Tuesday Afternoon, November 11, 2014

Vacuum Technology
Room: 303 - Session VT-TuA

Vacuum Quality Analysis, Outgassing, and Control
Moderator: James Fedchak, National Institute of Standards and Technology (NIST), Marcy Stutzman, Thomas Jefferson National Accelerator Facility

2:20pm VT-TuA1 Our Present Understanding of Outgassing, *Manfred Leisch*, Graz University of Tech., Austria **INVITED**
Outgassing means basically the diffusion of atoms usually hydrogen through the bulk material, entering the surface and desorbing from it. The important consequence is it limits the lowest achievable pressure in a vacuum chamber and is a central issue in vacuum science with respect to ultra high (UHV) and extreme high vacuum (XHV). Stainless steel (SS) is one of the most commonly used constructional materials for vacuum chambers and components. A considerable body of work is documented on the hydrogen outgassing behaviour of SS. For the description of the outgassing rate basically two models common as diffusion limited model (DLM) and recombination limited model (RLM) have been discussed so far. Experimental studies in the last decade show that the real situation on the complex SS surface cannot be fully described by DLM or RLM. Hydrogen atoms approaching the surface from the bulk are desorbing in a second-order process. The rate of recombination depends strongly on the atomic structure of the surface and is e.g. generally higher on stepped surfaces than on flat close packed planes. A new insight was gained by atomic level studies on the real morphology of SS with atomic force microscopy (AFM) and the scanning tunnelling microscopy (STM).

Beside surface morphology surface composition additionally controls the desorption kinetics. Auger electron spectroscopy (AES) gives reason for a composition change. Since the information depth of AES covers several atomic layers complementary atom probe analysis were performed, measuring the chemical composition on the surface atomic layer by layer. Energy calculations using the ASED method (Atom superposition and Electron Delocalization) result in lower energy levels in Fe vacancies. It supports the picture that surface and subsurface defects form traps with different energetic levels. They may control the recombinative desorption process and give explanation for the observed outgassing behaviour of stainless steel. From this results a more complete description of the outgassing process may be given by a more or less dynamic equilibrium between diffusion, sojourn in different level traps and recombinative desorption.

This work was supported by the Austrian „Fonds zur Förderung der wissenschaftlichen Forschung" P 12099 and "Zukunftsfonds Steiermark" P 119.

3:00pm VT-TuA3 Hydrogen Traps in the Outgassing Model of a Stainless Steel Vacuum Chamber, *Robert Berg*, National Institute of Standards and Technology (NIST)
The outgassing model accounts for the geometry of the chamber components, the hydrogen dissolved in those components, and the processes of diffusion, recombination, and trapping. Strongly bound or "trapped" hydrogen, which occurs at heterogeneities such as dislocations and grain boundaries, can hold most of the dissolved hydrogen even though those locations comprise fewer than 0.1% of all lattice sites. Four simplifications allowed practical use of the model: (1) Each component was described as a one-dimensional object. (2) The hydrogen initially dissolved in each component was described as a uniform concentration. (3) Accurate, consistent values were used to describe diffusion and recombination in stainless steel types 304 and 316 [Grant et al., J. Nucl. Mater. 149, 180 (1987); 152, 139 (1988)]. (4) Only one type of hydrogen trap was considered, and trapping was ignored in components made from vacuum remelted stainless steel. The simple model was developed and validated by comparing it to outgassing measurements. Traps were required to describe the outgassing from a component made of drawn stainless steel 304. The initial hydrogen concentration in that component was comparable to concentrations found elsewhere by thermal desorption and almost 100 times larger than in the components made of vacuum remelted 316 stainless steel. The model's usefulness is illustrated by using it to predict the outgassing of a vacuum chamber made of type 304 stainless steel.

3:20pm VT-TuA4 A Mild Steel Ultrahigh Vacuum Chamber Appropriate for Magnetic Shielding, *B. Cho, S.J. Ahn,* Korea Research Institute of Standards and Science (KRISS), Republic of Korea, *C.D. Park, Taekyun Ha*, POSTECH, Republic of Korea
Mild steel, i.e. low carbon steel, is a soft magnetic material and widely used for shielding sensitive experimental apparatuses from stray magnetic field because of its relatively low price and high magnetic permeability. Mild steel vacuum chambers are usually nickel-plated in order to prevent corrosion and improve the vacuum. For example, electron microscopes employ nickel plated mild steel for constructing their specimen vacuum chambers in which the electron beam propagates and interacts with specimens; presence of stray magnetic field deteriorates proper propagation of the electron beam, degrading the resolution of the electron microscope.

