

44th IUVSTA Workshop: Sputtering and Ion Emission by Cluster Ion Beams

Book of Abstracts and Final Programme

23-27 April 2007

(with reception on 22 April 2007)

Barony Castle,
Eddleston by Peebles,
Scotland, UK

Conference Website
www.npl.co.uk/iuvsta

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Barony Castle, Edinburgh, Scotland, UK

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Welcome

On behalf of the scientific organising committee, it is a great pleasure to welcome you to the 44th IUVSTA Workshop: Sputtering and Ion Emission by Cluster Ion Beams. The purpose of this workshop is to provide a forum for discussion to advance the field of sputtering and ion emission by cluster ion beams. We are delighted with the very positive response we have received from the community leading to an excellent programme which, we hope, will provide stimulating discussion and debate.

We are very grateful to our sponsors for supporting this workshop and to the scientific community for your contributions making the workshop possible. We hope that you have an enjoyable stay in Scotland!

Ian Gilmore
Felicia Green

The Scientific Organising Committee

Ian Gilmore, National Physical Laboratory, UK
John Vickerman, University of Manchester, UK
Peter Sigmund, University of Southern Denmark, Denmark
Greg Gillen, National Institute of Standards and Technology, USA
Felicia Green, National Physical Laboratory, UK

Social programme

An informal evening drinks reception will be held on Sunday 22nd April between 5 pm and 7 pm. On Tuesday the 24th there will be an evening of whisky tasting. The conference excursion is on the afternoon of Wednesday 25th April to Edinburgh and Edinburgh castle. Coaches will leave the castle after lunch so please be ready to meet at 2 pm in reception. The conference dinner will be held at the castle on the evening of Thursday 26th April where we will be piped in to a traditional Scottish banquet with haggis (vegetarian haggis available too). The workshop will close after lunch on Friday 27th April.

Partners programme

A programme for Monday, Tuesday and Thursday has been arranged for partners with a local guide. Activities will include exploring the Scottish Borders, a trip to New Lanark to see an old water driven textile Mill and a trip to Edinburgh city including a tour of the new Parliament. Entry fees are payable locally. Of course, partners are included in all the workshop social activities given above

Workshop Format

The workshop format has been developed to provide a forum for discussion and debate. There are seven themes covered by thirteen Discussion Sessions as well as two poster sessions. **We very much encourage workshop participants to come prepared with material for the discussion.**

Discussion Sessions

The following provides information on the way the discussion sessions will operate. A very important aspect of this is the role of the Discussion Leader, rapporteur and, of course, contributions and discussion from the workshop participants.

1. Each session will be chaired by a Discussion Leader.
2. The Discussion Leader has responsibility for keeping the session to time.
3. Each session begins with an invited keynote lecture of 45 mins followed by one or two contributed talks of 15 min (these times do not include question time which is incorporated into the discussion). The audience may ask questions after talks for technical clarification but discussion questions should be saved for the discussion period.
4. The Discussion Leader has a 45 min slot to have an open discussion. His or her role is to ensure that everyone gets an opportunity to contribute and to stimulate discussion. The Discussion Leader may come prepared with material to focus discussion.
5. We very much encourage workshop participants to come prepared with material for the discussion. The time allocated to participants is at the discretion of the Discussion Leader and as a guide, typically 2 slides taking no more than 5 minutes may be appropriate. If using powerpoint, please bring this on a memory stick. An overhead projector will also be available for more impromptu slides.
6. With the aid of a rapporteur, the Discussion Leader summarises the discussion. A blank poster will be provided for each Discussion Leader to provide a summary. These can then be discussed at the two poster sessions and modified as necessary as a result of feedback. The final summary will be presented on Friday.
7. At the final session on Friday, all the Discussion Leaders will form a panel and we will try to summarise the key items of the workshop, areas of recommended future research, potential collaborations and outlook. Note that IUVSTA does not allow a published proceedings but we do need to provide a summary.

Oral Presentations

Invited talks are 45 minutes in length and contributed talks are 15 minutes in length. This does not include time for questions which is incorporated into the discussion time – see above. The preferred format is powerpoint slides on a memory stick or as a second choice on CD. You will also be able to use your own laptop (but as you will know this sometimes causes problems) and we will have an overhead projector. There will be no facility for the projection of 35 mm slides. It would be a great help if you could upload your talk to the conference computer in advance of your session.

Poster Presentations

The poster should be no larger than A0 in landscape format (841 mm by 1189 mm). We will provide appropriate fixing material for mounting the poster on the poster boards. The poster session is on Tuesday afternoon and the poster should stay up all week for discussion.

Sponsorship

This workshop has been made possible through generous sponsorship from the following organisations:

International Union for Vacuum Science, Technique, and Applications (IUVSTA)
Physical Electronics Inc
ION-TOF GmbH
Ionoptika Ltd
UK Surface Analysis Forum (UKSAF)
Surface and Interface Analysis, Wiley
The British Vacuum Council (BVC)
Valid Analytical Measurements Programme of the UK Department of Trade and Industry
The National Physical Laboratory



Sponsored by the journal *Surface and Interface Analysis*, a leading international research forum on major surface science techniques, including SIMS



Outline Programme

	Sunday 22	Monday 23	Tuesday 24	Wednesday 25	Thursday 26	Friday 27
Morning Session 1 08:40 * to 10:40		Welcome: Ian Gilmore <i>Fundamentals I</i> IS: Herbert Urbassek DL: Peter Sigmund	<i>Sputtering & Ion emission I</i> IS: Martin Seah DL: Hans Henrik Andersen	<i>Depth Profiling I</i> IS: Greg Gillen DL: Dae Won Moon	<i>Biological Analysis</i> IS: John Vickerman DL: Dave Castner	<i>Massive clusters II</i> IS: Emile Schweikert DL: Amy Walker
Tea/Coffee						
Morning Session 2 11:00 to 13:00		<i>Fundamentals II</i> IS: Hans Henrik Andersen DL: Klaus Wittmaack	<i>Sputtering & Ion emission II</i> IS: Serge Della Negra DL: Peter Williams	<i>Depth Profiling II</i> IS: Andreas Wucher DL: Matt Wagner	<i>Cluster beam technology</i> IS: Nick Winograd DL: Patrick Betrand	Summary and panel discussion: Chair Ian Gilmore Close: Ian Gilmore
Lunch		Lunch	Lunch	Lunch	Lunch	Lunch
Afternoon Session 1 14:00 to 16:00		<i>Molecular Dynamics I</i> IS: Zbigniew Postawa DL: Roger Webb	<i>Sputtering & Ion emission III</i> IS: Arnaud Delcorte DL: Ian Gilmore	Excursion to Edinburgh castle and Edinburgh city.	<i>Massive clusters I</i> IS: Jiro Matsuo DL: Nick Lockyer	
Tea/Coffee						
Afternoon Session 2 16:20 to 18:20		<i>Molecular Dynamics II</i> IS: Barbara Garrison DL: Kristin Krantzman	Poster Session I – Contributed posters and session summary posters		Poster Session II - Session summary posters	
Dinner	Drinks reception before dinner				Conference Dinner with Piper.	
Other events			Whisky tasting			

Notes:

IS = Invited Speaker (click on name to go to abstract)

DL = Discussion Leader

* See full programme for exact timings

**44th IUVSTA Workshop: Sputtering and Ion Emission by Cluster
Ion Beams Programme
23 – 27 April 2007**

Sunday 22nd April

Welcome drinks reception before dinner 17:00-19:00.

Monday 23rd April

8:40 *Welcome address and introduction*
Ian Gilmore

Fundamentals I

Discussion Leader: Peter Sigmund

8:55 **Invited:** *Fundamental and general principles of sputtering*
Herbert M Urbassek, Technische Universität, Kaiserslautern, Germany

9:40 *Cluster ion emission produced via gas - flow mechanism during sputtering of niobium
with gold projectiles*
S.F. Belykh and M.G. Dowsett, University of Warwick, UK

9:55 Discussion

10:40 Coffee

Fundamentals II

Discussion Leader: Klaus Wittmaack

11:00 **Invited:** *Fundamentals of sputtering by ion cluster beams in the nuclear stopping
energy region*
Hans Henrik Andersen, Niels Bohr Institute, University of Copenhagen, Denmark

11:45 *Effect of primary ion mass and composition on MCs_x^+ ion formation*
E. Niehuis, T. Grehl, F. Kollmer, R. Moellers, D. Rading, ION-TOF GmbH, Germany

12:00 *The effect of incident velocity on secondary ion emission from Si and Arginine with
large Ar cluster ions*
Satoshi Ninomiya, Yoshihiko Nakata, Kazuya Ichiki, Yoshiro Honda, Toshio Seki,
Takaaki Aoki and Jiro Matsuo, Kyoto University, Japan

12:15 Discussion

13:00 Lunch

Molecular Dynamics I
Discussion Leader: Roger Webb

- 14:00 **Invited:** *Molecular dynamics simulations of sputtering of organic overlayers by slow, large clusters*
L. Rzeznik^a, Ch. Palombo^b, B. Czerwinski^a, B.J. Garrison^b, N. Winograd^b, Z.Postawa^a,
^aJagiellonian University, Kraków, Poland, ^bPenn State University, USA
- 14:45 *Cluster induced chemistry at solid surfaces: molecular dynamics simulations of keV C₆₀ bombardment of Si*
Kristin D. Krantzman¹ and Barbara J. Garrison², ¹College of Charleston, USA, ²Penn State University, USA
- 15:00 *Investigation of cluster dynamics through bombardment of water*
Michael F. Russo Jr., Kathleen E. Ryan, Christopher Szakal, Joseph Kozole, Nicholas Winograd, Barbara J. Garrison, Penn State University, USA
- 15:15 Discussion
- 16:00 Coffee

Molecular Dynamics II
Discussion Leader: Kristin Krantzman

- 16:20 **Invited:** *Computational models to understand the interaction of cluster primary ions with surfaces and molecule emission*
Barbara J. Garrison^a, Michael F. Russo Jr^a, Kathleen E. Ryan^a, Edward J. Smiley^a,
Zbigniew Postawa^b, ^aPenn State University, USA, ^bJagiellonian University, Poland
- 17:05 *The effect of cluster density on the behaviour of energetic cluster impacts*
Roger Webb, University of Surrey, UK
- 17:20 *Effect of cluster size in keV cluster bombardment of solid benzene*
K. E. Ryan, E. J. Smiley, M. F. Russo, Jr., N. Winograd, and B. J. Garrison, Penn State University, USA
- 17:35 Discussion
- 18:20 Session close
- 19:00 Dinner

Tuesday 24th April

Sputtering and Ion Emission I
Discussion Leader: Hans Henrik Andersen

- 8:40 **Invited:** *Cluster ion sputtering yields: generic relations for sputtering yields and ion yields*
M. P. Seah, National Physical Laboratory, UK
- 9:25 *Influence of primary ion species and primary ion energy on the emission of secondary ions from surfaces*
F. Kollmer^a, R. Kersting^b, D. Rading^a, R. Möllers^a and E. Niehuis^a, ^aION-TOF GmbH, Germany, ^bTascon GmbH, Germany
- 9:40 *The mechanism of secondary ion yield enhancements using Bi²⁺ and Bi₃²⁺ primary ions*
Gabriella Nagy, Amy V. Walker, Washington University in St. Louis, USA
- 9:55 Discussion
- 10:40 Coffee

Sputtering and Ion Emission II
Discussion Leader: Peter Williams

- 11:00 **Invited:** *Cluster ion beam sputtering and secondary ion emission using experimental techniques with a wide range of energies and cluster sizes.*
S. Della-Negra, Institut de Physique Nucléaire d'Orsay, France
- 11:45 *Cluster Analysis of Organic and Inorganic Samples*
F.M.Green, I.S.Gilmore & M.P. Seah, National Physical Laboratory, UK
- 12:00 *Sputtering and ion emission by cluster ion beams*
R. Kersting^a, F. Kollmer^b, B. Hagenhoff^a, E. Niehuis^b, ^aTascon GmbH, Germany, ^bION-TOF GmbH, Germany
- 12:15 Discussion
- 13:00 Lunch

Sputtering and Ion Emission III
Discussion Leader: Ian Gilmore

- 14:00 **Invited:** *Probing molecular solids and polymers with fullerenes: computer simulations and chemical surface analysis*
A. Delcorte^a, N. Nieuwjaer^a, C. Poleunis^a, P. Bertrand^a, B. J. Garrison^b, ^aUniversité Catholique de Louvain, Belgium, ^bPenn State University, USA.

