JPRS-JST-88-017 270087
17 AUGUST 1988

FOREIGN BROADCAST INFORMATION SERVICE

JPRS Report

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

Science & Technology

Japan

SURFACE REFORMING BY ION IMPLANTATION SYMPOSIUM

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

10
44
A03

JPRS-JST-88-017
17 AUGUST 1988

SCIENCE & TECHNOLOGY

JAPAN

SURFACE REFORMING BY ION IMPLANTATION SYMPOSIUM

43067592 Tokyo ION CHUNYU NI YORU HYOMEN KAISHITSU in Japanese 20 May 88

[Selections from the Symposium on Surface Reforming by Ion Implantation held 20 May 88 in Tokyo, sponsored by the Metal Engineering Research and Coordination Committee and the Materials Engineering Research and Coordination Committee Under the Science Council of Japan]

CONTENTS

Features of Ion Implantation, Surface Layer Processing

43067592a Tokyo ION CHUNYU NI YORU HYOMEN KAISHITSU in Japanese 20 May 88
pp 1-8

[Article by Masaya Iwasaki, Surface Analysis Office, Institute of Physical and Chemical Research: "Features of Ion Implantation and Use of Processed Materials; A Description of Ion Implanted Layers; Ion Implantation and Surface Layer Processing; Ion Implantation and Membrane Formation; Strange Material--Nitrogen Ion Implanted Steel"]

[Text] I. Introduction

The heart of a computer, the leading actor in the "information revolution," is, needless to say, LSI. It is ion implantation that plays an important role in adding impurities in the LSI manufacturing process. It is not going too far to say that but for this technology, the present LSI would not exist. Energy used for this technology has usually been 200 keV and below, while new technology which follows from this technology and uses emergy of 1 MeV and above is being developed. It is pointed out that this new ion implantation technology is likely to solve various problems which have accompanied the development of newer devices and micronization of devices.

In any event, R&D on ion implantation has been conducted as an impurity addition method for semiconductors, silicon in particular, and is still under way. Ion implantation, like lasers and plasma process, has never been brought into focus. It has always been unseen, but is a technology playing an important role in the background. Ion implantation is now beginning to be brought into focus, and is expected to pave the new way for surface layer modification of metals and ceramic polymers.

Ion implantation for metals has targeted improved corrosion resistance and wear resistance of surface layers of metals by applying alloys and ceramics. On the other hand, ion implantation into ceramics has targeted making their surface layers a different kind of ceramics or metallizing or forming buried metal layers, which is to reinforce the ceramics/ceramics junction and to compensate for the brittleness of ceramics by metallizing their surface.

Recently ion implantation for polymers has begun to draw attention. Polymers are materials found much more often than inorganic materials. They are said to be more susceptible to damage caused by radiation and it was considered that they would undergo great destruction during ion beam radiation, thereby making it difficult to obtain particle added effects. Some research results obtained so far, however, have experimentally shown that, though the carbonization phenomenon can be found, the apparent impurity doping effect can be obtained and that new radicals are produced, which has led to the beginning of a study of applying ion implantation to polymers.

Research into ion implantation for a pure carbon material has been actively pushed. Diamond, a single crystal carbon, is an attractive material as an ornament and as a machine tool material. There have been attempts to improve its life for machine tools and to form p-n junction. In addition, a carbon material is light in weight compared to other inorganic materials and less reactive chemically, thus a study on applying it to materials for artificial organs is being conducted.

As stated, ion implantation is expanding from the semiconductor field to penetrate into the vast area of material science. It is rare that a single technique is used for so many materials. The following are descriptions of the features of ion implantation, the use of processed materials, a comparison between ion implantation technology and conventional surface layer processing technology and relevant technologies such as ion beam accelerated deposition using the advantages of ion implantation, followed by the presentation of a mechanism for improving the wear resistance of a strange material--nitrogen ion-implanted steel.

II. Features of Ion Implantation and Use of Processed Materials

Ion implantation is a particle addition method involving ionizing particles intended for a vacuum (10^{-4} pa), accelerating them in an electrostatic field, and radiating them onto a solid substrate. Figure 1 shows the outline of ion implantation equipment. The equipment consists of an ion source to ionize particles, an accelerator to retrieve ions from the ion source and accelerate them, a mass separator to select necessary ions, an ion beam scanner to keep ion beams homogeneous on the radiation substrate surface, an implantation chamber to radiate ion beams and an exhaust device to produce a vacuum through the entire system. Energy used at present ranges from several tens of keV to several hundreds of keV, while the range of energy available is expanding from keV to MeV levels along with the progress in ion beam technology.

Ion implantation includes the following features derived from the construction of ion implantation equipment:

(1) The particle addition process under nonthermal equilibrium permits a free selection of a combination of ions desired and a substrate to add them to.

(2) The depth of ions to be added can be controlled by accelerating energy.

(3) The quantity of ions to be added can be controlled by ion beam current density and processing time.

(4) Mass separation results in excellent purity of added particles and ion beam scanning permits good surface homogeneity of added particles.

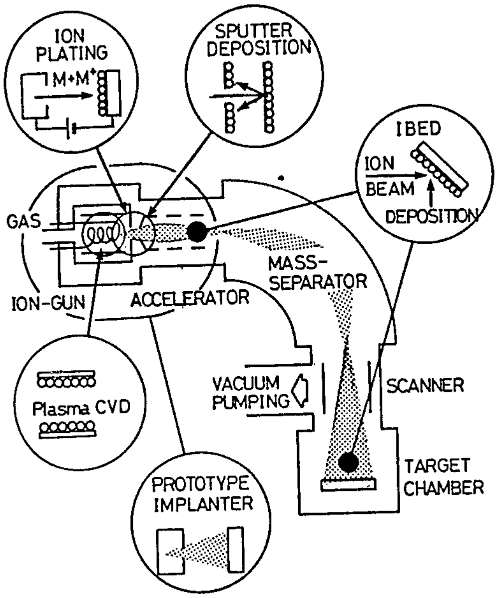


Figure 1. Outline of Ion Implantation Equipment

Of the above, the greatest feature of ion implantation is feature number (1). Any substrate to which ions are added can be selected if it is a solid and the selection is made in a vacuum and particles of any element to be added are also freely selectable from the periodic table. The addition and the depth of addition of necessary particles which have undergone mass separation can be precisely controlled. There are no such particle addition methods. Ion implanted materials can be used in the following three areas: (1) new materials as they are, (2) model products of new materials, and (3) standard materials.

Such materials are finding steadily growing applications as new materials in various machine tools, special parts and biomaterials, for example, an application to Ti-6Al-4V which is used as an artificial joint (in the United States). Implanting nitrogen ions into a Ti alloy results in excellent conformability with its partner material (ultrahigh density polyethylene) and improved corrosion resistance and wear resistance. They are also used for shuttle-related bearings in the aerospace parts field. With regard to machine tools, ion implantation is being attempted, aimed at improving cutting ability and life of drills and punches in the electron device manufacturing process.

There are no application examples of model products (2). This concept originates due to the fact that since 1 eV corresponds to about 10,000 degrees, ion implantation can be regarded as a kind of ultimate technology--manufacturing a model product through ion implantation in which a free selection of a substrate and adding particles is possible and thereby manufacturing products using ultimate technologies such as ultrahigh pressures and temperatures.

As for standard materials (3), they have already been used for standard samples in the surface analysis method, for example when creating calibration curves in the secondary ion mass analysis method. They will be applied in the future to Auger electronic spectroscopy, photoelectric spectroscopy and Rutherford back scattering.

III. Description of Ion Implanted Layer

The interaction between ion beams and a solid yields three kinds of effects in terms of modification--deposition effect when ions are accelerated at several tens of eV, sputtering effect by some-keV ion radiation, and implantation effect when ions are radiated at several tens of keV and above. These effects, however, cannot be distinguished strictly according to energy used, and they can be found mixed in some cases. Therefore, ion implantation is a particle addition method using this third effect and when the implantation effect is great in modifying surface layers through ion beam radiation, it should be regarded as ion implantation technology or ion implantation-related technology irrespective of energy used.

When ions are radiated on a solid to penetrate it, the ions which have penetrated it repeat elastic and nonelastic collisions between them and substrate atoms, lose energy, and stay within the solid. As shown in Figure 2, around the track of an ion which has penetrated, a substrate atom which has been knocked out in collision repeats collisions, causing a great quantity of radiation damage. The track of one implanted ion differs from that of another, so ions are distributed. As shown in Figure 2, the distribution shape of implanted ions can approximate Gauss distribution with a given depth as its maximum concentration. The distribution of radiation damage is maximum at a position shallower than the depth of the maximum concentration of implanted ions, each ion converting several hundred atoms. Thus, particle penetration under nonthermal equilibrium results in new materials or structures formed on the surface layer of a solid substrate, the surface layer coming to show properties different from its parent material.

A criterion of the depth permitting modification through ion implantation is the depth of maximum concentration in the distribution of implanted ions. The depth to which implanted ions penetrate can be determined by a substrate, a type of ion and ion accelerating energy to be used. Energy of about 100 keV so far permits a maximum concentration depth of about 0.1 μm and an extremely shallow modification depth. Possible MeV-level ion implantation in the future will result in modification depths of the μm level, thereby realizing processing depths equal to those by the conventional surface processing methods. For this reason, great expectations are placed in the development of MeV-level ion implantation equipment.

