Cambridge University Press
978-1-107-40865-4 - Ion-Beam-Based Nanofabrication: Materials Research Society Symposium Proceedings: Volume 1020
Editors: Daryush ILA, John Baglin, Naoki Kishimoto and Paul K. Chu
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Ion Beam Nanofab:
Tools, Techniques, and Applications

Mater. Res. Soc. Symp. Proc. Vol. 1020 © 2007 Materials Research Society 1020-GG01-02

Cluster Ion Beam Process for Nanofabrication

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Abstract. This paper reviews gas cluster ion beam (GCIB) technology, including the generation of cluster beams, fundamental characteristics of cluster ion to solid surface interactions, emerging industrial applications, and identification of some of the significant events which occurred as the technology has evolved into what it is today. More than 20 years have passed since the author (I.Y) first began to explore feasibility of processing by gas cluster ion beams at the Ion Beam Engineering Experimental Laboratory of Kyoto University. Processes employing ions of gaseous material clusters comprised of a few hundred to many thousand atoms are now being developed into a new field of ion beam technology. Cluster-surface collisions produce important non-linear effects which are being applied to shallow junction formation, to etching and smoothing of semiconductors, metals, and dielectrics, to assisted formation of thin films with nano-scale accuracy, and to other surface modification applications.

HISTORICAL MILESTONES IN GCIB TECHNOLOGY

In 1950, Becker et al first studied cluster formation for thermonuclear fuel applications using gaseous materials passed through supersonic nozzles wchichi were cooled by liquid nitrogen and helium shrouds [1]. The supersonic expansion approach was successful in producing cryogenic beams containing large numbers of clusters. This original work opened the way to employ gas clusters for materials processing.

During the late 1970's and 1980's, an ionized cluster beam (ICB) technique which employed metal vapor clusters from heated Knudsen cells for thin film formation was studied at Kyoto University and elsewhere. Kyoto University investigations of metal vapor clusters ended when collaborative work with W.L.Brown at Bell Laboratories showed the cluster ion intensities within the metal vapor streams to be too low for most practical purposes [2,3]. Subsequent work at the Kyoto University Ion Beam Engineering Experimental Laboratory then focused upon cluster beam formation employing gas expansion through simple supersonic nozzles.

Initial research on gas cluster beam formation showed that supersonic nozzles having converging-diverging shapes operating at room temperature could produce intense beams of gas clusters. This then led to research and development of gas cluster ion beam (GCIB) techniques [4] and to investigations of new ion-solid interactions produced by gas cluster ion impacts. These studies demonstrated that GCIB produces unique ion/solid interactions and offers new atomic and molecular ion beam process opportunities in areas of implantation, sputtering, and ion beam assisted deposition. Most of the original technical results through to the year 2000 have been summarized in a monograph. [5].

Over the first 10 years of GCIB studies, low energy surface interaction effects, lateral sputtering phenomena and high chemical reaction effects were observed experimentally and were

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explained by means of molecular dynamics (MD) modeling. Japanese government funding through JST (Japan Science and Technology), MEXT (Agency, Ministry of Education), METI (Ministry of Economy, Trade and Industry) and others provided long term support for the research at Kyoto University. Difficulty in developing GCIB equipment within Japan resulted in development of commercial GCIB equipment by Epion Corporation in the U.S. beginning in 1995 [6].

In 2000, a four year R&D project for development of GCIB industrial technology began in Japan under funding from the New Energy and Industrial Technology Development Organization (NEDO). This project involved subjects in areas of semiconductor surface processing, high accuracy surface processing and high-quality film formation. The project was supported by the formation of a new Collaborative Research Center of Cluster Ion Beam Technology at Kyoto University and University of Hyogo.

In 2002, another major GCIB project which emphasized nano-technology applications was started under a contract from the Ministry of Economy and Technology for Industry (METI). This METI project currently involves development related to size-selected cluster ion beam equipment and processes, and development of GCIB processes for very high rate etching and for zero damage etching of magnetic materials and compound semiconductor materials.