- 14:45 *A simple model for the fluence dependent yields of biomolecules observed in SIMS analysis of organic matter bombarded with molecular ions*
Klaus Wittmaack, GSF – National Research Centre for Environment and Health, Germany
- 15:00 *Molecular depth profiling of polymers with C₆₀ beams: the role of chemistry*
Antonino Licciardello^a, Rudolf Moellers^b, Vanna Torrisi^a, Nunzio Tuccitto^a, ^aUniversità di Catania, Italy, ^bION-TOF GmbH, Germany
- 15:15 Discussion
- 16:00 Coffee
- 16:20 Poster Session I : Contributed posters and poster summaries of discussion sessions on days 1 and 2
- 18:20 Session close
- 19:00 Dinner
- Whisky tasting evening

Wednesday 25th April

Depth Profiling I

Discussion Leader: Dae Won Moon

- 8:40 **Invited:** *Cluster SIMS depth profiling: fundamentals and applications*
Greg Gillen, Christopher Szakal, Albert Fahey and Christine Mahoney, National Institute of Standards and Technology, USA
- 9:25 *ToF-SIMS depth -profiling of thin polymer layers: comparison between Ga⁺ and C₆₀⁺ ion bombardment*
 N. Nieuwjaer, C. Poleunis, A. Delcorte, P. Bertrand, Université Catholique de Louvain, Belgium
- 9:40 *Characterization of thin polymer films after Bi cluster ion bombardment*
Matthew S. Wagner, Michael R. Mootz and Brandon M. Dunphy, Procter & Gamble Company, USA
- 9:55 Discussion
- 10:40 Coffee

Depth Profiling II

Discussion Leader: Matt Wagner

- 11:00 **Invited:** *Molecular depth profiling using cluster beams*
Andreas Wucher, Universität Duisburg-Essen, Germany

11:45 *SF₅⁺ depth profiling of polymeric materials*
Christine Mahoney, National Institute of Standards and Technology, USA

12:00 *C₆₀ sputtering of layered organic materials*
A. Shard, Ian Gilmore, National Physical Laboratory, UK

12:15 Discussion

13:00 Lunch

14:00 Leave for the excursion to Edinburgh and Edinburgh castle

19:00 Back from excursion

19:30 Dinner

Thursday 26th April

Biological Analysis

Discussion Leader: Dave Castner

8:40 **Invited:** *Do cluster primary ion beams advance the capability of bio-molecule analysis by SIMS?*
John C. Vickerman, University of Manchester, UK

9:25 *Depth profiling brain tissue sections with a 40 keV C₆₀⁺ primary ion beam, from salt adducts to 3-D imaging*
Emrys A. Jones, Nicholas P. Lockyer, John C. Vickerman, University of Manchester, UK

9:40 *Challenges of 2 and 3D bio-analysis using cluster ion ToF-SIMS*
John S. Fletcher, Seetharaman Vaidyanathan, Nicholas P Lockyer and John C. Vickerman , University of Manchester, UK

9:55 Discussion

10:40 Coffee

Cluster Beam Technology

Discussion Leader: Patrick Bertrand

11:00 **Invited:** *What's special about cluster ion beams?*
Nicholas Winograd, Penn State University, USA.

11:45 *A study of C₆₀-sputtered bulk and thin film organics: mechanistic insights using TOF-SIMS, XPS and nanoindentation*
Gregory L. Fisher and Scott Bryan , Physical Electronics, USA

12:00 *Molecular depth profiling of alternating Langmuir-Blodgett multilayers*
Leiliang Zheng and Nicholas Winograd, Penn State University, USA

12:15 Discussion

13:00 Lunch

Massive Clusters I
Discussion Leader: Nick Lockyer

14:00 **Invited:** *Cluster size effect on secondary ion emission*
Jiro Matsuo, Kyoto University, Japan

14:45 *Shock-heating phenomena in impacts of massive electrosprayed clusters*
Peter Williams¹, Sergei Aksyonov¹ and Leonid Zhigilei², ¹Arizona State University, USA, ²University of Virginia, USA

15:00 Discussion

15:45 Coffee

16:05 Poster Session II : Poster summaries of discussion sessions on days 3 and 4

18:05 Session close

19:00 Conference Dinner

Friday 27th April

Massive Clusters II
Discussion Leader: Amy Walker

9:00 **Invited:** *Massive projectiles for the characterization of surfaces*
Emile A. Schweikert, Texas A&M University College Station, USA

9:45 *Ion emission of solids under gold clusters bombardment with various sizes and energies*
Nimer Wehbe, Mireille Fallavier, Serge Della Negra, Institut de Physique Nucléaire de Lyon, France

10:00 Discussion

10:45 Coffee

11:05 Final summary session and conference end

13:00 Lunch

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Oral Abstracts

Listed in Chronological Order

Invited

Fundamental and general principles of sputtering

Herbert M. Urbassek

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Kaiserslautern, Germany

urbassek@physik.uni-kl.de

The physical mechanisms and processes underlying the sputtering of surfaces induced by atom and cluster bombardment are reviewed. Linear or collision-cascade sputtering occurs when recoiling target atoms can surpass the surface barrier. When the average energy delivered per atom in the vicinity of the surface becomes comparable to the cohesive energy of the solid, sputtering from a so-called spike may result. This scenario is particularly pronounced in the case of cluster impact.

This talk discusses sputter yields, the energy and angular distributions of emitted particles, as well as the size distribution of emitted clusters. The depth of origin of sputtered particles is of particular interest to the application of sputtering as a depth profiling tool. Ion irradiation of compound targets induces preferential sputtering which leads after prolonged irradiation to composition changes at the target surface. Due to the violent nature of energetic particle impact, the surface topography of the target will be changed; in particular, large craters can be formed. Such surface topography will, on the other hand, influence the sputter process.

Cluster Ion Emission Produced via Gas - Flow Mechanism during Sputtering of Niobium with Gold Projectiles

S.F. Belykh* and M.G. Dowsett

Department of Physics, University of Warwick, Coventry CV4 7AL, UK

(*s.belikh@warwick.ac.uk)

In our previous work [1] a nonlinear effect has been documented with cluster ions ejected as a whole from the metal surface bombarded with keV polyatomic gold projectiles. A mechanism of such an emission has been developed [2]. Recently it was shown that sputtering of indium with polyatomic gold ions produces an additional low-energy contribution to a flux of sputtered neutral atoms [3]. These results indicate a spike emission mechanism which resembles a free expansion of a super-critically heated subsurface volume. It is in agreement with a gas-flow model [4] which predicts a nucleation of flow atoms into clusters at the some distance from the surface. The difference in cluster origin start points can be used as a key for separating of clusters produced due to mechanisms [2 and 4].

Here, we present the first results on the emission of two groups of cluster ions sputtered from niobium with keV gold projectiles: one of them includes clusters ejected as a whole from the surface while a second group consists of clusters originated outside of the surface. The relationship between contributions of these clusters to a total cluster flux, their energy spectra, and a model for the explanation of results obtained are reported.

[1] S.F.Belykh, B.Habets, U.Kh.Rasulev, A.V.Samartsev, L.V.Stroev, and I.V.Veryovkin, Nucl. Instrum. Meth. Phys. Res. **B 164-165** (2000) 809

[2] S.F. Belykh, V.I. Matveev, I.V. Veryovkin, A. Adriaens, and F. Adams, Nucl. Instrum. Methods Phys. Res., **B 155**, 409 (1999)

[3] A.V. Samartsev, A. Duvenbeck, and A. Wucher, Phys. Rev. **B 72**, 115417 (2005)

[4] H.M. Urbassek and J. Michl, Nucl. Instrum. Methods Phys. Res. **B 22**, 480 (1987)

Invited

Fundamentals of sputtering by ion cluster beams in the nuclear stopping energy region

Hans Henrik Andersen

Niels Bohr Institute, University of Copenhagen

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The sputtering yield was nearly 40 years ago shown theoretically to be proportional to the nuclear stopping and inversely proportional to the target surface binding energy. Experimentally, that prediction worked excellently in the region where nuclear stopping was dominant, and for metal targets to even much higher energies. It was, however, found that where the deposited energy density was high, an experimental enhancement in yield was found. Through the use of cluster ion beams, this enhancement was found to be non-linear in nature. Detailed experimental investigations have more recently shown the non-linear enhancement in some cases to be very substantial, i.e. to amount to more than a factor of 20 in yield. The non-linearity is found to reside in the relation between the deposited energy density and the yield, not in the nuclear stopping of clusters.

While the phenomenology of yield enhancements has been studied in some detail, other parameters have been much less investigated. It has been found that the enhancement of the yield is due to particles ejected later than those of the linear part of the cascade and that these particles have on the average much lower energy than those of the linear cascade. The angular distribution for energies, where the collision cascade is fully developed is more cosine-like than the collision cascade part, and the yield dependence on angle of incidence is weaker than for atomic particle bombardment. The size distribution of the ejected aggregates is not known in detail, particularly because such data to a large extent depends on the measurements of charged clusters, and hence is dependent on knowledge of the charge state of clusters emitted from hot collision regions. That aspect will not be discussed in the present presentation. Finally, the behaviour of binary and ternary targets under cluster bombardment is virtually unknown, although the behaviour under such conditions is very important for the use of cluster beams for sputter profiling. Some evidence exists for diffusional redistribution within the hot collision spike.

Effect of Primary Ion Mass and Composition on MCs_x^+ Ion Formation

E. Niehuis*, T. Grehl, F. Kollmer, R. Moellers, D. Rading,
ION-TOF GmbH, Heisenbergstr. 15, 48149 Muenster, Germany
(*ewald.niehuis@iontof.com)

In contrast to the understanding of the sputtering process the theoretical description of the ionisation phenomena in SIMS is still in an early state. This is a major problem for quantitative surface analysis by SIMS. In 1988 Gao demonstrated the advantage of using molecular MCs^+ ions instead of M^+ ions for a quantitative compositional analysis of matrix elements [1].

TOF-SIMS dual beam depth profiling is ideal to study the MCs_x^+ ion formation as the Cs sputtering and the analysis process is completely de-coupled. The Cs-Xe-cosputtering technique allows to change the Cs surface concentration and hence, the work function in a systematic way to study ionisation mechanisms.

We have investigated the yield of MCs_x^+ ions as a function of mass and composition of the analysis beam for various sample systems. We used atomic primary ions like Ga^+ and Bi^+ as well as cluster primary ions like Bi_3^+ and C_{60}^+ while keeping the Cs sputtering conditions constant. For some sample systems we found an increase in MCs^+ ion yields up to a factor of 1000 by using clusters instead of Ga^+ .

[1] Y. Gao, J. Appl. Phys. **64** (7) 1988, 3760-3762.

The Effect of Incident Velocity on Secondary Ion Emission from Si and Arginine with Large Ar Cluster Ions

Satoshi Ninomiya^{a,*}, Yoshihiko Nakata^b, Kazuya Ichiki^b, Yoshiro Honda^b, Toshio Seki^a, Takaaki Aoki^c and Jiro Matsuo^a

^a Quantum Science and Engineering Center, Kyoto University, Gokasho, Uji, Kyoto 611-0011 Japan

^b Department of Nuclear Engineering, Kyoto University, Sakyo, Kyoto 606-8501, Japan

^c Department of Electronic Science and Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo, Kyoto 615-8510, Japan

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Secondary ions emitted from solids with cluster ions such as Au_3^+ and C_{60}^+ ions have been recently and frequently studied [1]. It was shown that yields of both sputtering and secondary ions increase considerably when cluster ions are incident on solids. These effects are called “nonlinear effects” or “cluster effects” and their mechanisms are still not fully understood. In previous studies, we have reported the unique secondary-ion emission for solid targets using cluster ions that are much larger than the molecular ions as primary ions [2]. In this study, secondary ions were measured for Si and Arginine bombarded with size-selected Ar cluster ions using a time-of-flight technique, and a method for generation of large cluster ion beams with high current density ($> \mu\text{A}/\text{cm}^2$) has been developed at Kyoto University [3]. Examples of secondary ion spectra for Si bombarded with large Ar cluster ions (Fig. 1) show strong variations with incident velocity (incident energy per atom). Fig. 2 shows the dependence of relative secondary ion yields for Si and Arginine targets on incident energy. The relative Si^+ yield increased rapidly with increasing incident energy per atom, whereas the arginine ion yields remained constant. It was found that secondary-ion emission depends strongly on incident cluster ion velocity, when cluster ions that consisted of more than 100 atoms were incident.