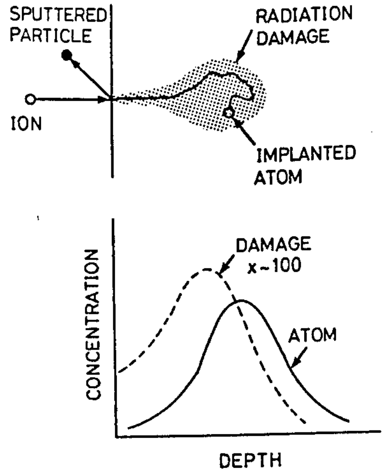


Figure 2. Ion Implantation Effect and Depth Distribution of Implanted Ions and Radiation Damage

Since ion implantation is one of the ion beam radiation methods, it causes sputtering and the surface is cut off without fail. In other words, ion implantation is a method for adding particles while cutting off the surface. Therefore, the effect of sputtering on the distribution of implanted ions must be taken into consideration. Figure 3 shows the distribution of implanted ions in Ti (titanium) ion implantation into Fe (iron) and N (nitrogen) ion implantation into Al (aluminum) in terms of functions of the quantity of their implantation. The sputtering rates in Ti-ion implantation into Fe and N-ion implantation into Al were 3 atoms/ion and 0.3 atoms/ion, respectively. With a high sputtering rate, the distribution of implanted ions deforms from Gauss distribution as implantation quantity increases and a maximum concentration is finally shown on the surface. Such distribution has already been approved experimentally in ion implantation at 10-100 keV. In MeV-level ion implantation, the sputtering rate will become low, little affecting implanted ion distribution, which will permit an alloy layer to be buried inside of a solid.

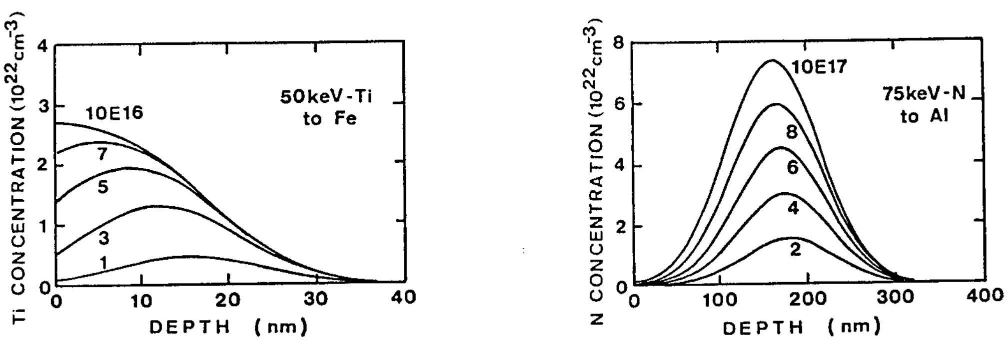


Figure 3. Theoretically Predicted Distribution of Implanted Ions in Ti-Implanted Fe and N-Implanted Al

Meanwhile, when the sputtering rate is low, it can be predicted that a maximum concentration of implanted ions will exceed an atomic concentration of the parent material. The experimental result, however, showed that the concentration of implanted ions does not exceed that of the parent material and that crystal growth of a compound is made internally. Internal crystal growth of a compound is a feature unique to ion implantation and MeV-level ion implantation will make it possible to bury new alloys or compounds.

IV. Ion Implantation and Surface Layer Processing

In industrial applications, ion implantation can be used for processing surface layers. As shown in Figure 1, ion implantation equipment includes a plasma CVD and PVD device. For example, an ion source of ion implantation equipment is a kind of plasma CVD device. In other words, a gas introduced into the ion source collides against electrons to be ionized, but an ionization chamber is in plasma where electrons coexist with ions. In ion implantation, ions are retrieved from this plasma to be accelerated. On the other hand, a kind of plasma CVD involves not retrieving ions out of plasma, but confining plasma within the ionization chamber and coating a membrane on its inner wall. Therefore, in obtaining carbon ion beams by introducing an acetylene gas, carbon beams cannot be obtained depending on discharge conditions and carbon membrane coating occurs on the inner wall of the ionization chamber.

A large gas flow into the ionization chamber and ions and a large quantity of neutral particles coming out of the ion takeoff port result in a kind of PVD, namely, equivalence to ionization plating. When an ion beam retrieved diverges to radiate a pulling electrode, the electrode material undergoes sputtering to be coated on the external wall of the ion source. This is ion beam sputter deposition. A simplified ion implanter uses the process up to the mass separator in Figure 1 as a system on the assumption that an ion beam has been retrieved. The commercial nitrogen dedicated ion implantation equipment uses this system.

Dynamical mixing (referred to as ion bean assist deposition or ion beam accelerated deposition) combining ion beam radiation and vacuum deposition which has recently begun to be researched actively, uses an ion implanter or a simplified ion implanter with a deposition device in its implantation chamber. This deposition method includes electron beam deposition and sputter deposition, selected according to usage.

In ion implantation, the place where ions are generated as a tool and processing chambers such as an accelerator, mass separator and implantation chamber which make ions a high performance beam, are distant from one another and controlled independently. Ion implantation, therefore, is superior in controllability in creating materials, but inferior to other PVD and CVD in processing ability. In other words, it can be said that PVD and CVD are relatively high in processing ability, but inferior in controllability. Ion beam accelerated deposition can be regarded as a technique between this conventional method and ion implantation, namely, a method combining the advantages of ion implantation and those of PVD. Table 1 shows a summary of a comparison of these techniques.

Table 1. Comparison of Ion Implantation, Ion Beam Accelerated Deposition, PVD and CVD

Processing method	Ion implantation	Ion beam accelerated deposition	PVD	CVD
Feature	Particle addition under nonthermal equilibrium	Coating at room temperature	Coating at low temperatures	Coating at high temperatures
Processing temperature	Free, room temperature permissible	Free, room temperature permissible	Hundreds of degrees C	~1,000°C maximum
Processing thickness	0.1-1 µm	0.1-several µm	Several µm	Several µm
Processing speed	Low	Medium	Medium	High
Crystallization	Degree of freedom available	Degree of freedom available	Temperature control	Temperature control
Processing pressure	0.0001 pa	0.01-0.001 pa	0.1 pa	100 pa

V. Ion Implantation and Membrane Formation

One of the important fields of ion implantation technology is diversifying types of ions. The number of types of ions used for surface layer modification at the Institute of Physical and Chemical Research amounts to 47, about half the elements in the periodic table. Ion beams, like ions themselves, have their own features, which result in different degrees of difficulty in generating ion beams. For materials for which direct addition of particles by an ion beam is difficult, a surface layer modification method by ion beam mixing combining membrane formation and an ion beam has been developed.

Ion beam mixing, mainly using cascade collision by radiated ions, is a method for mixing membrane atoms and substrate atoms without using heat, which is likely to permit creation of a surface layer the same as one created through ion implantation. The depth of modification by this method, however, depends on ion beam range. The methods for making the modification depth greater using an ion beam include ion beam assist deposition and ion beam accelerated deposition. These methods, involving ion implantation while depositing, put no restrictions in principle to the membrane thickness. The composition of a membrane to be created depends on ion beam current and deposition speed.

Figure 4 shows a summary of these approaches. In the figure, technology (a) shows direct ion implantation for forming semistable surface layer alloys through metal ion implantation into metals and forming metal buried layers through metal ion implantation into ceramics. Technology (b) shows ion beam mixing involving forming a layer where substrate atoms and membrane atoms are mixed by implanting ions through a membrane. Technology (c) is interface mixing involving mixing peripheries alone of a membrane and a substrate, while technology (d), involving ion beam assist deposition and ion beam accelerated deposition, is a method for simultaneously conducting vacuum deposition and ion beam radiation (ion implantation).

Ion beam assist deposition and ion beam accelerated deposition are used without strictly being distinguished. Therefore, for the sake of future reference, let us define these terms as follows: ion beam radiation used in assist deposition is a case where a compound of added ions is formed. Therefore, the former is to improve the adhesion between a membrane and a substrate and to control the crystallization of membranes, while the latter is the same except that a compound of added ions is formed. The technology combining vacuum deposition and ion implantation with an electron beam has been put to practical use for processing blades of electric shavers.

VI. Strange Material--Nitrogen-Implanted Steel

The type of ion used most for improving wear resistance is a nitrogen ion. Nitrogen ion implantation into steel, in particular, ranges from basic to applied research. The reasons for this include ready availability of a large quantity of nitrogen ion beams and nitrogen ion implantation being taken for ion nitriding. Nitrogen ion implantation, however, is substantially different from ion nitriding. The former is processing under nonthermal equilibrium, while the latter uses a thermal equilibrium process. In addition, ion implantation permits a nitrified layer to be formed from inside and substrate temperatures and additions to be freely controlled, while ion nitriding enables a nitrified layer to be formed from the surface and needs high processing temperatures.

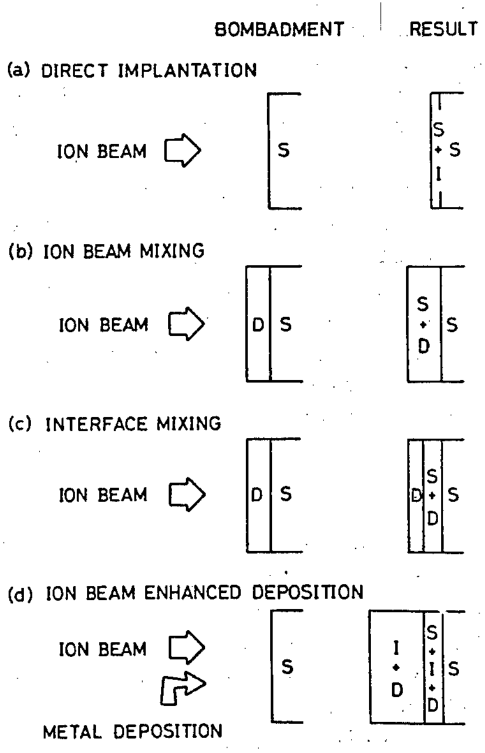


Figure 4. Ion Implantation Related Technologies

Assuming that the depth of ion implantation processing is the depth where a maximum concentration of implanted ions exists, a processing depth through nitrogen ion implantation will be around 0.1 μm. In order to find the reasons for wear resistance and how it can be improved in such a shallow modification layer, a great number of studies have been conducted. The common results obtained so far can be summarized in the following three points:

(1) Nitrogen ion implantation causes hardening in a surface layer.

