganite spinels have profound effects on their electrical conduction. As these materials are being widely used for thermistor applications, it is important to find a way of controlling the oxidation states of transition metal cations in these mixed oxides. We have therefore undertaken our research developing a unique method fabricating thermistor composition by chemical solution deposition where cations with unusual coordination and unusual oxidation state can be obtained. Organometallic films deposited on silicon and glass substrates by spin-coating of a liquid precursor solution were decomposed in air at 550°C followed by furnace-annealing at temperatures ranging from 600° to 800°C to obtain single-phase cubic spinel of chemical composition Ni@sub 0.48@Co@sub 0.24@Cu@sub 0.6@Mn@sub 1.68@O@sub 4-x@. XPS, FTIR, and Mossbauer spectroscopy have been used to study oxidation states of transition metal ions.

Octahedrally coordinated Cu@super +1@ observed from the specimens (prepared below 700°C) showed unusually large negative binding energy shifts in Cu(2p) peak relative to metallic Cu, of which origin was attributed to the difference in the Madelung potentials. Annealing at higher temperatures causes oxidation of copper to Cu@super 2+@ and reduction of manganese cations from Mn@super 4+@ to Mn@super 3+@. The annealing temperature can precisely control oxidation state distribution of copper and manganese cations.

9:20am SS+MC-FrM4 Behavior of Lightly Doped-electrons on the Electronic Structure of SrTiO@sub 3@: An Angle-resolved Photoemission Study, Y. Aiura, H. Bando, I. Hase, Electrotechnical Laboratory, Japan; T. Yasue, Tsukuba University, Japan; T. Saitoh, D.A. Dessau, University of Colorado

Behavior of lightly doped-electrons on the electronic structure of SrTiO@sub 3@ has been studied using angle-resolved photoemission spectroscopy (ARPES). Two states in the band gap region of SrTiO@sub 3@ (in-gap states) are observed; a state with a sharp Fermi cut-off (metallic state) and a broad state centered at ~1.5eV below the Fermi level (~1.5eV state). In order to study the origin of the metallic state, we have calculated the energy-band of non-doped (stoichiometric) SrTiO@sub 3@ and lightly electron-doped SrTiO@sub 3@ based on the full-potential linearized augmented plane wave (FLAPW) method. From comparison between the calculated results and the experimental ones from ARPES, it was shown that the metallic state can be quite well explained by the rigid-band behavior based on one-electron band theory. For the ~1.5eV state, on the other hand, ARPES spectra showed that there is no visible empirical energy dispersion and that its spectral intensity is very sensitive to the surface condition. These experimental results means that the ~1.5eV state is not caused by the bulk electronic structure, but the surface one due to the surface defects.

9:40am SS+MC-FrM5 Reactions of Acetaldehyde over UO@sub2@(111) Single Crystal Surfaces: Evidence of Benzene Formation, S.V. Chong, H. Idriss, The University of Auckland, New Zealand

The reactions of aldehydes on metal oxide surfaces have exposed some of the most exquisite chemistry compared to their alcohol and carboxylic acid counterparts. Due to the intermediate oxidation state of the carbonyl carbon on an aldehyde, reactions such as the Cannizzaro reaction (forming alcohol and carboxylate) and Tishchenko reaction (forming ester) have been observed on various metal oxide surfaces. Furthermore, condensation reactions have also been observed on aldehydes possessing alpha-H atom(s) over stoichiometric metal oxide surfaces, while surface defect sites are able to reductively couple two aldehyde adsorbates to yield alkene. Herein, we present the reactions of acetaldehyde over the stoichiometric, electron irradiated, and H@sub2@ reduced surfaces of UO@sub2@(111) single crystal. TPD results over the three surfaces show evidence of benzene formation, and it appears that electron irradiation slightly increases the conversion to benzene, while H@sub2@ reduction doubles it. Thus, the amount of benzene yield might be a novel way to quantify the extent of surface defects. No C@sub4@ hydrocarbon (crotonaldehyde nor butadiene) traces were observed, indicating that the formation of benzene through aldol condensation pathways might be ruled out.

