

Monday Afternoon, October 20, 2008

Vacuum Technology

Room: 205 - Session VT-MoA

Vacuum Cleanliness, Outgassing, Contamination, and Gas Dynamics

Moderator: J.H. Hendricks, National Institute of Standards and Technology

2:00pm **VT-MoA1 A Review of the Development of Cleaning Processes and Cleanliness Assessment at Daresbury Laboratory.** *J.D. Herbert, K.J. Middleman, R.J. Reid, A.N. Hannah*, STFC Daresbury Laboratory, UK
INVITED

Over the last 30 years the cleaning and processing of vacuum components at Daresbury Laboratory has changed considerably. Although some aspects remain quite similar, others are very different. There are two key reasons for the changes. Firstly, project requirements at Daresbury have changed significantly. Early projects like the Synchrotron Radiation Source (SRS), a 2nd Generation Synchrotron Light Source, required clean Ultra High Vacuum (UHV). Things became more complex when designing DIAMOND, a 3rd Generation Synchrotron Light Source, due to higher photon desorption yields and narrow vacuum chambers. Current projects like ALICE (Accelerators and Lasers In Combined Experiments) and the NLS (Next Light Source) demand vacuum levels in some parts to be in the eXtreme High Vacuum (XHV) region. To achieve this very low levels of contamination are required and very tight restrictions on particles are needed. Secondly, legislation has restricted the range of cleaning processes available. In the early years it was possible to use chlorinated solvents with relative freedom. Environmental legislation then restricted the use of Ozone depleting chemicals and COSHH added further restrictions. Over the last few years both Environmental and Health & Safety legislation has been tightened further. This paper will describe how the vacuum science group at Daresbury Laboratory have adapted to these changes and will describe some of the qualification methods used to determine cleanliness. Also, a recent study of cleaning methods has been conducted, some of the results will be presented and how the results have helped to determine a strategy for the future.

2:40pm **VT-MoA3 The Stainless Steel Bellows with Inner Surface Polishing.** *O. Koizumi*, Osaka Rasenkan Kogyo Co., Ltd., Japan, *N. Ogiwara*, Japan Atomic Energy Agency, *S. Sawa*, Osaka Rasenkan Kogyo Co., Ltd., Japan, *K. Suganuma*, Japan Atomic Energy Agency, *M. Matsue*, Osaka Rasenkan Kogyo Co., Ltd., Japan

One of the performances required for gas feed system in semiconductor manufacturing equipment is to be particle free. To meet this requirement the inner surface of the bellows must be smoothed and cleaned. This problem for the pipe and mechanical processed parts has been already resolved by combination with electro polishing or electro mechanical buffing, etc., and cleaning. However, for the bellows we could polish the inner surface smooth but not evenly because it is formed in bellows shape. Therefore we established wet mechanical polishing with which it is possible to polish the inner surface of the bellows smooth and even. The feature of this polishing is that you can completely polish the entire inner surface of the bellows by mixing abrasive in the liquid. We finally obtained the inner surface roughness less than $Ra=0.05\mu\text{m}$ for the bellows. Furthermore we realized to be particle free by combing this polishing and cleaning. Also we are planning to report the outgassing rate from the bellows which applied this wet mechanical polishing.

3:00pm **VT-MoA4 A Sensor for Detecting Extremely Low Concentrations of Heavy Hydrocarbons in Vacuum Systems.** *N.B. Koster, R. Jansen*, TNO Science and Industry, The Netherlands

At present vacuum systems are becoming more and more complex and are growing towards a full industrial scale. Together with this growth in size and complexity the cleanliness demands are also becoming more strict. Especially for Extreme Ultra Violet Lithography (EUVL) the requirements on hydrocarbon concentration are high. Typically the total concentration of hydrocarbons in such a tool must be below $1*10^{-12}$ mbar integrated over the mass range 45 to 200 in order to maintain the optics quality during lifetime of the EUVL tool. This also means that the requirements for components and sub-assemblies are even more strict and because the tool cannot be baked the cleanliness has to be verified before integration in the tool. These type of cleanliness demands are also becoming more important for other applications like ALD, CVD, fusion and accelerator systems. We present a sensor, that we are currently developing, that is able to measure the total concentration of heavy hydrocarbons (including fluor compounds) from

mass 100 up to infinity in a single channel. The sensor is based on a ionisation source in combination with a magnetic analyser that is used as a low mass filter for removing the species that are of no interest. The masses of interest are led towards a single channel detector for readout of the hydrocarbon partial pressure. Unlike an ordinary RGA the mass range is not scanned but acquired on a single detector, which leads to a significantly higher signal. Also, unlike a RGA, the noise level of the detector is not summed over the scanned mass range, but remains constant. As the sensor is a one channel detector it acts as a Mass Filtered Ion Gauge (MFIG) giving a signal for total concentration of heavy molecules. The benefit of such a sensor is that it gives a single output which enables a go / no go decision for vacuum qualification of chambers and components or in-situ monitoring of contamination levels in a tool. We expect that the sensor has a lower detection limit below $1*10^{-13}$ mbar when operating in faraday mode. The detection limit can be further increased by adding a Secondary Electron Multiplier (SEM) like a Multi Channel Plate (MCP) in front of the faraday detector. This can increase the sensitivity with a factor 100 to 1000. We will present our first results of the sensor when operating at vacuum levels between $1*10^{-6}$ and $1*10^{-9}$ mbar.

3:20pm **VT-MoA5 Low Outgassing, Low Permeability Elastomeric Seals for High Purity PVD Processing.** *G.A. Foggiato, W.B. Alexander*, Greene Tweed Co.

New processes associated with semiconductor manufacturing and in related industries require very clean, high vacuums. Systems utilized for such processes employ a multitude of seals with emphasis in elastomeric seals for transfer handling of substrates. The process environments require such seals to have very low outgassing and low permeability to the atmosphere as well as the gases used in processing. Recent developments of new elastomer seals employing perfluoroelastomers provide the characteristics suitable for these applications. Various material and fabrication technologies are described as used for fabricating seals for high vacuum, ultra high purity environments. This paper will review the new technologies and their effect on the properties of seal materials, the seals themselves and associated equipment performance. Examples of such optimization of seal technology will show the achieved characteristics for seals capable of sustaining vacuums of 10^{-9} Torr and at temperatures to 280 °C. The outgassing characteristics of a variety of seals will be shown for H₂O, HF, H and O₂, all potential contaminating gases during depositions of films for semiconductor and photovoltaic thin films. The low level of outgassing attainable by the more recently developed materials and the technology associated with such properties will be described. Through the use of a "tighter" bonding perfluoro molecular structure, combined with molecular based fillers, a molecular structure has been developed which greatly reduces permeability. Through a uniquely developed molding process, key of which is the cooling cycle, a tighter molecular structure is achieved. These new materials provide both the characteristics required for high performance PVD deposition equipment as well as addressing the highly corrosive and aggressive environments found in semiconductor etching and CVD equipment. The progress made in increasing the longevity of seals in such applications is described as this is becoming very critical in future technology nodes manufacturing. Data for use with NF₃, CF₄ and O₂ plasmas is presented to better understand the deterioration of the elastomers and associated mechanisms. The impact of temperature is also described showing that at chamber temperatures approaching 300 °C, such new seal materials still function suitably. Descriptions of these extended applications will be given along with the resultant enhanced performance.

4:00pm **VT-MoA7 Novel Leak Testing Methods for High Reliability Hermetic Devices.** *J.M. Hochrein, S.M. Thornberg, J.R. Brown, M.I. White*, Sandia National Laboratories

Traditionally, leak testing is done using helium leak detectors, which are specially designed for the detection of helium. Helium leak tests are often limited to room temperature which does not allow information to be gathered at elevated temperatures. This type of test only provides information about the leak rate under ambient conditions and not about the temperature at which a leak occurs during a thermal profile or how the leak magnitude changes as a function of temperature. In other cases, components may be sealed and contain gases that cannot be detected using traditional techniques rendering them ineffective. Two newly developed experimental methods for leak testing high reliability hermetic devices will be discussed. The first method is used to conduct real-time leak monitoring at temperatures ranging from ambient to 900°C while subjecting one side of the parts to continuous vacuum and monitoring for air components. Any loss of hermeticity will result in increases in air components detected. The second method that will be discussed is a method that involves monitoring for the presence of a specific organic target molecule (in this case, a

perfluorinated hydrocarbon) to localize the source of a leak. These experiments are conducted at ambient pressure using solid phase micro extraction (SPME) combined with gas chromatography/mass spectrometry.

4:20pm VT-MoA8 Direct Conductance Measurements of Small Leaks with Simple Geometries, J.A. Fedchak, R.F. Berg, D.R. Defibaugh, National Institute of Standards and Technology

The Pressure and Vacuum Group at NIST utilizes two constant pressure flowmeters as primary standards to calibrate helium leak artifacts, spinning rotor gauges, and ion gauges, using an orifice flow technique. A molar flow rate is produced by allowing gas to leak out of a small volume through a leak valve. By driving a piston into the volume such that the pressure within the volume remains constant, the gas flow rate through the leak valve is determined from the pressure measurement times the volume displacement of the piston per unit time (L/s). In the absence of other sources or sinks of gas, the conductance of the leak is identical to the volume rate of change of the piston. Therefore, the NIST flowmeters can be directly used to measure the conductance of leaks in the range of 10^{-6} to 10^{-5} L/s. Similar measurements have been done by other labs with primary flow standards (see Jousten et al.,¹ for example), but with limited success due to the inability to accurately model the conductance of leaks with complicated geometries. We directly use the flowmeter to measure the conductance of small leaks with simple geometries, such as thin orifices (OD~10 μ m) and capillaries. Small leaks with a known, precisely measured conductance may be used as check standards and in a variety of other applications. The conductance measurements and the applications will be presented.