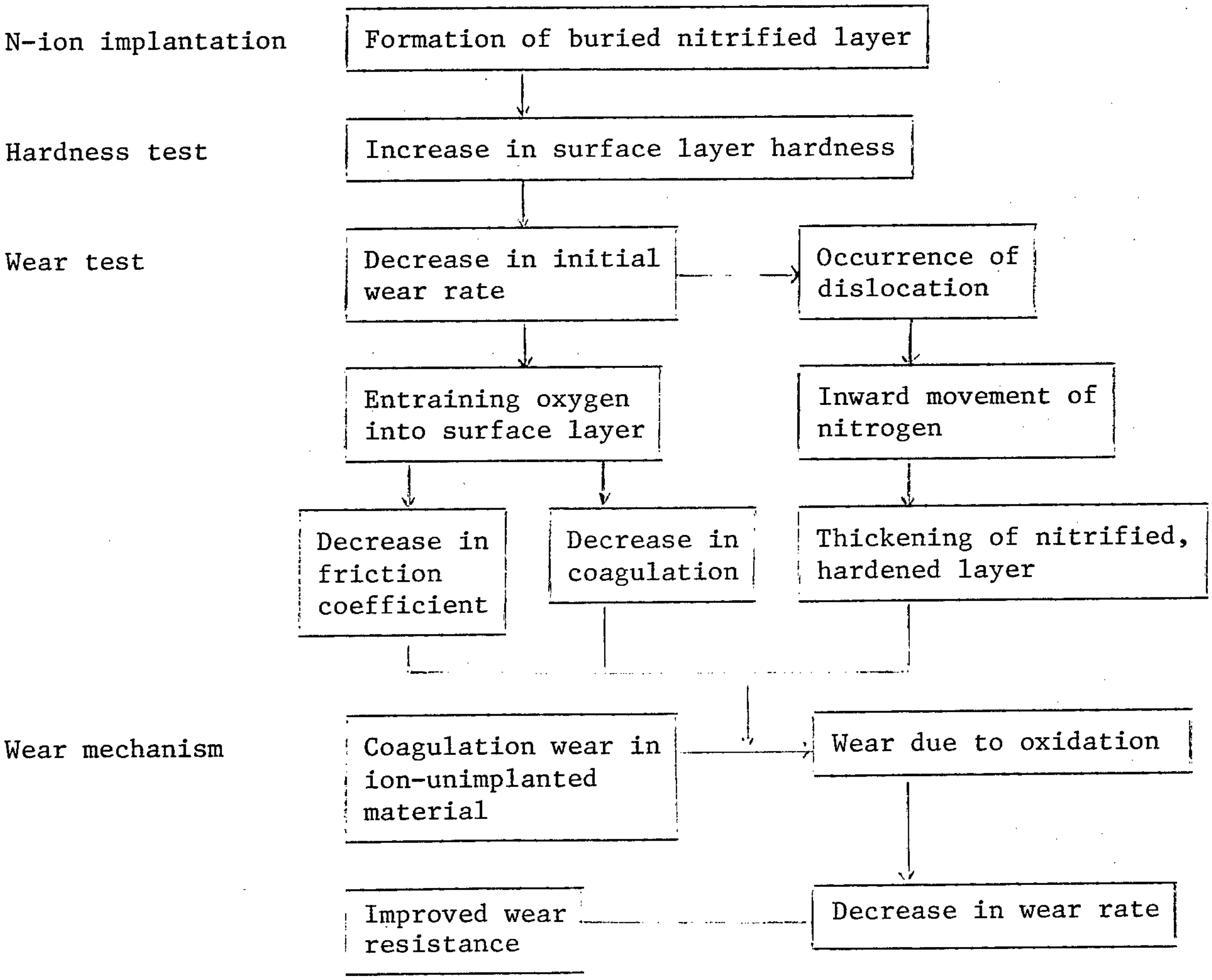
(2) Nitrogen ions implanted during a wear test penetrate deep inside.

(3) The analysis result of the composition on wear track shows that the presence of oxygen not discernible in ion unimplanted materials can be discerned in ion implanted materials.

Hardening in a surface layer (1) can be explained through the formation of nitride, while (2) is regarded as a result of nitrogen moving via a dislocation net which occurs during a wear test. In addition, the presence of oxygen (3) can be discerned with nitrogen ion implanted materials with low wear rates compared to ion unimplanted materials, the reason for which is unknown.

From the above results and analysis results of wear powder, the mechanism of improving wear resistance through nitrogen ion implantation is summarized in Table 2: A buried nitrified layer is formed in the surface layer of steel through nitrogen ion implantation. The formation of this nitrified layer causes hardening in the surface layer, resulting in a decrease in initial wear rates. Oxygen entrained during initial wear results in a decrease in friction coefficients engineeringwise and a decrease in coagulation physically. In addition, nitrogen implanted via dislocation which occurs in friction at low wear rates partially moves inside. Inner movement of nitrogen via dislocation promotes thickening of a buried nitrified hardened layer. These phenomena show that coagulation wear discerned in wear tests of ion-unimplanted materials shifts to oxidation wear through nitrogen ion implantation. Therefore, it is considered that a shift in the wear mechanism from wear due to coagulation (severe) to wear due to oxidation (mild) results in decreased wear rates and improved wear resistance. Such results have been discerned also with nitrogen ion implanted titanium alloys.

Table 2. Outline of Improving Wear Resistance of N-Ion Implanted Steel



From these results, it is understood that one of the requirements for improved wear resistance of a steel to be obtained through nitrogen ion implantation is the occurrence of oxidation from its surface, or its surface layer coming into contact with air. Proof of this was found in a wear test using a chuck and rods. Sliding contact conditions with these materials are continuous contact for chuck materials and repetition of contact and non-contact (in contact with air) for rods. Improved wear resistance through nitrogen ion implantation has been found with rods, but not with a chuck, which shows that wear resistance of a steel can be improved if its surface layer comes into contact with air.

In any event, the primary requirement of improving wear resistance of a steel through nitrogen ion implantation is hardening in its surface layer. Substrate temperatures during ion implantation is related to the degree of hardening in the surface layer of a steel. Also, it is believed that the distribution of nitrogen implanted is related to the presence of oxygen which improves wear resistance of a steel, so that it is important to conduct further study on it. In this context, in order to put nitrogen ion implanted steel to practical use, it is necessary to conduct a detailed study of the optimization of implantation conditions such as implantation energy of up to the MeV level, a dose and substrate temperatures for implantation together with their service conditions.

VII. Conclusion

A study on improving wear resistance of the carbon material through ion implantation has recently been drawing attention from the standpoint of its application to biomaterials. The reasons for this are the carbon material's superiority in adaptability to organisms, compactness and light weight and large penetration depths of implanted ions due to its low Z number. In the relation between ion beam technologies including ion implantation and the carbon material, forming carbon membranes from gaseous carbon has been studied most actively, the formation of diamond membranes drawing greatest attention. Crystallization transformation control for formed membranes is also an important subject, but few research examples involving it are available. It is considered that ion implantation plays a great role in particle addition because adding different types of elements to the carbon material is limited in the thermal equilibrium process. In this field, a vast research area is left untouched. Anyway, ion implanted materials are very rare to be found in the world.

References

1. Kiyota Yoshida, Susumu Namba and Masaya Iwaki, "Surface Layer Modification Technology Through Ion Implantation," SCIENCE FORUM, 1987.

2. S. Tamura, Semiconductor World, 6, No 14, 67, 1987.

3. Masaya Iwaki, NEW DIAMOND, 4, No 1, 13, 1988.

4. Masaya Iwaki, JITSUMU HYOMEN GIJUTSU, 34, No 10, 402, 1987.

5. Mrs Bullentin, 12, No 2, 1987.

6. Masaya Iwaki, HYOMEN, 25, 676, 1987.

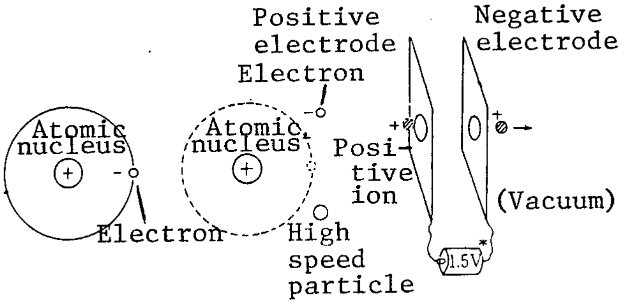
Large Scale Ion Source, Applications to Fine Processing, Membrane Processing Equipment

43067592b Tokyo ION CHUNYU NI YORU HYOMEN KAISHITSU in Japanese 20 May 88
pp 27-33

[Article by Tadashi Sato, Hitachi Research Institute, Hitachi, Ltd.: "Large Scale Ion Source; Applications to Fine Processing Equipment; Applications to Membrane Processing Equipment"]

[Text] I. Introduction

Any material usually exists as an electrically neutral atom with a negative electron centering around a positively charged atomic nucleus, as shown in Figure 1 (a). When an atom is heated at high temperatures or it collides with other electrons or atoms, as shown in Figure 1 (b), part of the outside electron is lost which results in a positively charged atom, i.e., an ion. As shown in Figure 1 (c), an ion can be accelerated with an ordinary 1.5-V dry cell up to a speed of 1.5 eV. Considering that heating an ion to more than 10^4°C is required to provide the same speed through thermal motion, this is the simplest method for providing matter with high energy (high speed).