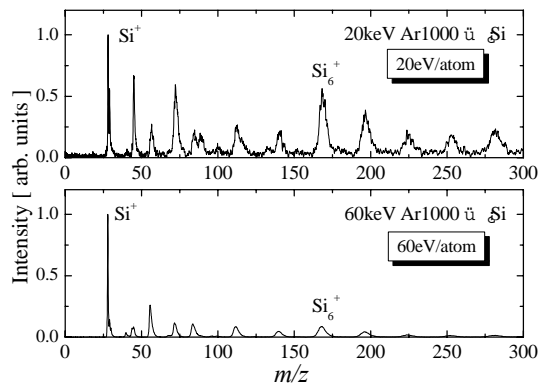


Fig. 1 Secondary ion spectra for Si.

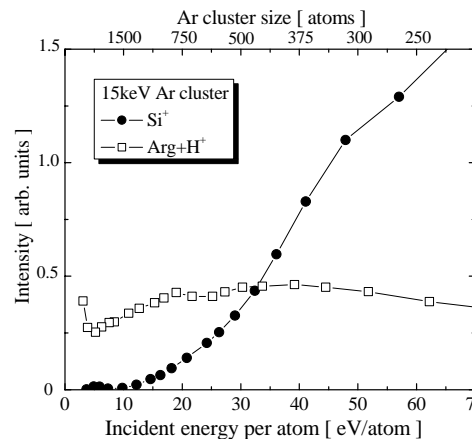


Fig. 2 The effect of incident energy (eV/atom) on secondary ion yields.

- [1] D. Weibel, S. Wong, N. Lockyer, P. Blenkinsopp, R. Hill and J.C. Vickerman, *Anal. Chem.* **75** (2003) 1754.
- [2] S. Ninomiya, Y. Nakata, K. Ichiki, T. Seki, T. Aoki and J. Matsuo, *Nucl. Instr. and Meth. B* (2007) in press.
- [3] T. Seki, J. Matsuo, G.H. Takaoka, I. Yamada, *Nucl. Instr. Meth. B* **206** (2003) 902.

Invited

Molecular dynamics simulations of sputtering of organic overlayers by slow, large clusters

L. Rzeznik¹, Ch. Palombo², B. Czerwinski¹, B.J. Garrison², N. Winograd², Z. Postawa^{*,1}

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Large cluster projectiles have been demonstrated to be useful for both processing of important electronic materials [1] and mass spectrometry [2,3]. In order to understand the ejection mechanisms of organic molecules in these experiments, the ion-stimulated desorption by impact of large and slow clusters is examined using molecular dynamics (MD) computer simulations. The investigated systems are represented by thin layers of benzene and polystyrene deposited on Ag{111}. The investigated surfaces are irradiated with projectiles composed of hundreds and tens of thousands noble gas atoms having a very low kinetic energy per atom (0.1-20eV). The sputtering yield of molecular species and their mass as well as internal, angular, and kinetic energy distributions are analyzed depending upon the type of the projectile and the type of a formed overlayer.

The simulations demonstrate quite clearly that the physics of ejection by these large and slow clusters is distinct from the ejection events stimulated by the popular SIMS clusters, C₆₀, Au₃ and SF₅. In this presentation, the essential processes leading to ejection of neutral organic molecules by large and slow clusters will be discussed and the predictions valuable to the mass spectrometry community will be given.

- [1] I. Yamada, N. Toyoda, Nucl. Instrum. Methods B **242** (2004) 143 *and references therein*.
- [2] R.D. Rickman, S.V. Verkhoturov, G.J. Hager, E.A. Schweikert, Int J. Mass Spectrom. **245** (2005) 48.
- [3] R.G. Cooks, Z. Odyang, Z. Takas, J.M. Wiseman, Science **311** (2006) 1566; Z. Takats, J.M. Wiseman, B. Gologan, R.G. Cooks, Science **306** (2004) 471.

**Cluster induced chemistry at solid surfaces:
Molecular Dynamics Simulations of keV C₆₀ bombardment of Si**

Kristin D. Krantzman*¹ and Barbara J. Garrison²

¹*College of Charleston, Department of Chemistry and Biochemistry, Charleston, USA*

²*The Pennsylvania State University, Department of Chemistry, University Park, USA*

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Depth profiling experiments with C₆₀⁺ projectiles on Si have shown puzzling results [1]. At lower kinetic energies, there is a buildup of solid material and no sputtering yield is observed, whereas a transition to net erosion of material is found at higher impact energy. Molecular dynamics simulations of the impact of C₆₀ onto Si show that the experimental results can be explained by bombardment induced surface chemistry, which is unique to the pairing of the C₆₀ projectile with the Si target. [2]. The simulations reveal the formation of strong covalent bonds between the C and Si atoms, which result in nearly all of the C atoms remaining embedded in the surface. This suggests the formation of SiC as a consequence of prolonged irradiation. In order to investigate possible effects caused by projectile fluence accumulation, additional simulations are therefore performed with SiC as target material. The influence of bombardment parameters such as impact energy and angle is investigated in the context of characteristic energy deposition footprints.

[1] G. Gillen, J. Batteas, C.A. Michaels, P. Chi, J. Small, E. Windsor, A. Fahey, J. Verkouteren and K.J. Kim, *App. Surf. Sci.* **252** (2006) 6521.

[2] K.D. Krantzman, D.B. Kingsbury and B.J. Garrison, *App. Surf. Sci.* **252** (2006) 6463; -
ibid, *Nucl. Instrum. Methods B*, in press.

Investigation of Cluster Dynamics through Bombardment of Water

Michael F. Russo Jr. *, Kathleen E. Ryan, Christopher Szakal, Joseph Kozole, Nicholas

Winograd, Barbara J. Garrison

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Due to the vast number of advantages associated with polyatomic projectiles, the use of cluster ion beams has rapidly become a staple of the SIMS community. In an effort to elucidate the fundamental physical phenomena that govern these bombardment events, we have performed a series of comparative molecular dynamics simulations for two of the predominant cluster sources currently used in experiment, C₆₀ and Au₃. Two sets of simulations on amorphous water were performed which involved either rigid [1] or dissociative [2] descriptions of the molecules. Several aspects of the collision event were examined including penetration depth, size and shape of the removed and damaged volumes, and the path of the incident particle's constituents. The C₆₀ cluster shatters upon impact, creating a crater region in which the individual carbon atoms are confined and the vast majority of the reactions occur. The Au₃ exhibits similar crater characteristics, however, the individual gold atoms became embedded deep into the sample and consequently the reactions also occur deep in the sample. Similarly designed simulations explain the experimental differences in emission of Ag⁺ ions from thin water layers adsorbed on a Ag substrate [3]. These results establish a foundation for the development of simple models [4] to be discussed in the talk by Barbara Garrison.

[1] M. F. Russo, I. A. Wojciechowski and B. J. Garrison, *Appl. Surf. Sci.* **252** (2006) 6423.

[2] I. A. Wojciechowski and B. J. Garrison, *J. Phys. Chem. B* **109** (2005) 2894.

[3] C. Szakal, J. Kozole, M. F. Russo Jr, B. J. Garrison and N. Winograd, *Phys. Rev. Lett.* **96** (2006) 216104.

[4] M. F. Russo, Jr and B. J. Garrison, *Anal. Chem.* **78** (2006) 7206.

Invited

Computational models to understand the interaction of cluster primary ions with surfaces and molecule emission

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The use of polyatomic projectiles in secondary ion mass spectrometry (SIMS) has greatly expanded applications in imaging and depth profiling of molecular substrates [1]. Computer modeling in this kinetic energy range for realistic molecular solids is problematic, however, since the size of the system must be increased to a very large number of atoms in order to contain the important energy dissipation processes [2-4]. The calculation of a single trajectory may require several months or years of computer time under these conditions. Because of this difficulty, performing simulations on multiple targets for multiple sets of initial conditions are challenging. Based on results from full simulations, we are developing models to predict ejection yields by using short-time MD simulations on limited sized targets [5]. Results and speculations from our work will be presented.

[1] N. Winograd, *Anal. Chem.*, **77** (2005) 142A.

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[3] M. F. Russo, Jr., I. A. Wojciechowski, B. J. Garrison, *Appl. Surf. Sci.*, **252** (2006) 6423.

[4] E. J. Smiley, Z. Postawa, I. A. Wojciechowski, N. Winograd, B. J. Garrison, *Appl. Surf. Sci.*, **252** (2006) 6436; E. J. Smiley, N. Winograd, B. J. Garrison, *Anal. Chem.*, **79** (2007) 494.

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The Effect of Cluster Density on the Behaviour of Energetic Cluster Impacts

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The effects of the impact of large energetic clusters on surfaces is being studied by many groups both experimentally and with the use of computer simulation. Computer simulations have been able to provide insight into many of the mechanisms that take place when a number of simultaneous particles strike a solid surface at the same time as is the case with cluster bombardment. Studies have been made that have investigated the effects of varying many parameters of the system such as the cluster velocity, the cluster size, the elemental make-up of the cluster. Investigations have also been made looking at the effect of the target properties, solid, liquid and gaseous targets have been used. The enfusion doping process pioneered at Kyoto and Epion has introduced the large frozen gas cluster to the system. These clusters are produced by mixing gases in the gas phase and using an aerosol effect to produce uniform sized quenched cluster of several thousand in size. It is not obvious what the density of these clusters might be. They might be frozen gases, with a low density, or they may have relaxed to a liquid or solid form with a higher density. The objective of the work reported here is to systematically explore the difference between a set of impacts from clusters that have been compressed to a solid form and clusters which have been frozen in a gas structure.

The pictures below show the difference between the two types of cluster with the same number of atoms. Clearly the deposited energy in each case is spread over a different area of the target and hence the behaviour of the target after the impact is different. These differences will be explored in detail.

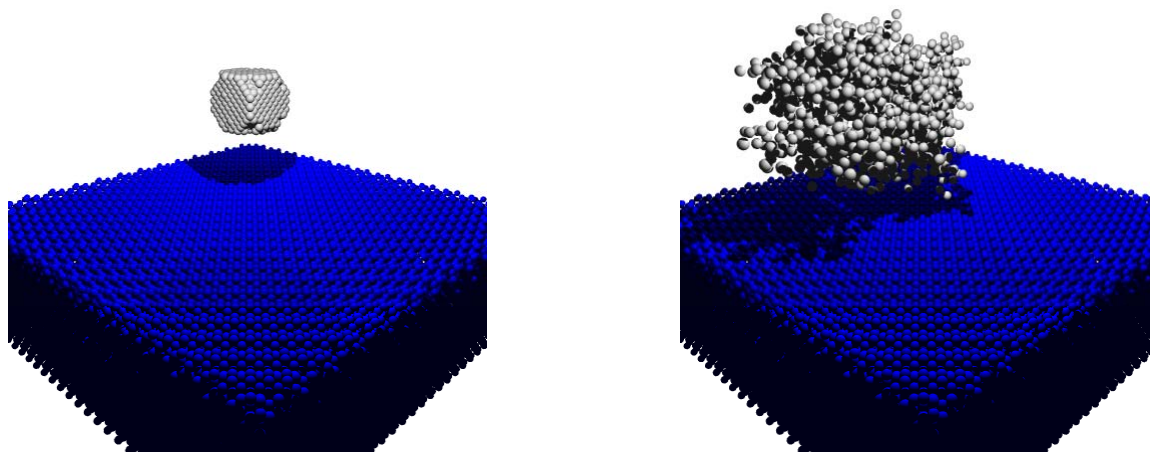


Fig. 1 Condensed solid cluster

low density gas cluster

Effect of cluster size in keV cluster bombardment of solid benzene

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Emission of benzene molecules by 5 keV cluster bombardment of a range of carbon projectiles from C₆H₆ to C₁₈₀ is studied by a coarse-grained (CG) molecular dynamics (MD) technique. This approach permits calculations that are not feasible using more complicated potential energy functions, particularly as the interesting physics associated with the ion impact event approaches the mesoscale. These calculations show that the highest ejection yields are associated with clusters that deposit their incident energy 15 to 20 Å below the surface. The highest yield for the projectiles is produced by the C₂₀ and C₆₀ projectiles [1]. Because similar MD simulations are not tractable for kinetic energies of relevance to experimentalists, we use short time MD simulations and an analytic model [2] to determine how the optimal cluster size depends on incident kinetic energy.