¹ K. Jousten, H. Menzer, and R. Niepraschk, *Metrologia*, 39, 519 (2002).

4:40pm VT-MoA9 Modeling of Diffusion Processes in Vacuum Technology with Finite Element Method, J. Setina, Institute of Metals and Technology, Slovenia

Diffusion of gasses is a frequent phenomenon in vacuum technology. Examples are: permeation of atmospheric gasses through parts of chamber wall (elastomeric seals and plastics), diffusion of dissolved hydrogen gas in a chamber wall and its evolution into vacuum, and permeation of gasses through membranes in permeation leak elements. The process can be mathematically represented with a diffusion equation, which is a second order partial differential equation. Its solutions depend on the geometry of the system and on initial and boundary conditions. Solutions can be found in analytical form for simple geometries and selected simple initial and boundary conditions only. Diffusion equation can be solved also numerically with finite element method (FEM). Numerical calculations can be applied for arbitrary initial and boundary conditions. In the presentation we will discuss a simple one dimensional case, which can be applied when the problem can be approximated with planar geometry. Numerical calculation of a time dependency of the concentration profile within the sample can be easily performed in a widely use spreadsheet program Excel. The reliability of FEM calculations was checked for a special case of initial and boundary conditions, when the analytical solution is known also. We will also present a practical example of FEM modeling of He gas flow into a vacuum system through a Viton gasket after short-time exposure to He at atmospheric side. Such problem is often observed when He leak detection is performed.

5:00pm VT-MoA10 Rarefied Gas Flow through a Slit into Vacuum, F. Sharipov, Universidade Federal do Parana, Brazil, D. Kozak, Pontificia Universidade Catolica do Parana, Brazil

The rarefied gas flow through a thin slit represents a great practical and scientific interest. Such kind of flow takes place in many engineering applications, e.g. vacuum equipment, microfluidics, spacecraft design, metrology of gas flow etc. In the present work, such a flow is studied, based on the direct simulation Monte Carlo method. The mass flow rate is calculated with an accuracy of 0.5% over the whole range of the gas rarefaction, from the free molecular regime to viscous one. The flowfield is also provided.

5:20pm VT-MoA11 Moving Surfaces in DSMC: Implementation, Validation and Applications, R. Versluis, M.E. Roos, L. Thielen, TNO Science and Industry, The Netherlands

Applications in vacuum technology exist where moving surfaces play a role. Under rarefied conditions, moving surfaces influence heat and momentum transfer and surface stress. Several methods have been used to model moving surfaces in Test Particle and Direct Simulation Monte Carlo methods. In simple situations, such as plane Couette flow, one can add an extra velocity vector to molecules hitting a moving surface (the modeled surface stays at rest in an inertial domain). In other examples the flow field is simulated by using a moving calculation domain and the molecule trajectory is corrected for this. Both methods are limited to only one moving surface. But in cases where the domain contains both moving and non-

moving surfaces these methods cannot be applied or separate domains need to be defined and the interaction at the interface needs to be prescribed or iteratively determined. We have developed an algorithm to simulate an arbitrary number of moving and non-moving planes in one domain for DSMC methods. The planes can have any velocity vector but should not change the geometry. The method uses periodic boundary conditions (especially implemented for this) and is grid independent. In the DSMC scheme molecule trajectories are determined in two steps: particle movement between collisions and particle collisions. Boundary interaction is taken into account during the particle movement phase. In our method the moving surface is a special boundary with all properties of a normal boundary (temperature, accommodation coefficient, reflection velocity distribution). The difference is that the trajectory of each surface is determined and the exact time and place of interaction between the boundary and a molecule is determined. This way, the exact molecule trajectory is determined during its movement phase taking into account the plane movements during that time. Multiple collisions in one time step between moving and non-moving surfaces are taken into account. The current algorithm is limited to 2D with planes moving in a straight line, but the principle is valid for 3D and planes moving with arbitrary and changing velocities (although the calculation of collisions between plane and molecules becomes more tedious). Results will be shown of validation simulations and possible applications, such as simulations of displacement pumps, moving stages or surfaces in lithography, CVD, PVD and ALD systems, sample manipulation, vacuum conveyor belts etc.

Vacuum Technology

Room: 205 - Session VT-TuM

Vacuum Pumping Technologies, Large Vacuum Systems, Vacuum Modeling

Moderator: M.L. Stutzman, Jefferson Lab

8:00am **VT-TuM1 Modeling a Turbomolecular Pump with Direct Simulation Monte Carlo (DSMC)**, *M.E. Roos, R. Versluis, L. Thielen*, TNO, the Netherlands

Three flow regimes can be distinguished (ordered in decreasing pressure): the continuum regime, the transitional or rarefied regime and the molecular regime. Modeling of the continuum flow regime is covered by Computational Fluid Dynamics. The fluidum is regarded as a continuum and the discrete character of molecules is not taken into account. For the molecular regime network modeling can be applied. This is the equivalent of electric network modeling applied to flows. It has always been a problem to model the transitional regime. Transitional flow conditions appear in a wide range of applications where vacuum is applied or small dimensions prevail. Some examples: the design of precision instruments (newest generation lithography machines), physical and chemical vapour deposition processes (fabrication of solar cells or coating of metals) or space technology (plume from a rocket nozzle). TNO has developed in cooperation with the Delft University of Technology a tool to model the transitional regime. This tool is based on the Direct Simulation Monte Carlo (DSMC) method. In this model flow properties are determined by simulating the movement and collisions of molecules. A mixture of different gases can be modeled as well as chemical reactions between gases and on surfaces. The DSMC model is implemented in the parallelized numerical 3D flow solver CVD-X (developed in-house by TNO). The DSMC model is also valid in the molecular and continuum regime. The development of the model is an ongoing process. Recently the model has been extended to be able to simulate moving parts in the transition regime. In our method moving parts are implemented as special boundaries which are moving through the domain. A moving boundary has all properties of a normal stationary boundary (like temperature and accommodation coefficient). In addition the exact time and position in space of the interaction between molecules and a moving boundary is determined throughout time. Multiple collisions of molecules in one time step with moving and non-moving surfaces are taken into account. This method makes it e.g. possible to model the spinning rotors of a turbomolecular pump and optimize the efficiency. We are performing DSMC simulations on a turbomolecular pump using this method. The results of these simulations and the validation with experimental data are presented.

8:20am **VT-TuM2 Evaluation of Metallic Films of TiZrV and Au used in Ultra-High Vacuum**, *M.J. Ferreira, R.M. Seraphim*, Brazilian Synchrotron Light Laboratory - LNLS, *P.A.P. Nascente*, Federal University of Sao Carlos - UFSCAR, Brazil

The construction of ultra-high vacuum chambers (UHV) for particle accelerator demands pressure in the range of 10^{-8} Pa. It is particularly more difficult to obtain this vacuum level in chambers with a length to traverse section rate of 150:1. Among several methods used to obtain this condition, it stands out the internal coating with a metallic film capable of absorbing gases, called NEG (non-evaporable getter). Metallic films used in synchrotron accelerators cannot have gas molecules adsorbed on the surface and should be deposited on the internal surface of the chamber, making it a vacuum pump. Usually these materials are constituted by elements of great reactivity and solubility (such as Ti, Zr, and V) at room temperature, for oxygen and other gases typically found in UHV (H_2 , CO, and CO_2), besides having considerable diffusibility at low temperature (< 700 K), the so-called activation temperature. The objective of this work is to prepare and evaluate films of TiZrV alloy and Au produced by magnetron sputtering. The film structure, morphology, and aging have been characterized in order to know how much of the gas absorption property at low temperature can be attributed to the chemical reactivity of the elements and to the structure formed by the deposition process. The morphological, structural, and chemical characterization was carried out by atomic force microscopy (AFM), high-resolution scanning electron microscopy (FEG-SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and photon stimulated desorption (PSD). The produced materials were compared with commercial TiZrV samples, and this comparison made clear that the desired characteristics are related to the nanometric structure of the films and that the structure is clearly sensitive to the heating treatments.

Acknowledgements: we would like to thank Vinicius L. Pimentel and Roosevel Droppa Jr. for their assistance on some of the experiments.

8:40am **VT-TuM3 Sorption Properties of Non Evaporable Getter Pumps for Selected Hydrocarbons and Organic Compounds**, *A. Conte*, SAES Getters S.p.A. Italy **INVITED**

Non Evaporable Getter (NEG) pumps are very clean, vibration-free, compact UHV pumps able to deliver large pumping speeds for all active gases, including water and hydrogen. Plenty of literature is available describing the sorption characteristics of NEG pumps toward the gases typically present in UHV system, e.g. hydrogen, carbon oxides, water, nitrogen and oxygen. Fewer papers can be found describing the behaviour of NEG pumps toward hydrocarbons. Most of the experimental data available in the literature are related to pumping of methane or relatively simple hydrocarbons like the lower alkanes. Very few data are available for more complex molecules. On the other hand, pumping of volatile and organic compounds is an issue in a variety of vacuum applications, especially those related to silicon and semiconductor materials processing, wafer in-line inspection, e-beam and Extreme Ultra Violet Lithography (EUVL). In the present study we report the results of specific tests aimed at measuring the pumping speed for some selected organic compounds, namely toluene, decane and methyl methacrylate (MMA). The study shows that NEG pumps can effectively sorb these large organic molecules with high speed and capacity even at room temperature. This opens up the possibility of using NEG pumps in combination with other typical UHV pumps in those systems where organic volatile compounds can be present to improve the ultimate vacuum and mitigate the carbon/oxygen contaminations.