*: Technically easy at 100 V and above

(a) Atom (b) Positively charged atom (positive ion) (c) Acceleration of positive ion

Figure 1. Method of Ionizing and Electrically Accelerating an Atom

Thermal motion is each atom's motion in random directions with speed distribution, while the motion in Figure 1 (c) is referred to as an ion beam as it is motion of an atom in a specific direction. On the above principle, any atom can be accelerated with ease after it is made into an ion and has been applied to various uses where matter must be accelerated at high speeds. Examples of this are: 1) an accelerator to clarify the material structure in detail and 2) an ion implanter indispensable for adding impurities to semiconductors. In comparison to the conventional impurity-adding method using heat, the ion implanter has permitted for the first time the accurate addition of specific matter at a constant depth and in a constant quantity necessary at room temperature, thereby making precision control of semiconductor properties possible. As a result, ion beam technologies are playing an active role at present in manufacturing semiconductor parts which are a central part of devices from a desk-top calculator for everyday use to a national-scale large computer for seat reservations for the new trunk lines' bullet trains.

In research into nuclear fusion aimed at developing energy for the next age, technology for generating a great quantity of ion beams to meet the need of stably maintaining plasma heated up to 0.1 billion degrees C has been developed. With regard to a plasma heating system, for example, as shown in Figure 2, a great quantity of high speed hydrogen ion beams generated at the ion source is implanted into nuclear fusion plasma at high efficiency and the plasma is heated with high speed hydrogen caught by it. The ion source in this case must be capable of generating beams with large area and high speeds in quantities. In this context, a large scale ion source capable of providing 40 A for 30-100 keV--a large ion beam output more than 1,000 times the conventional output--has been developed[1,2]. This ion source features facilitating large aperture, large current and high voltage acceleration because of its simple structure. Consequently, this has resulted in the development of fine processing equipment for mass processing of fine patterns of membrane devices such as membrane magnetic head utilizing its feature of large aperture[3] and membrane-producing equipment for nonsemiconductor materials such as metals and ceramics into which a large quantity of ions are implanted[4]. This equipment is used for developing new devices and materials at present.

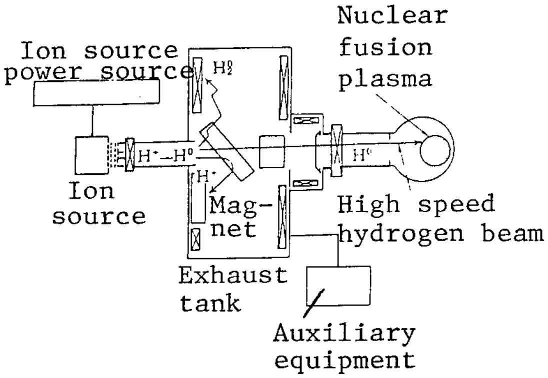


Figure 2. Nuclear Fusion Plasma Heating System Using Ion Source

The following are descriptions mainly of the basic structure of the large aperture ion source developed for nuclear fusion and of fine processing equipment and membrane producing equipment applying the large aperture ion source.

II. Large Aperture Ion Source

Various ion sources had been proposed for use in nuclear fusion early in the decade beginning with 1975, but finally the current mainstream in applications both in fine processing and producing membranes is the bucket type ion source[5] developed by Britain's Culham Atomic Power Research Institute, due to its ease in obtaining large aperture and simple structure.

Figure 3 shows an example of the section of a bucket type ion source. First, primary electrons discharged from the cathode (heated tungsten filament) are accelerated by a voltage of about 100 V impressed between the cathode and the anode (plasma chamber's vessel wall) and allowed to collide against gas molecules on the way, permitting plasma to be made through arc discharge with doubled electrons. Next, voltage is impressed, as shown in Figure 1 (c), between more than one pulling electrode with multiple holes, accelerated in the electric field, and retrieved as an ion beam. Types and uses of ion beams depend on the gas introduced into the plasma chamber. In nuclear fusion, hydrogen or deuterium gas is introduced, while in fine processing, argon, a chemically inert gas, and a chemically active fluorine compound gas are used. Gas pressures in the plasma chamber range from 0.1 to 0.5 Pa (0.1 P $\cong 10^{-6}$ atmosphere) and about 1 percent of this gas is changed into plasma.

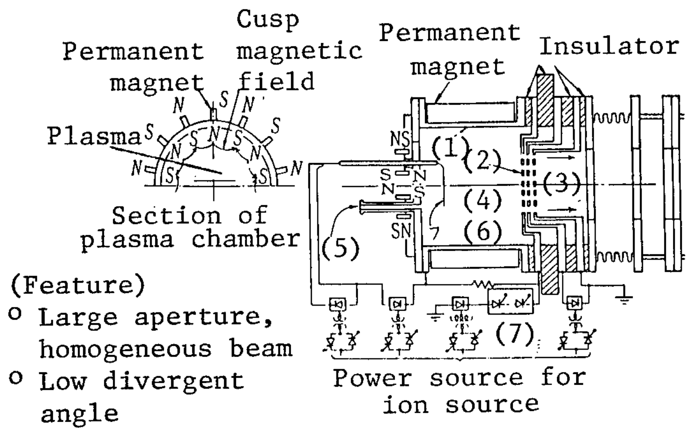


Figure 3. Bucket Type Ion Source

Key:
1. Anode
2. Pulling electrode
3. Ion beam
4. Plasma chamber
5. Gas inlet
6. Filament
7. High speed switch

As shown in Figure 3, a bucket type ion source has permanent magnets arranged around its plasma chamber and plasma confined by permanent magnets whose magnetic poles change alternately, so that plasma loss on the chamber wall surface is insignificant. The central part of the plasma chamber, free from a magnetic field, permits homogeneous plasma to be created. In addition, since the magnetic field on the wall surface of the plasma chamber moves together with the wall, little presence of a magnetic field can be detected. This permits the central part of the plasma chamber where homogeneous plasma is confined to be provided with a large aperture by expanding the inside diameter of the chamber. Figure 4 shows a computer simulation of an orbit of a primary electron from its popping out of the filament cathode to reaching the anode consisting of walls of magnetic fields generated by permanent magnets. The result shows how a primary electron which is near the anode is reflected repeatedly by the walls of the magnetic fields and confined in the plasma chamber.

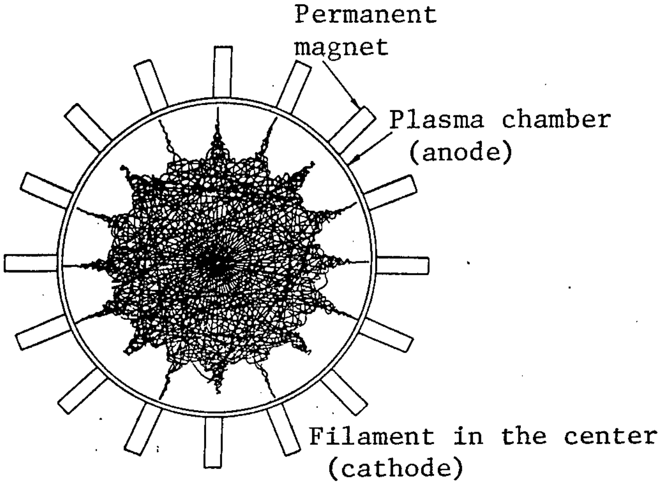


Figure 4. Computation Example of Orbit of Primary Electron Confined by Magnetic Fields of Permanent Magnets

III. Application to Fine Processing Equipment

In the magnetic recording field whose most important developmental target is improved recording density, in order to substantially increase recording density by miniaturizing a magnetic head for recording and playback, membrane magnetic heads shown in Figure 5 produced in the membrane process are being developed actively[6]. With respect to permalloy used for membrane magnetic heads, for example, a permalloy membrane and a fine photoresist pattern used on it are cut at the same time, as shown in Figure 6, with the use of an accelerated argon beam, applying photography. As a result, permalloy in the portion where a photoresist remains, permalloy in the portion where there is none is cut, and finally a permalloy membrane with the same pattern as that in the photograph can be obtained on a wafer. A magnetic head (Figure 5) can be made by repeating the membrane producing process to produce a membrane with a homogeneous membrane thickness on a wafer and the fine processing process to process a fine pattern on a membrane.