[1] E. J. Smiley, N. Winograd, and B. J. Garrison, *Analytical Chemistry* **79** 494-499 (2007).

[2] M. F. Russo, Jr., and B. J. Garrison, *Analytical Chemistry*, **78** 7206-7210 (2006)

Invited

Cluster ion sputtering yields: generic relations for sputtering yields and ion yields

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An assessment is made of the behaviours in ion sputtering and static secondary ion mass spectrometry (static SIMS) to provide a framework to understand the enhanced secondary ion yield of molecular fragments, from molecules on defined substrates, achieved by using primary ion clusters. First, an analysis is made of the published ion sputtering yield data for mono-elemental solids sputtered by mono-elemental primary ion clusters, mainly of the type Au_n^+ . These are evaluated using existing theory which is an excellent description of published data for a number of elemental targets over a wide energy range for primary ion cluster sizes from 1 to 13 for gold primary ion clusters and for a number of different primary ion species including clusters of more than one elemental specie. This is then used to provide a description of the molecular ion yield behaviour that is of interest in static SIMS. A simple extension allows a description of the primary ion source dependence of the disappearance cross section. This approach provides a unified model that relates the effects of different sources and also enables recommendations for future sources of higher efficiency for the analysis of organic materials.

Influence of primary ion species and primary ion energy on the emission of secondary ions from surfaces

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In this study we investigated the influence of different primary ion species and energies on the secondary ion emission from thin organic films. As model systems we used spin coated samples of the polymer additives Chimassorb 944 and Irganox 1010 on polyethylene. The film thickness is estimated to be in the monolayer range. Chimassorb 944 is a polymeric light stabilizer ($M_w \approx 2500-4000$ u) and Irganox 1010 ($M_w \approx 1177$ u) is used as an anti-oxidant.

The chosen preparation guarantees that the collision cascade takes place completely in organic material and that the secondary ions of the analyte originate only from the uppermost monolayer. We determined the secondary ion yield, the disappearance cross section, the efficiency as described in [1] and the fragmentation behavior [2] for monoatomic Bi ions as well as for different polyatomic Bi_n and C_{60} cluster ions.

The results will be presented and discussed with respect to mass, energy, and the number of cluster constituents of the respective projectile.

[1] F. Kötter, A. Benninghoven, Applied Surface Science 133 (1988) 47-57

[2] I.S. Gilmore, M.P. Seah, Applied Surface Science 161 (2000) 465-480

The Mechanism of Secondary Ion Yield Enhancements using Bi^{2+} and Bi_3^{2+} Primary Ions

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We have investigated the mechanism of secondary ion yield enhancement using Bi^{2+} and Bi_3^{2+} primary ions and *DL*-phenylalanine, Irganox 1010 and polymer thin films adsorbed on silicon and aluminum. For Irganox 1010, in the negative ion mode the molecular ion yields ($m/z = 1175$; $[\text{M}-\text{H}]^-$) are 1-2 times larger when using Bi^{2+} and Bi_3^{2+} primary ions than with Bi^+ and Bi_3^+ at the same primary ion velocities. In the positive ion mode, the quasimolecular ion yield ($m/z = 899$) is ~ 1.3 times larger for Bi^{2+} ions than for Bi^+ . For Bi_3^{2+} the quasimolecular ion yield is only $\sim 50\%$ of the ion yield using Bi_3^+ , but the secondary ion yields of the fragment ions at $m/z = 57$ and 219 are enhanced. For all polymer films studied, using Bi^{2+} and Bi_3^{2+} secondary ion intensities from the oligomer regions are substantially decreased (Figure 1). Secondly, for polymers that are able to undergo allyl radical reactions, the intensities of monomer ions are greatly increased, and secondary ion yield enhancements typically range from 1.2 to 4. No secondary ion yield enhancement is observed for *DL*-phenylalanine. We discuss differences in the ionization mechanisms for Bi^{2+} and Bi_3^{2+} primary ion bombardment compared with Bi_n^+ bombardment.

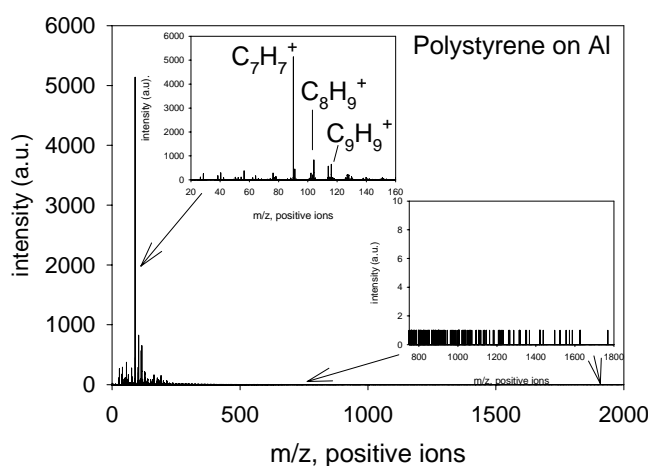


Fig.1 – Positive ion mass spectrum of polystyrene adsorbed on Al. The primary ion beam employed was Bi_3^{2+} with a kinetic energy of 12.5 keV and primary ion dose of 7×10^7 ions cm^{-2} . The mass spectrum is greatly simplified and is dominated by the monomer ions ($m/z = 90-120$), while the oligomer ion intensities ($m/z = 750-1800$) are suppressed.

Invited

Cluster ion beam sputtering and Secondary ion emission using experimental techniques with a wide range of energies and cluster sizes.

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More than fifteen years ago, the fundamental interest of the cluster ions was quickly shown and within a few years we had a whole set of source and accelerator facilities allowing to cover a large energy and mass range: from keV to MeV and clusters from some carbon or gold atoms to the molecules like fullerenes.

The object of my talk is to synthesize the information which can be extracted from this vast projectile energy and mass range.

The first part of my talk will be related to the ion velocity influence and will show it is possible to compare the two modes of energy deposition: elastic and inelastic collisions. I will point out certain results obtained a few years ago but in illustrating the cluster-solid interaction by presenting results about the modifications induced in the material by cluster impacts. This first part will end by recent results concerning the differences between ion yield and total sputtering rate behaviour as a function of the projectile velocity between 20 and 200 keV/atoms. In this energy range, the characteristics of the ionic emission will be also presented.

The second part of my talk will concentrate on the massive clusters of a few hundred atoms with a comparison of the advantages and limitations of these ions with respect to the now more traditional projectiles that are the beams of gold and bismuth clusters and also fullerenes. To illustrate this part of my talk I will again associate ionic emission and material modification which makes it possible to follow the projectile in the solid and to visualize the final state of the solid. As for the high energy field, I hope to extract from these results the projectile characteristics after its interaction with the solid, i.e. its range and its possible fragmentation. This information is necessary to determine the energy deposited in the medium and especially the density of energy which is the discussion thread of my talk.

In conclusion I will recall the outstanding facts of this search. Is there really a universal probe? Which is the best mass-energy-velocity compromise which makes it possible to sublime and ionize the largest volume of matter near the surface?

Cluster Analysis of Organic and Inorganic Samples

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The molecular analysis of organic films on si wafer or similar substrates is, today, of growing importance to sectors of industry developing sensors for bio assays to organic electronics. In this work we use Irganox 1010 organic molecular films of thicknesses > 10 nm on a silicon wafer as a model system to investigate sputtering yields, molecular ion yields and the depth resolution. There is wide debate over the effectiveness of different clusters for enhancement of the molecular yield without damage to the sample. In this work we compare small clusters such as Bi_n^+ and the larger C_{60}^+ primary ion beams. It is found that Bi_7^{++} gives the highest sputtering and molecular ion yields. Although C_{60}^{n+} primary ions have lower yields, the reduced primary ion range allows a high steady state $(\text{M-H})^-$ secondary ion yield in depth profiles, making C_{60}^{n+} good for organic depth profiling. Prior to the interface the signals for highly fragmented ions increases and that for the $(\text{M-H})^-$ ion shows a very pronounced peak. These could be interpreted as a significant change in the molecular film close to the si wafer. Modelling of the sputtering behaviour close to the interface using the non-linear result of the thermal spike theory shows that these effects are caused by the sputtering process and do not reflect changes to the material. A simple model based on the roughness induced by sputtering explains large interface widths seen with C_{60}^+ . Irganox depth profiles agree with the model and show that lower energies of bombardment give better depth resolution.

Sputtering and Ion Emission by Cluster Ion Beams

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Within our known model system of spin-coated Irganox 1010 monolayers on low density polyethylene we will concentrate on a description of the fragment formation of the antioxidant molecule as function of primary ion parameters (mass, number of constituents, energy). In order to study the fragmentation during the actual emission process it is essential to perform the investigation with primary ion dose densities below the static SIMS limit.

Our observations indicate significant changes of the energy distribution close to the sample surface and/or of the energy transfer to analyte molecules when polyatomic instead of monoatomic projectiles are used.

Invited

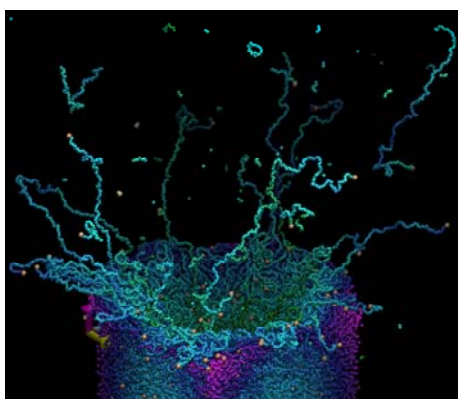
Probing Molecular Solids and Polymers with Fullerenes: Computer Simulations and Chemical Surface Analysis

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Polyatomic ions such as SF_5^+ , Au_n^+ , Bi_n^+ , C_{60}^+ are now routinely used as projectiles for surface analysis by secondary ion mass spectrometry (SIMS), because they induce large sensitivity enhancements for molecular ions. Among them, fullerenes appear to be particularly adequate for the analysis of bulk organic films and also for depth profiling, because, in many cases, the signal of molecular ions is retained upon erosion. To understand the underlying physics, confronting experimental observations to a model based on classical molecular dynamics (MD) constitutes a powerful combination [1,2]. MD simulations help us to establish a microscopic view of the processes occurring in the solid upon projectile impact while time-of-flight SIMS provides the yields and energy distributions of desorbed fragment and molecular ions. In this contribution, we focus on the mechanisms of energy transfer and sputtering induced in molecular solids such as polymers by kiloelectronvolt C_{60} projectiles, in contrast with monoatomic (Ar, Ga) projectiles. Then, we broaden the scope by addressing important questions for surface analysis that are not (yet?) tackled by the models, concerning e.g. ionization mechanisms, molecular depth profiling, projectile-induced chemistry, etc. These issues help us delineate limitations and perspectives for surface analysis with polyatomic projectiles.



Molecular emission and crater formation under 5 keV C_{60} bombardment of polyethylene.

- [1] B. J. Garrison, in "ToF-SIMS: Surface Analysis by Mass Spectrometry", Eds. J. C. Vickerman and D. Briggs, SurfaceSpectra/IMPublications, Manchester (2001) p. 223.
[2] A. Delcorte, Phys. Chem. Chem. Phys. 7, 2005, 3395.

A Simple Model for the Fluence Dependent Yields of Biomolecules Observed in SIMS Analysis of Organic Matter Bombarded with Molecular Ions

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It is well known that the yields of biomolecules observed in SIMS analysis of organic matter can be enhanced significantly or even strongly if one uses molecular instead of atomic primary ions for sample erosion. Even more important is the observation that, in contrast to bombardment with atomic ions, molecular primary ions generate signals of sample molecules that do not exhibit an almost unlimited exponential decrease with increasing primary ion fluence, reflecting progressive sample damage, but stabilizes at a sometimes remarkably high level [1-3]. This observation has tentatively been attributed mostly to a high sputtering yield brought about by bombardment with molecular ions.

