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Cluster Ion Beam Processing: Review of Current and Prospective Applications

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ABSTRACT

Cluster ion beam processes which employ ions comprised of a few hundred to several thousand atoms are being developed into a new field of ion beam technology. The processes are characterized by low energy surface interaction effects, lateral sputtering phenomena and high-rate chemical reaction effects. This paper reviews the current status of studies of the fundamental cluster ion beam characteristics as they apply to nanoscale processing and present industrial applications. As new prospective applications, techniques are now being developed to employ cluster ions in surface analysis tools such as XPS and SIMS and to modify surfaces of bio-materials. Results related to these new projects will also be reviewed.

INTRODUCTION

In cluster ion beam bombardment of solid surfaces, the concurrent energetic interactions between many atoms comprising a cluster and many atoms at a target surface result in highly non-linear sputtering and implantation effects. Following successful accomplishment in 1988 of intense beams of gas clusters from small nozzles at room temperature, an extended series of investigations was conducted at Kyoto University and at the University of Hyogo to develop gas cluster ion beam (GCIB) fundamentals and applications [1].

By 1995, it was recognized that it would not be practical to use substantially greater gas flows in order to increase cluster ion beam currents to the levels to be required for production processors. No other groups or institutes in the world had yet paid attention to the concept of cluster ion beam equipment and to possible uses of gas cluster ions for surface processing. In collaboration with the author's group (IY) at Kyoto University, in support of work sponsored by the Japan Science and Technology Agency (JST), Epion Corporation in the US began development of commercial GCIB equipment in 1995 [2]. Efforts to increase cluster generation, to improve efficiency of cluster ionization, and to optimize beam transport without increasing gas consumption or pumping requirements, were successful. Cluster ion beam currents of several hundred microamperes on target became possible with source gas flows that could be handled by standard vacuum pumps. Commercial GCIB equipment by Epion was introduced in 2000.

Historically, cluster ion beam processing efforts expanded into two different but closely related major categories: gas cluster ion beam (GCIB) processing and polyatomic ion beam processing. GCIB has become useful in a number of nanotechnology areas by employing its unique characteristics of very low effective energies, its lateral sputtering effects and its high chemical reactivity effects. Polyatomic ion beam technology investigations were initially started during the early GCIB research in order to experimentally demonstrate the low energy interaction effects which are associated with bombardment by multiple atom particles. Because a GCIB beam contains a wide range of cluster sizes, typically from a few hundred atoms to many thousands of atoms, it had during early investigations been difficult to quantitatively describe the dependence of low energy interaction effects upon cluster size. In order to obtain clear experimental evidence, it was desirable to use cluster ions of a single specific number of atoms per cluster. The idea then emerged to use a molecular ion consisting of a relatively large number of primary atoms of one single element. The polyatomic material candidate selected was decaborane ($B_{10}H_{14}$) which consists of 10 boron atoms bonded together by low mass hydrogen atoms. Note that a GCIB system equipped with a cluster size selection system had not yet been developed at that time. As the research proceeded, experimental implantation of decaborane ions into Si showed clearly that the effective energy of each boron atom of a polyatomic cluster ion is essentially equal to the total energy of the cluster divided by the number of boron atoms contained in the cluster. As the research continued, successful fabrication of a P-MOSFET with 40 nm gate was accomplished for the first time in 1996 [3].

In order to develop commercial polyatomic cluster ion implantation equipment, the author (IY) arranged JST sponsorship for a "risk-taking technological development project" (in Japanese, Itaku-Kaihatsu) which started in 1998 at Sumitomo Eaton Nova. The program was selected from among candidates involving JST held patents which originated from university research projects where patented technology was considered to have high probability of being successfully developed for practical use and for promoting further research. The risk-taking contract ended in 2001, but the technology was not yet fully developed and serious concerns still existed regarding whether the aggregate atoms from molecular clusters could be adequately annealed into substitutional sites and whether end-of-range effects and transient enhanced diffusion issues could be overcome. Further collaboration was subsequently made between Kyoto University, Nissin Ion Equipment Co., Ltd. and Fujitsu under JST support. This project was started in 2003 and was successfully completed in 2005. The resulting polyatomic ion implantation concept has become a major low energy processing method for ultra-shallow junction formation.

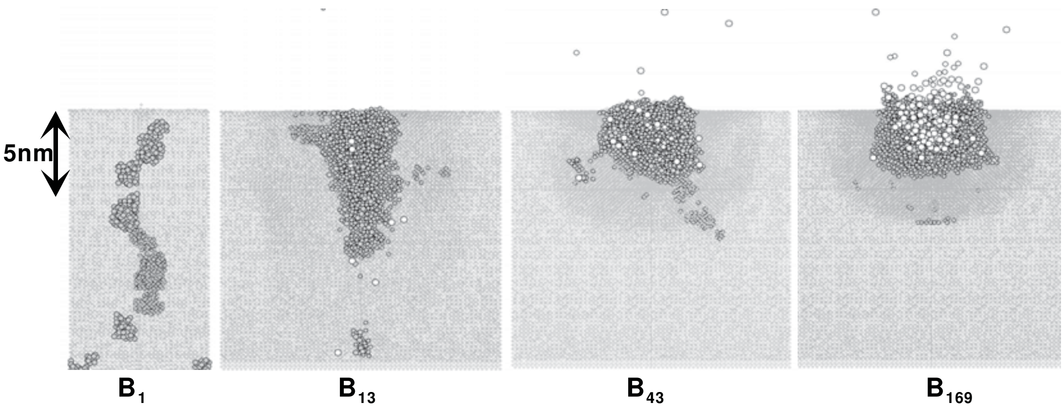

Figure 1. MD simulation results of atomic and cluster Boron ion implantation into Silicon at 7keV after 385fs.