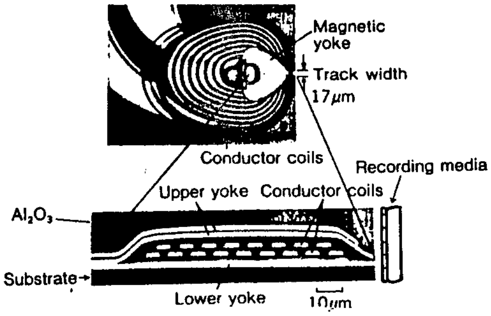


Figure 5. Structure of Membrane Magnetic Head

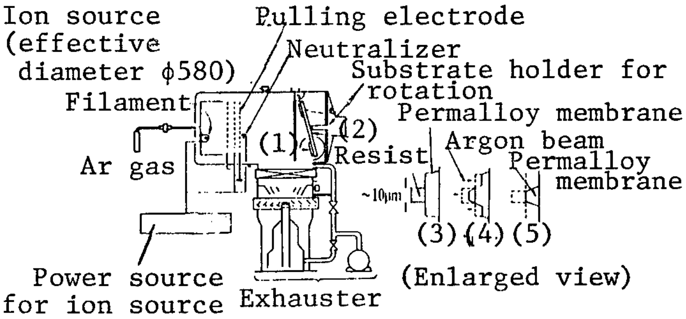


Figure 6. Ion Milling Equipment

Key:

1. Substrate
2. Shutter
3. Before processing
4. In processing
5. After processing

A voltage between 500-1,000 V is impressed on the electrode (Figure 1 (c)) and an argon ion is accelerated to 2-3 km/sec to collide against the surface of a photoresist and permalloy membrane. Part of the ion's kinetic energy is absorbed by atoms on the surface and the surface is gradually cut through sputtering coming off the surface. Surface cutting speeds usually range from 20 to 50 nm/min, depending upon incident angles, energy, ion densities and membrane materials. This process is referred to as ion milling and when chemical reactions are applied to this, it is called reactive ion beam etching.

Compared to the semiconductor field where ion chemical reactions are mainly used, fine processing using argon ion beams which cut membrane surfaces by kinetic energy generated in collision, provides low cutting speeds irrespective of membrane materials. Consequently, fine processing equipment--capable of simultaneously radiating an ion beam on multiple wafers thanks to a large aperture ion source and suitable for mass production on an industrial scale--has been developed and put to practical use. Figure 7 shows equipment capable of simultaneously radiating an ion beam on 16 3-inch wafers using a large aperture ion source with a diameter of 580 mm applying an ion source for nuclear fusion[3]. The equipment is capable of processing tens of thousands of magnetic heads per month per unit.

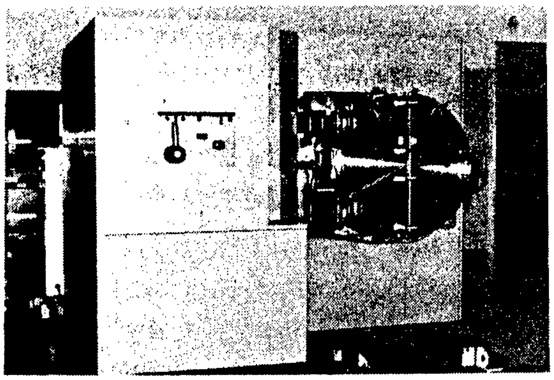


Figure 7. Appearance of Ion Milling Equipment Applying Large Aperture Ion Source for Use in Nuclear Fusion

IV. Application to Membrane Producing Equipment

When ion energy is raised to more than about 10 keV, a high speed ion itself can penetrate up to a constant depth while repeating collisions within a solid as well as cut the surface through sputtering. A method for adding specific matter to materials is referred to as ion implantation. When prospects of ion implantation into semiconductors were seen, some researchers began ion implantation into metals and ceramics[7,8]. Of the results, the most noteworthy industrially is improving the life of tools and dies through nitrogen ion implantation. An example shows that the life of some tools into which nitrogen ions--more than 100 times the dose for semiconductors--accelerated to about 100 keV were implanted, was extended more than 10 times[9]. This can be said to be surprising, considering the implantation depth of about 0.1 μm from the surface. When temperatures exceed 500°C, nitrogen on the surface diffuses internally, causing no effect.

Spurred by these facts, attempts to improve corrosion and wear resistance of various bearings and concrete applications of ion implantation to artificial bones, have begun in the United States. In order to further develop this method as an industrial technology, however, it is necessary to improve the above-mentioned membrane (about 0.1 μm) and the limit in temperatures (below 500°C). To attempt this, as shown in Figure 8, there is dynamic mixing simultaneously combining other membrane-producing means such as deposition and ion implantation. It is a method involving depositing a metal membrane on the sample surface, simultaneously implanting ions of several tens of keV, producing a compound membrane on the surface with the implanted ions and the deposited membrane, and permitting any membrane thickness to be obtained by preventing thermal diffusion under high temperatures and increasing processing time. Therefore, the above restriction incurred by ion implantation can be reduced. This method also permits a mixed layer of mutual atoms between the specimen and the membrane[11], and has the possibility of controlling crystal growth irrespective of surface materials.

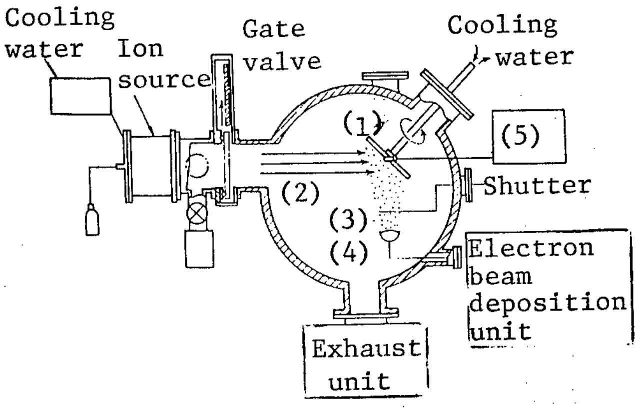


Figure 8. Construction of Dynamic Mixing Equipment

Key:

1. Sample holder
2. Ion beam
3. Metal
4. Vapor
5. Membrane thickness monitor

The ion source of dynamic mixing equipment must supply as large a quantity of ions as deposited metal over a wide area. To this, large aperture ion source technology for nuclear fusion shown in Figure 3 is applicable. As for output of an ion source, a nitrogen ion (N^+ - 50 percent, N_2^+ - 50 percent) provides up to 600 mA. A metal ion with specific energy cannot be retrieved out of compound gas plasma as mass separation has not been conducted, but a large quantity of nitrogen ion beams suitable for iron and aluminum materials can be generated. In the case of oxygen ions, filament exhaustion results in their short life, so that an ion source not using heated filaments is required. To this end, an ion source (Figure 9) which has plasma made of microwaves as its cathode provides direct current discharge with electrons pulled out of cathode plasma, and has plasma confined in the cusp magnetic field[12]. This ion source provides homogeneous, large aperture plasma and is suitable for chemically active gases as well as oxygen ions.

Figure 10 shows electronography of a section of titanium nitride with a membrane thickness of 15 μm produced on the surface of an aluminum alloy at room temperature with dynamic mixing equipment[13]. The total number of nitrogen ions implanted is $10^{20}/cm^2$, 10^5-fold that of a semiconductor and 10^3-fold that for implantation only into metal materials. It can be said that the application of ion source technology for nuclear fusion has paved the way for membrane-producing technology using a large quantity of ions on an industrial basis. In the ion source for nuclear fusion, however, it is difficult to make a filter to retrieve ion beams with homogeneous mass and energy, so it is not suitable for use in impurity addition to semiconductors requiring a small quantity of, yet high-precision, ion implantation.

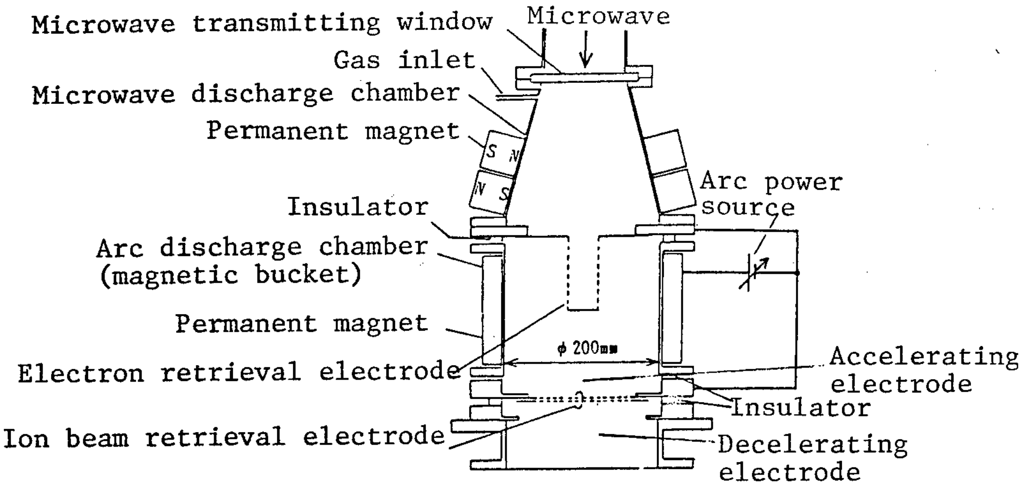


Figure 9. Ion Source With Microwave Plasma as Its Cathode

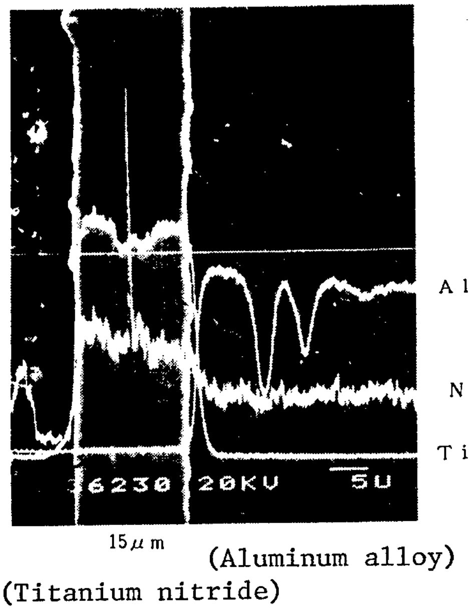


Figure 10. Scanning Type Electronography of a Section of Titanium Nitride Produced on Aluminum Alloy Surface at Room Temperature Through Dynamic Mixing

V. Conclusion

The above has described a large aperture ion source whose development has made progress through nuclear fusion and its applications. Plasma and its application technologies including ion source applications are a field of great interest expected to develop in the future.