To provide a more detailed interpretation of published data, the evolution of fluence dependent molecular secondary ion yields is described by a model which is based on the assumption that the observed yields constitute the sum of contributions from two different emission sites, one representing the virgin original surface, the other a surface region that has already been exposed to ion bombardment. The amount of damage actually generated in this region will depend on the properties of the sample material as well as on the ability of the primary ion to remove sample molecules efficiently. The input parameters that enter into the model characterize (i) the rate at which the virgin sample is converted into a material with a damaged near-surface region and (ii) the yield of molecular ions from the damaged region relative to the yield from the virgin matter. By an appropriate choice of the input parameters all features of previously reported fluence dependent molecular ion yields can be reproduced, including the high-damage case usually encountered when using atomic primary ions. It is also shown that with samples exhibiting a very high sputtering yield, measurements need to be performed at small fluence increments in order to separate the contributions due to the virgin and the damaged areas.

[1] C.M. Mahoney, S.V. Roberson, *Anal. Chem.* **76** (2004) 3199.

[2] J. Cheng and N. Winograd, *Anal. Chem.* **76** (2005) 3651

[3] J.S. Fletcher, X.A. Conian, E.A. Jones, G. Biddulph, N.P. Lockyer, and J.C. Vickerman,

Molecular depth profiling of polymers with C₆₀ beams: the role of chemistry

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Molecular depth profiling of organic materials has been, since a long time, a “forbidden fruit” for SIMS people. Indeed beam irradiation of organics (and polymers in particular) produces severe chemical modifications (such as bond formation/breaking, radical formation, preferential loss of hydrogen and heteroatoms, compaction, formation of graphite and/or amorphous carbon and so on ...) that made unrealistic even to think about molecular depth profiling. However, in the recent years the development of polyatomic primary ion sources made molecular depth profiling something more concrete than a dream. Relatively recent literature [1-4], obtained by using C₆₀ primary ions beyond the static limit, reports interesting data in this direction. In particular, results on PMMA [4] suggested that in general molecular depth profiling of polymers is feasible. Such finding could be connected with the high sputter yield and the very low penetration depth of the C₆₀ ions, that indeed “sputter away” the damaged region leaving behind a more or less undamaged surface. On the other hand, polymers are known to undergo - under ion-irradiation - several competing phenomena, including chain-scission and cross-linking phenomena, although in different experimental conditions (typically hundred keV of monoatomic beams). If similar phenomena are active under keV C₆₀ bombardment, as already shown in a previous paper of our group [5], the removal of the damaged layer would be strongly depending on the radiation chemistry of the particular polymer under consideration (i.e. prevailing chain scission or cross-linking). In this contribution new data will be presented, both on polymers with opposite ion-beam induced chemistry and their copolymers, that emphasize the importance of chemical factors in the erosion behaviour under dynamic SIMS conditions and suggest that molecular depth profiling of polymers with C₆₀ (and presumably with other cluster beams), although feasible in the case of certain systems, is nevertheless not applicable to all classes of polymers.

[1] D.E.Weibel, N. Lockyer, J.C. Vickerman, Appl. Surf. Sci **231–232** (2004) 146.

[2] A.G. Sostarecz, S. Sun, C. Szakal, A. Wucher, N. Winograd, Appl. Surf. Sci. **231–232** (2004) 179.

[3] R. Moellers, R. Kersting, F. Kollmer, D. Rading, T. Grehl, E. Niehuis, proc. SIMS Europe 2004, Muenster, (2004), p. 106.

[4] C. Szakal, S. Sun, A. Wucher, N. Winograd, Appl. Surf. Sci **231–232** (2004) 183.

Invited

Cluster SIMS Depth Profiling: Fundamentals and Applications

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The use of novel cluster primary ion beams for SIMS depth profiling of both organic and inorganic materials has been an area of intense study in recent years. For inorganic surface analysis of semiconductor materials cluster SIMS results in a reduced penetration depth for the constituent atoms of the cluster which may improve SIMS depth resolution and minimizes the sputter depth over which the build up of the primary beam gives non-linear sputter and ion yield enhancements (the so-called transient region). Optimal selection of the cluster beam can be used to maximize secondary ion yields for dopants and trace elements. Cluster bombardment has also proven useful for reducing sputter-induced topography during ion beam analysis of metal films. However, in some cases, such as C_{60}^+ bombardment of silicon at lower impact energies, surface chemical effects can dominate leading to the deposition of surface carbon which prevents depth profiling. For organic surface characterization, cluster primary ion beams offer large improvements in molecular secondary ion yields and, in selected cases, immunity to primary-beam-induced degradation of the sample. The reduction in the accumulation of beam-induced damage allows for molecular depth profiling which is an entirely new application for SIMS that has been widely pursued by numerous research groups over the last several years. In our laboratory at NIST we have explored applications of cluster primary ion beam SIMS for practical surface analysis. Several types of cluster ion sources are currently being used on both TOF and ion microscope SIMS instruments including; SF_5^+ , C_8^- , Bi_3^+ and C_{60}^+ . A variety of materials have been analyzed with these ion sources including low energy ion implants in silicon, delta-doped layers, metal films, organic thin films, biomolecules, polymers and biological tissues. Our most recent efforts have been focused on extending the cluster SIMS technique for the 3D molecular depth profiling of organic thin films and polymeric drug delivery systems. This presentation will provide an overview of selected examples of cluster SIMS depth profiling for both inorganic and organic materials. Experiments leading to optimization of the depth profiling conditions including selection of appropriate cluster beam species and impact energy/angle will be discussed. The possible role of sample temperature and sample rotation on organic depth profiling will be examined. Current limitations of the cluster SIMS approach will be described including organic systems that are not amenable to depth profiling and molecular signal recovery from heavily damaged surfaces or surfaces that have been metal-coated. Finally, we will discuss issues associated with interpretation of molecular depth profiles and possible strategies for improving secondary ion yields.

ToF-SIMS depth -profiling of thin polymer layers: comparison between Ga^+ and C_{60}^+ ion bombardment

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Cluster ions beams appear to be very attractive for depth profiling molecular samples. Indeed, polyatomic ions, such as SF_5^+ , were successfully used to depth profile biopolymers [1], and recent reports have shown that C_{60}^+ ion beams can be used for depth profiling some organic samples [2,3].

This work aims at comparing the sputtering produced by either atomic or cluster ion beams for thin organic layers made of two different polymers: polystyrene (PS) and poly(methyl-metacrylate) (PMMA). For this purpose, 15 keV- C_{60}^+ and 15 keV - Ga^+ ions were used in the same ToF-SIMS equipment to sputter and analyse the same samples. They consisted in polymer layers produced with different thicknesses (40 -100 nm range) by spin -coating from solutions onto silicon wafers. For polystyrene, samples with different molecular weight distributions were investigated.

The ToF-SIMS results confirm that an important secondary ion yield enhancement is obtained for both polymers when C_{60}^+ ions are used. However, the influence of the integrated ion fluence is dramatically different for the two polymers. During the C_{60}^+ sputtering of the PMMA layer, after an initial decrease of the secondary ion yields, a steady state is observed for characteristic fragments. In contrast, for PS, an exponential decay of the characteristic fragment intensities is immediately observed, leading to an initial disappearance cross section that is even higher than the value observed for Ga^+ .

The results are discussed on the basis of the difference in the irradiation induced chemical modifications between the two polymers [4] and the difference in the sputter mechanisms between atomic and Buckminster fullerene bombardment, as highlighted by recent molecular dynamics simulations [5]. Fullerenes break upon impact and, due to the low energy per constituent atom, their penetration depth and the damage created in the subsurface region are strongly reduced.

In conclusion, our results confirm that the success of molecular depth profiling of polymers with C_{60}^+ beam is not universal but sample chemistry dependent.

[1] C.M. Mahoney; S. Roberson; G. Gillen, Appl. Surf. Sci. **231-232** (2004) 174

[2] J. Cheng; N. Winograd, Anal. Chem. **77** (2005) 3651

[3] J. S. Fletcher, X. A. Conlan, E. A. Jones, G. Biddulph, N. P. Lockyer, J. C. Vickerman, Anal. Chem. **78** (2006) 1827

[4] R. Möllers, N. Tuccitto, V. Torrisi, E. Niehuis, A. Licciardello, Appl. Surf. Sci. **252** (2006) 6509

[5] Z. Postawa; B. Czerwinski; M. Szewczyk; E.J. Smiley; N. Winograd; B.J. Garrison; J. Phys. Chem. B **108** (2004) 7831

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Characterization of Thin Polymer Films after Bi Cluster Ion Bombardment

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Relaxation of the static SIMS limit can increase the sensitivity of ToF-SIMS analysis and open the possibility for the depth profiling of organic materials if ion-induced damage accumulation in the sample is minimized. The effect of extended cluster ion bombardment on damage accumulation in thin polymer films has been studied for SF_5^+ [1] and C_{60}^+ [2] bombardment; however, these studies have not been performed for commonly used Bi cluster ions. In this study, the effect of Bi cluster ion bombardment of poly(methyl methacrylate), PMMA, and poly(octyl methacrylate), POMA, thin films was examined, these polymers having been shown to behave quite differently under SF_5^+ bombardment [3]. The effects of cluster size, primary ion dose, and polymer chemistry were characterized using ToF-SIMS, AFM, and XPS. Bi cluster ions showed significantly higher sputter rates and damage removal rates in comparison with Bi_1^+ , with PMMA faring better than POMA. Additionally, Bi cluster size and the chemistry of the polymer target significantly affected topography formation during sputtering. This study agreed with previous studies which showed that both the cluster size and sample chemistry affect sample stability under extended primary ion bombardment. Implications for sensitivity enhancement, depth profiling, and depth resolution will be discussed.

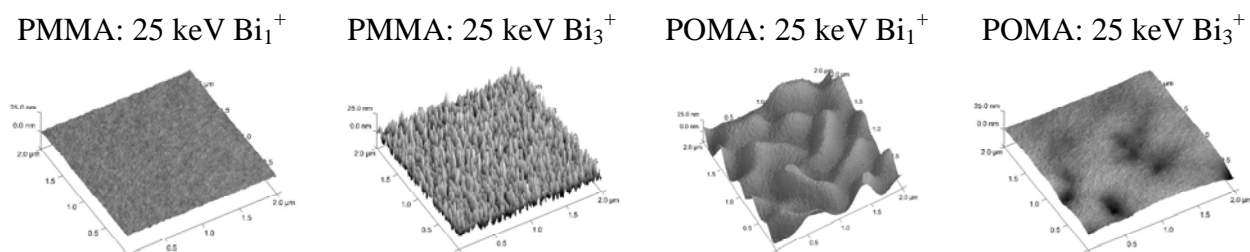


Fig. 1 – Tapping mode atomic force micrographs (topography) of thin polymer films after bombardment with 25 keV Bi_1^+ or Bi_3^+ (primary ion dose = 5×10^{13} ions/cm²).

[1] S. Roberson and G. Gillen, *Rapid Commun. Mass Spectrom* **12** (1998) 1303. E.R. Fuoco et al, *J. Phys. Chem B* **105** (2001) 3950. C.M. Mahoney, S.V. Roberson, G. Gillen, *Anal. Chem.* **76** (2004) 3199. M.S. Wagner, *Anal. Chem.* **76** (2004) 1264.

[2] D.E. Weibel et al, *Anal. Chem.* **75** (2003) 1754. C. Szakal et al *Appl. Surf. Sci.* **231-232** (2004) 183. R. Mollers et al, *Appl. Surf. Sci.* **252** (2006) 6509. J.S. Fletcher et al, *Appl. Surf. Sci.* **252** (2006) 6513. R.M. Braun et al, *Appl. Surf. Sci.* **252** (2006) 6615.

[3] M.S. Wagner, *Surf. Interface Anal.* **37** (2005) 53.

Invited

Molecular Depth Profiling Using Cluster Beams

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One of the great advantages of cluster ion beams in mass spectrometric surface analysis is that molecular surfaces can be investigated beyond the static limit. In many cases, high-fluence bombardment of organic solids with cluster projectiles does not induce the accumulation of chemical damage typical for atomic ions. As a consequence, molecular information can be preserved even if projectile fluences are applied which lead to significant removal of material from the bombarded surface. In fact, it was demonstrated that even the damage accumulated under previous atomic ion bombardment can efficiently be removed by subsequent cluster beam irradiation. Hence, cluster ion beams open the possibility of sputter depth profiling of molecular solids, a task which for long appeared virtually impossible. In combination with i) high lateral resolution provided by focused cluster ion beams and ii) atomic force microscopy investigating the topography of the eroded area, high resolution three-dimensional imaging of molecular species emerges as a new powerful application in SIMS. The talk will illustrate a few recent examples of such an analysis. In order to assess the prospects of the technique, we will then illuminate the underlying concepts by means of a simple model describing the erosion and damage dynamics of a molecular surface under cluster impact.