The mild steel has not been employed, to the best of authors' knowledge, for ultra-high vacuum (UHV) use because its outgassing rate has been known to be too high; reported values were on the order of 10^{-8}~10^{-9} mbar l s^{-1} cm^{-2} or higher [1]. Ishimori *et al*. [2] reported that the outgassing rates of a mild steel (carbon ~0.15%), a chromium-plated mild steel and a stainless steel were 2~3×10^{-11} mbar l s^{-1} cm^{-2}, 7~9×10^{-11} mbar l s^{-1} cm^{-2} and 2~3×10^{-12} mbar l s^{-1} cm^{-2}, respectively, after baking at 300 °C for 3 hours. The outgassing rate of UHV chambers are normally on the order of 10^{-12} mbar l s^{-1} cm^{-2} or less after baking at 100 ~ 200 °C.

The outgassing rates of a mild steel and a stainless steel 304 chamber were measured by using the so-called rate-of-rise (RoR) method [3]. We present that the outgassing rate of the mild steel purchasable on the market is much smaller than that of a stainless steel type 304L which is most widely used as a UHV vacuum chamber material. The ultimate pressure of a vacuum chamber made of the mild steel was 2.7x10^{-11} mbar, and its outgassing rate was of < 3×10^{-14} mbar l s^{-1} cm^{-2}, which indicates the mild steel is even appropriate for extreme high vacuum use. Vacuum annealing of the mild steel at 850 °C reduced the outgassing rate further.

[1] B. B. Dayton : 6th Nat. Symp. Vac. Tech. 101 (1959).

[2] Yoshio Ishimori, Nagamitsu Yoshimura, Shuzo Hasegawa, and Hisashi Oikawa, SHINKU 14(8), 295(1971).

[3] C. D. Park, S. M. Chung, Xianghong Liu and Yulin Li, J. Vac. Sci. Technol. A 26(5), 1166(2008).

4:20pm VT-TuA7 Ultimate Limits in the Gas Composition Determination Within Small Sealed Volumes by Quadrupole Mass Spectrometry, *Vincenc Nemanič*, Jozef Stefan Institute, Slovenia **INVITED**
Miniaturization of modern sealed vacuum devices and higher demands for their stable operation on the long-term scale require accurate determination of the gas composition in the early stage of their operation, as well as after a long operating period. Since particular gases may have detrimental effect on the device performance even at low concentrations, accurate quantification of the gas mixture is an important as well as a challenging task. Among a few highly gas-sensitive methods capable to detect quantities below 10^{-4} mbar L, the quadrupole mass spectrometry seems to be the most appropriate one for this task.

A two-step procedure, consisting of sample puncture inside an expanding chamber, followed by opening the leak valve to the quadrupole mass spectrometer, kept in the analytical chamber at ~3x10^{-11} mbar, is proposed. A limited number of ion current readings are used for the reconstruction of the original total pressure and gas composition. Calibration of such instruments at particular partial pressure is regularly achieved at stable gas influx and constant pumping speed. Several discrete points have to be recorded to get the sensitivity of the instrument expressed in A/mbar.

In this presentation, a systematic approach for preparing the instrument for routine quantification of small gas amounts is described. In the first stage, the instrument was calibrated as the precise partial gas flow meter by an innovative *in-situ* calibration procedure by three different gases, hydrogen, argon and nitrogen. Each gas was admitted into the expanding chamber, having a precisely determined volume of 0.312 L and equipped by a capacitance manometer. By opening the leak valve, ion currents versus gas flux were recorded over three orders of magnitude, expressing the partial flux sensitivity in As/(mbar L). In the second stage, known gas quantities ~10^{-4} mbar L of pure gas were admitted at different leak valve conductance to determine the instrument's response. This data enabled minimizing the error by searching for a compromise between the number of the readings and the level of recorded ion currents. In the third stage, gas mixtures with various contents of three gases were prepared and analyzed. This evaluation enabled a much better prediction of the ultimate limits in reconstructing of the unknown gas mixture in a real device. Anyhow, uncertainty in

evaluation increases by lowering the gas amounts as ion currents become indistinguishable from the background readings of the instrument.

5:00pm VT-TuA9 The Importance of Competitive Langmuir Adsorption Kinetics for Vacuum Cleanliness, *Richard Versluis*, TNO Technical Sciences, Netherlands

There are numerous examples of systems that rely on a very clean vacuum. Gaseous contamination and surface contamination may influence the process or even damage the machine (such as beam scattering accelerators and e-beam equipment or background contamination in gas analyzers) or may contaminate samples (XPS, SEM, HIM etc) or may contaminate sub-components of the machine (such as mirror contamination in EUV systems, space systems, spectral analyzers etc). The usual methods of contamination inspection are measurement of the residual gas compositions (RGA's) or the use of witness plates to determine surface contamination. The requirements on residual contamination (either gaseous or adsorbed on surfaces) are becoming more stringent with the development of equipment that is becoming more sensitive for contamination. A good understanding of the kinetics of contamination transport and gas-surface interaction is crucial when developing or using these requirements. This is important for both equipment users and equipment developers.

