Negative-ion source applications (invited)[a)]

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In this paper heavy negative-ion sources which we developed and their applications for materials science are reviewed. Heavy negative ions can be effectively produced by the ejection of a sputtered atom through the optimally cesiated surface of target with a low work function. Then, enough continuous negative-ion currents for materials-science applications can be obtained. We developed several kinds of sputter-type heavy negative-ion sources such as neutral- and ionized-alkaline metal bombardment-type heavy negative-ion source and rf-plasma sputter type. In the case where a negative ion is irradiated on a material surface, surface charging seldom takes place because incoming negative charge of the negative ion is well balanced with outgoing negative charge of the released secondary electron. In the negative-ion implantation into an insulator or insulated conductive material, high precision implantation processing with charge-up free properties can be achieved. Negative-ion implantation technique, therefore, can be applied to the following novel material processing systems: the surface modification of micrometer-sized powders, the nanoparticle formation in an insulator for the quantum devices, and the nerve cell growth manipulation by precise control of the biocompatibility of polymer surface. When a negative ion with low kinetic energy approaches the solid surface, the kinetic energy causes the interatomic bonding (kinetic bonding), and formation of a metastable material is promoted. Carbon films with high constituent of sp^3 bonding, therefore, can be formed by carbon negative-ion beam deposition. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2814250]

I. INTRODUCTION

Heavy negative ions can be effectively produced by the way in which a sputtered atom passes through the optimally cesiated surface of a sputter target with the lowest work function. We have shown clear that the maximum negative-ion production probability can be quite high.[1] We obtained submilliampere-class, heavy negative-ion beams, in the dc mode by cesium ion beam sputter-type negative-ion sources,[2] and milliampere-class ion beams from rf-plasma sputter-type negative-ion sources.[3–5] These developments then opened various applications of negative-ion beams for materials science.

The surface charging voltage of insulators or insulated conductive materials during positive-ion implantation is quite large, and it rises up to the ion acceleration voltage in worst case, so this situation sometimes becomes troublesome. The surface charging voltage of the same material during negative-ion implantation, however, is extremely low and is, in fact, negligible. It is because the incoming charge due to the ion flux is negative and the outgoing charge due to secondary electron is also negative; thus, the charge balance could be easily obtained at the surface.[5–8] By using the negative-ion implantation technique, we could perform the following applications such as surface modification of micrometer-sized particles without scattering of the target particles,[9] nanometer metal-particle formation in a thin insulator film for quantum devices,[10,11] and cell adhesion control of a polymer surface by implantation.[12,13]

In negative-ion-beam deposition atomic-bonding processes through ion's kinetic energy (kinetic bonding) take place because of the ion's small internal potential energy (electron affinity) and it promotes the formation of metastable materials. For example, tetrahedrally bonded carbon films and CN films with high sp^3 structure could be prepared by using carbon and CN negative-ion-beam deposition.[6,14–16]

II. SPUTTER-TYPE HEAVY NEGATIVE-ION SOURCES

A. Optimal heavy negative-ion production

In a negative ion an electron is weakly attached to an atom, and its adhesion energy is as low as 1 eV (electron affinity). This weak attachment between atom and electron is an important aspect in production of the negative ion. Negative-ion production is quite different from positive-ion production. An effective way to produce a heavy negative ion is a surface effect method; a tunneling shift of electron from Fermi level of conductive material to electron affinity level of atom. In particular, heavy negative ions can be effectively produced by the way in which a sputtered atom passes through the optimally cesiated surface of sputter target with the lowest work function.[17] This negative-ion production mechanism is called secondary negative-ion emission.

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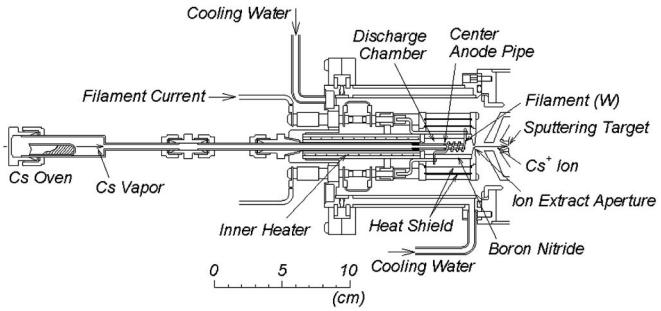

FIG. 1. Sputter-type heavy negative-ion source: NIABNIS with an electron bombardment-type Cs ion source.