SF_5^+ Depth Profiling of Polymeric Materials

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Cluster primary ion sources have revolutionized the field of organic SIMS, allowing for significant enhancement in sensitivities (up to 1000-fold increases in signal), and in many cases decreased damage accumulation, therefore enabling 3-D compositional depth profiling through organic and polymeric layers. However, this technology still has several limitations for polymeric depth profiling. For example, some polymers are more amenable to depth profiling with cluster SIMS than others [e.g. poly(lactic acid) performs better than poly(methylmethacrylate) (PMMA)] while still others experience extensive beam-induced degradation (e.g. polystyrene and polyethylene) resulting in a complete loss of the characteristic secondary ion signal. More research is required to acquire a better understanding of the fragmentation mechanisms that result from interactions between polyatomic primary ion beams and various polymeric materials.

This talk will focus on the recent efforts at NIST to better understand the sputter process in polymeric materials. The effects of temperature will be revisited with new evidence describing the theory behind the observed effects [1,2]. In addition, the importance of polymer structure will be discussed. Figure 1 shows depth profiles taken at 3 different temperatures, -75 °C, 25 °C and 105 °C, of both atactic (Fig. 1a) and isotactic (Fig. 1b) PMMA. Similar to previous results, temperature effects were shown to be significant for atactic PMMA, yielding the least amount of damage accumulation at low temperatures, with evidence of ion induced depolymerization effects at high temperatures. Isotactic PMMA showed very little damage accumulation, even at room temperature, as evidenced by the relatively constant steady-state region in the profile. There was however a modest decrease in the interface width at low temperatures. This difference clearly illustrates the importance of polymeric structure in the depth profile process.

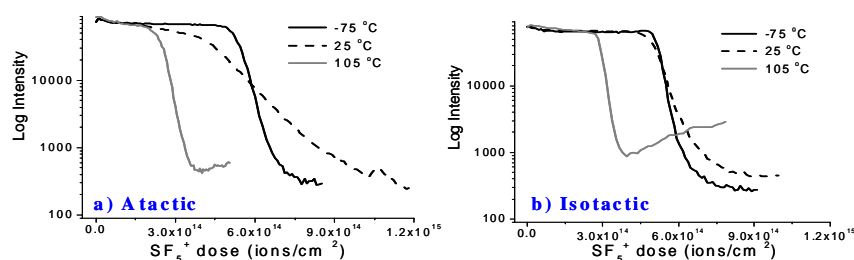


Fig.1: Plots of intensity (log scale) vs. SF_5^+ dose at varying temperatures for: a) Atactic PMMA, and b) Isotactic PMMA.

[1] Mahoney, C. M.; Fahey, A. J.; Gillen, G. Accepted for publication in *Analytical Chemistry*, 2007, 79.

[2] Mahoney, C. M.; Fahey, A. J.; Gillen, G.; Xu, C.; Batteas, J. D. Accepted for publication in *Analytical Chemistry*, 2007, 79.

C₆₀ Sputtering of Layered Organic Materials

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Sputter-depth profiling of organic layers using C₆₀ primary ions has been a major analytical development for technology applications from organic electronics to drug delivery systems. For analysts, it is essential to understand the mechanisms involved to optimize performance, interpret data, provide valid data and be aware of limitations. At the National Physical Laboratory we are conducting research to help address these issues. In this study we two types of molecular films of Irganox 1010 on a silicon wafer substrate using thermal evaporation. Firstly, a uniform layer of Irganox with controlled thickness and secondly, a novel "delta layer" system comprising of alternating layers of 2.5 nm of Irganox 3114 followed by 50 nm of Irganox 1010 [1]. The latter multilayers are a molecular analogue of the delta-layer systems used so successfully in the dynamic SIMS community to characterise many of the fundamental sputtering parameters. These two materials are employed to determine the energy dependence of sputtering yield, depth resolution and damage accumulation during C₆₀ depth profiling [1]. We show that sputtering yield increases with C₆₀ ion energy and that depth resolution concomitantly becomes poorer. The multilayers are also used to demonstrate how the depth resolution degrades with depth, as indicated in Fig. 1 below.

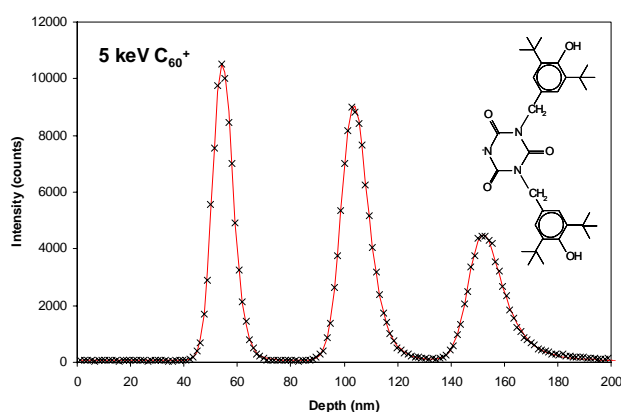


Fig.1 – Secondary ion intensity of a characteristic ion from 2.5 nm thick Irganox 3114 layers in an Irganox 1010 matrix. The red line denotes an analytical description.

[1] A. G. Shard, P. J. Brewer, F. M. Green and I. S. Gilmore, *Surf. Interface Anal.*, in press and available on line as an [early view document](#).

Invited

Do cluster primary ion beams advance the capability of bio-molecule analysis by SIMS?

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The analysis of bio-molecular systems using SIMS with atomic primary ion beams has been bedevilled by three principal limitations – the static limit, the inability to sputter large molecules intact and the very low ionisation probability.

The static limit, imposed because of the extensive bombardment induced chemical damage generated by high energy atomic primary ions, limits the amount of material accessible for analysis to 1% of the surface layer, greatly limiting detection sensitivity, the pixel size that can be usefully imaged and eliminating the possibility of molecular depth profiling. Atomic primary ions do not appear to be capable of sputtering intact organic molecules molecular weight much above 500 daltons in significant quantities. This places a major limitation on the value of SIMS in bioanalysis. Finally in common with all desorption mass spectrometries, the ionisation probability of the sputtered species is usually well below 10^{-3} , placing a further limitation on detection sensitivity and the useful minimum pixel size in SIMS imaging. It is clear that making progress into lifting some or all of these limitations would have a dramatic effect on the value of SIMS in bio-analysis.

Over the last 10 years the possibility that cluster primary ion beams would lift some of these limitations has been increasingly investigated. This paper will review the progress that has been made and will suggest that to fully exploit the benefits of cluster primary ions new approaches analysis may be required.

Depth Profiling Brain Tissue Sections with a 40 keV C₆₀⁺ Primary Ion Beam, from Salt Adducts to 3-D Imaging

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A particularly exciting development in SIMS is that some polyatomic primary ion beams allow the movement away from the traditional ‘static’ mode of analysis due to low damage accumulation with certain sample types. Projectile ions such as SF₅⁺ and C₆₀⁺ have enabled the depth profiling of organic layers without the loss of useful molecular signal from the spectrum, a problem seen with monoatomic beams. The combination of this avenue of interest and the continuing focus on studying the natural world has resulted in an exciting new direction for the technique, *the 3D imaging of biological samples*. Publications in this area are currently few [1-2], however interest is high; and thus systematic studies are required to characterise the behaviour of these sample types under this form of analysis.

Here we discuss the effect of high C₆₀⁺ primary ion dose on the chemical information that is available from the surface of a section of rat brain. Initial studies demonstrate the rapid loss of molecular signal from the bombarded area. Analysis of the data indicates a correlation between this effect and the appearance of sodium and potassium adducts of phosphate and protein fragments; this is supported by model systems. By using an ammonium formate wash to reduce the salt levels within the tissue this effect is removed, allowing the chemistry of the tissue section to be better probed. Results collected from multiple sections suggest that at room temperature under vacuum conditions there is a migration of lipids to the surface of the tissue, as reported by Sjövall et al. [3]. 3-D imaging is used to demonstrate that once these lipids are removed other species, such as proteins, are uncovered. By depth profiling the sample in a frozen state, the degree and importance of lipid migration to the observed localisation of native compounds is assessed.

This investigation into the behaviour of biological tissue under high C₆₀⁺ fluxes not only allows an evaluation of the potential accuracy of 3-D SIMS mapping of important biological molecules, but also demonstrates the possibility of using ion doses beyond the ‘static limit’ to provide higher secondary ion yields that could lead to greater detection limits within such analyses.

[1] G. Gillen; A. Fahey; M. Wagner; C. Mahoney; *App. Surf. Sci.* (2006), **252**, 6537-6541

[2] J. S. Fletcher; N. P. Lockyer; S. Vaidyanathan; J. C. Vickerman; *Anal. Chem.* (2007), In Press.

[3] P. Sjövall; B. Johansson; J. Lausmaa; *App. Surf. Sci.* (2006), **252**, 6966-6974

Challenges of 2 and 3D bio-analysis using cluster ion ToF-SIMS

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The use of cluster ion beams in ToF-SIMS analysis offers a considerable advantage over conventional monoatomic primary ion sources in many applications, none more so than the probing of biological systems. For such analyses the use of cluster ion beams such as Au_n^+ , Bi_n^+ and C_{60}^+ greatly enhance the ability to detect higher mass, more biochemically characteristic fragments. In a large number of cases the increased *efficiency* of these cluster and polyatomic ion sources can also aid in the generation of clear images by generating increased secondary in signal within a given pixel size.[1]

It has been demonstrated that the very high efficiency of beams such as C_{60}^+ , and to a certain degree SF_5^+ , can provide the ability to perform molecular depth profiling and that this concept has been developed further and has been used to perform 3D biochemical imaging of cell and tissue samples.[2,3]

Here we present a synopsis of what has been accomplished thus far, with a particular emphasis on the 3D imaging aspects, highlighting the challenges that need to be met as we move to image the chemistry of more and more complex bio-systems. Such challenges being both experimental, *i.e.* sample preparation and analysis conditions, but also computational where there is a need to aid interpretation and visualization the large data sets that are inevitably generated.

[1] Touboul D, Kollmer F, Niehuis E, et al. *J. Am. Soc. Mass Spectrom.* **16 (10)** (2005) 1608

[2] Fletcher JS, Lockyer NP, Vaidyanathan S, Vickerman JC, *Anal. Chem. In press.*

[3] Debois D, Brunelle A, Laprevote O, *Int. J. Mass. Spectrom.* **260 (2-3)** (2007) 115.

Invited

What's special about cluster ion beams?

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The emergence of cluster projectiles has certainly opened new ways to think about the ion/surface interaction problem. To varying degrees, bombardment of surfaces with cluster beams has led to enhancement of the yield of neutral species and the enhancement of the yield of ionized species. There is plenty of evidence that cluster bombardment at high fluences produces smooth surfaces both for inorganic and organic targets with no evidence for the formation of topography normally associated with atomic bombardment, and that depth profiling with high depth resolution is possible. Surface and subsurface chemical damage is generally greatly reduced using cluster projectiles opening the possibility of molecular depth profiling. And finally, with the advent of focused cluster beam sources, both 2-D and 3-D imaging experiments are possible using a variety of targets, especially biologically related ones. All of these properties are being addressed at this conference.

These special properties of cluster/solid interactions obviously change the rules of the game for traditional dynamic and static SIMS experiments. To properly take advantage of these properties, it is desirable to consider new instrumentation modalities. In this talk, the incorporation of a C₆₀ source into an orthogonal time-of-flight analyzer with tandem mass spectrometry capabilities will be examined in detail. This geometry is particularly suited to cluster beam experiments since it utilizes a dc ion beam, providing 4 orders of magnitude higher ion current over traditional tof experiments along with the possibility of better lateral resolution. Moreover, the mass resolution of about 10,000 is easily achieved with a mass accuracy of a few ppm, since the mass spectrometer is effectively decoupled from the desorption process. Several examples will be given that illustrate these features, particularly those involving bioimaging and a number of future experiments will be scoped out with preliminary data.