10:00am SS+MC-FrM6 Synchrotron-based XPS Study of 1-Decanethiol Chemisorbed on Au(111), Y.W. Yang, Synchrotron Radiation Research Center, Taiwan; L.J. Fan, National Tsing Hua University, Taiwan; L.J. Lai, Synchrotron Radiation Research Center, Taiwan

Self-assembled monolayers have been the subject of intense research due to their potential applications in areas of lubrications, corrosion inhibitions, gas sensors, etc. We combined TDS and synchrotron-based, high resolution core level spectroscopy to study the chemisorption of 1-decanethiol monolayer on Au(111) surface with the molecular films prepared from both gas-phase dosing and solution immersion. On heating to temperatures higher than 400 K, decanethiolate starts to decompose, forming 1-decene via @beta@-hydrogen elimination, and leaves atomic sulfur on the surface. For thin films produced by both methods, S2p core level exhibits a single, well-characterized spin-orbit doublet with S2p@sub 2/3@ at 162.1 eV, indicating identical chemical interaction between sulfur and gold atoms in the films. However, C 1s core level starts from 284.0 eV at low coverage, develops a high-binding shoulder at intermediate coverage and eventually becomes a single peak at 285.0 eV for the high coverage prepared from solution phase. Angle-resolved XPS measurements of substrate core level signal provide a direct measure of the film thickness. The increases of C 1s binding energy is found to be associated with the incomplete final-state

Friday Morning, October 6, 2000

relaxation of the carbon atoms due to the thickness increase of the film as the carbon chains tilt toward the surface normal. Moreover, the implication of observing only a well-defined doublet of S 2p signal will be discussed in relation to the sulfur dimer model.

10:20am SS+MC-FrM7 STM Studies of Pyrrole-sdsorbed Si(111)-7*7 Surfaces, Z.L. Yuan, National University of Singapore, Singapore

The Si(111)-7*7 surfaces is particularly appropriate in Si surface chemistry, because it contains dangling bonds on several different sites within the surface unit cell, and also STM has been used to provide direct and local information on an atomic scale.@footnote 1@ In the present work, the topographic and spectroscopic analysis of pyrrole adsorption on Si(111)-7*7 surfaces at room temperature under different pyrrole exposures is investigated by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). No significant changes in the surface reconstruction are observed, some adatoms become dark, however this is not due to the vacancies of Si adatoms, because these adatom are visible under the higher sample bias, the disappearance of adatoms is the result of changes in electronic structure upon reaction with pyrrole. the preservation of the 7*7 reconstruction suggests that the reaction with pyrrole has primarily saturated existing dangling bonds on Si(111)-7*7 surfaces. The adsorption is site selective, the faulted center adatoms are most favored for adsorption among the adatoms. The rest atoms also react with pyrrole from STS observation. Based on our STM/STS and HREELS data, a possible adsorption mechanism of pyrrole chemsorption on Si(111)-7*7 surfaces is also discussed. @FootnoteText@ @footnote 1@R. Wolkow and Ph Avouris, Phys. Rev. Lett. 1988, 60:1049; Phys. Rev. B,1989, 39:5091; J. Yoshinobu et al, Phys. Rev. B 1992, 46:9520; Jpn. J. Appl. Phys. 1993, 32:1171; M. N. Piancastelli et al, Phy. Rev. B 1993, 48:17892, R. A. Wolkow, Annau. Rev. Phys. Chem. 1999, 50:413.

10:40am SS+MC-FrM8 Characterization of Bound Ultrathin Perfluoropolyether-Functionalized Polysiloxane Films on Silicon Oxide Surfaces, F. Parsapour, Colorado State University; D.G. Castner, University of Washington; D.W. Grainger, Colorado State University

Current technological demands for magnetic recording media lubrication include a reduction in the head-disk gap, elimination of stiction, and fabrication of a low adhesion protective surface which can withstand thermal and mechanical stresses associated with hard disk drive operation. Perfluoropolyethers (PFPE) are the most commonly used lubricants in the magnetic recording media. These polymers are typically applied thin films to the hard drive overcoat to which they are generally physisorbed. As a result, they are subject to thermal degradation and "spin-off", ultimately resulting in tribological failure modes. Direct attachment of PFPE films is potentially interesting as a foundation for improved friction and wear performance. We have previously reported fabrication of ultrathin films of polysiloxanes functionalized with perfluoropolyether side chains chemisorbed to surfaces and exhibiting structural anisotropy due to separation of various polymer-grafted components normal to the interface. We now report analogous polymer monolayers but with the important chemical and functional distinction of surface bonding to silicon oxide through alkylsilane anchoring groups. These copolymers were synthesized in a single step through the respective PFPE functional and alkylsilane anchor group coupling reactions. Monolayer films were formed on silicon oxide surfaces through the dip-coating method, resulting in hydrophobic immobilized films ~3 nm thick. XPS measurements support a stratified three-layer film chemistry within the monolayer, and an outer interface enriched with the PFPE moiety. AFM experiments show a high degree of coverage of the oxide surface by the copolymer film, and a relatively uniform surface. LFM measurements exhibit low frictional forces in the areas covered by the monolayer film. Force-displacement curves obtained in a fluid environment reveal a low adhesion surface compared to films prepared from copolymers without the PFPE functional group.