Previously, we have measured the negative-ion production probability by this secondary negative-ion emission process, and its maximum value was found to be quite high, ranging from 0.3% to 18%.[1] We could obtain high-current heavy negative-ion beams by using this method.

Another very important aspect of negative-ion production is the gas pressure of the discharge and the transport regions. We measured the electron-detachment cross section[18] and the value was found to be quite large to be around 10^{-15} cm^2. Negative ions, thus, are easily detached and destroyed if they pass through a badly evacuated region. The discharge (less than 10^{-4} Torr) and the transport (less than 10^{-6} Torr) of negative ions in a low-pressure gas are essential to avoid extinction of negative ions.

B. Heavy negative-ion sources

We developed several kinds of sputter-type heavy negative-ion sources such as neutral- and ionized-alkaline metal bombardment-type heavy negative-ion sources[2,19] (NIABNISs) and rf-plasma sputter-type negative-ion sources[3–5] for materials-science applications. In NIABNISs, cesium ions and neutral particles are extracted from an electron-bombardment-type ion source or a compact microwave ion source and they are irradiated onto a cone-shaped sputter target. Figure 1 shows the NIABNIS with an electron-bombardment-type cesium ion source. From these sources, submilliampere dc ion currents, such as negative carbon ions, can be extracted. In these sources, no carrier gas for discharge is used, then, no unnecessary gas particles are emitted from the source. Thus, they are suited for ion-beam-deposition applications where high vacuum conditions are often required because ultrahigh vacuum can be obtained with a simple differential pumping system.

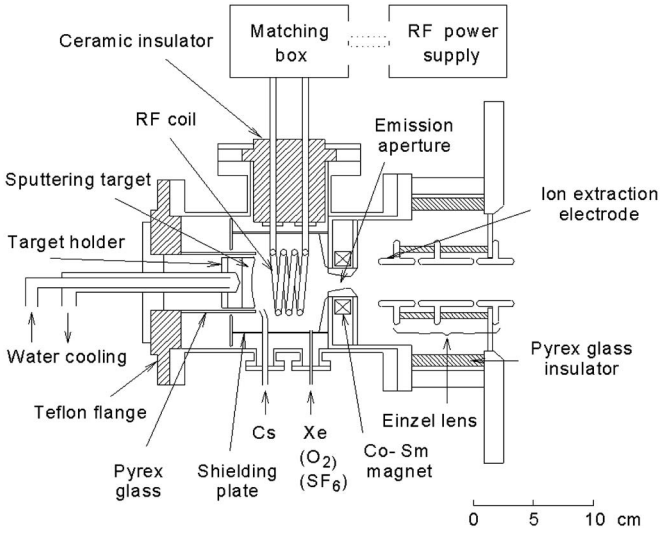

FIG. 2. Sputter-type heavy negative-ion source: rf-plasma sputter-type negative-ion source.

For the material science applications high-current negative-ion sources were eagerly awaited. We developed rf-plasma sputter-type heavy negative-ion source to obtain milliampere-class heavy negative ions.[3–5] Figure 2 shows the prototype of rf-plasma sputter-type negative-ion source. In the source, xenon gas is effectively ionized by using a rf (13.56 MHz) discharge at a relatively low gas pressure of about 10^{-4} Torr. The sputter target is negatively biased by several hundred volts; then, xenon ions bombard the sputter target surface. When a sufficient neutral cesium flux is supplied to the sputter target surface to bring the lowest work function, efficient negative-ion production process takes place. Then, milliampere-class negative-ion beams are generated, as indicated in Table I, including negative oxygen and fluorine,[20,21] and CN ions.[16] A small version of a rf-plasma sputter-type negative-ion source was also developed for a negative-ion implanter.[5]

III. NEGATIVE-ION IMPLANTER AND NEGATIVE-ION-BEAM DEPOSITOR

A. Negative-ion implanter

We developed several types of negative-ion implanters equipped with NIABNIS or rf-plasma sputter-type negative-ion source. Figure 3 shows a negative-ion implanter with a small version of a rf-plasma sputter-type negative-ion source.[7] In this implanter the acceleration voltage is as large

TABLE I. Negative-ion currents obtained from a rf-plasma sputter-type heavy negative-ion source.