Over the 20 years of cluster ion beam investigations, low energy surface interaction effects, lateral sputtering phenomena and high-rate chemical reaction effects were explored experimentally and were explained by means of molecular dynamics (MD) modeling [4]. The fundamental results concerning ion/solid surface interactions have become useful and valuable information and they have become a base for a considerable amount of application technology. Cluster ion beams which have such distinctive characteristics have been applied for nanoscale processing such as shallow junction formation, low damage surface modification and etching, ultra-smooth surface formation and high quality thin film formation.

A fundamental question in cluster ion interactions, as compared to interactions by traditional atomic and molecular ions, was how large must a cluster ion be in order for it to produce non-linear effects during bombardment of a solid surface? The answer became clear when theoretical modeling done in 1996 by Takaaki Aoki was able to correctly predict the experimental observations [5]. Figure 1 shows MD modeling snapshots of monomer (B_1), small cluster (B_{13}) medium cluster (B_{43}) and large cluster (B_{169}) ions impacting at 7 keV onto crystalline Si at an elapsed time of 385fs following impact. The results of these simulations have shown that cluster-like bombardment phenomena, ie. the nonlinear effects which are typical of cluster impact, are already evident at a size of 13 atoms. The result for B_{13} does exhibit concentration of displacement damage, but damage from larger gas clusters is seen to be much more concentrated and more localized. It was predicted that complete self-amorphization resulting with cluster impact could help cause better solid phase epitaxy during low temperature annealing.

Recent successful industrial applications of GCIB are for fabrication of thin film transistors (TFT) using the low energy effect [6], for local corrective etching in bulk acoustic wave devices using the lateral sputtering effect [7] and for surface planarization of patterned hard disk drive (HDD) media using the low energy and lateral sputtering effects [8]. In these applications, nanoscale dimensional precision has been achieved, for example in formation of shallow junctions of depths less than a few nm, and in smoothing of surfaces to roughness less than 1 nm. Figure 2 illustrates some of the milestones of GCIB equipment and process development.

New GCIB applications are now being developed, for example in shallow surface analysis