This talk will highlight some important aspects of gas-surface interaction in vacuum chambers by focusing on the dynamical behavior of gas species competing for adsorption sites. We will show how the adsorption energies and concentrations influence the equilibrium that is reached, but we will also show how the adsorption energies and the concentrations determine the kinetic behavior before equilibrium is reached and how they influence surface coverage by different species during non-equilibrium. A simple model solving the coupled kinetic equations is able to predict the time dependent behavior, which can be used to determine for instance outgassing times and sampling times and the relationship between measured gas concentrations and surface coverage during non-equilibrium.

5:20pm VT-TuA10 Diagnostic Tool to Identify Volatile Molecules in Vacuum, *Freek Molkenboer, A. Van de Runstraat, J.A. Van der Meer, T. Van Groningen, O. Kievit*, TNO Technical Sciences, Netherlands

Residual gas analyzers (RGAs) are commonly used in ultra-high vacuum applications to measure vacuum quality. The RGA fragments and ionizes the molecules that are present in the gas phase in the vacuum system. These fragments of all the molecules make up the RGA spectrum. The RGA spectrum has to be interpreted to identify the contaminants that are present in the vacuum system. This is complicated and often impossible in case of complex mixtures of organics in the vacuum atmosphere.

The goal of this project is to develop a simple-to-use diagnostic tool that is able to identify the contaminant molecules in vacuum directly. After a trade-off of various options, we selected a removable cold trap in combination with an off-line gas chromatography–mass spectrometry (GC-MS) system for analysis of the samples.

The cold trap is installed on a vacuum flange. A removable sample tube is positioned inside the cold trap in connection with the vacuum system. The cooling of the cold trap is achieved with Peltier elements, which makes it simple to operate as well as independent of supply of coolants such as liquid nitrogen. After sampling, the sample tube can be removed without venting the vacuum system and a new sample tube can be installed to continue measurements if required.

After sampling of the vacuum vessel, the sample tube is connected to a GC-MS system for analysis of the sample and identifying and partly quantify the organic molecules present.

The first results are promising and we continue to improve the system. In this presentation we will present our sampling method and the results of vacuum quality measurements using the new diagnostic tool.

5:40pm VT-TuA11 Quantitative Gas Analysis of Small Batch Samples by Quadrupole Mass Spectrometer, *Lily Wang*, Los Alamos National Laboratory

In our studies of static gas release properties of various solid materials at low temperatures ranging from 25 to 80 °C, we find the amounts of gas collected from the experimental samples in sealed vacuum vessels over extended times (weeks to months) are only a few to less than 100 torrs in a free volume of 10 - 50 cc. In order to analyze these small batch gas samples, a quantitative method was developed using a quadrupole mass spectrometer. This method involves introducing a small pulse of the gas with a custom-designed sample manifold into a quadrupole mass spectrometer and analyzing the gas component quantity in a few seconds. The method is relatively quick and is particularly suitable for gas components that have low sticking coefficients to stainless steel surfaces. This method was evaluated for hydrogen, methane, and argon. In this presentation, the setup, the calibration and measurement procedures, and the performance of the method are presented and discussed.

6:00pm VT-TuA12 A Novel Vacuum Mini-Environment Design For Thin Film Sputter Deposition Apparatus, *Jun Xie, R.L> Ruck, C. Liu, P. Leahey, T. Bluck*, Intevac, Inc.

In microelectronics manufacturing, many critical process steps are carried out in high vacuum apparatus. Trace quantities of residual gaseous species, such as hydrogen and water (H2O), are always present within such system, which are of great concern to state-of-the-art device fabrication. In the hard-disk drive industry, for example, metallic thin films of a magnetic recording disk are especially susceptible to H2O, which could affect film growth adversely and compromise the device performance. It becomes a top priority to prevent the trace contaminants in the vacuum system, especially H2O, from interacting with these metallic thin films during a sputter deposition process. The goal of this study is to create a pristinely clean mini-environment inside a general vacuum apparatus for ultrapure thin film sputter deposition. The approach consists of two innovative features. The first is a retractable enclosure that seals off a volume around the sputter target and the substrate. The second is a series of pumping channels of pre-determined sizes and shapes through the wall of the enclosure that facilitate the evacuation of the gases or byproducts from the enclosure in a controlled manner while minimizing the probability of outside contaminants entering the enclosure. Experiments were conducted by sputter-depositing chromium thin films in such an enclosure to getter contaminants and assess its effectiveness with secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) analysis.

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