Negative ion	Cu^-	C^-	O_2^-	Si^-	B_2^-	P^-	O^-	F^-	CN^-
Maximum current (mA)	12.1	1.6	2.3	3.8	1.0	0.92	4.7	4.5	0.88
Material to be ionized	OFHC	Graphite	Graphite	Poly-Si	Sintered LaB6	Poly-GaP	O_2 gas	SF_6 gas	Graphite $+N_2$ gas

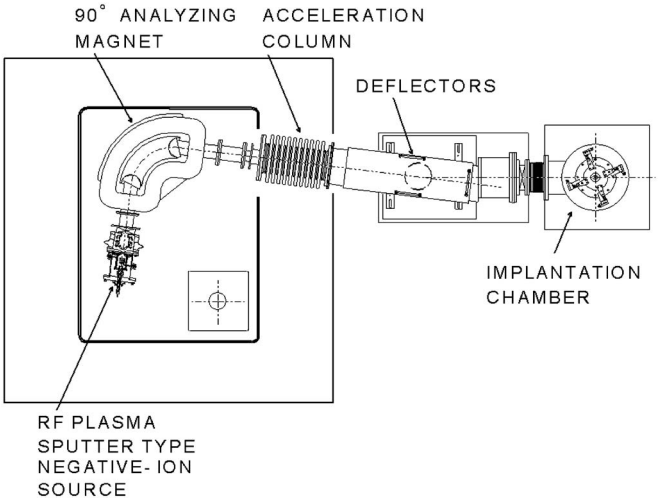

FIG. 3. Negative-ion implanter equipped with a small version of a rf-plasma sputter-type negative-ion source.

as 100 kV, and negative-ion currents are several tens of microamperes. The implanter has an extraimplantation chamber for powder particle implantation.

B. Negative-ion-beam depositor

We developed a negative-ion-beam depositor as shown in Fig. 4.[22] In this depositor a NIABNIS with an electron-bombardment-type cesium ion source is equipped. The NIABNIS emits no gas particle and the deposition chamber can be evacuated to ultrahigh vacuum, thus pure film deposition can be performed. In the depositor, a mass separated negative-ion beam is decelerated to a low energy (several tens of eV) suited for deposition just before the target.

IV. NEGATIVE-ION IMPLANTATION

A. Charging voltage by negative-ion implantation

When a positive ion irradiates material such as insulator or insulated conductive material, the electric charge of the ion accumulates on the surface, and the surface potential may rise, in the worst case, to the ion acceleration voltage. Therefore, the insulator may be destroyed by breakdown due to discharge through it. On the other hand, in the case of the negative-ion irradiation, the number of charges incoming to and outgoing from the surface are well balanced because both charges (incident on material surface by negative-ion irradiation and released from material surface as secondary electrons) are negative.[23] Therefore, the material surface potential is fixed within several volts which is by two to four orders of magnitude lower than that due to positive-ion irradiation. No insulator damage by breakdown may occur.

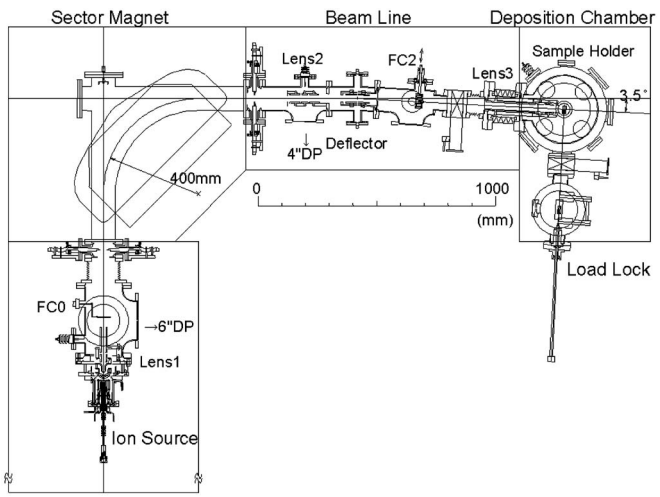

FIG. 4. Negative-ion beam depositor equipped by a NIABNIS with an electron-bombardment-type Cs-ion source.

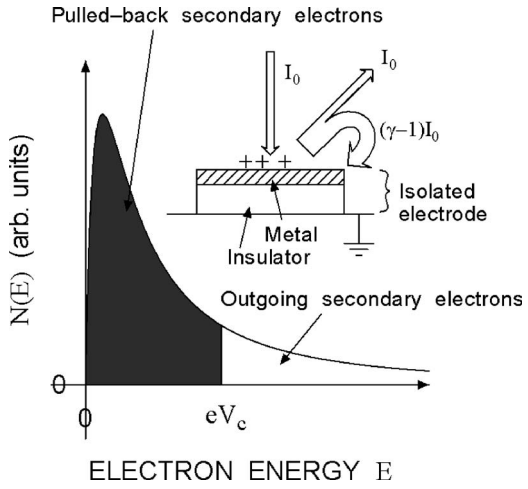

FIG. 5. Schematic diagram illustrating the charge equilibrium of an isolated electrode during negative-ion implantation.