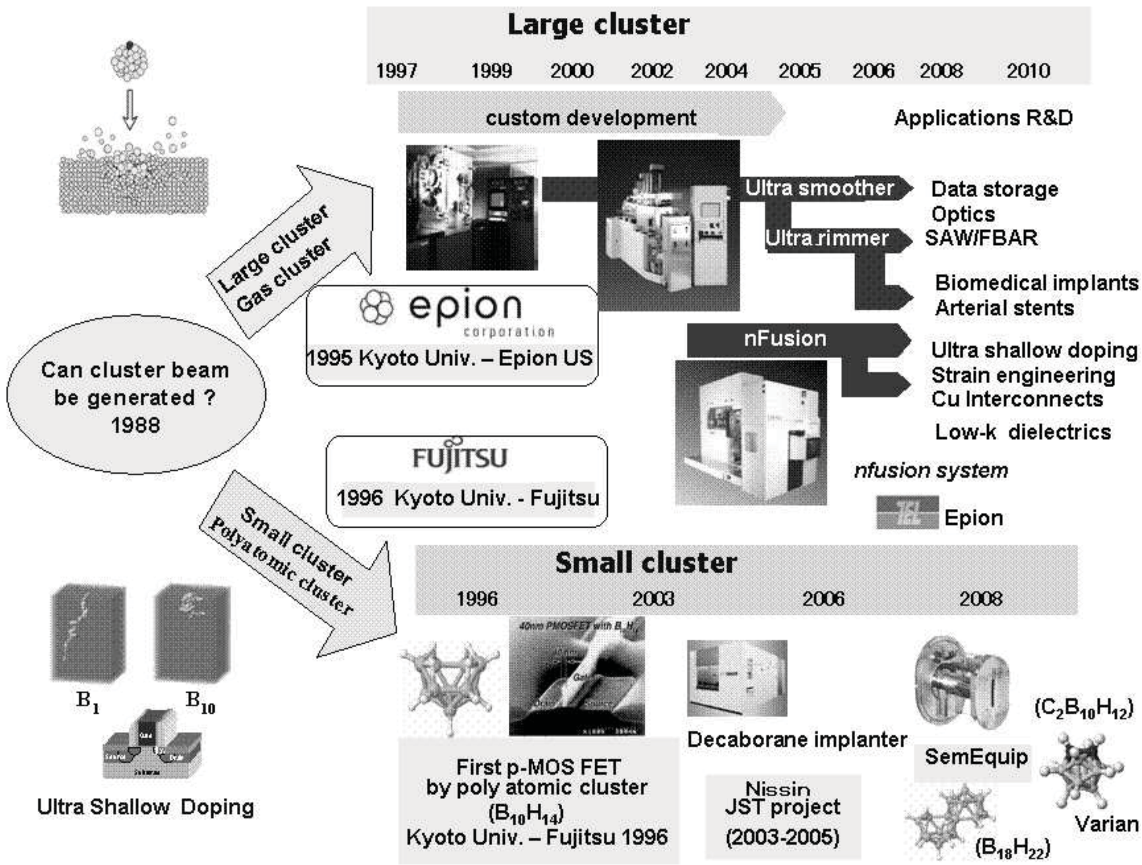

Figure 2. Development history of industrial cluster ion beam equipment

techniques such as XPS and SIMS. Because a large cluster can sputter from a much shallower volume of material than in the case of a smaller projectile, GCIB can be beneficially employed to accomplish extremely surface-sensitive analyses of organic thin films. Another new area of application is in surface modification of bio-materials. It has been shown by Exogenesis Corporation in the US that GCIB modification of medical device materials such as titanium can greatly enhance osteoblast proliferation and bone formation. Exogenesis has also demonstrated a novel method of drug delivery from metal vascular stents in which GCIB is employed to control rate of drug elution without requiring the use of any binding polymer.

This paper reviews some of the present industrial nano-scale applications of GCIB and discusses new results related to surface modification of bio-materials.

APPLICATIONS TO NANOSCALE PROCESSING

Ability to modify ultra-thin surfaces under extremely low damage conditions and with nanometer precision has become important in recent device fabrication. The METI (Japanese Ministry of Economy and Trade and Industry) R&D Program & Technology Strategy Map has been published as a tool for strategic planning and implementation of R & D investment in several industrial areas [9]. METI roadmaps published in 2007 through 2010 have recommended cluster ion beam processing for uses in the nanotechnology fields of next-generation semiconductor devices (TFT's of Si, SiC, GaN), data storage devices (HDD, MRAM, MEMS), sensors and transducers, extremely small optical lenses, photonics devices, etc. In working upon such industrial applications, the capabilities and limits of GCIB relative to smoothing, surface damage and nm-depth etching have become recognized.

Extremely smooth surface processing

Lateral sputtering is an important characteristic of GCIB which is not associated with other atomic and molecular ion beam processes. During early investigations it was found that GCIB can produce surface smoothing of many materials, such as CVD diamond, glasses and metals, even when its etching rate in these materials is greater than that of monomer ion beams by two to three orders of magnitude [2]. Because GCIB is an energetic beam process, it was reasonable to expect that it might not be able to produce smoothing to sub-nanometer levels, but on the contrary it has been shown to offer excellent ability to smooth to such levels.

The limits of the ability of GCIB for surface smoothing have been evaluated for many applications, for example, in planarization of a HDD surface. In order to increase the capacity of a HDD, discrete track media (DTM) and bit patterned media (BPM) are being developed [8]. However, for these approaches, nano-level smoothing and planarization of the patterned media are required. To utilize GCIB to achieve such accurate nano-level surfaces, the lateral sputtering behavior of GCIB processing can be employed. For evaluation purposes, test substrates with several different line-and-space patterns were used. The substrates were made by nano-imprint lithography on CVD-deposited TiCr films. The substrate groove intervals were 100 nm and the depth of each groove was 18 nm. Figure 3 shows AFM images of the surface patterns after irradiation by GCIB at 20 keV and by monomer ions at 400 eV. Before the irradiations, the roughness, Ra, was 2.47 nm and the P-V (peak-to-valley) value was 4.75 nm. After the GCIB irradiation, surface roughness Ra was reduced to 0.46 nm and P-V value was reduced to 0.50 nm. The identical sample irradiated by the Ar monomer ion beam resulted in surface roughness Ra of 0.9 nm and P-V of 2.88 nm. This example exhibits the capability of GCIB irradiation for decreasing surface roughness even in the sub-nm region. In order to investigate the dimensional range characteristics of smoothing effects produced by GCIB, atomic force microscope (AFM) examinations have been made on Ar-GCIB bombarded amorphous carbon film line & space patterns with groove intervals from 100 to 400 nm [10]. Spatial wavelength dependence of the reduction in roughness caused by the GCIB exposures was studied using the power spectrum of the AFM images. As is shown in figure 4, the reduction of power spectrum intensity decreased monotonically with decreasing groove interval and was particularly remarkable at spacings below 200 nm. Because surface planarization by GCIB is dominated by the lateral motion of atoms induced by individual cluster ion impacts, structures with very small spatial dimensions are removed preferentially.

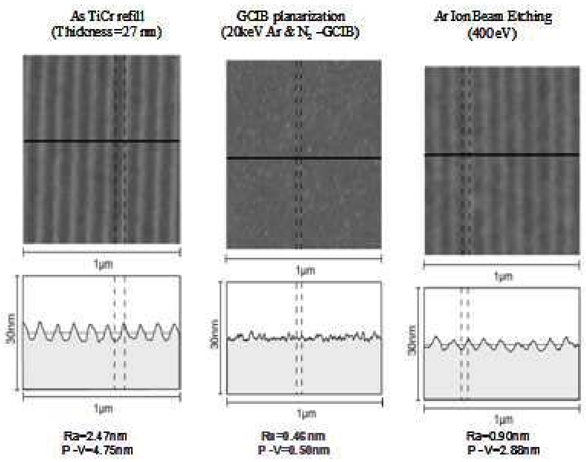

Figure 3. AFM images of surfaces before irradiation, after GCIB irradiation and Ar monomer ion irradiation.