9:20am **VT-TuM5 New Methods to Achieve XHV/UHV with Refrigerator Cooled Cryopumps**, *B. Rock, D. Muller, M. Ahlers, T. Brown*, Oerlikon Leybold Vacuum

Cryopumps have a higher effective pumping speed compared to ion pumps or turbomolecular pumps, especially for the typical gases which limit the ultimate pressures in UHV devices like water vapor or Hydrogen. In addition, they are absolutely hydrocarbon free. The ultimate pressure of commercial refrigerator cooled cryopumps is mostly limited by 2 factors: they cannot be baked completely and they cannot be operated while attached to a chamber during bakeout due to the high thermal load. This paper presents a simple modification of a standard cryopump including the ability to cool the radiation shield with LN2 during bakeout. Pressures below 1×10^{-12} mbar have been reached even in larger vacuum chambers. The possibilities to measure these pressures via the Extractor gauge are shown too.

9:40am **VT-TuM6 The KATRIN Experiment: Vacuum Performance of the Large Main Spectrometer Vessel**, *J. Wolf*, Universität Karlsruhe, Germany

The scientific objective of the Karlsruhe TRitium Neutrino experiment (KATRIN) is to measure the electron neutrino mass from the β -decay of tritium with an unprecedented sensitivity of $200 \text{ meV}/c^2$. The kinetic energy of the decay electrons will be measured by an electrostatic spectrometer. Background considerations require a very good vacuum of 10^{-11} mbar or better in the large spectrometer vessel (volume 1240 m^3 , surface: 690 m^2). A combination of NEG pumps ($S = 10^6 \text{ l/s}$) and turbo-molecular pumps will provide the necessary pumping speed. In addition a very clean surface and low outgassing rates are mandatory. This talk reports on the manufacturing, vacuum performance before and after bake-out at 350°C .

10:40am **VT-TuM9 LHC Beam & Insulation Vacuum Systems**, *J.M. Jimenez*, CERN, Switzerland **INVITED**

In May'08, the world largest vacuum system was fully commissioned and consolidated in the Large Hadron Collider (LHC), a CERN accelerator built near the City of Geneva in Switzerland. Its more than 100 km of vacuum systems are operating over a wide range of pressures and integrates an impressive variety of vacuum technologies. These vacuum systems are composed of 54 km of UHV vacuum for the circulating beams and two times 24 km of insulation vacuum around the cryogenic magnets and for the cryogenic helium transfer lines. 48 km out of the 54 km are operated at a cryogenic temperature (1.9 K). The remaining 6 km of beam vacuum containing the insertions is at ambient temperature and uses non-evaporable getter (NEG) coatings, a vacuum technology that was born and industrialized at CERN. The pumping is completed using 600 ion pumps to remove noble gases; 1000 gauges are used to monitor the pressures. The cryogenic insulation vacuum of the magnets, while technically less demanding, impresses by its 24 km in length and a diameter of 900 mm for a total volume of 640 m^3 . Once cooled at 1.9 K, the cryogenic pumping allows reaching pressure in the 10-6 mbar range. This talk will introduce the vacuum systems and the challenges of its design, manufacturing, installation, commissioning and consolidation phases.

11:20am **VT-TuM11 The Modeling of Large and Distributed Vacuum System**, *A.D. Chew, M. Galtry, J. Luby*, Edwards, UK

As the size and complexity of vacuum systems increases the financial and technical challenges do so also. Accurate modeling allows system optimisation in advance of engineering efforts and negates the need for inefficient empirical iterations. This paper will describe a computational modeling technique which allows the modeling of vacuum systems incorporating any number of primary and secondary pumps and all other elements of a vacuum system. Real examples will be used to illustrate accuracy and efficacy.

11:40am **VT-TuM12 Introduction to Molflow+, a New GPU-Based Monte Carlo Code for Simulating Molecular Flows and for Calculating Angular Coefficients in the CUDA Environment**, *R. Kersevan, J.L. Pons*, European Synchrotron Radiation Facility, France

Molflow+ is a new test-particle (TP) monte carlo (MC) code developed for the simulation of molecular flows. It is the natural evolution of the code Molflow which had been developed by one of the authors (R.K.) and used by many laboratories since 1991. Molflow+ implements modern computing trends, such as the use of the OpenGL graphical interface and C\C++ code, and takes advantage of recent developments in the field of graphical processing units (GPUs) which allow a substantial parallelization of the TP MC algorithm for a modest capital cost. The Compute Unified Device Architecture (CUDA) environment has been chosen for its ease of use and portability to different computing environments. A second version of the program will let a similar code run on computers which have no GPUs or non CUDA-compatible GPUs, and only single or multi-core CPUs. As for the original code Molflow, in Molflow+ the geometry of the vacuum component under study is described in terms of planar polygonal surfaces to which attributes such as transparency, sticking coefficient, desorption profiles and more are assigned. The geometry is defined either by using a built-in editor program or by importing files obtained by using a popular computer-assisted design program which generates a triangularization of the surfaces. A very large period random number generator has been implemented into the code, in order to minimize systematic statistical errors. It will be shown how Molflow+ can also be used to calculate the angular coefficients of arbitrarily complex geometries, which can then be used to perform vacuum calculations based on the resolution of matrix operations. It will also be shown how using the GPU yields a dramatic improvement of the processing speed, thus allowing the simulation of complex vacuum systems which could not hitherto be carried out unless powerful and expensive computing tools were used. The paper will outline the early stages of development of the code, its benchmarking against existing analytical as well as numerical results, and will hint at possible fields of application where the dramatic computational power of the GPU could make a difference as compared to CPU-only cases. It will also discuss possible future developments such as the inclusion of intramolecular collisions which could extend the domain of application to flow regimes other than molecular.

Tuesday Afternoon, October 21, 2008

Vacuum Technology

Room: 205 - Session VT-TuA

Vacuum Gauging and Calibration

Moderator: J. Setina, Institute of Metals and Technology

1:40pm **VT-TuA1 Pirani Vacuum Gauge for J-PARC 3GeV Synchrotron Vacuum System**, *M. Kuroiwa, S. Fujii, N. Matsumoto, M. Sasaki*, Tokyo Electronics Co., Ltd., Japan, *N. Ogiwara, Y. Hikichi*, Japan Atomic Energy Agency

Turbomolecular pumps (TMPs) are used for not only rough pumping but also evacuation during beam operation. The backing pressure of the TMPs is always monitored with Pirani gauges. The control unit for the gauge has been newly designed, as the unit should be placed far from the gauge head which is located in a high level of radiation and electrical noise. We have adopted the combination of the constant current method with four-point probe method. Thus, with these techniques the output has been confirmed experimentally to be independent of the cable length, and less influenced by the noise. Generally the constant current method is not so suitable for measuring the higher pressure than that with constant temperature method, because the change in the output voltage so drastically decreases increasing the pressure over than about 100 Pa. As we have to measure the pressure up to about 1000 Pa precisely in order to monitor the backing pressure of TMPs, we have carried out the experiment about the change in the output as a function of the current. And, we have confirmed that the higher pressure can be measured when the higher current is passed. For example, we can measure the pressure less than 20 Pa at 50 mA, and the pressure ranging from 20 Pa to 1000 Pa at 90 mA, respectively. Thus the current is controlled in such a way that the set value is increased with the increasing pressure in several stages. On the other hand, to minimize radiation exposure during maintenance, it is necessary for the gauge head to have high toughness against the vibration and abrupt air inlet etc. Thus we tried to use W wire as the filament instead of Pt wire. However W wire would be unstable characteristic in high temperature status (over the 300C). It had might be affected by oxidation. So we have investigated other material for the filament. Now we have got good data by using W wire with gold coating 30 micrometer in a diameter. 30mA, 10ohm. Still we continue to have investigation to get more toughness and good condition for filament.

2:00pm **VT-TuA2 Hot Cathode Ionization Gauge Life Extension in the mTorr range by Operational Modifications**, *P.C. Arnold*, Brooks Automation, Inc.

Improvement of hot cathode ionization vacuum gauge lifetime in the mTorr range by reducing the sputtering of gauge electrodes onto other components of the gauge will be demonstrated. Of special interest with respect to the sputtering are deposits on the cathodes and on the feedthrough insulators which result in impaired electron emission and leakage currents, both ultimately causing gauge failure. Analytical procedures which led to the sources of the sputtered material will be described. The sputtering reduction is accomplished by reducing the potential difference through which ions are accelerated, consequently reducing the impact energy on low potential electrodes and thus reducing the yield of the sputtering. Empirical data results will be shown to agree with theory and calculations. Other changes in gauge operation to implement these modifications and other improvements to enhance high pressure gauge life will be discussed.

2:20pm **VT-TuA3 Vacuum Metrology in Korea, Value Innovation for Customers**, *K.H. Chung*, Korea Research Institute of Standards and Science (KRISS) **INVITED**

The Korea Research Institute of Standards and Science (KRISS) is the National Metrology Institute of Korea and responsible for the establishment, maintenance and dissemination of the national measurement standards. The Vacuum Technology Center (VTC) in KRISS has maintained the vacuum and leak standards from the atmospheric pressure down to 5×10^{-7} Pa. The vacuum standards systems for low, high, and ultra-high vacuum have been developed. Through bilateral comparisons with NIST, PTB, NMIJ, NPL (UK), IMGC and CCM key comparison for CCM.P-K3 and CCM.P-K4, it is recognized that the KRISS vacuum standards have reached the top level. In an effort to apply the vacuum and leak standards, VTC drew up and carried out the project "Base Construction for Vacuum Technology" from the year 1999 to 2007. The goal of the project was to establish the center in which almost all kinds of vacuum parts, devices, and equipments can be evaluated and performance tested. Its purpose is to help vacuum industries by providing them technical data needed in their development of vacuum equipments or processes. The next

step for VTC is to develop the methods to diagnosis plasma processes in reaction chambers and precursor level and contaminations for advanced vacuum processes like semiconductor and display fabrication.