Figure 1 shows historical milestones of GCIB equipment and process development.

GAS CLUSTER FORMATION AND GCIB EQUIPMENT

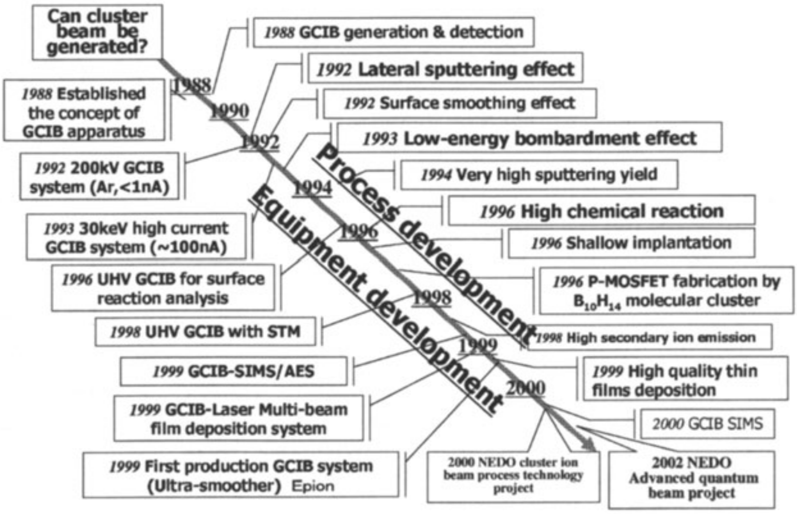

Figure 1. Historical milestones of GCIB equipment and process development.

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GCIB processing of materials is based on the use of electrically charged cluster ions consisting of a few hundred to a few thousand atoms or molecules of gaseous materials. A beam of neutral clusters is first formed from individual gas atoms by expansion of the gas through a nozzle at room temperature into vacuum. The clusters are subsequently ionized and accelerated.

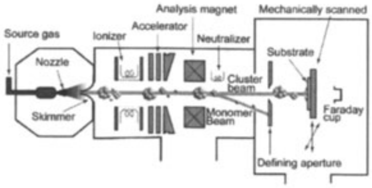

Figure 2. Typical configuration of GCIB equipment

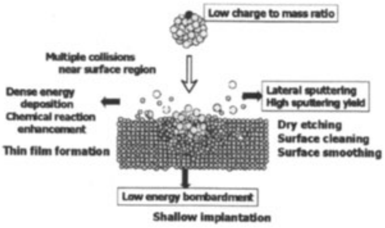

Figure 3. GCIB-solid surface interactions and their applications.

The typical configuration of GCIB equipment is as shown in Figure 2. A small aperture, or skimmer, transmits the primary jet core of gas clusters emerging from the expansion nozzle. Forward-directed neutral clusters are then ionized by impact of electrons accelerated from a filament so as to form positive ion gas clusters with nominally one charge per cluster. The ionized clusters are extracted and accelerated through typical potentials of between and 2 and 30 kV using a series of electrodes. Electrostatic lenses are utilized to focus the cluster ions, and monomers are filtered out by means of a strong transverse magnetic field. Usually the cluster ion beam is kept stationary and material to be processed is scanned mechanically through the beam so as to obtain uniform and complete coverage. The cluster ion fluence is measured by means of a Faraday cup.

When an energetic cluster ion impacts upon a surface, it interacts nearly simultaneously with many target atoms and deposits high energy density into a very small volume of the target material. The concurrent energetic interactions between many atoms comprising the cluster and many atoms of the target result in highly non-linear implantation and sputtering effects [7]. These effects, which are fundamentally different from those associated with the more simple binary collisions occurring during monomer ion impacts, include low energy bombardment phenomena, lateral sputtering effects and high chemical reaction effects. Figure 3 summarizes GCIB-solid surface interactions and their applications.