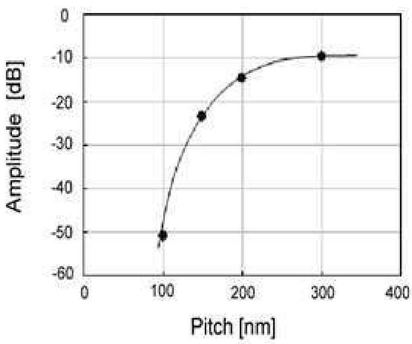

Figure 4. Power spectra of AFM images after GCIB irradiation.

Precise nanometer depth etch processing

Precise nm-depth etching utilizing the low energy effects of GCIB bombardment is becoming important in various industrial applications. To achieve such etching, the inherent GCIB character which combines a low energy bombardment process with the above mentioned lateral sputtering behavior seems to be unique among existing technologies. In conjunction with its low energy effects, GCIB can deliver a highly directional and controllable energetic chemical beam. These characteristics have been employed by Epion Corporation in several distinct nm-processing areas, for example in fabrication of Film Bulk Acoustic Resonator (FBAR) filters, EUV masks, OLED (Organic Light Emitting Diode) displays, etc [11]. An important approach to applying GCIB processes has been incorporation of a Location Specific Processing (LSP) control system which utilizes a scanning capability in which the dwell time is varied as a function of the amount of material to be removed at any specific location. A wafer metrology map is imported into the LSP control system to define the functional relationship between x,y position on the wafer and required etching depth. LSP is now being utilized in several surface smoothing applications such as production of large Si wafers, MEMS, and small molds for optical lens fabrication, etc.

Through cooperation between Epion Corporation in the US and EPCOS AG in Munich, Germany, FBAR processing using GCIB-LSP has been successfully developed. Operating frequencies of FBAR filter devices depend very critically upon thickness of a piezoelectric material (AlN) surface layer and adequate frequency uniformity across individual wafers and from wafer to wafer is difficult to achieve. In order to achieve increased production yields, GCIB-LSP is used to remove precisely controlled amounts of surface material in patterns which are adjusted for each individual wafer [7]. As shown in figure 5, a reduction of width of frequency distribution by factor of 5 over a typical 200 mm substrate area has been reported. Piezoelectric quality of the highly textured, polycrystalline, c-axis oriented columnar surface film is not affected by the GCIB exposure.

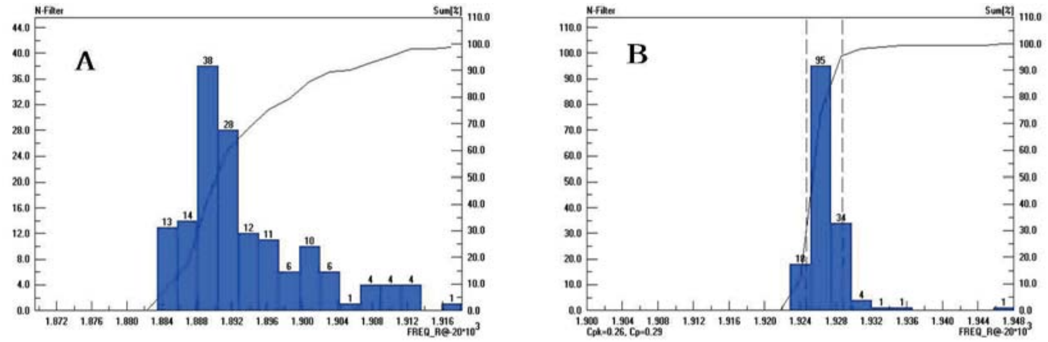

Figure 5. Frequency distribution of FBAR before (a) and after (b) GCIB etching.

Extremely low energy processing

After the characteristic low energy behaviors of GCIB were first experimentally demonstrated in 1993 [12], GCIB received attention from the nanotechnology community for various potential uses in semiconductor, magnetic, and optoelectronic devices. In addition to its characteristics for surface processing GCIB also became of interest for its secondary electron and ion emission characteristics.

In 1999, N. Toyoda described the dependence upon bombarding ion velocity of secondary ion yields from Au surfaces impacted by C cluster ions of size n (n=1, 7, 9, 11, 60) [13]. Figure 6 shows the reported secondary ion yields normalized to cluster size, i.e., the number of secondary ions produced per cluster atom, versus velocity of the clusters. For cluster sizes up to 7 atoms, the yields are seen to be almost same as that produced by the carbon monomer ions. However, an enhanced secondary ion yield was observed starting from cluster size of 9. These results were adopted for SIMS analysis for the first time by the author's group at Kyoto University in 2001 [14]. It was expected that high resolution depth profiling could be achieved because of the high sputtering yields and low energy irradiation effects in combination with minimal ion mixing behavior and absence of surface roughening. The experiments demonstrated a resolution of several nm achieved using Ar cluster ions as a primary ion beam.

Further development of GCIB TOF-SIMS was subsequently made by the J.Matsuo group at Kyoto University [15]. Figure 7 shows a schematic of a GCIB TOF-SIMS. A primary Ar cluster ion beam is size-selected by a double deflection method, and is then introduced upon the sample. Secondary ions produced by GCIB are accelerated to a kinetic energy of 2 keV and are detected with a microchannel plate (MCP). The timing of the secondary-ion chopping and the detection are used as the start and stop signals for the time-of-flight (TOF) measurement. SIMS depth profiling of ITO/PS, Si/DSPC and ITO/Alq3/NPD samples showed that the intensities of the molecular ions from these samples remained constant with increasing fluence. Stable intensities at steady state and at least two orders of magnitude of dynamic range have been reported and depth resolution of SIMS profiling with Ar cluster ion beams is estimated to be better than 10 nm [16]. These results have confirmed the potential for depth profiling analyses using beams of large Ar cluster ions.