3:00pm **VT-TuA5 Investigations of Gas Dynamics in Capacitance Diaphragm Gauges**, *M. Wüest*, INFICON Ltd, Balzers, Liechtenstein, *V. Kolobov, A. Vassenkov*, CFD Research Corporation

Industrial vacuum processes such as chemical vapor deposition (CVD) can affect the long-term stability of vacuum gauges. This sensor drift can be caused by deposition of process by-products on the surfaces of the sensor. Here, we present chemically reactive gas dynamics inside capacitance diaphragm gauges (CDG) in a CVD process. We present modeling results for the formation and deposition of process by-products in gauges with different geometries.

4:00pm **VT-TuA8 NIST Experience with New Non-Rotating Force Balanced Piston Gauges for Low Pressure Metrology**, *J.H. Hendricks*, National Institute of Standards and Technology

The NIST Low Pressure Manometry Project maintains and operates primary standard ultrasonic interferometer manometers (UIMs) over the pressure range 0.01 Pa (vacuum) to 360 kPa (3.6 times atmospheric pressure). The typical gauging technologies used to cover this important pressure range have included high-accuracy capacitance diaphragm gauges (CDG), resonance silicon gauges (RSG), piezoresistive transducers (PZT), and piston gauges (PG). Over the past 6 years, a new type of customer gauge, the non-rotating force-balanced piston gauge or FPG, has been compared to the NIST 140 Pa UIM and 160 kPa mercury UIMs. The results of these customer comparisons will be presented along with the advantages and disadvantages of using this new high-accuracy device to both generate and measure pressures between 1 Pa and 15 kPa.

4:20pm **VT-TuA9 UHV Gauges in Theory and Practice**, *M.L. Stutzman*, Jefferson Lab, *B.R.F. Kendall*, Elvac Laboratories

Many factors affect the measurement of pressure in the ultra-high vacuum regime. The operating theory of the various hot filament and cold-cathode gauges will be briefly reviewed, followed by a more in-depth discussion about the factors that affect the different gauges. Operational behavior and stability of both hot filament gauges, such as the Bayard-Alpert, Modulated BA and Extractor gauges, and cold-cathode gauges, particularly the inverted magnetron gauge, will be addressed.

4:40pm **VT-TuA10 A New Static Expansion System for the Spanish Metrology Center (CEM)**, *N. Medina, S. Ruiz*, Spanish Metrology Center (CEM), *J. Gómez-Goñi*, Universidad Politécnica de Madrid, Spain

The Spanish Metrology Center, in cooperation with the Technical University of Madrid (UPM) is developing a static expansion system to be used as pressure primary standard in the range from 0,0001 Pa up to 1000 Pa. This standard will be used to calibrate capacitance diaphragm gauges and spinning rotor gauges. The system consists of five vessels: two 100 L-vessels, two 1 L-vessels and one 0,5 L-vessel. It also has two 300 L/s turbopumps (for N2) in order to evacuate the system. The system has been designed to be bakable up to 150 C in order to facilitate its degasification. The system is also endowed with 16 Pt100 temperature probes in order to measure the temperature distribution on the vessels. As auxiliary pressure gauges it also has one mass spectrometer, two ionization gauges, two spinning rotor gauges and two capacitance diaphragm gauges. The expansion factor determination is performed by gas accumulation method. The use of a Ruska 2465 pressure balance and a DHi FPG8601 pressure balance connected to the system through a 1 Torr differential capacitive diaphragm gauge is a special feature of this expansion factor determination. In this way we expect to reduce our measurement uncertainties.

5:00pm **VT-TuA11 Precision Volume Measurements: Challenges to Reducing Uncertainties**, *S.M. Thornberg, J.M. Hochrein, J.R. Brown, R.D. Boyd*, Sandia National Laboratories

In order to reduce uncertainties in gas law calculations, one must address each of the major variables: pressure, temperature and volume. Very accurate temperature and pressure gauges are available and can be measured directly with commercial instruments. However, volume is typically the variable in the ideal gas law that consistently contributes greatly to the uncertainty when performing gas calculations. Reducing the volume uncertainty is particularly challenging because volume is not measured directly but is derived from other dimensional, pressure, volume, mass and/or temperature parameters. A $\Delta V/\Delta P$ method for accurately measuring volumes will be presented along with a discussion of ways used to reduce uncertainties and randomness. This method uses calibrated

micrometers and precision pressure gauges in an “isothermal” (the goal is to reach a thermal stability where the temperature drifts less than 0.001°C during the 15 minute measurement duration) environment, all of which provides measurement repeatabilities within +/- 0.005 cc for a nominal 10 cc volume.

5:20pm **VT-TuA12 Thermal Management of Temperature Controlled Capacitive Diaphragm Gauges**, *B. Andreaus, H. Hanselmann, M. Wüest, Ch. Berg*, Inficon AG, Liechtenstein

We present results from our thermal management studies for INFICON’s new, innovative family of SKY digital capacitive diaphragm vacuum gauges which covers a temperature range from controlled 45°C to hot 200°C as well as full-scales from 1000 Torr to 100 mTorr. A wide range of interface configurations is made possible by a flexible gauge power and communication interface platform. The heart of the design is a new programmable heater architecture that surrounds the high precision ceramic measurement cell and as well controls the temperature gradient between the gauge and the flange. Much thought has been put into heat distribution, material choice and mechanical design in order to achieve a compact and robust design that will provide stable measuring conditions while keeping electronics and software protected and functional in hostile process environments. We present results from our thermal management design studies, complemented by relevant performance characteristics of the gauges from validation experiments.

Tuesday Afternoon Poster Sessions

Vacuum Technology

Room: Hall D - Session VT-TuP

Poster Session, Including Student Poster Competition

VT-TuP1 Construction of a Laboratory Based Resistance Thermal Evaporator and/or Sputtering Module and the Associated Safety Systems, *V. Lambe, A. Pender*, Institute of Technology Tallaght, Ireland

Construction of a laboratory based resistance thermal evaporator and/or sputtering module and the associated safety systems. This student project involves building both the vacuum system consisting of bell jar, turbo and rotary vein pump and associated ducting and valves. The high voltage system consists of a 30A dc power supply and associated circuitry. The aim of the project was to evaporate and characterise aluminium deposition on silicon (thickness versus time, power versus thickness etc). An addition aim was to characterise the equipment and provide documentation for the user. A simple film thickness monitor is to be built and installed into the system. In particular the student has concentrated on the safety aspects of the design. These includes, 1. Half atmosphere switch to protect the turbopump 2. EMO and breaker circuitry for the high voltage power supply 3. Interlocks for the power supply 4. Air driven vacuum interlock to protect against high voltage.

VT-TuP2 A Study of a Method to Evaluate the Corrosion Resistance of Al_2O_3 Coated Vacuum Components for Semiconductor Equipment, *J.Y. Yun, S.W. Kang*, KRIS, Korea, *S.M. You, J.S. Shin*, Daejeon University, Korea

This study is concerned with the evaluation of the corrosion resistance of coated semiconductor equipment parts with various processes. To select the appropriate basis for evaluation, replacement parts were observed during the semiconductor manufacturing process. This study also ran a dry corrosion test using Al_2O_3 , which is mostly used as a coating material. This test quantitatively measured the efficiency of coated parts. Surface morphology, leakage current and breakdown voltage were also evaluated. This study showed that the leakage current increased and the dielectric strength largely decreased after a dry corrosion process that led to the drop of electrical properties. The surface morphology test produced found that surface impairment can be severe depending on exposure to corrosive environments. By using the values that changed during the corrosion process, it may be possible to contrive a method to evaluate the efficiency of coated parts with various processes.

VT-TuP4 The PM-IRRAS Study of Water Thin Film on Aluminum Alloy Surface with Vacuum Pumping Down Process Condition, *H.P. Hsueh*, NSRRC, Taiwan, *W.F. Liu*, NTHU, Taiwan, *C.K. Chan, G.Y. Hsiung*, NSRRC, Taiwan, *J.R. Chen*, NSRRC and NTHU, Taiwan

Baking is always a necessary step for achieving ultra high vacuum (UHV). For a previously baked system to have the vacuum parts replaced and to achieve the same level of vacuum without repeated baking is a challenge to today's large vacuum system like synchrotron radiation facility. With ongoing study on ultra-dry parts replacement system, the need to understand how dry is enough becomes essential for both scientific aspect and cost of ownership aspect. Previous studies have shown a phase change for water on crystal Al_2O_3 (0001) near 10 torr. In our study, polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS) results have shown a clear spectrum change at 8 torr on ozone water cleaned A6061-T6 aluminum alloy surface. We also measured the temperature change during pumping down process and found out the temperature can go as low as $-30^\circ C$ for this adiabatic expansion process. This pumping down process could cause the water molecules on the surface to be frozen and then to be melted during the whole pumping down process. The PM-IRRAS study has shown the phase change result. A more detailed PM-IRRAS study corresponding to the pressure and temperature during pumping process will be shown in this presentation for both A6061-T6 aluminum alloy and crystal Al_2O_3 (0001).