References

1. T. Obiki, et al., Rev. Sci. Instrum. 52, 10, 1445, October 1981.
2. S. Matsuda and M. Akiba, Symp. Proc. ISIAT '87, p 95, June 1987.
3. Arimatsu, et al., HITACHI HYORON, 68, 6, 49, June 1986.
4. T. Sato, et al., J. Vac. Sci. Technol. A4, 3, 784, May 1986.
5. T.S. Green, 10th Symp. Fusion Tech. 2, 873, September 1987.
6. M. Hanazono, et al., J. Appl. Phys. 61, 8, 4157, April 1987.
7. N.E.W. Hartley, Wear 34, 427, 1975.
8. Iwaki, OYO BUTSURI, 53, 8, 700, August 1984.
9. J.K. Hirvonen, Symp. Proc. Ion Implantation and Ion Beam Processing of Materials, p 621, November 1983.
10. P. Sioshansi, (private correspondence).
11. M. Kiuchi, et al., Japanese J. Appl. Phys. 26, 6, L938, June 1987.
12. Kamata, et al., 1988 National Convention of Electrology Society, Lecture No 61.
13. T. Sato, et al., NIM B 19/20, 644, 1987.

Ion Implantation Into Metal Materials

43067592c Tokyo ION CHUNYU NI YORU HYOMEN KAISHITSU in Japanese 20 May 88
pp 34-41

[Article by Naotake Okubo, Engineering Planning and Management Division, Nippon Steel Corporation: "Improvement of Surface Mechanical Properties; Improvement of Corrosion Resistance; R&D Status of Industrial Ion Implanting Equipment; Future Subjects"]

[Excerpts] I. Introduction

With regard to surface modification of metal materials, steel materials and steel manufacturing equipment in particular, plating, painting and thermal spray were used in the early years to improve their corrosion resistance, thermal resistance, wear resistance and ornamental adaptability. In recent years, the dry process such as vacuum deposition, P-CVD, sputtering and ion plating have been under development and a steel sheet with high corrosion and thermal resistance with ceramic membranes (SiO_2, TiN, etc.) coated on a steel coil in succession through the dry process has appeared[1].

As a matter of fact, plasma thermal spray, CDD and ion plating for steel manufacturing tools and rolls to improve their wear resistance are substantially involved in the problem of flaking due to poor adhesion between a coating membrane and a substrate and have not been put to practical use except for a few examples.

On the other hand, ion implantation, a nonthermal equilibrium process, is free from the flaking problem because it permits the surface layer of a substrate to be modified by directly implanting ions into it, enables any element ionizable to be used for implantation, and provides good controllability with respect to implantation depths, dosage and additional concentration beyond the conventional standard.

The following are descriptions of mechanical characteristics of metal materials surfaces which result from ion implantation, experimental examples of improving corrosion resistance, and subjects of research and development for the future involving industrial ion implanting equipment and ion implantation technology.

II. Improvement of Surface Mechanical Properties[2,3]

1. Experiment

The following are descriptions of examples of the modification of surface mechanical properties in implanting nitrogen, oxygen and titanium ions into four types of iron-chrome steel substrates with different chrome concentration. Their implantation conditions and test and analysis methods are as follows:

(1) Implantation conditions

a. Substrate: Fe-Cr binary chrome steel
Chrome concentration: 5, 10, 15, 20 wt percent
Polishing: 0.5 μm diamond buffing

b.

Ion to be implanted	Accelerating voltage	Dose
N_2^+	50 keV	5×10^{16} ion/cm^2
O_2^+	100 keV	5×10^{16} ion/cm^2
T_i^+	150 keV	1-3 $\times 10^{17}$ ion/cm^2

c. Implanting equipment: Riken low current type ion implanting equipment

(2) Surface mechanical properties

a. Hardness measuring: Micro-Vickers penetrometer (2 gf)

b. Friction test: BOWDEN-LEBEN testing machine

c. Surface analysis: X-ray photoelectric spectral analysis (XPS)

2. Nitrogen, Oxygen Ions Implantation Effects and Their Study

Figures 1 and 2 show changes in hardness of chrome steel materials against each chrome concentration after implanting nitrogen and oxygen ions into them and changes in their friction coefficient, respectively. Observing both figures shows that implanting nitrogen or oxygen results in increased hardness of chrome steel substrates and decreased friction coefficient. It also shows that with respect to hardness, implanting both nitrogen and oxygen results in almost the same hardness increase effect as the hardness of an unimplanted chrome steel substrate increases. With regard to friction coefficient, an unimplanted substrate shows almost constant values, ion implantation results in a remarkable decrease, with implanting oxygen ions resulting in a greater effect. In implanting either of them, changes in the abrasive effect accompanying an increase in hardness is responsible for a decrease in friction coefficient. It is believed that the difference in friction coefficient between a nitrogen ion and an oxygen ion results from the difference in depositing force on the surface after implantation between them.

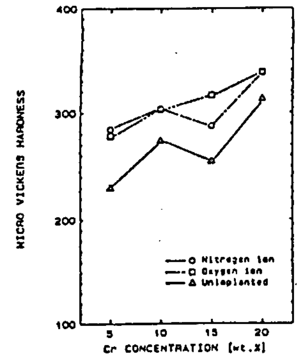


Figure 1. Micro-Vickers Hardness of of N_2^+ or O_2^+-Implanted Specimens as a Function of Cr%

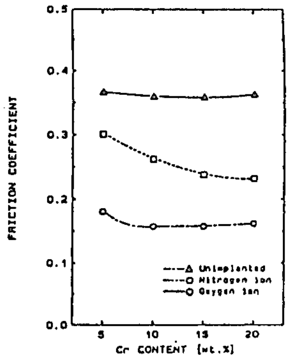


Figure 2. Friction Coefficient of N_2^+ or O_2^+-Implanted Specimens as a Function of Cr%

Analysis (Figure 3) by XPS of a coupling situation of implanted nitrogen ions in a substrate implanted layer finds that implanted nitrogen ions have formed chrome and Cr_2N. With oxygen ions, too, XPS analysis finds that Cr_2O_3 has been formed. In implanting either ion, a compound of it and chrome seems to cause increased hardness and decreased friction coefficient.

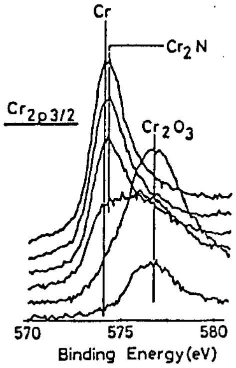


Figure 3. XPS Related to $Cr_{2p3/2}$ in the N_2^+-Implanted Specimen

3. Titanium Implantation Effect and Its Study

Figures 4 and 5, showing changes in hardness and friction coefficient respectively, reveal that the effect of implanting titanium ions is different from that of implanting nitrogen and oxygen ions in the previous section. Implanting titanium ions has resulted in an increase in hardness (Figure 4), while implanting titanium ions has caused friction coefficient of a high chrome material to increase reversely, approaching values of unimplanted materials (Figure 5). In other words, it is found that in implanting titanium ions, a decrease in depositing force has contributed to the decrease in friction on the ion-implanted surface more than the abrasive effect. With respect to implanted titanium ions, in-surface layer analysis in XPS analysis against each sputtering depth (Figure 6) shows that carbon has penetrated into the layer, resulting in the anticipation of TiC formation. However, TiC spector could not be observed, and it is assumed that an Fe-Cr-Ti-C semistable alloy which is different from metal coupling has been formed. The high chrome concentration of this tetra-semistable alloy results in an increase in its hardness but no change in its friction coefficient, while as its chrome concentration decreases, both its friction coefficient and hardness decrease. It is known that an Fe-Ti-C semistable alloy which is formed in a titanium ion-implanted layer of pure iron is amorphous and in this case, too, it can be assumed that an Fe-Cr-Ti-C semistable alloy will form an amorphous phase.

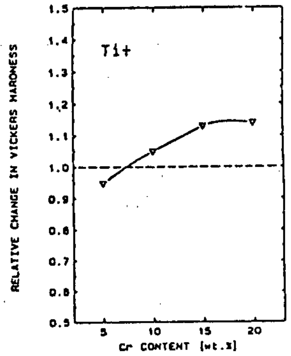


Figure 4. Relative Change in Micro-Vickers Hardness of Ti^+-Implanted Specimens as a Function of Cr Content

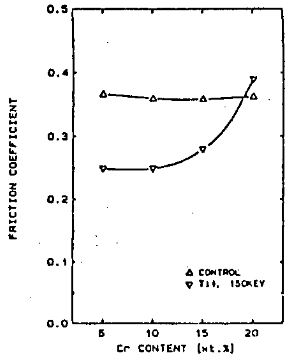


Figure 5. Friction Coefficient of Ti^+-Implanted Specimens as a Function of Cr Content

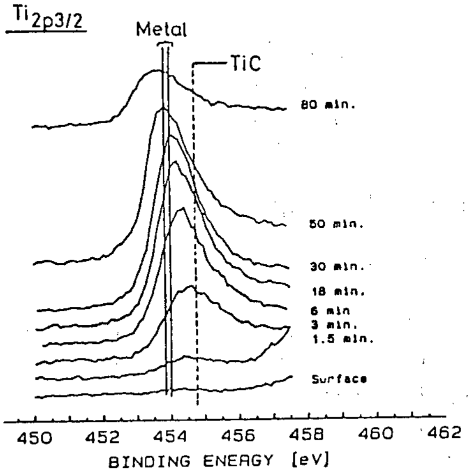


Figure 6. XPS Spectra of $Ti_{2p3/2}$ in the Ti^+-Implanted 5Cr Specimen

From the above study, it can be concluded that with respect to the modification of surface mechanical properties of chrome steel, implanting nitrogen ions and oxygen ions is more effective when chrome concentration is high, while implanting titanium ions is effective when it is low.