11:00am SS+MC-FrM9 Aerial Oxidation of Self-assembled Monolayers studied by SIMS, AFM and Contact Angle Measurement, *N.J. Brewer, G.J. Leggett,* University of Manchester Institute of Science and Technology, UK

For many applications, the long term stability of self-assembled monolayers (SAMs) is a critical issue. We have undertaken a systematic study of SAM oxidation using secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM) and contact angle measurements. Samples were left in an ambient environment for specific periods of time and then surface analytical techniques were used to observe any changes in the SAMs. SAMs were formed from long and short chain methyl, carboxylic acid and hydroxyl terminated alkanethiols. By using SIMS, we were able to monitor the rate of oxidation. We found that DDT, a long chain methyl terminated SAM, oxidised in seven hours, but the long chain carboxylic terminated SAM was unoxidised after seven hours. This shows that long chain carboxylic acid terminated SAMs exhibit increased stability in air. AFM was used to record the friction coefficients of the SAMs over a period of hours. The change in the coefficient of friction was slow and it was little changed after times when SIMS showed complete conversion of thiolates to sulfonates had occurred. This suggests that although the sulfur-gold bond is broken, the interchain forces still hold the structure together. The collapse of the system is gradual and this is reflected in the slow change in the friction coefficients. Advancing water contact angle measurements exhibited a sharp change in contact angle for carboxylic acid and hydroxyl terminated SAMs due to adsorption of contaminants, but a small change for the methyl terminated SAMs. It is concluded that SAMs may oxidise reasonably rapidly on exposure to air, but that the degradation of their structures and properties is much slower.

Author Index

- A --Aiura, Y.: SS+MC-FrM4, 1 - B --Bando, H.: SS+MC-FrM4, 1 Brewer, N.J.: SS+MC-FrM9, 2 - C --Castner, D.G.: SS+MC-FrM8, 2 Chong, S.V.: SS+MC-FrM5, 1 - D --Dessau, D.A.: SS+MC-FrM4, 1 - F --Fan, L.J.: SS+MC-FrM6, 1 - G --Grainger, D.W.: SS+MC-FrM8, 2 Gregg, M.C.: SS+MC-FrM3, 1

Bold page numbers indicate presenter

— H — Hase, I.: SS+MC-FrM4, 1 Hjortsberg, O.: SS+MC-FrM1, 1 -1 - 1Idriss, H.: SS+MC-FrM5, 1 -K-Kasemo, B.: SS+MC-FrM1, 1 KuKuruznyak, D.A.: SS+MC-FrM3, 1 -L-Lai, L.J.: SS+MC-FrM6, 1 Lee, M.-H.: SS+MC-FrM3, 1 Leggett, G.J.: SS+MC-FrM9, 2 -0-Ohuchi, F.S.: SS+MC-FrM3, 1 Omland, K.A.: SS+MC-FrM3, 1 Österlund, L.: SS+MC-FrM1, 1

— P —

Paderno, Y.: SS+MC-FrM2, 1 Parsapour, F.: SS+MC-FrM8, **2** — S —

Saitoh, T.: SS+MC-FrM4, 1 Singh, R.: SS+MC-FrM2, **1** — T —

Tanaka, T.: SS+MC-FrM2, 1 Trenary, M.: SS+MC-FrM2, 1 — W —

Werdinius, C.: SS+MC-FrM1, 1 — Y —

Yang, Y.W.: SS+MC-FrM6, **1** Yasue, T.: SS+MC-FrM4, 1 Yuan, Z.L.: SS+MC-FrM7, **2**