In early 1988, cluster formation was confirmed by electron diffraction. A strong Debye-Scherrer ring, as shown in Figure 4(a), was observed when electrons were diffracted through the beam emerging from a gas nozzle. Time of flight (TOF) measurements were subsequently used to show that the clusters contained several hundred to many thousand atoms [8]. The clusters were believed to be held together by van der Waals forces.

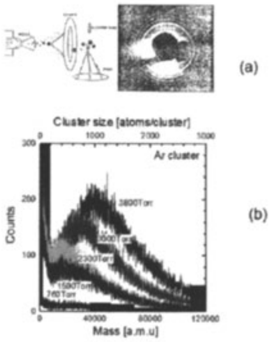

Figure 4. Cluster detection by e-diffraction (a) and TOF (b).

Figure 4(b) shows typical size distributions found for Ar gas clusters. Clusters of the sizes which are normally produced by room temperature nozzles were found to be particularly useful for materials processing. More recent experiments conducted with size-selected cluster beams have confirmed the fortuitous nature of the cluster size distributions which are typically produced [9]. It has been found that clusters can be formed from nearly all gases and gas mixtures, including rare gases such as Ar and Xe, most diatomic gases such as O_2 and N_2, and molecular compound gases such as B_2H_6, BF_3, CH_4, NF_3, SF_6, etc.

One of the advantages associated with the cluster ion is a very low charge to mass ratio. Cluster ions containing up to several thousands of atoms typically become only singly or doubly ionized. Consequently, a cluster ion beam at any given current density can transport up to thousands of times more atoms than a monomer ion beam at the same current density. For example, a 1μA beam of cluster ions with average size of 1000 atoms per cluster can transport the same number of atoms as a 1mA monomer ion beam. These characteristics make it possible to use GCIB for very low energy ion beam processes which are normally difficult by traditional ion beam technology. Available GCIB equipment is now able to produce cluster ion beam currents of hundreds of microamperes or more from gases such as Ar [6].

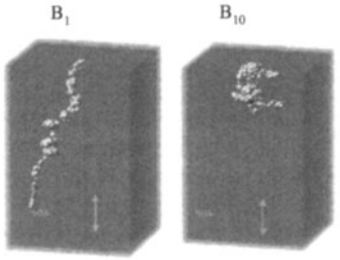

Figure 5. MD simulations of B monomer and B_{10} cluster ion implantations into Si at 5 keV.

LOW ENERGY EFFECTS AND SHALLOW JUNCTION FORMATION

From the beginning of cluster ion beam investigations, it was expected that clusters should produce low energy bombardment effects since the kinetic energy of each atom in a cluster ion is roughly equal to the total energy of the cluster divided by the number of atoms contained in the cluster. As an example, within a 20 keV cluster ion consisting of 2000 atoms, each of the individual atoms has energy of only 10 eV. Low energy effects were predicted by MD simulations and were confirmed by experiments, for example by comparing B monomer ion and B cluster ion implantation [10]. The results showed low-energy individual atomic interactions even when the total energy of the clusters was high. Figure 5 shows MD simulations of B monomer and cluster ions into Si illustrating the low energy effect of cluster ion bombardment relative to monomer ion bombardment. Important differences in range and density of the displacements produced are apparent. In the cluster ion case, the penetration range is extremely shallow and the displacements that are produced remain tightly concentrated within the impact region at the target surface.

While, due to space charge effects, it is exceptionally difficult to transport monomer ion beams at energies as low as 10 eV, equivalently low energy ion beams can be realized by using cluster ion beams at high acceleration voltages. The standard configuration of GCIB equipment inherently results in highly directional parallel cluster ion beams which are extremely well suited for ultra shallow doping applications and are known to produce thin film transistors which exhibit operational characteristics superior to those which result when conventional ion implantation is used for the shallow doping [11].