VT-TuP5 A Novel, UHV Analysis System for Detecting Electron Stimulated Reaction Products Generated during Field Emission Studies, *M. Bagge-Hansen, R.A. Outlaw, M.Y. Zhu, H. Chen, D.M. Manos*, The College of William and Mary

Carbon nanosheets (CNS) are a promising carbon allotrope for high current field emission cathodes and are grown by plasma-enhanced chemical vapor deposition (PE-CVD) from a C_2H_2/H_2 gas blend at substrate temperatures of $\sim 600^\circ C$. The resulting film consists of sp^2 , vertically oriented, honeycomb carbon arrays terminating in a single graphene sheet that serve as field

emission cathodes. A novel ultrahigh vacuum (UHV) system has been assembled for the study of gas products generated by etching of the CNS during field emission testing. A residual gas analyzer (RGA) located in direct line-of-sight of the field emission gap (254 μm) of the Cu diode geometry is used for measurement of reaction products generated during field emission tests. Electron bombardment of the Cu anode (up to 2 mA/mm²) generates atomic hydrogen (1-5 eV) by electron stimulated desorption (ESD) which, in turn, reactively etches the CNS cathode and produces predominantly CH_4 as a reaction product. The Cu anode assembly is actively water-cooled by an external chiller to 0 $^\circ C$ to minimize thermal effects. The typical operating pressure is $<2 \times 10^{-10}$ Torr. Mass spectral and I-V data are collected simultaneously by an integrated LabView program. Carbon monoxide and carbon dioxide were also observed during field emission and are also correlated with the emission current. Scanning electron microscopy of the CNS topography and cross section was used to confirm the etching rate (~ 2 nm/hr). These results are consistent with the density functional predictions reported by Kanai et al. of CH_4 generated by atomic hydrogen incident on graphene.¹

¹ C. Kanai, K. Watanabe, and Takakuwa, Phys. Rev B 63, 235311 (2001).

VT-TuP6 A Compact Deposition Chamber Design for Low Temperature Growth of Ultra-Thin Crystalline Films on Metal-Insulator-Semiconductor Devices, *R.E. Lake, J.R. Puls, M.P. Ray, C.E. Sosolik*, Clemson University

Fabricating ultra-thin crystalline metal films is especially important in new studies of ballistic electron transport at interfaces and energetic processes of atoms on surfaces. In order to probe physics at the atomic level without contamination these studies require that homogeneous, atomically ordered, and defect free thin films be deposited in the same ultra-high vacuum (UHV) system where they will be studied. With this constraint in mind, we have designed and built a compact deposition chamber that allows for in situ growth and analysis of atomically ordered epitaxial metal layers which are only a few monolayers thick. This UHV deposition chamber is attached to a port on the fast exchange load lock (FELL) of our Omicron variable temperature STM (VT-STM) and has an internal volume of 476 cm³. It contains an evaporation gun slot that can be equipped with either an electron beam evaporator or a simple thermal evaporator. The target substrates used for deposition are compatible with the VT-STM design and are held in place at the center of the deposition chamber in a specially-designed clamping slot fabricated into an oxygen-free high-conductivity copper stage. The copper sample stage facilitates rapid cooling of the substrates to the temperatures required for crystalline film growth. This is done using a continuous flow of liquid nitrogen through the hollowed out interior of the sample stage. Following film growth, samples can be kept under vacuum and transferred into the FELL via a rotary-linear manipulator and then directly into the VT-STM chamber for analysis. Our compact chamber design has made the VT-STM system more effective for measurements of as-grown surfaces and interfaces, and its low cost and ease of use should be of special interest to other physicists, chemists, and engineers with similar research goals.

VT-TuP7 HORST - A New Device for Digital In-Line X-ray Holography, *F. Staier, A. Rosenhahn, M. Grunze*, University of Heidelberg, Germany

The holographic x-ray scattering chamber (Holographische Röntgenstreuakammer HORST) is a new experimental station for coherent x-ray sources such as synchrotrons and free electron lasers. It is designed for digital in line holography but also flexible to have add ons like magnets or beamstops for diffraction imaging. HORST consists of a large vacuum chamber with three stage systems for pinhole, sample and camera positioning and a differential pumping stage to achieve a very good vacuum pressure at the beamline. All this is mounted on a mobile and height adjustable framework. The three motorized stage systems has 13 axes of motion: pinholes can be moved and tilted perpendicular to the beam axis, samples can be moved in all three dimensions as well as rotated for tomography and the CCD camera can be positioned. We present first images acquired at UE52SGM at BESSY which characterizes the imaging properties of the system. The applicability to handle biological samples and first holotomography results will be presented.

VT-TuP8 The Titan Blimp, *J.T. Hagen*, Cedarville University

The purpose of this project was to test the feasibility of an exploratory blimp in the harsh conditions present on Saturn's largest moon, Titan. A blimp would possess significant advantages over satellites due to Titan's enormously thick atmosphere, as well as over rovers due to the extremely cold temperatures that exist on the surface. These facts establish that a blimp with the flexibility to ascend and descend through the atmosphere and

land on the surface would be the most practical exploration vehicle. An insulated pressure/vacuum chamber was constructed to house a simulated atmosphere of Titan. This vacuum chamber was constructed from a steel dollar-coin changer measuring 26" x 19" x 13". The lid was sealed with an inch thick acrylic lid to allow for visible inspection as experimentation was run. Liquid nitrogen was poured into the chamber, and its evaporation created the -180°C temperature of Titan's surface, the 95% nitrogen gas composition of Titan's atmosphere, as well as the 147kPa surface pressure. A 12-liter mylar balloon was placed inside the chamber and filled with cryogenic helium gas to generate buoyancy. RTD temperature probes were used in the chamber to measure the chamber temperature as well as the balloon temperature. Two pressure transmitters were also installed to measure the pressure of both the chamber and the balloon. These pressure transmitters as well as electric solenoid valves were connected to pressure controllers, which could then regulate the pressure of both the chamber and balloon simultaneously. A pressure control program was used in conjunction with a vacuum pump to simulate an ascent and descent through the Titan atmosphere, reaching simulated altitudes of 16km. A feasible balloon was successfully kept fully inflated through various pressure changes without exploding.

VT-TuP9 Scaling of Low-Pressure Transport Coefficients for Gas Mixture Flow in a Tube, M. Vukovic, Tokyo Electron, US Holdings

Low pressure gas mixture flow in a tube can be analyzed with the linearized Boltzmann equation or the DSMC method. Alternatively, one can use the linearized Boltzmann equation to calculate gas transport coefficients that depend on the local concentration and density. These coefficients are then used in the gas flow analysis. This procedure requires repeated solution of the linearized Boltzmann equation, or preparation of coefficient tables for the whole range of expected gas concentrations and densities. Using the numerical results of Sharipov and Kalempa (J. Vac. Sci. Technol. A 20, 814 2002), we show how to rescale each transport coefficient for a gas mixture, collapsing the curves for various gas mixtures to a single curve. Once this re-scaling is done, to calculate the transport coefficients one needs the free-molecular value of the coefficient, the slip flow value, and interpolation of the dimensionless curve. This reduces the computational cost of the coefficient calculation to that of calculating the slip flow coefficients (for which relatively inexpensive methods are available) and interpolation of the dimensionless curves.

VT-TuP10 Vacuum Pressure Simulation for the Upgrade of Front-End at NSLS Insertion Device Beamline, J.-P. Hu, Brookhaven National Laboratory

The beamline 9 at X-ray storage ring of the Brookhaven Lab's National Synchrotron Light Source (NSLS) is being upgraded from a conventional bending magnet beamline to an insertion device beamline, with installation of a mini-gap undulator (MGU) at upstream of the dipole magnet. The new undulator, which is made of neodymium-iron-boron magnet and vanadium-permanium poles, will generate a high-brightness photon beam through the X-9 front-end to the experimental end-station enclosure, where sampling of nano materials will be conducted by small-angle X-ray scattering (SAXS). For the beam focusing and radiation shielding, most of the optical apparatus and vacuum systems at front-end of the beamline will be modified or replaced. To determine limit of conductance for gas pumping between the proposed aperture and collimator where the beam size is defined, vacuum pressure along the straight chamber from beam port of the undulator down to the differential pump (replacing beryllium window as vacuum barrier) is calculated, using two validated computer codes. In the statistical Molflow code which is a Monte-Carlo based software package, chamber conductance through different sections at front-end is estimated for pump arrangement. In the analytical Vaccum code which is a finite-difference formulated Fortran program, pressure distribution along the beam axis is calculated based on balanced diffusion-and-pumping of gas species in consecutive segments of the vacuum chamber. The result is verified by the output from code runs previously performed to optimize the beamline vacuum. Details of pressure profile versus component setup at X-9 front-end will be presented. (Work performed under auspices of the United States Department of Energy, under contract DE-AC02-98CH10886).

VT-TuP11 Thermistor Vacuum Gauge; High Sensitivity Shows Direction and Acceleration Which Enables Vacuum Leak Detection, D. Casilio, R. Kromer, Myers Vacuum

Thermistor gauge sensors are rugged sensors that have been used to measure vacuum indirectly for many decades. The single resistor element is employed in a bridge-type detector. A constant source to the heating element of the sensor is maintained to a fixed resistance. The amount of drive needed to maintain this value is measured. A decrease in pressure reduces the number of gas molecules available to transfer heat away from the heating element. This results in a temperature and resistance output change from the sensor. This signal is filtered and amplified, and then sent

to an analog to digital converter. The microprocessor reads this signal, does further filtering and uses the result as an index into a lookup table for pressure. This value is written to the display and to a digital to analog converter that generates the analog voltage output. High sensitivity over most of its range allows for direction indication as well as how fast pressure is accelerating in which direction. Due to its quick response, a solvent can be used to trigger the response near a chamber vacuum leak.