The charging voltage V_c is determined by the following equation, as shown in Fig. 5:

$$\gamma \int_{eV_c}^{E_{\max}} N(E)dE = 1, \tag{1}$$

where γ is the secondary electron emission yield, $N(E)$ is the energy distribution function of secondary electrons, and $E_{\max}$ is the maximum energy of secondary electrons. The charging voltage of insulators due to negative-ion irradiation is also very low, i.e., minus several volts, because an electric double layer is generated on the surface.[24,25] Since the charging voltage of insulated materials due to negative-ion irradiation is from plus several volts to minus several volts, essentially "charge-up-free" negative-ion implantation is possible.

B. Application of negative-ion implantation technique

1. LSI device fabrication

The ion implantation is a key technique in large scale integration (LSI) device fabrication process. Now positive ions are used for this implantation. Then, a charge neutralizer of electron shower is inevitable in order to avoid charging of the gate electrode of metal oxide semiconductor field effect transistor during implantation. This charging problem becomes more and more severe in near future. If we use negative ions instead of positive ones in implantation, this charging problem could be easily solved because the charging voltage by negative-ion implantation is below the breakdown voltage of a gate oxide film.

We tested an applicability of negative-ion implantation for LSI device fabrication by using test element group (TEG)

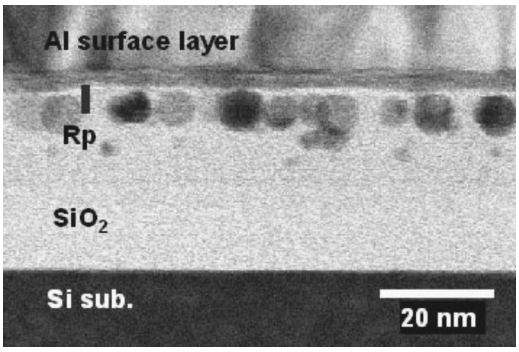

FIG. 6. TEM images of gold nanoparticles formed in thin SiO_2 films by negative-ion implantation.

devices with a gate oxide film thickness of 20 nm and various antenna ratios.[8] No damage was observed below an applied voltage of 18 V in TEG devices after 10 C/cm^2 Cu^- implantation. This result shows that the use of negative-ion implantation technique in LSI device fabrication would be very effective.

2. Powder surface modification

Ion implantation into surface of micron-sized powders, such as ceramic and polymer particles, is highly desirable for applications in medical and catalytic fields.[26,27] When positive ions are poured into a micron-sized particle, scattering of these particles happens due to surface charge. As a result, ion implantation processing of micron-sized particles is very difficult. The scattering begins from surface potential values beyond approximately 1 kV. On the other hand, negative-ion implantation can be performed smoothly because scattering of particles does not take place at all, the surface potential being within several volts.[9,28]

3. Nanoparticle formation

Insulators with film thickness of about several tens of nanometers, including nanoparticles, can be used to realize quantum devices such as single-electron devices.[29,30] The formation of delta-layered nanoparticles in a thin SiO_2 film without damage by negative-ion implantation was investigated. Figure 6 shows transmission electron microscope (TEM) image of gold nanoparticles formed in a thin SiO_2 film by using negative-ion implantation. The ion implantation energy of gold ion was 1 keV, which resulted in a very narrow distribution of implanted gold atoms. A delta layer of gold nanoparticles with diameters of 5–8 nm was formed around the projected range of gold atoms near the surface region.[10] Delta layers of Ag and Ge nanoparticles were also formed near the boundary of Si and SiO_2 and near the center of SiO_2 film, respectively.[11]

4. Biocompatibility control

Negative-ion implantation is a promising technique for nerve cell engineering. By the patterned negative-ion implantation on polymers, nerve cell adhesion patterning control can be precisely performed due to charge-up-free property of negative-ion implantation. Thus, this method can be