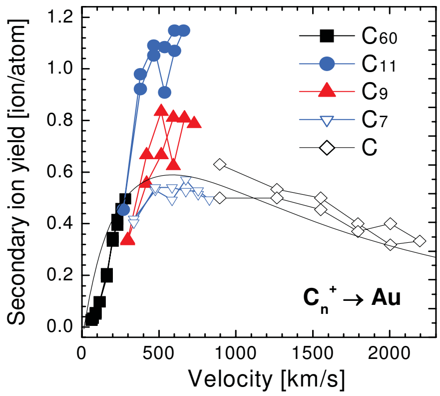

Figure 6. Secondary ion emission yields by carbon cluster ions form Au surface.

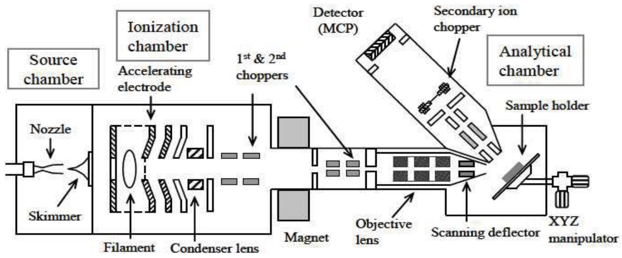

Figure 7. Schematic of GCIB TOF-SIMS

A size-selected GCIB SIMS developed by K.Mochiji and colleagues at University of Hyogo has emphasized damageless processes for large organic materials [17]. In organic materials evaluation by conventional secondary ion mass spectrometry (SIMS), the molecular weight of the intact ions currently detectable is at best only as high as 1000, which prevents the technique from being applied to biomaterials of higher mass. However the developed GCIB-SIMS could detect intact ions of insulin (molecular weight: 5808) and cytochrome C (MW: 12327). The results indicate that fragmentation could be substantially suppressed without sacrificing the sputter yield of intact ions when the kinetic energy per atom was decreased to the level of the target's dissociation energy.

Ar GCIB gas has been applied for low damage depth profiling by XPS and for removal of damaged layers of polymer materials. ULVAC-Phi Inc. announced commercial availability of GCIB mounted XPS equipment in 2011 [18]. XPS depth profiling of polyimide thin films using GCIB have shown the extremely low damage during the depth profiles, compared with the depth profiles obtained by C_{60} and coronene ion sputtering.

APPLICATIONS TO BIO-MATERIALS

Surface Integration using GCIB

It is well understood that for a cell to attach to a surface which will eventually lead to proliferation and differentiation depends on the wettability or hydrophilicity, the chemistry, the charge, and the roughness. Surface biocompatibility and cytocompatibility, therefore, are generally regarded as a need for integration of a device into the human body. Ranging from conductive metallic implants such as used in the dental and orthopedic fields, to insulating polymer implants such as polyester or polytetrafluoroethylene (PTFE, Teflon®) vascular grafts and polyether ether ketone (PEEK) spinal cages, to allograft tissues such as anterior cruciate ligament (ACL) repair or bone grafts, the more biocompatible a surface chemistry is, the less the body will react negatively towards it, and the more cytocompatible a surface is, the better it will integrate with the surrounding tissue. Many advances have been made in various surfaces over the last few decades. In the case of titanium, which is considered to be biocompatible, implants used in dentistry have gradually progressed from a smooth surface to a machined surface to a roughened surface by many means including sandblasting and/or acid etching [19, 20]. The changes in these surfaces, which increased cytocompatibility, merely led to increased surface area or roughess in which osteoblasts from the surrounding bone could latch onto and begin integration. However, at least one group has argued that these modifications lead to temporary increased surface hydrophilicity and hence the reason for better cell attachment [21].

Materials such as PTFE or PEEK, to name just a couple, while favorable for their inherent characteristics for various uses in medicine and are considered as biocompatible, are not generally considered to be cytocompatible and as such have poor integration potential. Increasing cytocompatibility for PTFE leading to rapid re-endothelialization in vascular grafts or for PEEK leading to better spinal fusions would be seen as a paradigm shift for their respective uses. In our studies, we sought to understand the effects of GCIB treatment of various surfaces in order to increase bio- and cyto-compatibility and bio-integration.

Here, we review some findings performed at Exogenesis in which the effects of GCIB were analyzed in respect to enhancement of cell adhesion, proliferation, and differentiation allowing better integration of a surface into the body.