Wednesday Morning, October 22, 2008

Energy Science and Technology Focus Topic

Room: 203 - Session EN+AS+EM+TF-WeM

Electrochemical Storage

Moderator: S. Haile, Caltech, K. Thornton, University of Michigan

8:00am **EN+AS+EM+TF-WeM1 Molybdenum Oxide Nanoparticles for Improved Lithium Ion Battery Technologies**, *A.C. Dillon*, National Renewable Energy Lab., *S.-H. Lee*, University of Colorado, *Y.-H. Kim*, National Renewable Energy Lab., *R. Deshpande*, Lam Research, *P.A. Parilla*, *D.T. Gillaspie*, *E. Whitney*, National Renewable Energy Lab., *S.B. Zhang*, Rensselaer Polytechnic Institute, *A.H. Mahan*, National Renewable Energy Lab. **INVITED**

Lithium-ion batteries are current power sources of choice for portable electronics. Further improvement of performance and simultaneous reduction in cost could allow for the deployment in hybrid electric vehicles or plug-in hybrid electric vehicles (PHEVs). The development of PHEVs will enable reduced oil consumption in the transportation sector. Importantly, PHEVs will also enable increased use of intermittent renewable energy resources such as solar and wind. By charging PHEVs during peak solar generation times, the load on the grid is effectively "leveled", and the average output of coal-fired power plants will be decreased. Recent efforts for electric vehicle applications are focused on new anode materials with slightly more positive insertion voltages to minimize any risks of high-surface-area Li plating while charging at high rates, a major safety concern. The state-of-the-art anode is graphite with a reversible capacity of ~ 350 mAh/g and a potential of 0.1 V relative to lithium metal. Metal oxides have long been known as Li-insertion compounds and typically operate at higher potential than graphite. Unfortunately they suffer from poor kinetics and/or capacity fade with cycling, especially at higher rates. Hot-wire chemical vapor deposition has been employed as a scalable method for the deposition of crystalline metal oxide nanoparticles at high density. Under optimal synthesis conditions, only crystalline nanostructures with a smallest dimension of ~ 10 - 40 nm are observed. Anodes fabricated from crystalline MoO₃ nanoparticles display both an unprecedented reversible capacity of ~ 630 mAh/g and durable high rate capability. Porous thin film nanoparticle anodes, deposited by a simple electrophoresis technique, show no degradation in capacity for 150 cycles when cycled at high rate (C/2 corresponding to one discharge in 2 hrs.). Micron sized MoO₃ particles are shown to fail after several cycles, under the same conditions. Both x-ray diffraction and in situ Raman spectroscopy studies reveal that upon Li-ion insertion the crystalline nanoparticles become highly disordered. Density functional theory calculations elucidate the complex Li-ion insertion process and reveal a novel mechanism confirming the nanoscale, high-rate, reversible capacity despite the loss of structural order. The synthesis of these novel nanostructured materials and their potential for improving lithium-ion battery technologies will be discussed in detail.

8:40am **EN+AS+EM+TF-WeM3 Boron Oxynitride: An Emerging Dielectric for High Temperature Capacitor Applications**, *N. Badi*, *S. Vijayaraghavan*, *A. Bensaoula*, University of Houston, *A. Tempez*, *P. Chapon*, Horiba Jobin Yvon, France, *N. Tuccitto*, *A. Licciardello*, University of Catania, Italy

Among the many technical challenges encountered in the development of high temperature electronics, the role of a passive component like capacitor is very important. Dielectric integrity at temperatures greater than 250 °C has however, up till now, been one of the major impediments to bringing out a capacitor with suitable performance characteristics at these high temperatures. In this work, we investigate applicability of boron oxynitride (BO_xN_{1-x}) thin films to fabricate capacitors for high temperature applications. Deposited BO_xN_{1-x} layers by a filamentless ion source assisted physical vapor deposition technique show a high thermal stability up to 400 °C and a very high breakdown voltage (BDV) above 400 V/μm. BO_xN_{1-x} samples of thickness varying from 70nm - 200nm were grown in a high vacuum reactor. Prototype capacitors with boron oxynitride dielectric and titanium metal electrodes have been fabricated on 3" Si wafers followed by electrical and thermal characterization. Preliminary results indicate a very small variation (~3%) of capacitance over the frequency range of 10 KHz - 2 MHz and <10% variation in capacitance for the temperature range of 25 °C-400 °C. The device electrical characteristics studies (capacitance, leakage current, breakdown voltage), as a function of temperature and frequency for (BO_xN_{1-x}) dielectrics with varying oxygen to nitrogen ratio, are currently underway and their results will be presented at the conference.

This research was supported in part by USDOE grant # DE-FG02-05ER84325 to Integrated Micro Sensors, Inc.

9:00am **EN+AS+EM+TF-WeM4 Improving Efficiencies of Electrochemical Systems Through Microstructure Optimization**, *H.Y. Chen*, University of Michigan, *J.R. Wilson*, *P.W. Voorhees*, Northwestern University, *S.B. Adler*, University of Washington, *S.A. Barnett*, Northwestern University, *K. Thornton*, University of Michigan

The properties and performance of a wide range of materials depend on their microstructures. This is especially true in multifunctional, multiphase or composite materials in which different phases perform different functions. Therefore, controlling microstructures in these materials is one of the main routes for materials design to achieve optimal performance. Various simulation methods that can be applied to examine processing, property, and degradation during operation, including the phase-field simulations and finite element modeling, will be discussed. Through coupling of simulations of microstructural evolution and transport that use realistic microstructures, microstructural design for optimized performance is investigated. Specific examples will include microstructures found in solid oxide fuel cell electrodes and those resulting from phase separation.

9:20am **EN+AS+EM+TF-WeM5 Layer-By-Layer Approaches to Electrochemical Energy and Storage**, *P.T. Hammond*, MIT **INVITED**

New advances in multilayer assembly have involved the development of ionically conductive multilayer thin films and the introduction of electrochemical functionality. These systems have allowed the formation of a range of ultrathin electrochemical devices including electrochromic displays, proton exchange membranes in fuel cells, and the use of these multilayers in other power and micropower devices. The use of this water based electrostatic assembly method has enabled the use of simple processing conditions, such as salt content and solution pH, to act as tools for the manipulation of ion and electron transport characteristics in the film, as well as the morphology of these unique nano-assemblies. Examples of this approach include the ability to integrate highly water soluble polymers with large sulfonic acid content into mechanically stable ultrathin films has led to new membranes with ionic conductivity approaching that of Nafion, and methanol permeability two orders lower, thus lowering fuel crossover and leading to large enhancements in methanol fuel cell performance with the application of nanometer thick thin films. On the other hand, the incorporation of both organic and inorganic nanoscale objects using the electrostatic assembly approach has enabled the incorporation of genetically engineering virus biotemplates in collaborations with the Belcher research group that have resulted in new developments in battery electrodes, and the integration of titania and other materials systems for reactive electrodes. Ultimately, the use of layer-by-layer systems have led to a range of organic and inorganic materials systems that have incorporated metal oxide nanoparticles, semiconducting carbon elements, and organic polymers to yield systems of interest for solar cells, capacitor/battery and electrochemical energy electrode and separator applications.

10:40am **EN+AS+EM+TF-WeM9 Material Solutions for Solid State Energy Storage**, *L.F. Nazar*, University of Waterloo, Canada **INVITED**

The increasing demand for energy world-wide and inherent pressing environmental needs, have jump-started efforts to develop energy storage systems that can be coupled to renewable sources, and/or viable energy conversion systems. Traditional electrode materials for lithium-ion storage cells are typically crystalline, single-phase layered structures such as metal oxides, and graphitic carbons. These materials power billions of portable electronic devices in today's society. However, large-scale, high-capacity storage devices capable of powering hybrid electric vehicles (HEV's) or their plug-in versions (PHEV's and EV's) have much more demanding requirements. This in turn, means that demands are on chemists to create novel materials, and address fundamental scientific issues relating to mass (ion) and electron transport at rapid rates. Recently, nanostructured solid state materials comprised of two more compositions, are being increasingly exploited. These can take the form of "surface modified nanocrystallites", or stuffed nanoporous materials. For example, we employ porous frameworks as electrically conductive scaffolds to encapsulate active electrode materials, where both components play a role in controlling the electrochemical performance. This presentation will provide an overview of how the nanostructured approach provides benefit over the bulk, using selected examples from a range of promising new solid state materials with targeted, and tuneable structures.