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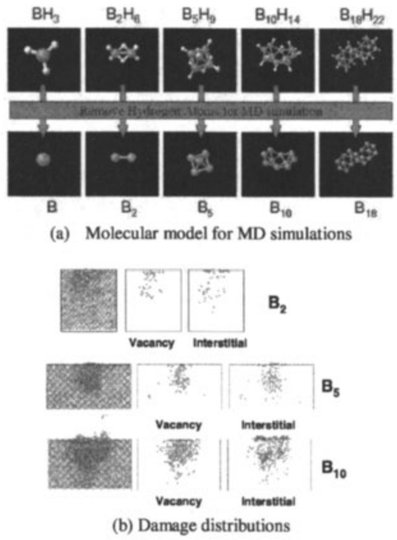

Figure 6. MD simulation models of B clusters (a) and typical implant damage distributions for B_2, B_5 and B_{10} ions (acceleration energy: 500eV/atom)

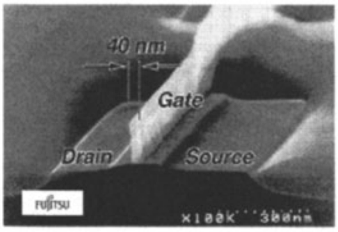

Figure 7. First p-MOSFET by $B_{10}H_{14}$ implantation

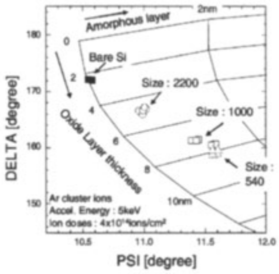

Figure 8. Cluster size dependence of Ψ and Δ after 5keV Ar-GCIB irradiation with ion dose of 4×10^{14}ions/cm^2.

POLYATOMIC CLUSTER IMPLANTATION

The concept of performing polyatomic cluster implantation into Si by using decaborane ($B_{10}H_{14}$) molecules was first investigated in 1996 by Kyoto University researchers working together with researchers at Fujitsu [12]. Effects upon range and damage distributions resulting from implantation of different sizes of B polyatomic clusters have been studied by MD simulations employing B_1, B_2, B_5, B_{10}, B_{18} molecular models shown in Figure 6(a) [13]. The results of these simulations indicate that cluster-like bombardment phenomena, the nonlinear effects which are typical of cluster impact, begin to be observed with clusters containing at least five or more atoms. Figure 6(b) shows the implant damage distributions resulting from the model clusters of 2 atoms, 5 atoms and 10 atoms. From MD simulations of bombardment by even larger clusters, it has been shown that the displacement damage increases with increasing cluster size and very clusters, as in the case of GCIB, cause complete self amorphization [5].

P-MOSFETs with 40nm gates, as in the device shown in Figure 7, were successfully fabricated by Fujitsu in 1996 using $B_{10}H_{14}$ implantation for ultra shallow junction and source/drain formation [12]. Decaborane implantation at 30 keV to a dose of 1×10^{13} ions/cm^2 followed by annealing at 1000°C for 10 seconds was reported to have resulted in a junction depth of 20 nm. For source/drain extensions, $B_{10}H_{14}$ ion implantation at 2 keV was carried out to a dose of 1×10^{12} ions/cm^2 followed by annealing at 900°C for 10 seconds.

Under a 2002 contract from JST (Japan Science and Technology Agency) Nissin Ion Corporation has successfully developed equipment for $B_{10}H_{14}$ ion implantation. A beam current of 3 mA at an acceleration energy of 3 keV has been achieved [14]. Using this equipment, Nissi and Fujitsu have worked to advance the decaborane process technology. Recently they hav reported devices with significantly reduced threshold voltage deviation and higher forwar currents than similar devices made by conventional B implantation [11]. Other polyatomi cluster implantation, such as that using $B_{18}H_{22}$, has also been developed because of th decaborane success [15].