GCIB modifications of surfaces of implantable medical devices

Due to its inert properties, argon gas (Ar) was selected to produce the clusters in which to modify the surface. Ar clusters dissipate upon impact with the surface, leaving no residue behind; therefore, nothing is added onto or into the surface. A wide range of doses as determined by clusters per cm^2 were studied, here we present findings using $5x10^{14}$ ions/cm^2 unless otherwise noted. At first we sought to understand the physical characteristics of the GCIB- modified surfaces. Surfaces become more hydrophilic following GCIB-treatment. The hydrophilicity of a surface is recognized to be important for initial cell attachment [21]. The hydrophilic properties, however, vary from surface to surface. The effect of enhanced hydrophilicity on titanium is relatively short lived, lasting from 3 to 48 hours (Figure 8a). The effect on PTFE, on the other hand, lasts much longer. We have patterned a sheet of PTFE using a mask and the GCIB-treated pattern has remained hydrophilic for over two years so far, and still counting (Figure 8b). The next change that we describe matches an earlier finding showing amorphization of surface crystallinity [22]; amorphous surfaces have been shown to be beneficial for cell proliferation [23, 24]. Earlier work also previously demonstrated the effect of the cluster bombardment on the formation of surface craters [25]. We believe that for bio-medical purposes these nano-craters lead to the formation of nano-roughness on the initial micro-roughness of the surface, thereby creating more surface area, and as described earlier, increased surface area leads to better cell growth. Finally, a modification that is currently being studied is change in surface charge potential. Since the Ar clusters that bombard the surface are charged, we believe that at impact charges transferred to the surface can cause beneficial alteration of surface charge potentials. Although the exact mechanism for enhanced cell attachment and proliferation on GCIB-treated surfaces has not been elucidated, a combination of enhanced hydrophilicity, crystalline amorphization of the surface, nanoscale roughness, and changes in surface charge potential are responsible for enhanced cytocompatibility.

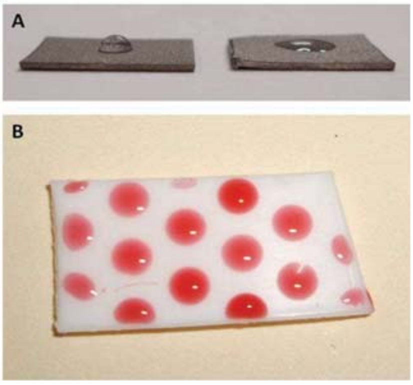

Figure 8. GCIB enhances hydrophilic properties of surfaces. A: shows a 5µl drop of water on titanium control surface (left) and GCIB treated surface (right). B: colored water remains on the GCIB-patterned surface of PTFE.

GCIB modification of surfaces leads to enhanced cell attachment and proliferation

Vascular grafts using PTFE or polyethylene terephthalate (PET, Dacron®) is commonplace; the idea to use PTFE or PET, very hydrophobic surfaces, is that cells do not bind to the surface and decrease the incidence of thrombosis. However, smaller-diameter grafts (<6mm) display an increased level of in-graft thrombosis [26, 27]. Rapid re-endothelialization of the graft lumen would be the ideal anti-thrombogenic surface. Many groups have attempted to address this issue by modifying PTFE or PET by adding Arg-Gly-Asp (RGD) attachment peptides, coating with adhesive proteins such as fibronectin or collagen, gas plasma treatment, or by chemically modifying the surface [28]. Such modifications, however, either do not last long term in the case of plasma treatment [29], or are not favorable due to potential changes in biocompatibility. Our studies have shown that GCIB treatment of both PTFE and PET leads to significant cell attachment and proliferation as compared to controls (Figure 9a-e). Further, these surface changes appear to be permanent as evidenced both by wettability of PTFE as shown in Figure 8b and in shelf life studies where the significant increase in cell attachment and proliferation were observed one year after GCIB treatment.

These changes have not only been demonstrated on PTFE and PET, but also successfully on titanium, polystyrene, glass, sapphire, PEEK, tissues derived from the body such as bone, ligament, and tendons, and many other surfaces. Enhancing cytocompatibility of these materials could lead to better integration of implantable medical devices and allografts or to better cell adhesion and growth for stem cell research. Studies on titanium have yielded very favorable results in significantly increased cell proliferation by day 10 time point 74% increase of cell number on GCIB as compared to controls ($p<0.03$) (Figure 10a-b). This increase could result in GCIB treatment of dental or orthopedic implants which osseointegrate in significantly decreased times. Similarly, PEEK which is now commonly used in spinal applications is preferred over titanium due to its elastic and compression properties more closely matching bone, however, due to its poor cytocompatibility, results in intra-body fusions that do not integrate properly. In initial studies, we have demonstrated that GCIB-treated PEEK result in cell attachment and proliferation comparable to native titanium (Figure 10c). Increasing the cytocompatibility of PEEK by GCIB would allow for inter-body fusions to occur without the addition of materials such as Bone Morphogenic Protein-2 (BMP-2) or demineralized bone powder.

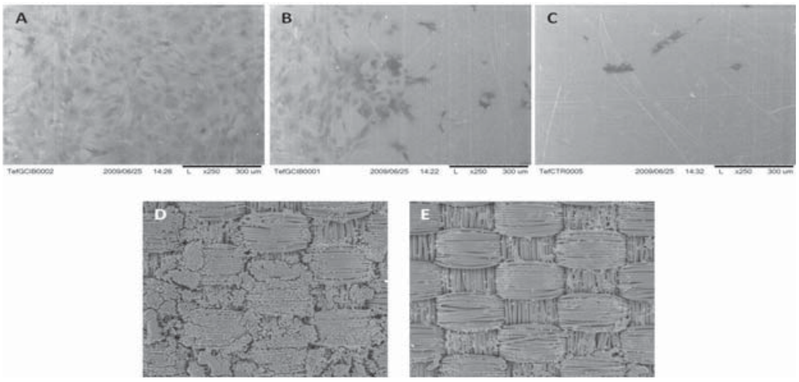

Figure 9. GCIB enhances cell attachment on surfaces. Osteoblast cells adhere and proliferate on PTFE that has been GCIB-treated (A) while no apparent cell attachment is seen on control PTFE (C). The portion that is half-masked (B) displays the difference in cell attachment on the surface of GCIB-treated PTFE. Endothelial cells seeded onto PET for 24 hours attach significantly more to GCIB-treated surfaces (D) as compared to control (E).