A Study of C₆₀-Sputtered Bulk and Thin Film Organics: Mechanistic Insights Using TOF-SIMS, XPS and Nanoindentation

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We have studied C₆₀ sputtering of organic materials for many years in conjunction with XPS which has led to a better understanding of optimum sputtering conditions. More recently, pulsed C₆₀ ion probes have been applied in the TOF-SIMS analysis of organic materials. The advent of C₆₀ sputtering in TOF-SIMS was initially driven by the analytical necessity to affect maximum enhancement in high m/z , molecular, or quasi-molecular ion formation. Sputtering of organic materials using a C₆₀ primary ion beam has been demonstrated to produce significantly less accumulated damage compared to sputtering with monatomic and atomic-cluster ion beams. This discovery has enabled molecular depth profiling of organic materials because the structural integrity of the organic analyte(s) remains, in many instances, virtually undisturbed. In this presentation we will introduce new data regarding TOF-SIMS depth profiles of C₆₀-sputtered organic materials. By combining the quantitative and chemical state information obtained by XPS with the structural information obtained by TOF-SIMS, a better understanding of the C₆₀ sputtering process emerges. The mechanical properties of the C₆₀-sputtered materials are also evaluated by nanoindentation as a function of primary ion energy and sputter depth. Preliminary observations concerning the correlations between chemical and mechanical properties as a function of sputter dose will also be discussed.

Molecular Depth Profiling of Alternating Langmuir-Blodgett Multilayers

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Cluster bombardment has resulted in reduced damage accumulation and less interlayer mixing, which makes it possible to achieve molecular depth profiling and potentially 3-dimensional imaging by SIMS. In order to investigate the depth profiling capability of the C₆₀ cluster ion source, we have made well-defined Langmuir-Blodgett (LB) multilayers with 2 molecules, 1,2-dimyristoyl-sn-glycero-3-phosphatidic acid (DMPA, MW = 593 g/mol) and arachidic acid (AA, MW = 312 g/mol), alternating in varying thicknesses. The LB films were successfully characterized by molecular ion peaks of both species as a function of depth. The interfacial width between DMPA and BA layers was calculated to be around 15 to 20 nm and increased with depth. The depth profile of LB films was performed at different C₆₀ kinetic energies and experimental temperatures and their effect will also be discussed in detail.

Invited

Cluster size effect on secondary ion emission

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Cluster ion beam has been developed for novel ion beam processing, such as shallow junction formation, surface smoothing, nano-fabrication and thin-film formation. Multiple collisions and high energy density collisions of cluster ions are responsible for “non-linear phenomena”, which play an important role in these processes. Large gas cluster ions, such as Ar or O₂ have been utilized recently as the primary ion beam for SIMS[1-4]. Cluster size is a unique parameter for cluster ions. One of the fundamental questions is what size of cluster is most suitable for each technique [5].

There are very few studies on the effect of cluster size on secondary ion emission. We have examined the effect of size on secondary ion emission with large cluster ions ($N > 100$) at the energy of about 100eV/atom by using the double deflection technique. When the total energy of the cluster ion is fixed, the secondary ion emission (SI) yield increases with size due to the non-linear effect. However, when the size of the cluster is too large, the SI yield decreases, because the energy per atom becomes too low to emit secondary ions. For instance, the maximum SI yield was observed for the Ar cluster with the size of a few hundred at the energy of 20keV. The size effect in secondary ion emission and the mechanism of non-linear phenomena will be discussed.

- [1] J. Matsuo, C. Okubo, T. Seki, T. Aoki, N. Toyoda and I. Yamada Nucl. Instrum. and Methods B, **219-220** (2004) 463-467
- [2] T. Aoki and J. Matsuo Nucl. Instrum. and Methods B, **242** (2005) 517-519.
- [3] S. Ninomiya, T. Aoki, T. Seki and J. Matsuo, Appl. Surf.Sci. **252** (2006) 6550-6553
- [4] S. Ninomiya, K. Ichiki, Y. Nakata, T. Seki, T. Aoki and J. Matsuo, Nucl. Instrum. and Methods B **256** (2007) 528-531
- [5] T. Seki, T. Murase and J. Matsuo Nucl. Instrum. and Methods B, **242** (2006)179-181

*This work is partially supported by the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

Shock-heating Phenomena in Impacts of Massive Electrosprayed Clusters

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The electrospray process can produce massive, highly-charged liquid clusters, or microdroplets that can be used as projectiles or can themselves carry analyte molecules. Massive cluster impact (MCI) was shown about 15 years ago to be capable of desorbing large biomolecules from liquid or solid surfaces [1] in an impact process best described as a shock-heating event [2]. More recently we have demonstrated that biomolecule analytes dissolved in electrosprayed microdroplets can be liberated and desolvated when the cluster is vaporized in a supersonic impact on a solid surface [3]. Experimental results will be described together with a molecular dynamics simulation that clearly illustrates the shock heating and disintegration of a large cluster in a supersonic impact.

[1] J.F. Mahoney, J. Perel, S.A. Ruatta, P.A. Husain, T.D. Lee, *Rapid Commun. Mass Spectrom.* **5** (1991) 441-115

[2] J.F. Mahoney, J. Perel, T.D. Lee and P. Williams, *J. Am. Soc. Mass Spectrometry*, **3** (1992) 311-317

[3] S.A. Aksyonov and P. Williams, *Rapid Commun. Mass Spectrom.* **15** (2001) 2001-2006

Invited

Massive projectiles for the characterization of surfaces

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We report on SIMS experiments with massive projectiles, specifically Au_n^{q+} (where: $100 \leq n \leq 400$; $q = 1 - 4$) with impact energies of up to 136 keV. The observations were made in the event-by-event bombardment-detection mode with identification of negatively charged ejecta from single projectile impacts. The bombardment of vapor deposits of phenylalanine, glycine, histidine, guanine generates secondary ions, SIs, with yields of up to ~ 100%. SI multiplicities are in the order of 5 to 10. Probabilities of co-emission of two molecular ions are in the range of 10 %. A distinct impact regime prevails, the projectiles are implanted as virtually intact nanoparticles. The impact causes ultra-fast chemistry evidenced with a new mode of synthesis of Au-adducts where a single projectile is the source of energy stimulating the emission and the donor of Au atoms. The features of “nanoparticle-SIMS” are those intrinsic to a single projectile impact. The deposition of a high density of energy within picoseconds is key for the emission of fragment and molecular ions. The volume sampled (~ 10-20 nm in diameter, ~ 5 nm in depth) delineates the probability of molecular signals as a function of molecular size.

Ion emission of solids under gold clusters bombardment with various sizes and energies

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The use of polyatomic ions increase considerably the energy density deposited in the first nanometers of solid. It results an extraordinary amplification of sputtering phenomena of surface [1] with in particular an intense emission of ions characteristic of the species present on the surface. Recent studies showed the interest of the clusters, in particular gold clusters Au_n^+ , to increase the sensitivity in TOF-SIMS analysis [2,3]. The VAN DE GRAAFF 2.5 MV accelerator of the IPN of Lyon was equipped with a LMIS source of gold clusters. We used Au_n^+ clusters of various sizes ($n = 1-9$) and of energy ranging from 17 to 230 keV/atom. The secondary ions were detected by a time of flight mass spectrometer (direct ToF) equipped with the multi-anode detector LAG 256 of the IPNO. This detector allows us to measure the multiplicity distribution of the ions emitted each impact. The targets were thin films (200 nm) of phenylalanine and (100 nm) of Cesium iodide deposited by evaporation on an aluminum substrate. In all the cases we observed a strong non-linear dependency on the ion emission yield Y with the size n of the clusters projectiles ($Y \sim n^\alpha$; $2 < \alpha < 3$). We found for example that one impact with Au_9^+ can eject on average 4 phenylalanine molecular ions $(M-H)^+$ while this yield is only about 0.05 for Au^+ projectile. In addition the mass spectra obtained under cluster bombardment show the emission of ions with much higher masses (up to 6000 Da). The emission yields increase with the clusters energy and reach a maximum located at around 100 keV/atom.

[1] S.Bouneau, A. Brunelle, S. Della Negra, J. Depauw, D. Jacquet, Y. Le Beyec, M. Pautrat, M. Fallavier, J.C. Poizat, H.H. Andersen. Phys. Rev. B 65, 144106 (2002).

[2] M. Fallavier, R. Kirsch, S.N. Morozov, J.C. Poizat, J.P. Thomas, N. Wehbe. Phys. Rev. B 68, 140102(R) (2003).

[3] Wehbe nimer ,Ph.D. Thesis, Université Claude Bernard Lyon 1, 2006.

**44th IUVSTA Workshop: Sputtering and Ion
Emission by Cluster Ion Beams**

23rd – 27th April 2007

Barony Castle, Edinburgh, Scotland, UK

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Poster Abstracts

Bio-imaging of Skin Tissues Using Cluster Ion Beams

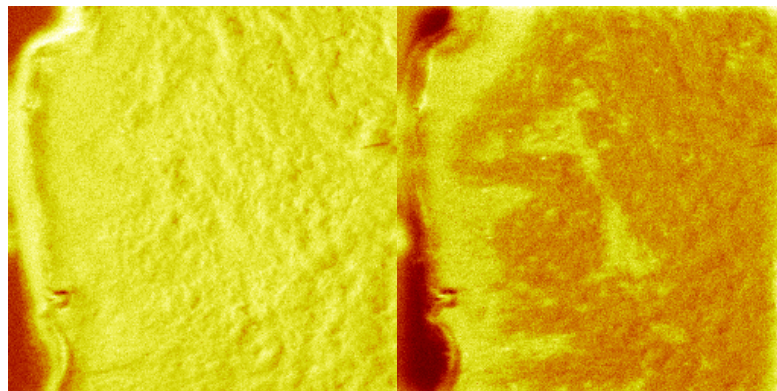
Dae Won Moon^{*,1}, Hyun Kyon Shon¹, Tae Geol Lee¹, Won Woo Choi² and Jin Ho Jung²

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Cross-sectional TOF-SIMS images of human skin tissues were obtained by using Bi cluster ion beams to study photoaging and chronological aging effects. There were significant changes in the TOF-SIMS images of fragments from lipid molecules and amino acid fragments from peptides due to UV-irradiation and chronological aging. These changes were consistent with previous results reported by dermatologists [1-2]. To remove the surface contamination layer and the damaged layer due to sectioning, Bi or C₆₀ re-sputtering were used to study the difference. For detailed understanding of the sputtering process of tissue bio-specimen with cluster ion beams of Bi and C₆₀, the crater bottoms were surface analyzed with micro-XPS, AES, and AFM, respectively. Details of sample preparation effects and mass calibration for TOF-SIMS imaging of skin tissues, medical information that can be extracted from the SIMS images, and relevant problems are discussed.



(A) before C₆₀ sputtering (B) after C₆₀ sputtering

Fig.1 – Effect of C₆₀ sputtering on TOF-SIMS images of a skin tissue.

[1] Y. Uchida et. al, The J. of Investigative Dermatology, 120, 662 (2003).

[2] G.J. Fisher et. al, Arch Dermatol, 138, 1463 (2002).

The preferential sputtering of DNA molecule on HOPG surface by the Ar cluster ion beam

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We demonstrate the Ar gas cluster ion beam (GCIB) induced sputtering of DNA molecule on HOPG surface. The Ar cluster beam was generated by the free jet expansion from the laval-type nozzle and accelerated in the electric field of 2~10 kV after ionized by the electron impact. The typical cluster size of Ar-GCIB is 750 atoms/cluster and its FWHM is 1000 atoms/cluster. Figure 1 shows the scanning tunneling microscopy (STM) images of the DNA on HOPG before (a) and after (b) irradiation of Ar-GCIB of 2.5×10^{11} ions/cm² at the acceleration energy (E_a) of 10 keV. After irradiation, the constituent part of DNA and the crater like defects was observed on the surface. Figure 2 shows the STM image of the DNA on HOPG after irradiation of Ar-GCIB of 2.5×10^{13} ions/cm² at $E_a=2$ keV. In this case we observed no constituent part of DNA. And noticeably, the HOPG surface maintained its lattice structure with no defects. These results indicate that the DNA molecules are sputtered preferentially from the surface by the 2-keV-Ar-GCIB. We discuss these experimental results from the view point of the kinetic energy of a constituent atom of the cluster ion.