11:20am EN+AS+EM+TF-WeM11 **Platinum Nanorods as PEM Fuel Cell Electrodes**, *M. Gasda, R. Teki, T.-M. Lu, N. Koratkar, G. Eisman, D. Gall*, Rensselaer Polytechnic Institute

Platinum catalyst layers were deposited by magnetron sputtering from a variable deposition angle α onto gas diffusion layer (GDL) substrates and were tested as cathode electrodes in polymer electrolyte membrane (PEM) fuel cells. Layers deposited at normal incidence ($\alpha = 0^\circ$) are continuous, and approximately replicate the rough surface morphology of the underlying GDL. In contrast, glancing angle deposition (GLAD) with $\alpha = 85^\circ$ and continuously rotating substrates yields highly porous layers consisting of vertical Pt nanorods. At 0.40 mg/cm^2 total Pt loading, the rods are 100-500 nm long and ~ 300 nm wide, separated by 20-100 nm wide voids. The dramatic difference in microstructure is due to atomic shadowing during GLAD that causes Pt flux from highly oblique angles to preferentially deposit on surface protrusions, leading to nucleation and columnar growth on substrate mounds while surface depressions remain uncoated. Fuel cell testing at 70°C using Nafion 1135 membranes, Teflon-bonded Pt-black electrodes (TBPBE) at the anode, and atmospheric pressure hydrogen and air reactants shows a monotonic increase in performance of GLAD cathodes from 0.05 to 0.40 mg/cm^2 total Pt loading. Nanorod cells exhibit approximately 2x higher mass activity than continuous layers at 0.50V (corrected for iR, shorting, and gas crossover); for example, GLAD and continuous layers with approximately the same Pt loading (0.18 and 0.25 mg/cm^2 , respectively) show 1.7 and 0.8 A/mg . In contrast, at low current density of 0.10 A/cm^2 , the continuous layers (0.70 V with 0.25 mg/cm^2 Pt) outperform GLAD cells even with relatively high Pt loadings (0.65 V with 0.40 mg/cm^2 Pt). The GLAD cells' higher mass-specific performance at high current densities is due to their high porosity which facilitates reactant transport, while the low-current performance of the continuous layer is attributed to a higher active Pt surface area. The sputter-deposited electrodes exhibit a higher platinum utilization in comparison to TBPBE reference cathodes, with GLAD cells (1.7 A/mg) performing better than TBPBE (0.75 A/mg) at high current densities (0.50 V), while continuous layers (0.07 A/mg) outperform TBPBE (0.035 A/mg) at 0.80 V . These results indicate the promise of nanoengineering to boost catalyst utilization in PEM fuel cells.

Energy Science and Technology Focus Topic

Room: 203 - Session EN+EM+NS+P+A+T+V-ThM

Energy: Tools and Approaches

Moderator: S.P. Williams, Plextronics, Inc.

8:00am **EN+EM+NS+P+A+T+V-ThM1 Nano-Structured and Micro-Structured Semiconductors for Better Efficiency of Solar Cells, C.-F. Lin, J.-S. Huang, S.-C. Shiu, J.-J. Chao, C.-Y. Hsiao, K.-H. Tsai**, National Taiwan University **INVITED**

The foreseeable depletion of fossil fuel and the global warming caused by the carbon dioxide had led to the increasing attention of alternative renewable energy, especially photovoltaic. Therefore, crystalline Si-PV devices are quickly spreading. Unfortunately, the large consumption of Si materials hinders their vast applications. Many efforts have been switched to developing thin-film PV devices. In this talk, we will discuss the use of nano-structured and micro-structured semiconductors that enable the fabrication of thin-film solar cells with improved efficiency. Several types of such thin-film solar cells will be discussed, including the organic-semiconductor-nanowire composite film, organic-semiconductor micro-structure composite film, nano-wire semiconductor thin film, and micro-structured semiconductor thin film. In the thin-film solar cells using organic-semiconductor-nanowire composite film, different types of semiconductor nanowires such as ZnO, Si, and GaAs nanowires are used to replace the acceptor-type organics for two purposes: increasing the electron mobility and assisting the formation of nano-morphology for better inter link between the donor organics and acceptor materials. The fabrication procedures of those nanowires as well as the formation of the organic-semiconductor-nanowire composite film with controlled nano-morphology will be presented. For the other solar cells using nano-structured and micro-structured semiconductors, we will particularly describe the technique of nanowire/micro-structure transfer. In our approach, the nanowires and micro-structures are made from the bulk semiconductors or epitaxial semiconductors, so they will have much better crystal quality than the usual thin-film materials. In addition, after nanowires and micro-structures are transferred to other transparent substrates, the original wafer can be reused, so the material cost can be lowered considerably. In addition, it offers the advantages of the bending flexibility, not being limited by the brittle property of semiconductors. Furthermore, in comparison with current III-V tandem solar cells taken by monolithic approach, which requires lattice match and current balance, our approach enables mechanically stacking. Thus each cell could be designed individually to match the entire solar spectrum for optimal solar usage. Therefore, such new-type thin-film solar cells are expected to be potentially efficient and low cost.

8:40am **EN+EM+NS+P+A+T+V-ThM3 Endohedral Metallofullerenes as Improved Acceptor Materials for Organic Solar Cells, M. Drees, Luna Innovations Incorporated, R. Ross, Georgetown University, C. Cardona, Luna Innovations Incorporated, E. Van Keuren, Georgetown University, D. Guldi, Friedrich-Alexander-Universitat Erlangen-Nurnberg, Germany, B.C. Holloway, Luna Innovations Incorporated**

Cost factors in inorganic solar cells have opened up a new path to less expensive manufacturing techniques using bulk heterojunction polymer/fullerene based solar cells. Using empty cage fullerene derivatives as the acceptor material, state-of-the-art organic photovoltaics currently display ~5% overall conversion efficiency. One of the main factors limiting the efficiency in organic solar cells is the low open circuit voltage. The open circuit voltage is governed by the molecular orbitals of the donor and acceptor material; therefore better matching of the orbitals will lead to improved voltages. Here we present a novel acceptor material based on Trimetaspere® carbon nanomaterials (TMS). Trimetaspere® are endohedral metallofullerenes that consist of a trimetal nitride cluster enclosed in a C80 cage. First-generation Trimetaspere® carbon nanomaterial derivatives have been synthesized and show behavior consistent with C60 but with improved molecular orbitals. Electrochemical data suggests a maximum voltage increase of up to 280 mV over C60-PCBM-based devices and photophysical characterization of shows efficient and stable charge separation. Initial bulk-heterojunction devices have been synthesized with open circuit voltages that are 280 mV higher than reference devices using C60-PCBM and conversion efficiencies exceeding 3.1%.

9:00am **EN+EM+NS+P+A+T+V-ThM4 Morphology Study of Vacuum-Deposited Pentacene:C60 Mixed Thin Films for Photovoltaic Applications, J. Xue, Y. Zheng, J.D. Myers, J. Ouyang**, University of Florida

The efficiency of organic photovoltaic (PV) devices has gained steady increase in past 20 years, showing a potential to provide clean and low-cost electrical energy in the near future. Bulk heterojunction (HJ) composed of nanoscale percolation of donor and acceptor phase have been demonstrated to improve the efficiency of organic PV device. Such improvement is attributed to the creation of a spatially distributed interface, which enhances exciton dissociation, and the presence of continuous conducting paths for efficient charge collection. However, ideal nanoscale percolation is not readily achievable. Therefore, understanding the morphology inside the bulk heterojunction plays an important role on achieving efficient PV device. Here, phase separation in donor-acceptor (D-A) mixture composed of pentacene:C60 and how it contributes to a percolated morphology are studied. The pentacene:C60 mixed films are fabricated by co-deposition of two molecules with vacuum thermal evaporation (VTE) method. The mixing ratio of pentacene and C60 is controlled by varying the deposition rate of each species. X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to characterize the vacuum deposited pentacene:C60 mixed film. XRD patterns of pentacene:C60 mixed films indicate phase separation inside the mixture, which is reflected by appearance of characteristic diffraction peaks of thin film phase pentacene. SEM and AFM images reveal the change of surface morphology of the mixed films with varied mixing ratio and deposition rate, suggesting different degree of phase separation inside. Base on these information, PV devices are fabricated and their performance is investigated. It is found that by suppressing the phase separation between pentacene and C60 to nanoscale the PV performance is improved significantly. The open circuit voltage (Voc) and short circuit current (Jsc) increase from 0.45 V and 9.7 $\mu\text{A}/\text{cm}^2$ in pentacene:C60 = 1:1 (by weight) device to 0.58 V and 1.3 mA/cm^2 in pentacene:C60 = 1:5.5. All these suggest that degree of phase separation of molecular mixtures can be controlled by varying the process conditions, which may lead to new pathways to generate nanoscale percolation for application in efficient organic PV devices.

9:20am **EN+EM+NS+P+A+T+V-ThM5 Tailoring the Morphology of Organic Solar Cells with Surface Templates, S. O'Donnell**, University of Virginia and The MITRE Corporation, P. Reinke, University of Virginia

One of the most important applications of fullerenes is their incorporation in organic solar cells, where they function as an electron acceptor in conjunction with photoactive molecules such as porphyrin. The photoyield is intimately linked to the morphology, which determines the efficiency of exciton diffusion and separation, and the effectiveness of charge transport to the electrodes. Control of the morphology across lengthscales, spanning the range from the molecule to the several hundred nm, is critical to optimization of solar cell functionality. We control the morphology by using tailored substrate templates on which we assemble ultrathin films with well-defined regions of acceptor and photoabsorber molecules. This approach enables us to measure the morphology and interface structure with atomic resolution with scanning probe methods, and to subsequently investigate the photocurrent distribution. A pattern with variable geometry is written on the surface of highly oriented pyrolytic graphite (HOPG), our model surface, with a focussed ion beam (Ga^+ , 30 keV ion energy), which creates regions with a high density of surface defects interspaced with largely undamaged graphite surface. The surface defect structure, its extension and density within the pattern is characterized prior to molecule deposition. Surface defects interact strongly with the fullerene molecules, and thus provide nucleation centers for the formation of fullerene islands whose position is in registry with the artificial pattern. The boundary of the ion damaged region serves as the primary nucleation center for the formation of C60 islands, whose shape is controlled by the pattern geometry and the diffusion length of the molecules. We will describe how the artificial pattern can be used to tailor the morphology across lengthscales and discuss the extension of this method to other, technically relevant surfaces such as quartz which possesses a natural patterning in the form of ledges. The complete 2D nanostructure can be built by deposition of fullerene on the templated HOPG, and the remaining "empty" graphite surface is then filled with photoabsorber molecules. We will show the movement of porphyrin molecules into the pattern, and how the interfacial region between fullerenes and porphyrins evolves, and discuss the resultant morphologies. This hierarchical assembly of organic solar cells will enable us to tailor morphologies and link them uniquely to the photophysical processes.