Enhancing cell proliferation alone is not indicative of better integration into the body if the proper differentiation of the cells to the desired tissue is not observed. In order to determine if the cells growing on the GCIB-treated surfaces are indicative of enhanced integration into the body, we looked at osteoblasts growing on titanium surfaces to verify if they are differentiating along the requisite pathway for bone development. An early indication of differentiation of the osteoblast cells is the increase in messenger RNA (mRNA) of various genes known to be involved in bone formation. Up-regulation of the ALPL gene is known to be involved in matrix mineralization leading to bone formation. Osteoblast cells growing on GCIB-treated titanium surfaces display 3.4 fold increase in ALPL gene as compared to cells growing on control surfaces by qPCR at 10 days ($p<0.02$). To verify the increase of the ALPL gene, we assayed mineralization by a well known method applying Alizarin Red to quantify the level of mineralization produced by osteoblasts growing on GCIB-treated or control titanium. Osteoblasts growing on GCIB-treated titanium produced 2.2 fold increase in mineralization as compared to growing on control surfaces, this is indicative of the osteoblasts undergoing osteogenesis and producing bone tissue.

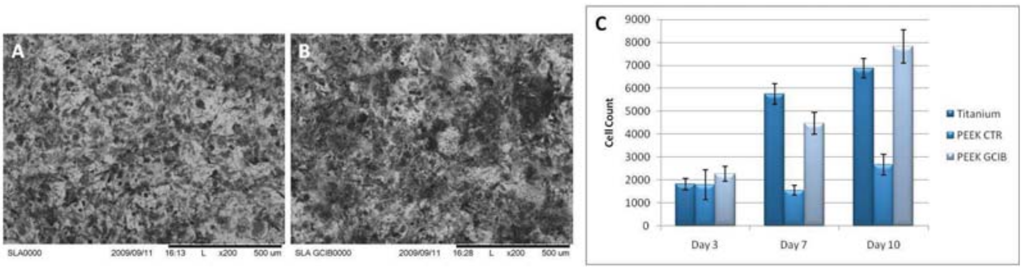

Figure 10. GCIB GCIB enhances cell attachment and proliferation. Titanium surfaces that were left as controls (A) did not allow osteoblast proliferation to occur to the same extent as GCIB-treated surfaces (B) by day 10. Analysis of the cell proliferation on PEEK surfaces shows GCIB-treated PEEK have a similar ability to allow osteoblasts to grow on the surface as untreated titanium (C).

In order to show proof of concept that GCIB surface modification leads to better integration, we did an *in vivo* study using a rat calvarial critical size defect model to show bone growth on the surface of GCIB-treated and –untreated PEEK. Following 4 weeks after implantation into the calvarial defect, histology was performed to determine the amount of bone re-growth on the surface. It was found that GCIB-treated PEEK resulted in a bone ledge growing on top of the disk covering approximately 50% of the surface whereas the control PEEK resulted in no bone growth at all (Figure 11).

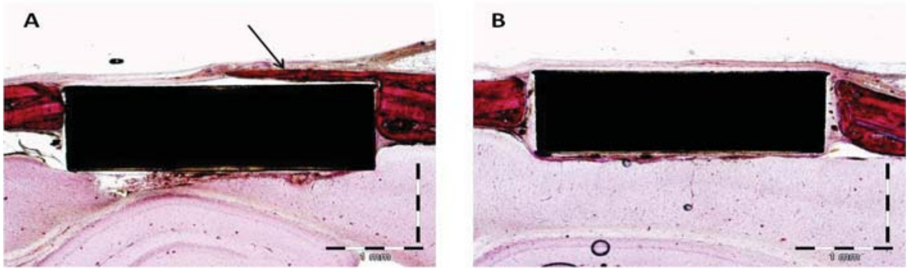

Figure 11. GCIB-treated PEEK results in bone formation in an in vivo model. GCIB-treated PEEK disks (A) result in significant bone coverage as indicated by the arrow as compared with control disks (B) in a four week study using a rat calvarial defect model.

CONCLUSIONS

GCIB processes involve low energy interaction effects, lateral sputtering behavior and high rate chemical reaction phenomena which are distinctly different from the characteristics exhibited by other types of atomic and molecular ion beam processes. The unique capabilities of GCIB are being utilized in surface smoothing, nm-depth etching and low-damage surface processes. Examples which have been described, including planarization of HDD media surfaces, fabrication of film bulk acoustic resonator filters, and low-damage depth profiling in XPS/SIMS analyses, demonstrate that GCIB can be employed for precise nanometer level processing in a broad range of industrial applications.

Other new prospective applications of GCIB in the processing of bio-materials have been introduced. GCIB shows potential to be used to enhance integration of implantable medical devices into the body by allowing better cell attachment, proliferation, and differentiation of surrounding tissue.

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REFERENCES

1. I. Yamada, in *18th International Conference on Ion Implantation Technology IIT 2010*, edited. by J. Matsuo, M. Kase, T. Aoki and T. Seki, AIP Conference Proceedings 1321, (2010) pp.1-8.
2. I. Yamada, J. Matsuo, N. Toyoda, and A. Kirkpatrick, Materials Science and Engineering, R34, (2001) pp.231-295.
3. K. Goto, J. Matsuo, T. Sugii, H. Minakata, I. Yamada, in *IEDM Tech Dig. 1996*, IEEE, (1996) pp. 435-438.