III. Improvement of Corrosion Resistance

1. Experiment: The following is a description of improved corrosion resistance of chrome ion-implanted SUS304.

(1) Implantation conditions:

a. Substrate: SUS304

b.

Ion to be implanted	Accelerating voltage	Dose
Cr^+	50 keV	1×10^{17} ion/cm^2

(2) Corrosion resistance test:

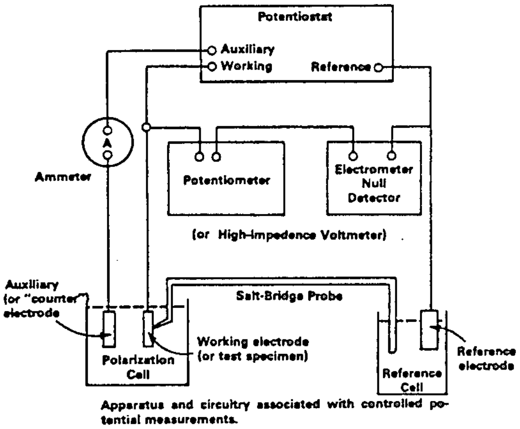
a. 3.5 percent Nacl solution electrochemical test

b. 5.0 percent H_2SO_4 solution electrochemical test

(3) Surface analysis: Glow discharge spectral analysis (GDS)

2. Corrosion Resistance Test Result and Its Study

As for a corrosion resistance test, an electrochemical test through positive polarization to examine the solubility (corrosion resistance) of specimens' surfaces with 3.5 percent Nacl solution and 5.0 percent H_2SO_4 solution (Figure 7) was conducted. Figure 8 shows a GDS analysis result of the surface layers of specimens in this test.



Apparatus and circuitry associated with controlled potential measurements.

Figure 7. Corrosion Resistance Testing Method

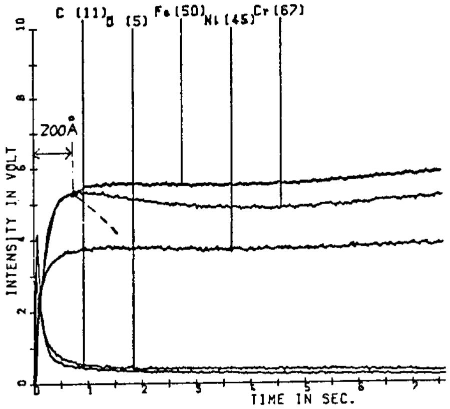


Figure 8. GDS Analysis Chart

Figure 9 shows a comparison between Cr-implanted SUS304 material and an unimplanted SUS304 material in the 3.5 percent Nacl solution test. Here, Vc' 100 potential causes $C\ell^-$ to break passive membranes and corrosion to occur, and the higher a potential, the higher the corrosion resistance of a passive membrane. It can be seen (Figure 9) that the potential of the unimplanted material is the same as that of the implanted material. This can be explained (Figure 8) that since implanted ions are present--not in a passive membrane (30-40 A) naturally existing on the unimplanted material surface, but in the substrate surface layer (200 A)--the implanted ions have not contributed to the improvement of the corrosion resistance of a passive membrane itself.

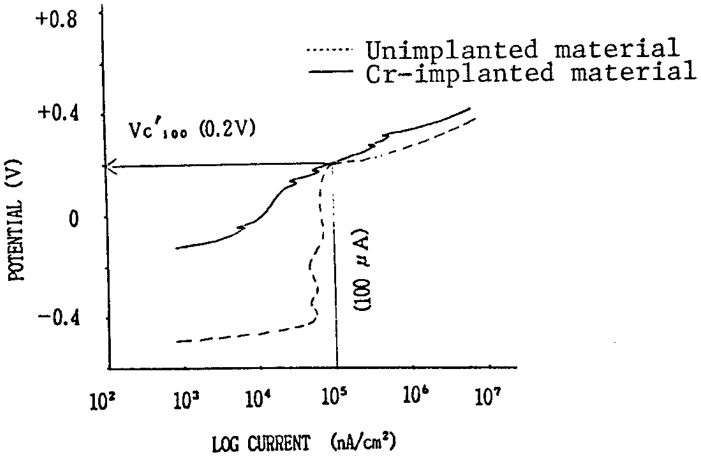


Figure 9. 3.5 Percent Nacl Solution Test

Meanwhile, Figure 10 shows a comparison between a chrome ion-implanted material and an unimplanted material in a 5.0 percent H_2SO_4 solution test. A passive membrane normally existing dissolves in this solution, and then a new passive membrane is produced in positive polarization. The test reveals the corrosion resistance of the passive membrane newly produced in an aqueous solution; ip indicates the solubility of a passive membrane and the smaller its value, the higher the corrosion resistance, while imax shows the solution speed of the substrate when no passive membrane exists and the smaller its value, the higher the corrosion resistance. A comparison between a chrome ion-implanted material and an unimplanted material in Figure 9 finds that the former is low both in ip and imax, showing high corrosion resistance, thereby resulting in a great difference between the corrosion resistance of the passive membrane newly produced in an aqueous solution.

From the above, the following methods can be considered as extremely interesting material designs to realize highly corrosion-resistant surfaces through ion implantation: two-phase processing involving implanting ions into both a substrate itself and a passive membrane and a method involving implanting ions only into a substrate and reproducing a stronger passive membrane by removing the existing one through acid processing.

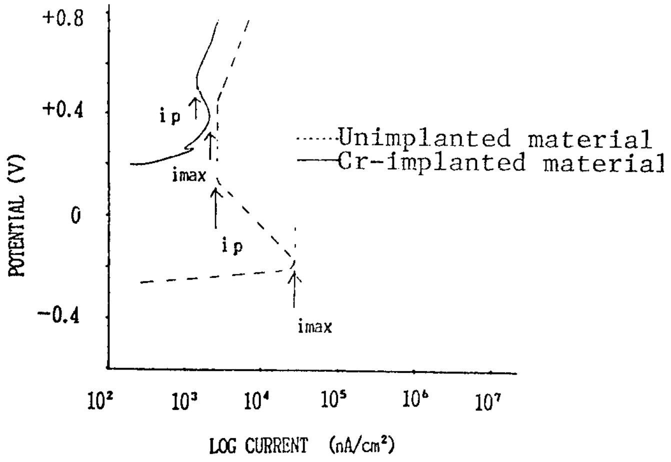


Figure 10. 5.0 Percent H_2SO_4 Solution Test

IV. R&D Status of Industrial Ion Implanting Equipment

For the surface modification of general industrial materials through ion implantation, the development of ion implanting equipment with a large capacity and large aperture is indispensable. Since the surface modification of metal materials needs a dose of more than 10^{17} ion/cm^2--about 1,000-fold that for semiconductors--and ion-implanting materials are greater in dimension, ion implanting equipment needs ion beam current values of more than several tens of mA and large apertures of more than several hundreds of cm^2. And, with respect to metal materials, the development of their multiple surface functions including alloying cannot be made possible until not only such gas ions as N^+ and O^+ but also various metal ions are implanted into them. Thus it is desirable that as many ion types as possible are available.

N^+- and O^+- gas ion sources of a bucket type with a large capacity (500 mA, 15 x 15 cm^2) are commercialized, while such metal sources as Cr^+ and Ti^+ with large capacities cannot be found. The MEVVA ion source recently released by LBL is extremely interesting equipment in that it has the possibility of providing a large capacity and permits multiple types of metal ions to be obtained[4].

2. Metering and Analyzing Instruments

Various metering and analyzing instruments are necessary in order to utilize excellent controllability resulting from ion implantation, namely, good controllability for any dose and implanting depth, and its feature of low temperature process. For the surface modification of general industrial materials, a computing control ion implanter is desired which is equipped with an ion beam ammeter metering the distribution of an ion beam current on the ion-implanted surface, a surface thermometer to meter the distribution of substrate temperatures during ion implantation, a substrate temperature controller and various analyzing instruments (RBS, etc.) and controls them with process parameters preprocessed by a computer.

V. Future Subjects

1. R&D on Ion Implanted Materials

Surface modification through ion implantation offers multiple attractions, while its optimization needs setting well defined conditions and a constant concept because of countless combinations of ion types and substrates coupled by multiple control factors such as accelerating voltage, dose and substrate temperature. Otherwise, the composition, structure and ion distribution in the surface layer after implantation change in each experiment, which results in a great difference in surface mechanical properties and corrosion resistance, causing great difficulty in designing materials. To solve this and develop full-fledged practical ion implanted materials, more systematic basic research is necessary, for example, research into interaction between ions and various substrates depending on the former's size and research into the effect of ion dose on depths and directions of the ion distribution in a substrate and surface sputtering and a basic implantation experiment focusing on the difference in chemical affinity depending on ion types. Also, with respect to experimental methods of modified performance after implantation, testing conditions are different depending on its use, so it is necessary to integrate testing methods of basic data. The accumulation of this systematic data and utilization of computation science in R&D in the future are needed in order to realize early practical use of ion implantation.