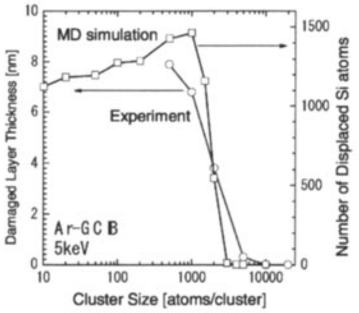

Figure 9. Cluster size dependence of number of displaced Si atoms by MD simulations and damage layer thickness

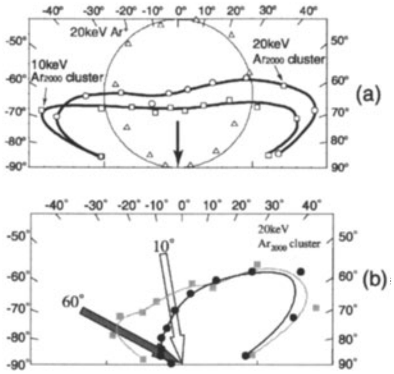

Figure 10. Angular distribution of sputtered atoms by Ar monomer and Ar cluster ions.(a) normal incidence (b) oblique incidence.

CLUSTER SIZE EFFECTS AND LOW DAMAGE PROCESSES

The influence of cluster size upon surface damage production has been studied experimentall using GCIB apparatus which incorporates a strong permanent sector magnet for cluster siz

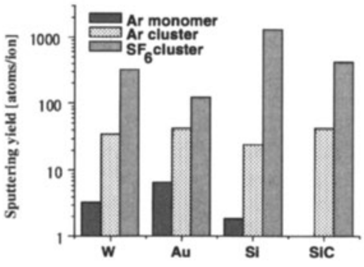

Figure 11. Reactive and physical sputtering for various materials at 20keV acceleration energy.

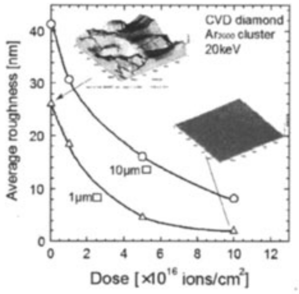

Figure 12. Ion dose dependence of the average roughness of a CVD diamond surface bombarded with a 20keV Ar cluster ion beam at normal incidence

selection [9]. Displacement damage within the Si surfaces has been evaluated by ellipsometry using a two-layer analysis model which assumes that oxide and amorphous layers are formed by the GCIB bombardment. From ellipsometry measurements, the intensity ratio Ψ and phase difference Δ of p and s waves can be determined. An increase in amorphous layer thickness is indicated by an increase of Ψ and an increase in the oxide layer thickness is indicated by a decrease of Δ. From the Ψ and Δ behaviors, estimates can be made of the damage formation due to Ar-GCIB bombardment.

Studies have been made of Si surfaces bombarded by size-selected 5 keV Ar cluster ion beams to dose levels of $4x10^{14}$ ions/cm^2. Mean cluster sizes utilized were 540, 1000 and 2200 atoms per cluster, resulting in average energies of 9.2, 5.0 and 2.3 eV per atom respectively. At the fixed 5 keV beam energy, both the oxide thickness and the amorphous layer thickness were found to decrease monotonically with increasing cluster size, ie., with decreasing energy of the cluster atoms. Figure 8 shows Ψ and Δ plots after Ar-GCIB irradiation of the Si.

Figure 9 shows plots of estimated damaged layer thickness and total displacements versus cluster size as determined experimentally and also by MD simulations [9]. From the MD simulations, the number of Si atoms displaced from their lattice cites increased with Ar cluster size from 10 to 1000, showed a peak at around 1000 atoms/cluster and then rapidly decreased with further increase of cluster size. At cluster sizes above 4000 atoms per cluster, MD simulations showed almost no displaced atoms after Ar-GCIB irradiation. The experimental results have shown almost the same trend as the MD simulations. These results suggest that shallow implantation and doping can be possible by using large cluster ions. From MD simulations, it is predicted that there is no damage formation in Si when the energy per atom in Ar cluster ion is below 1eV even though large cluster ions having such conditions can still deposit approximately 30% of their acceleration energy into a target Si substrate.

LATERAL SPUTTERING AND ATOMIC LEVEL SMOOTHING

An important characteristic of large gas-cluster ion bombardment is an effect known as lateral sputtering. Angular distributions of surface atoms ejected by cluster ions are considerably different from the distributions produced by monomer ions. Figure 10 shows experimentally measured angular distributions of sputtered atoms by Ar_{2000} cluster ions at (a) normal incidence and (b) oblique incidence. The angular distribution produced by monomer ions, which indicates the usual cosine distribution, is also shown. The angular distribution of sputtered atoms produced by the Ar cluster ions illustrates the lateral ejection. [8].

