Michael Eller Research Activity at IPNO with Andromede Project

1. Project Goals:

The goals of the research project are several fold involving the first stages of the Andromede Project. The Andromede Project is part of a pulidisciplinary research center at IPNO (IGLEX). In the Andromede part of this project a 4MeV accelerator will be coupled to several primary ion sources for performing experiments such as cluster MeV SIMS (Secondary Ion Mass Spectrometry), atomic MeV SIMS, and Ion Beam Analysis (e.g. RBS, PIXIE). The two main ion sources are a gold LMIS (Liquid Metal Ion Source) and ECR (Electron Cyclotron Resonance). The ECR is capable of producing a range of projectile from gaseous species, including Ar^{+1-8}, He^{+}, as well as molecular species SF_5^{+}, CO_2^{+} and C_{60}^{+n}. The gold LMIS is capable of producing a range of gold projectiles including atomic gold Au_1^{+}, gold clusters e.g. Au_2^{+}, Au_3^{+}, Au_5^{+}, and Au_9^{+} and gold nano-particles Au_{400}^{+4}. The large molecular secondary ion yields (detected ions per projectile) measured from nano particle impacts on surfaces (e.g. Au_{400}^{+4}) especially at high impact energies allow for one to obtain a complete mass spectrum from a single projectile impact. As these secondary ions originate from a small area ~20nm in diameter, this allows one to probe the molecular surface chemistry and chemical environment at the nano-metric level. By coupling this effective source of secondary ions to a mass spectrometer, a mass spectrum of a sample at the nano-metric level can be generated. Additionally, this system will be equipped with an EEM (Electron Emission Microscope) to collect the electrons emitted from these impacts and determine the impact coordinates (X,Y) of each projectile impact. The assembly of these various elements (4MeV cluster ion source, mass spectrometer, and EEM) allow for an instrument to be realized that generates molecular ion images with chemical information from nano-metric domains on the surface.

2. Description of Work Achieved:

The Andromede project was started in 2011 and has consisted of the collaboration of several different departments at IPNO and international collaborations. During the time since I have arrived the work has focused around the designing, building and commissioning of several elements to be included in the project, such as the analysis chamber, the ion sources, mass spectrometer and EEM. Also, a more ambitious design of the EMM termed EPEM (Electron/Proton Emission Microscope) has been simulated and incorporated into the total design of the instrument. Additionally several fundamental studies using the projectiles to observe ion surface interactions with novel materials has been performed.

The design of the different elements in the instrument have been performed in collaboration with the accelerator and detector divisions at IPNO, specifically Philippe Blache, Bernard Mathon, Emmanuel Rindel, Christine Le Galliard, and Philippe Rosier.

While working with these two groups, the cluster MeV SIMS analysis chamber was designed, then built by MDC, and received here at IPNO. The chamber has several inlets for the introduction of different projectiles, one at 45° for MeV ions provided by the accelerator, and one at 120° for gaseous argon clusters to be provided by an argon cluster ion source. Inlets for monitoring the vacuum, controlling the 3 axis sample stage, sample stage cooling, and high and low voltage connections are also provided at the necessary positions. An inlet is provided at 90° for connection of the mass spectrometer. Lastly a port at 135° has been provided for the EEM/EPEM. This chamber has been received in the fall of 2013 and the first elements have been installed into the chamber such as the 3-axis sample stage. Additionally the vacuum has been tested, with and without these elements, and the vacuum is between $1*10^{-9}$ and $1*10^{-7}$ mbar, which is within the specifications of the chamber.

As the geometry of the chamber depends greatly on the design of the mass spectrometer and EEM/EPEM, these elements were designed in parallel with the chamber. As with the chamber, the accelerator and detector divisions were greatly involved in the design of the mass spectrometer and EEM/EPEM. The EEM consists of five einzel lenses and a magnet to turn the electrons 45° with respect to the path of the secondary ions, as well as three sets of steerers to adjust the trajectory of the electrons. The distances between the lenses as well as the geometry of the lenses were designed based on the original design of Stanislav Verkhoturov at Texas A&M University. To design the EEM three software packages were used, SIMION, COSY, and Transport. In each case the design was changed to reduce aberrations introduced by the lenses and magnet. After simulation/calculation of the EEM the design was incorporated into the design of the chamber and will be machined in May 2014. The design of the EEM allowed us to envision a new microscope which will use the emitted protons from an ion impact to determine the impact coordinates. This new microscope was termed EPEM, which uses a pulsed electro-spherical energy analyzer (ESA) to defect the H^+ emitted from a single projectile impact toward the subsequent transfer optics and magnification lenses. Calculations of this microscope/ESA were done using SIMION in order to determine the aberrations or asymmetries introduced into the ion image by the ESA. The results were positive and indicated we would receive a similar or better performance compared to the magnet deflection. Therefore the ESA was incorporated into the design of the chamber. A precise timing scheme has also been designed to correctly deviate the H^+ while reducing the deviation of other species.

The most recent results using the EEM at Texas A&M University and the new design of the EPEM have been presented at two different conferences: IVC19 in Paris France (September 2013) and Desorption 2014 in Montreal (April 2014).