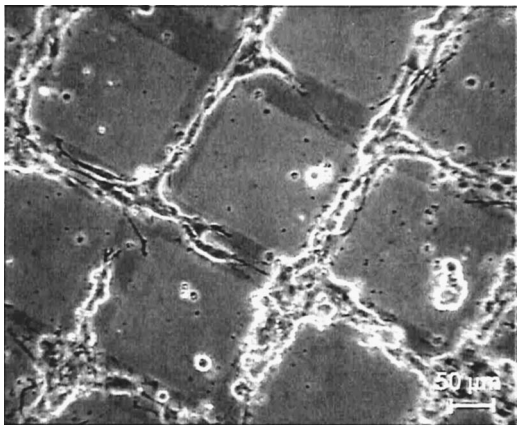

FIG. 7. PC-12h nerve cell and neurite outgrowth adhesion properties on polystyrene surfaces after grid-patterned-implantation by carbon negative ions.

applied to the developments such as artificial nerve network with living cells and guide tube of nerve regeneration, i.e., tabulation.[12,13]

Nerve cell adhesion patterning control. Contact angle for de-ionized water of polystyrene surface was decreased by about 15° by carbon negative-ion implantation with a dose of an order of 10^{15} ions/cm^2 at an energy of around 10 keV, and then the biocompatibility of this surface is improved by a large margin.[31] Figure 7 shows the PC-12h nerve cell and neurite outgrowth adhesion properties on grid-patterned-carbon-negative-ion-implanted polystyrene surface. Good nerve cell adhesion properties were obtained on the modified area by negative-ion implantation.

Nervous-system repair. Tubulation as shown in Fig. 8(a) is a very prospective method for the regeneration of a nerve system. However, the regenerated length was only less than 10 mm by using a silicon rubber tube without surface treatment by ion implantation. A longer regeneration length is desired for real treatment. We used carbon negative-ion implantation to improve the inside wall of the silicon rubber tube. The implantation conditions were as follows: ion dose of 3×10^{15} ions/cm^2 and an energy of 10 keV. By using the modified silicon rubber tube, the rat sciatic nerve system of regenerated length of 15 mm was perfectly repaired at 24 weeks after tabulation operation, as shown in Fig. 8(b).[12]

V. NEGATIVE-ION-BEAM DEPOSITION

In ion-beam deposition the kinetic energy of the ion usually ranges between several tens of eV and a few hundreds of

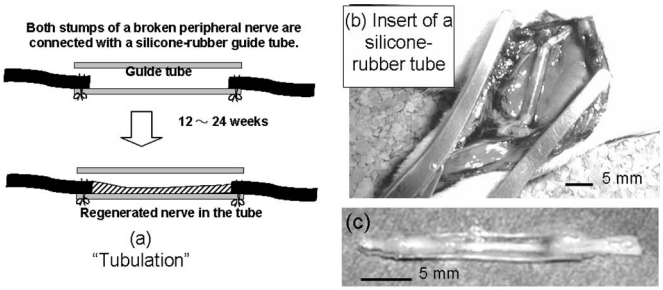

FIG. 8. Tubulation for regeneration of rat sciatic nerve: (a) a schematic diagrams of the "tubulation" method, (b) photograph of tubulated sciatic nerve of a rat, and (c) regenerated sciatic nerve in the tube.

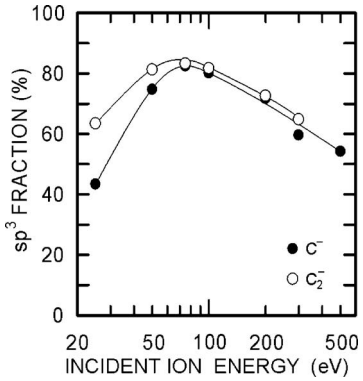

FIG. 9. sp^3 fraction as a function of the incident ion energy for films formed by C^-- and C_2^--ion-beam deposition.

eV. In positive-ion-beam deposition, the ionization potential strongly affects the atomic-bonding process and sometimes covers the effect of atomic bonding due to the ion's kinetic energy because the internal potential energy of positive ions (ionization potential) is comparable to the kinetic energy. On the other hand, in negative-ion-beam deposition atomic-bonding processes due to the kinetic energy (kinetic bonding) can occur because of the ion's small internal potential energy (electron affinity).

When we use a low-energy ion beam for film formation, the film material is formed through the kinetic-bonding process, which is quite a different process from thermal equilibrium chemical reaction. In the former process, metastable material formation is strongly promoted by the kinetic energy of ions.

Figure 9 shows the sp^3 fraction as a function of the incident ion energy for films formed by using C^- and C_2^- ion-beam deposition on silicon substrates.[6,14,15] The incident ion energy in the figure is the kinetic energy per atom. The sp^3 fraction strongly depends on the negative-ion kinetic energy, and it has a peak of 80% at an energy of around 50–100 eV. Therefore, tetrahedrally bonded carbon films were obtained under this deposition condition.

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