Sputtering yields due to cluster ions are very high relative to those associated with monomer ions at similar energy. Very high sputtering yields on metal, semiconductor and insulator surfaces due to bombardment with cluster ions have been observed experimentally. Experimentally measured sputtering yields of various materials due to 20 keV Ar (physical) and SF_6 (chemically reactive) cluster ions and monomer ions are shown in Figure 11.

Lateral sputtering produces surface smoothing behavior which does not occur with monomer ions. Smoothing of surfaces to atomic levels has been the first production use for cluster ion beam processing. Figure 12 shows typical ion dose dependence of the average roughness of a CVD diamond surface bombarded with a 20 keV Ar cluster ion beam at the normal incidence. The average roughness decreased monotonically with increasing ion dose from the initial value of 26 nm to a value of 1.3 nm after an ion dose of $8x10^{16}$ ions/cm^2. In the case of monomer ion irradiation at normal incidence, surface roughness typically increases with ion dose due to erosion or bubble formation inside the target.

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GCIB APPLICATIONS IN INDUSTRY

Epion Corporation in the U.S. has developed GCIB equipment for industrial applications under a license from Japan Science and Technology Agency (JST). As is shown in Figure 13, concurrent with the development of increasingly capable commercial GCIB equipment has been the development of applications for GCIB process technology in the manufacturing of semiconductor devices and other advanced technical devices [16].

GCIB applications in semiconductors

As is suggested in Figure 14, a number of candidate applications are being developed for GCIB in the manufacturing of coming generations of semiconductor devices. These applications include ultra shallow junction doping, SiGe alloy formation, film deposition, silicon-on-insulator thinning and uniformity correction, etching of dielectrics, ashing of photoresist, and surface modification of metals and dielectrics for integration of improved Cu interconnects.

GCIB offers excellent characteristics for producing ultra shallow junctions with pre-activation depths ranging from less than 10 nm to a maximum of approximately 30 nm. The mechanism of doping by GCIB, which is referred to as "infusion", depends upon the intense localized temperature/pressure transient which is created at the point of cluster impact. During the moment of impact, molecular gases such as B_2H_6 contained within the cluster undergo dissociation and solid species such as B which they contain then undergo mixing into the targ-t

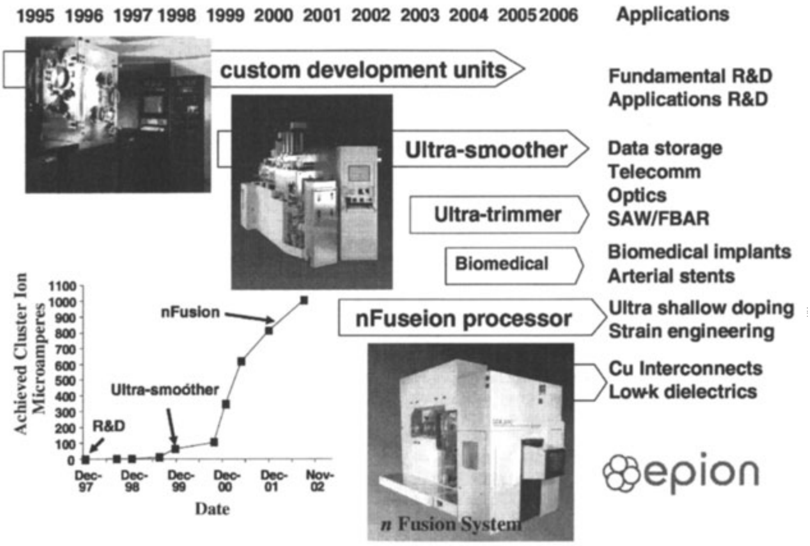

Figure 13. Industrial GCIB application areas