Surface Modification and implantation studies in collaboration with Gabriel Lippmann in Luxembourg were started in summer 2013. The goal of the project was to implant gold nanoparticles provided by the gold LMIS source into organic surfaces to promote the production of cationized species and adduct formation. This was done in order to increase the molecular specific information from a sample but also to understand the formation processes of adduct ions and the amount of cationized. A series of samples have been irridated with Au_{400} particles with different doses and different energies. The various doses were performed to study the cationization and adduct formation as a function of dose. The different energies were used to look at the effect of depth of implantation on the cationization and adduct formation. These studies are still on going, however the initial results show that the local dose of nano-particles can be calibrated based on the detected amount of Au_3 emitted under Bi_3^+ bombardment. Additionally, several adducts display a non-linear dependence versus nano-particle dose, this gives us insight into their formation. Specifically the formation of $Au(CN)_2^-$ increases non-linearly with the dose, indicating that additional CN fragments are created with successive bombardments, allowing for these more complex adducts to be formed more easily. The future experiments on low energy implantation will allow us to study the nano-particle analyte interface more easily, and depth profiling experiments to investigate this have been envisioned.

Fundamental studies of nano-particle interactions with ultra-thin samples: In a collaboration with Texas A&M University, the interaction of Au_{400}^{+4} nano-particles at 520keV impact energy (~36km/s) with single and multi-layer graphene was studied. This ion-surface interaction of the nano-particle with a 2-D material. In this experiment the ions generated from the "transmission" and "reflection" direction with respect to the path of the projectile were collected, allowing us to study the interaction in a very unique way. Additionally, it is possible to perform the experiment with a bombardment angle of 90°, allowing for detection of the nano-particle after interacting with this 2-D material. In the case of the secondary ion, SI, emission from this material, we see a range of carbon clusters, C_n^- n=1-10, emitted in negative mode. These clusters are detected in both the reflection and transmission directions which is surprising as one could have envisioned a situation where all the species were emitted in the direction of the projectile (transmission direction). The SI yields (number of ions detected per projectile impact) are extremely high approaching 1.0 in some cases. As the number of emitted atoms must be small (~3000 estimated from TEM images of holes created in the graphene ~10nm in diameter) this implies that the ionization probability is several orders of magnitude higher compared to bulk graphite. This indicates that some very interesting processes are happening in the confined space of the 2-D material. Interestingly, in positive ion mode $H_{1\text{-}3}^+$ are all detected with high yields in both transmission and reflection directions. This result in addition to C_1^+ detection indicates that there is a high charge with in the interaction volume. As this is not provided by the projectile (average charge of 1/100 per atom) the interaction of the particle with the graphene must be generating this large charge. Experiments while collecting the nano-particle after the interaction have given us additional insights but no comprehensive explanation as of yet has been found. Further experiments at low energy are underway to expand our knowledge on the system.

3. Publications 2013-2014

1. SIMS Instrumentation and Methodology for Mapping of Co-localized Molecules, M. J. Eller; S. V. Verkhoturov; S. Della-Negra; E. A. Schweikert; *Review of Scientific Instruments*, **2013**, 84, 103706;
2. Nanoscopic Cylindrical Dual Concentric and Lengthwise Block Brush Terpolymers as Covalent Preassembled High-Resolution and High-Sensitivity Negative-Tone Photoresist Materials, G. Sun; S. Cho; C. Clark; S. V. Verkhoturov; M. J. Eller; A. Li; A. Pavía-Jiménez; E.A. Schweikert; J. W. Thackeray; P. Trefonas; K. L. Wooley; *Journal of the American Chemical Society*, **2013**, 135 (11), 4203–4206.
3. Metal-assisted SIMS with Hypervelocity Gold Cluster Projectiles, J. D. DeBord; A. Prabhakaran, M. J. Eller, S. V. Verkhoturov, A. Delcorte, E. A. Schweikert; *International Journal of Mass Spectrometry*, **2013**, 343–344, 28-36.
4. Bottom-up / Top-down High Resolution, High Throughput Lithography using Vertically Assembled Block Bottle Brush Polymers, P. Trefonas; J. W. Thackeray; G. Sun; S. Cho; C. Clark; S. V. Verkhoturov; M. J. Eller; A. Li; A. Pavía-Jiménez; E. A. Schweikert; K. L. Wooley; *Journal of Micro/Nanolithography, MEMS, and MOEMS*, **2013**, 12(04), 043006
5. Simultaneous Detection and Localization of Secondary Ions and Electrons from Single Large Cluster Impacts, M.J. Eller; S.V. Verkhoturov; F.A. Fernandez-Lima; J.D. DeBord; E.A. Schweikert; S. Della-Negra, *Surface and Interface Analysis*, **2013**, 45(1), 529–531.

4. Relevance of the project within P2IO

This project focuses on the interaction of nano-objects with surfaces. These studies are important to understand the fundamental interactions taking place at the nano-scale. The effects of cationization of materials by introduction of Au or other metal which promotes cationization, can be thoroughly studied by this approach. The interaction with ultra-thin materials gives us insight into the interaction which could previously only be studied by simulation. The results of these experiments could not be predicted by simulation. Overall, these studies are within the pulidisciplinary aspect of the project and the impact of these nano-particles at high energies (4qMeV) will be used to generate a complete mass spectrum from nano-volumes. The mass spectrometry coupled to the EEM/EPEM allows us to generate ion images with nano-scale molecular information to study biological problems, such as lipid distributions on tissues. The ability of this technique to study the co-localization of two molecular species at the nano-scale is unique, and allows us to address problems with cannot be investigated using other techniques. This allows us to study surfaces from the nano-scale to the millimeter scale which corresponds well to the goals of the P2IO project.

5. For R&D only: Not Applicable
6. For R&D only: Not Applicable
7. For end of contract post-docs: Not Applicable