4. I. Yamada, "Development of Cluster Ion Beam Technology" in *IIT school book (2010)*, edited by J. Ziegler, (Ion Implantation Technology Co. Chester, MD, 2011) pp.13-1 - 13-62.
5. T. Aoki, N. Shimada, D. Takeuchi, J. Matsuo, Z. Insepov and I. Yamada, "The Molecular Dynamics Simulation of Boron Cluster Ion Implantation", IEICE Technical Report, 96, No.396, (1996) pp.49-54. (in Japanese).
6. Several papers in *18th International Conference on Ion Implantation Technology IIT 2010*, edited by J. Matsuo, M. Kase, T. Aoki and T. Seki, AIP Conference Proceedings 1321, (2010) and in *10th Workshop on Cluster Ion Beam Technology*, Kyoto, (2010).
7. C. Eggs, in *7th Workshop on Cluster Ion Beam Technology*, Tokyo, (2006) pp.46-51.
8. N. Toyoda and I. Yamada in *10th Workshop on Cluster Ion Beam Technology*, Kyoto, (2010) pp.75-78.
9. R&D Program & Technology Strategy Map (2007-2010), published by METI Japan. http://www.meti.go.jp/policy/economy/gijutsu_kakushin/kenkyu_kaihatu/str2010.html.
10. N. Toyoda, K. Nagato, H. Tani, Y. Sakane, M. Nakao, T. Hamaguchi, I. Yamada, J. Appl. Phys. 105, (2009) pp.07C127-1 - 07C127-2.
11. J. Weldon, R.MacCrimmon, S. Caliendo, Y. Shao, J. Hautala, B. Zide, M. Gwinn, in 5th *Workshop on Cluster Ion Beam Technology*, Kyoto, (2004) pp.47-57.
12. I. Yamada, W. L. Brown, J. A. Northby and M. Sosnowski, Nucl. Instr. and Meth. B79, (1993) pp.223-226.
13. N. Toyoda, Kyoto University Ph.D Thesis (1999).
14. N. Toyoda, J. Matsuo, T. Aoki, S. Chiba, I. Yamada, D. B. Fenner and R. Tori, in *Ion Beam Synthesis and Processing of Advanced Materials,* edited by S. C. Moss, K. Heinig and D. Poker, (Mat. Res. Soc. Symp. Proc. 647, Pittsburgh, PA, 2001) pp.O5.1.1-O5.1.6.
15. S. Ninomiya, K. Ichiki, T. Seki, T. Aoki and J. Matsuo, Nucl. Instr. and Meth. in Phys. Res, B 256, (2007) pp.493–496.
16. S. Ninomiya, Y. Nakata, K. Ichiki, T. Seki, T. Aoki and J. Matsuo, in *10th Workshop on Cluster Ion Beam Technology*, Kyoto, (2010) pp.43-47.
17. K. Mochiji, M. Hashinokuchiy, K. Moritani and N. Toyoda, Mass Spectrom. 23, (2009) pp. 648–652.
18. T. Miyayama, N. Sanada, S. R. Bryan, J. S. Hammond and M. Suzuki, Surf. Interface Anal. 42, (2010) pp.1453–1457.
19. T. Albrektsson, P.I. Brånemark, H.A. Hansson, J. Lindström, Acta Orthop. Scand. 52, (1981) pp.155-70.
20. D. Buser, N. Broggini, M. Wieland, R.K. Schenk, A.J. Denzer, D.L. Cochran, B. Hoffmann, A. Lussi and S.G. Steinemann, J. Dent. Res. 83, (2004) pp.529-33.
21. T. Suzuki, N. Hori, W. Att, K. Kubo, F. Iwasa, T. Ueno, H. Maeda and T. Ogawa, Tissue Eng Pt A 15, (2009) pp.3679-3688.
22. H. Isogai, E. Toyoda, T. Senda, , K. Izunome, K. Kashima, N. Toyoda, and I. Yamada, in *16th International Conference on Ion Implantation Technology IIT 2006*, edited by K. Kirkby, R. Gwilliam, A. Smith and D. Chivers, AIP Conference Proceedings 866, (2006) pp.194-197.
23. A.G. Mikos, G. Sarakinos, M.D. Lyman, D.E. Ingber, J.P. Vacanti, R. Langer, Biotechnol. Bioeng. 42, (1993) pp.716-23.
24. A. Park, L.G. Cima, J. Biomed. Mater. Res. 31, (1996) pp.117-30.
25. T. Seki, T. Kaneko, D. Takeuchi, T. Aoki, J. Matsuo, Z. Insepov, I. Yamada, Nucl. Instr. and Meth. in Phys. Res. B. 121, (1997) pp.498-502.
26. G. Leseche, J. Ohan, S. Bouttier, T. Palombi, P. Bertrand, B. Andréassian, Ann. Vasc. Surg. 9 Suppl., (1995) pp.S15-23.
27. A. Yeager, A.D. Callow, ASAIO Trans. 34, (1988) pp.88-94.
28. F.R. Pu, R.L. Williams, T.K Markkula, J.A. Hunt, Biomaterials, 23, (2002) pp.2411-28.
29. D. Eddington, J. Puccinelli, D. Beebe, Sensors Actuators B-Chem. 114, (2006) pp.170-172.