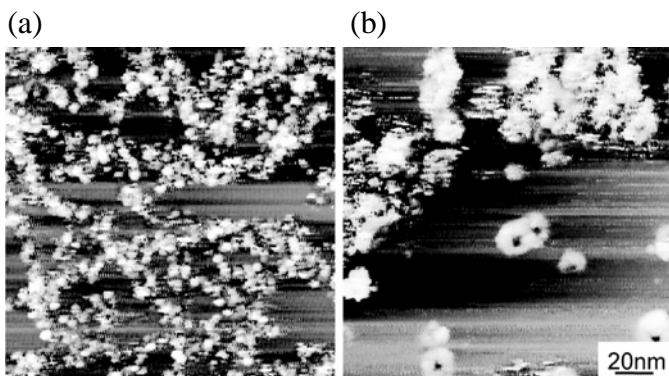


Fig. 1 – STM image of plasmid DNA on HOPG surface: (a) before irradiation of Ar-GCIB; (b) after irradiation of 10-keV-Ar-GCIB of 2.5×10^{11} ions/cm².

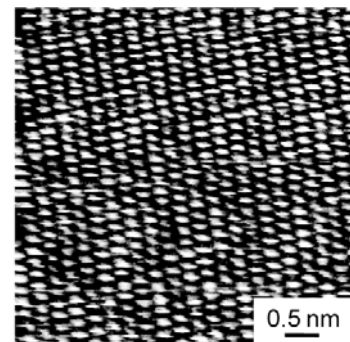


Fig. 2 – STM image of the sample surface after irradiation of 2-keV-Ar-GCIB of 2.5×10^{13} ions/cm².

**Secondary ion mass spectrometry under gold clusters bombardment:
influence of the cluster size and energy on the ion emission yield of the
phenylalanine**

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The ToF-SIMS analysis sees currently an enormous change with the introduction of the cluster as surface probe technique. The VAN DE GRAAFF 2.5 MV accelerator of the IPN of Lyon was equipped with a LMIS source of gold clusters. The cluster beams are mass sorted by magnetic analysis after acceleration, which leads to beam intensities much higher than those of SIMS apparatuses. We used Au_n^+ clusters of various sizes ($n = 1-9$) and of energy ranging from 17 to 230 keV/atom. The secondary ions were detected by a time of flight mass spectrometer (direct ToF) equipped with the multi-anode detector LAG 256 of the IPNO. This detector allows us to measure the multiplicity distribution of the ions emitted each impact. In order to compare the various cluster projectiles, all mass spectra were measured with the same number of cluster projectiles (10^5) and a fluence of about 5×10^8 projectiles/cm² thus under static SIMS conditions. The targets are thin films (200 nm) of phenylalanine deposited by evaporation on an aluminum substrate. The strong nonlinear effects characteristic of cluster impacts were quantified for the emission of the molecular ion $(M-H)^-$ of which the yield follows an n^2 dependency law. One Au_9^+ cluster eject on average 4 $(M-H)^-$ ions whereas an Au^+ ion of the same velocity was not able to eject more than only 0.05. In addition the mass spectra obtained under cluster bombardment also show the dimers and trimers emission $(M_2-H)^-$ and $(M_3-H)^-$ respectively. The emission yields increase with the clusters energy and reach a maximum located at around 100 keV/atom.

Increased sensitivity and quantification in SIMS by ion cluster bombardment with simultaneous cesium deposition?

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Owing in particular to its excellent sensitivity, its high dynamic range and its good depth resolution, Secondary Ion Mass Spectrometry (SIMS) constitutes an extremely powerful technique for analyzing surfaces and thin films. Up to now, the high sensitivity of SIMS analyses is guaranteed by bombarding the sample with an energetic beam of reactive ions (cesium and oxygen). For analyses requiring a good depth resolution, the beam energy has however to be lowered considerably in the sub-keV range. This lowering of the energy of the sputtering beam has important effects on the concentration of reactive species introduced into the sample and thus on the sensitivity of the analysis. By using in-situ Cs deposition with simultaneous non-Cs ion bombardment on SAM's CMS [1], sputtering has been decoupled successfully from Cs incorporation and quantitative analysis in the MCs_x^+ [2-4] and M^- [5-7] modes have been obtained. Up to now, sputtering has been realized by monatomic ion bombardment, resulting in low sputtering rates in the sub-keV range. This problem of low sputter rates can be circumvented by using cluster ion bombardment. However depth resolution and roughness formation have not been investigated in depth. A combination of cluster ion bombardment (for optimum erosion rates) and neutral cesium deposition (for high sensitivity and quantification) should open very interesting perspectives.

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X-ray Photoelectron Spectroscopy Study of Cluster Ion Beam Sputtered Organic Polymer Surfaces

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Chemical analysis of buried interfaces is of great interest by polymer and bio-material scientists. X-ray Photoelectron Spectroscopy (XPS) is being asked to provide detailed information on chemical composition of buried interfaces and thin films beneath the contaminated surface. We have applied buckminsterfullerene (C₆₀) ion beam sputtering to depth profiling and surface cleaning for XPS of organic polymers [1]. Initial investigations indicated that quantitative analysis of many organic polymers was promising. Sputter rates for some organic polymer were measured and proved to be 5 to 20 times faster than that for SiO₂. On the other hand, residual carbon was observed after sputtering with C₆₀ ion beam. The amount of residual carbon was affected by both incident angle and acceleration energy of the ion beam.

In this study, we examined the optimal sputtering conditions to reduce the amount of residual carbon which would interfere depth profiling, and also investigated the distribution of the residual carbon in samples for more precise data analysis.

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Cs/C₆₀ Depth Profiling of Inorganic-Organic Hybrid Thin Films

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Cs/C₆₀ depth profiles using Bi_n^{x+} (n=1, 3, 5 and x=1, 2) analysis beams were obtained from inorganic-organic hybrid thin films, which were fabricated by repeated 7-octenyltrichlorosilane (7-OTS) SAMs/TiO₂ molecular layer deposition under vacuum. Significant differences were observed in Cs depth profiles but not in C₆₀ depth profiles, as a function of primary analysis beams. For closer examination, sputter craters were also investigated using x-ray photoelectron spectroscopy and atomic force microscopy. Based on TOF-SIMS depth profiles, XPS and AFM data, we discuss how to perform proper depth profiling for inorganic-organic hybrid thin films.

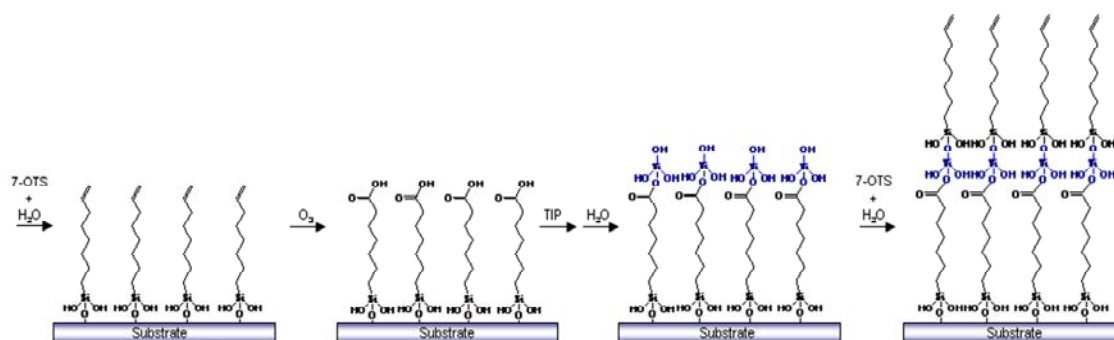


Fig.1 – Schematic diagram of layer-by-layer synthesis of SAMs.

Testing of Ultra-Low Energy Gold Cluster Ion Beams for SIMS Applications

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By now SIMS depth profiling has evolved to encompass the use of low-energy ions (<500 eV) to achieve the nm-scale depth resolution as a result of the reduced atomic mixing and altered layer thickness. Currently, a generation of intense and well focused low energy ion beams is achieved on commercial SIMS instruments using devices such as the floating low energy ion gun (FLIG) [1]. To further extend the performance of SIMS tools in the future, it is interesting to consider using cluster projectiles of heavy elements (like the Au_m^- ions) instead of atomic projectiles or light diatomic ones such as O_2^+ . However, the question of how effective the gold cluster ions might be for the SIMS depth profiling as well as for the other applications still remains open.

Here we describe the first test results from a combination of a sputter cluster ion source [2] modified for the generation of low energy gold cluster ion beams and a FLIG ion column similar to that used on the Cameca 4500/4550 quadrupole instruments and EVA 2000 at Warwick. Data on performance and sputtering behaviour will be presented.

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Artifacts in the Sputtering of Silicon by C_{60}^+

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Despite major efforts in the field, the mechanism behind sputtering using cluster ion beams is not yet well understood. Successful SIMS depth profiles have been obtained using C_{60} on a wide variety of organic materials. However, there are issues with the degradation of depth resolution caused by the development of topography, and the deposition of carbon on the surface, which are time and fluence dependent [1,2]. Conflicting theories currently exist on the identity of the deposited material on the bombardment of silicon by C_{60} , with evidence suggesting it may be amorphous carbon [2] or silicon carbide SiC [3]. There is as yet no explanation on the amount of deposition one should expect, and why C_{60} is able to sputter through some material but not others. Basic metrology and understanding of C_{60} sputtering is urgently required if its potential analytical capabilities in organic depth profiling for novel systems, such as organic electronics and drug delivery, are to be realised.

In the present study, we used a simple silicon wafer to understand the basic issues in C_{60} sputtering. We measured the sputtering yield of silicon by C_{60}^{n+} , over a range of impact energies from 5 – 30 keV, by sputtering a number of micro craters on to the surface and measuring their volumes using atomic force microscopy. At higher energies, the sputter yield is found to agree with the thermal spike model and varies roughly linearly with energy. As the impact energy is reduced, topography formation becomes increasingly pronounced at the bottom of the craters, and below a threshold energy of 9 keV net deposition of carbon occurs on the surface. Analysis of the bottom of a 12 keV crater using imaging SIMS with Bi^+ primary ions shows a significant enhancement of carbon clusters C_n^- as well as $Si_nC_m^-$. Depth profiling was also performed, showing a gradual, mixed layer. From this, we show that the thickness of this interface layer to be around 10 nm, in good agreement with the height of topographic features measured in AFM.

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Kinetic Energy Distributions of Secondary Ions Emitted From Metal and Organic Surfaces under Au, Au₃ and C₆₀ Bombardment

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A reflectron time-of-flight analyzer was detuned to act as a low-pass energy filter for the measurement of kinetic energy distributions of atomic and molecular ions sputtered from indium and polyethylene terephthalate (PET) surfaces under atomic and cluster ion bombardment. We report the kinetic energy distributions of various atomic and molecular secondary ions resulting from bombardment with 20 keV Au and Au₃ and with 20-120 keV C₆₀. The resulting distributions are shifted to lower kinetic energy from Au to Au₃ and lower still for C₆₀ projectiles. This shift towards lower kinetic energy with increased nuclearity of primary projectile may in part be responsible for the observed increased yield of intact high mass molecular ions with polyatomic ions [1]. Closer examination of the data reveals that for Au and Au₃ sputtering, higher mass secondary ions have a lower leading edge to the kinetic energy distribution compared to lower mass secondary ions. However C₆₀ sputtering results in identical energy distributions throughout the observed secondary ion mass range. We will discuss these observations in the context of the underlying sputtering mechanisms.

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Substrate effects on the analysis of biomolecular layers using Au^+ , Au_3^+ and C_{60}^+ Bombardment

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The enhancement in secondary ion yield observed under cluster and polyatomic ion bombardment is generally most dramatic when analyzing bulk molecular materials [1]. For thin molecular films on atomic substrates, experimental studies [2] and molecular dynamics simulations [3] have shown the importance of substrate properties in determining secondary ion yields under atomic (Au^+ , Xe^+) and cluster (Au_n^+ , SF_5^+) ion bombardment. The mechanism of enhanced sputtering has been linked to the characteristics of the energy deposition in the near surface region. We report an extension to this work, including biomolecular films (cyclosporin A, cholesterol and a phospholipid) supported on atomic and molecular substrates (Pt, Si, graphite, PET) bombarded with atomic, cluster and polyatomic projectiles (Au^+ , Au_3^+ and C_{60}^+). Under Au_n^+ bombardment thin film samples exhibit an increased ion yield on a Pt substrate whereas for C_{60}^+ the highest yield is observed with PET substrates. The lowest secondary ion yields are observed on graphite substrates. When samples are applied as thick, multilayer films the observed secondary ion yields are independent of the substrate and increase with nuclearity of the primary ion in agreement with previous studies.

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