9:40am **EN+EM+NS+P+A+T+V-ThM6 Photoemission Studies of Lead Sulfide Nanocrystals in Organic Films**, *A.T. Wroble, D.J. Asunskis, A.M. Zachary, I.L. Bolotin*, University of Illinois at Chicago, *D.J. Wallace, M. Severson*, University of Wisconsin-Madison, *L. Hanley*, University of Illinois at Chicago

Lead sulfide (PbS) nanocrystals have shown potential for use in optoelectronic applications including photovoltaics. PbS nanocrystals are grown directly into polymers or organic oligomer matrices to control the size and surface chemistry of the resulting nanocrystals. Transmission electron microscopy is used to determine the size distribution of PbS nanocrystals in organic films grown by either colloidal synthesis in polymer solutions or gaseous deposition using a cluster beam deposition source. Both the colloidal and cluster beam deposition methods are described in detail. Various techniques in photoemission spectroscopy are then applied to these PbS nanocrystal-organic films. X-ray photoelectron spectroscopy (XPS) confirms that PbS nanocrystals are present. Soft-XPS using 200 eV photon energies available at a synchrotron radiation source provides surface sensitivity to observe the interaction of the PbS nanocrystal surface with the organic matrix and is compared to XPS results obtained using 1487 eV photon energy. Little or no bonding between the PbS nanocrystals and the organic phase is observed. The core of the nanocrystals are found to be 1:1 Pb:S, but their surfaces are enriched in Pb. Finally, core level binding energy shifts in XPS under simulated solar irradiation are used for contact-free evaluation of element-specific photovoltaic electrical response of these PbS nanocrystal-organic thin films.

10:40am **EN+EM+NS+P+A+T+V-ThM9 Rational Design of Nanostructured Hybrid Materials for Photovoltaics**, *S.B. Darling, I. Botiz*, Argonne National Laboratory, *S. Tepavcevic, S.J. Sibener*, The University of Chicago, *T. Rajh, N. Dimitrijevic*, Argonne National Laboratory

Efficient conversion of photons to electricity in organic and hybrid materials depends on optimization of factors including light absorption, exciton separation, and charge carrier migration. Bulk heterojunction devices target these processes, but disorder on the nanoscale results in inefficiencies due to exciton recombination and poor mobility. By rationally designing the morphology at appropriate length scales, one can enhance the effectiveness of internal processes and, therefore, the performance of photovoltaic devices. In this work, we have implemented this approach in two hybrid material systems—both of which may provide pathways to low-cost, large-area fabrication.¹ The first involves a rod-coil block copolymer which is used both as an optoelectronically active material and as a structure-directing agent to pattern active material into ordered nanostructures. The second system uses electrochemically prepared titania nanotube arrays in concert with in situ polymerization of electron-donating material. In both cases, the characteristic donor-acceptor length scale is controlled to be comparable to the exciton diffusion length throughout the active layer, and the domains are oriented perpendicular to the incident light direction to encourage efficient charge migration.

¹ Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract #DE-AC02-06CH11357. Parts of this work were also supported by the NSF-MRSEC at the University of Chicago.

11:00am **EN+EM+NS+P+A+T+V-ThM10 Electronic Energy Level Alignment in Dye Sensitized Oxide Surfaces**, *S. Rangan, J.P. Theisen, E. Bersch, R.A. Bartynski*, Rutgers University

We have used direct and inverse photoemission to measure the occupied and unoccupied electronic states of N3 dye and determine their alignment with the band edges of single crystal and nanostructured TiO₂ and ZnO substrates. In dye-sensitized solar cell applications, the HOMO-LUMO gap of the dye molecule determines the useful portion of the solar spectrum, and charge transfer of photoexcited electrons to the substrate depends on the alignment of the LUMO to the substrate conduction band edge. We have compared the N3 dye properties on well characterized rutile TiO₂(110) and wurtzite ZnO single crystal surfaces to adsorption on more technologically relevant TiO₂ anatase nanoparticle and ZnO nanorod substrates. Samples were prepared and passivated with a pivalate layer in UHV, then sensitized ex-situ in a solution of N3 dye in acetonitrile. STM measurements show that the pivalic acid forms an ordered overlayer on the TiO₂(110) surface and that the N3 dye molecules can be imaged after sensitization. For N3 on TiO₂(110) as shown below, our spectroscopic measurements show that passivation significantly reduces contamination (presumably from water in the ambient) and that the N3 HOMO occurs at 0.9 eV above the TiO₂ valence band edge, while the LUMO is found 0.5 eV above the conduction band edge. On ZnO, the N3 HOMO occurs at 1.3 eV above the ZnO valence band edge but the N3 LUMO occurs 2.1 eV above the conduction band edge, much higher than what is measured on TiO₂. Comparison with experimental and theoretical values from the literature will be discussed.

11:20am **EN+EM+NS+P+A+T+V-ThM11 Preparation of Nanoporous ZnO Photoelectrode using PEG Template for the Fabrication of Dye-Sensitized Solar Cells**, *M.F. Hossain, S. Biswas, M. Shahjahan, T. Takahashi*, University of Toyama, Japan

Recently, great attention has been paid to dye-sensitized solar cells (DSCs) due to their low fabrication cost. The high light-to-energy conversion efficiencies achieved with dye sensitized solar cells (DSCs) may be attributed to the nanoporous TiO₂ electrode. Zinc oxide (ZnO) is a wide band gap semiconducting material with a similar band gap and electron affinity to those of TiO₂ and has been considered as an alternative material in DSCs applications. Among the various techniques for the preparation of ZnO photo-electrode, the relatively simple sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates. In our present study, the nanoporous ZnO films were deposited on SnO₂:F coated glass by sol-gel technique with polyethylene glycol (PEG) as organic template, Zn(CH₃COO)₂·2H₂O as precursor, ethanol as solvent and NH(C₂H₄OH)₂ as chelating agent. The ZnO films have been characterized by the TG-DTA, XRD, SEM AFM, FTIR and UV-VIS systems. The surface morphology of the nanoporous ZnO films strongly depend on the Zn(CH₃COO)₂ concentrations, PEG contents and number of coatings. It was revealed from optical study that the dye absorption increases with the increase of PEG concentrations. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different ZnO thin films to evaluate the economic viability of this technique. The variation of photoelectric conversion efficiency of the solar cells, deposited with different Zn(CH₃COO)₂ and PEG concentrations are discussed with the analysis of different microstructure of the ZnO thin films and the corresponding dye-incorporations.

11:40am **EN+EM+NS+P+A+T+V-ThM12 Metal / Polymer Interfaces: Ca on Polyfluorenes**, *J.A. Farmer, J.H. Baricuatro*, University of Washington, *E. Zillner*, Universitaet Erlangen-Nuernberg, Germany, *J.F. Zhu*, University of Science and Technology of China, *C.T. Campbell*, University of Washington

Conjugated polymers are being investigated for use in organic photovoltaic devices and organic electronics due to favorable cost and ease of processing compared to devices based on inorganic materials. The synthetic tunability of polymer-based devices makes them applicable to many technological applications. The creation of cheap organic photovoltaic devices would significantly improve our ability to harness solar energy and curb the use of fossil fuels. The development of organic LED and organic electronics may give rise to flexible computer displays and hardware that could revolutionize human interaction with computing devices. Crucial to the performance optimization of these devices is understanding the interaction between the metal electrodes and the polymer. The structure and energetics of the interface between Ca and two polyfluorenes, poly(9,9-di-n-hexylfluorenyl-2,7-diyl) (PDHF) and poly(9,9-di-n-hexylfluorenyl-2,7-vinylene) (PDHFV), were studied in ultrahigh vacuum using adsorption microcalorimetry, and low-energy ion scattering spectroscopy. The initial sticking probabilities of Ca on pristine PDHF and PDHFV at 300 K were 0.40 and 0.53, respectively. The sticking probability of Ca on PDHFV began decreasing after ~0.06 ML, and then increased toward unity after ~0.24 ML. Because no similar behavior was seen on PDHF, this decrease in the Ca sticking probability on PDHFV is tentatively ascribed to the presence of the vinyl group. At submonolayer coverages on both polymers, the integrated Ca ISS peak area increased slowly below 1 ML, with a value less than 1 % of a saturated Ca surface at 300 K. These results indicated that most of the Ca at low coverages were below the surface, and not visible to ISS. Beyond 1 ML the Ca peak area increased, and ultimately a continuous Ca film formed at ~50 ML. Based on the variation of Ca peak area with coverage, Ca grows as 3D islands on these polymer surfaces. The heat of adsorption of Ca on PDHF at 300 K was initially 240 kJ/mol and 315 kJ/mol on PDHFV. The heat of adsorption of Ca on PDHF decreased to the heat of sublimation of Ca in ~0.25 ML; the heat of sublimation was reached by ~0.50 ML for PDHFV. The interesting thermodynamic and sticking behavior below 0.50 ML, where Ca is interacting strongly with specific adsorption sites on the polymer will be discussed, and related to the use of these polyfluorenes in device applications.

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