2. R&D Involving Ion Implanting Equipment

The current status of ion implantation is such that the effect of ion implantation is recognized, but high implantation cost has limited its practical use to costly small parts such as bearings for space shuttles and titanium alloy artificial bones. Large capacity ion implanting equipment permitting the current cost to be reduced by at least one-tenth to one-hundredth is expected to be developed and widely used for surface modification in industry in general.

Ion implanting technology can be said to have just begun to develop practical general industrial materials through its practical application to semiconductors. The perfection of basic material research and the development of equipment technology will be increasingly important in the future for creating new materials focusing on the innovation of ion implanting technology.

References

1. M. Hashimoto, et al., Surface Modification of Stainless Steels by In-Line Dry Coating Technology, 15th ICMC, April 1988.

2. Jun Sasaki and Masaya Iwaki, Tribological Properties of Ion Implanted Fe-Cr Steels, EPI, September 1987.

3. Jun Sasaki and Masaya Iwaki, Surface Mechanical Properties and Micro-Characteristics of Ti^+ Implanted Fe-Cr Alloys Depending on Cr Concentrations, MRS, December 1987.

4. Ian Brown and Jack Washburn, Nuclear Instruments and Methods in Physics Research B21 (1987) 201-204.

Ion Implantation Into Ceramics

43067592d Tokyo ION CHUNYU NI YORU HYOMEN KAISHITSU in Japanese 20 May 88 pp 42-49

[Article by Tatsumi Hioki, Toyota Central Research Institute Co., Ltd.: "Structure of Ion Implanted Layer; Mechanical Properties; Surface Modification"]

[Text] I. Introduction

Mechanical properties of ceramics are extremely sensitive to surface conditions. Fracture of ceramics, for example, occurs from its surface flaws in many cases. When it comes into contact with something hard, cracks occur instantly, often leading to fracture. Considering its good sensitivity, surface modification of ceramics is expected to improve its mechanical properties. Current ion implantation permits a surface modification thickness of not more than 100 µm, while it has the great advantage of introducing a desired element with ease. Therefore, this method will be very effective in clarifying the relation between the mechanical properties of ceramics and its surface and in finding a proper surface processing method. Research into ion implantation aimed at improving the mechanical properties of ceramics has been initiated by several groups since around the beginning of the 1980's[1-4]. Targeting at Al_2O_3[5-7], ZrO_2[4,8,9], SiC[10,11], MgO[12], and TiB_2[13], the research has examined the effects of implanting various ions into ceramics on the structure of their ion-implanted layers and on their mechanical properties such as hardness, toughness and friction and wear properties. Many recent studies have examined effects of implanting ions into ceramics coated with a metal membrane on its mechanical properties[14-16]. The following are descriptions of some of these studies.

II. Structure of Ion-Implanted Layer

1. State of Ions as Implanted

(1) Vertical distribution of implanted ions and radiation damage

Ion implantation is a means of introducing impurity atoms into surface layers of substrate materials, which entails a large number of radiation defects. Therefore, the vertical distribution of implanted ions and the degree of radiation damage is the most basic information involving the structure of implanted surface layers. As a means of obtaining these pieces of information, surface layer analysis using a high speed ion beam as its probe is often used, along with the backscattering and the nuclear reaction methods[17]. When a sample is a single crystal, parallel incidence of a probe beam to the crystal axis results in a phenomenon in which backscattering yield is remarkably reduced, compared to its incidence in random directions (channeling effect). Use of this can permit the vertical distribution of the degree of radiation damage (displaced atom concentration) of substrates to be obtained. Figure 1 shows the vertical distribution of nitrogen atoms when 400 keV $^{15}N^+$ ions are implanted into a stabilized zirconia single crystal containing 14-mole-percent Y_2O_3, whose experimental results were obtained using resonant nuclear reactions $^{15}N(p, \alpha\gamma)\ ^{12}C$, (Ep = 898 keV)[9]. Figure 2 shows the vertical distribution of Zr displaced atom concentration obtained using the channeling effect[9]. The histograms in Figures 1 and 2 show calculated values of implanted ions and displaced atom concentration obtained through simulations by the Monte Carlo method, which agrees with the results of the experiment. As can be seen in these examples, a great advantage of ion implantation is the very precise forecast of the distribution of implanted ions or damage through calculation.

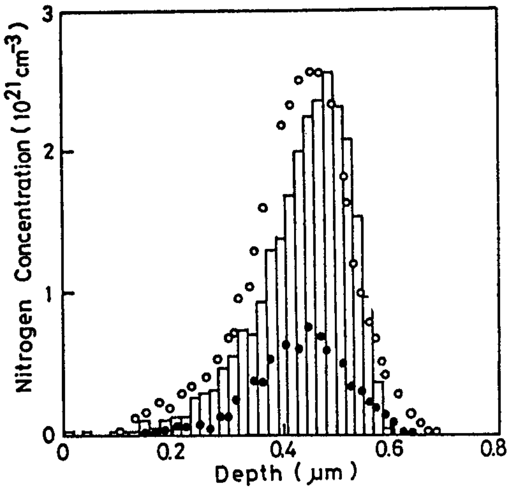


Figure 1. Depth Distribution of Nitrogen Ion Atoms Implanted Into Yttrium Stabilized Zirconia. Implanted ion: 400 keV $^{15}N^+$; Dose: o: 5 x 10^{16} pieces/cm^2, ●: 1 x 10^{16} pieces/cm^2. The histogram shows a simulated result by the Monte Carlo method.

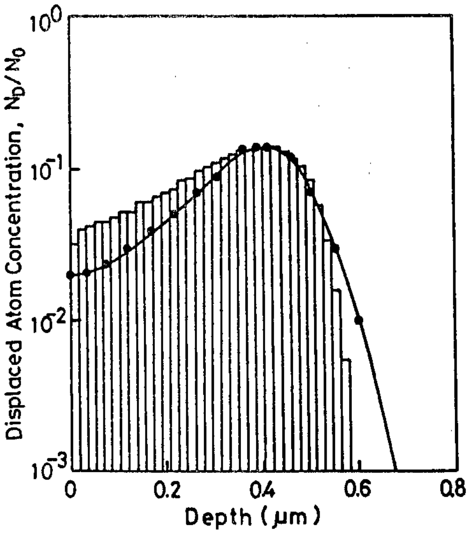


Figure 2. Vertical Distribution of Displaced Atom Concentration in Nitrogen Ion-Implanted Yttrium Stabilized Zirconia. Implanted ion: 400 keV $^{15}N^+$; Dose: 1 x 10^{16} pieces/cm^2. The histogram shows a simulated result by the Monte Carlo method.

(2) Noncrystallization

Incidence of a high-energy ion into a substrate material causes a cascade of collisions, knocking a great number of atoms composing the substrate out of the lattice point. This causes a large number of radiation defects, part of which are annihilated during implantation. Radiation damage of a substrate found after implantation results from the production and annihilation of defects during implantation. Under conditions where defects cannot be annihilated or recovered with ease, such as low-temperature implantation (ions are implanted into a substrate material retained at low temperatures), defects accumulate as dosage increases, finally leading to noncrystallization. Figure 3 shows backscattering channeling spector when 300 keV Ni^+ ions are implanted into sapphire (α - Al_2O_3 single crystal)[7]. From the figure one finds that in 300 K implantation, implanting 1 x 10^{17} pieces/cm^2 results in no noncrystallization, while in 100 K implantation, implanting ~2 x 10^{15} pieces/cm^2 causes noncrystallization. Ni maximum concentration in the latter's dosage is no more than ~0.1 at percent.

The difficulty of noncrystallization also depends on types of substrate materials. SiC and Si_3N_4, covalent bond materials, easily cause noncrystallization, compared to such materials with strong ionicity as Al_2O_3 and MgO.

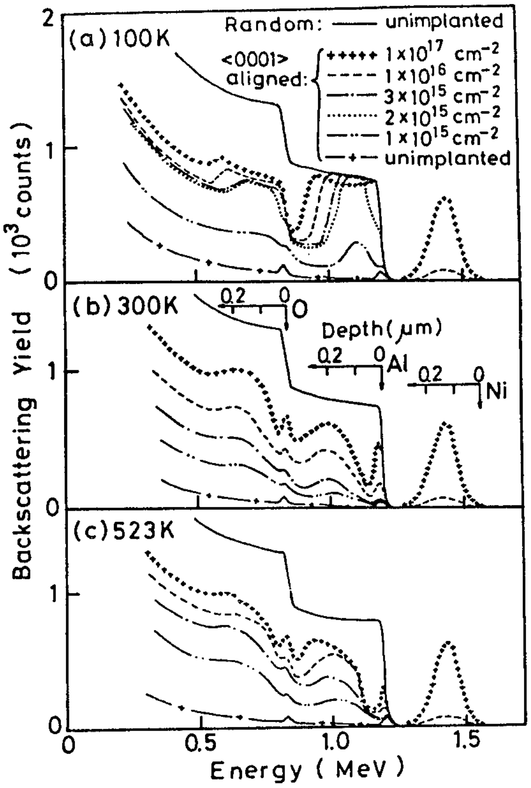


Figure 3. Backscattering Channeling Spector of 300-keV Ni^+ Ion-Implanted Sapphire

2. Structural Change Through Heat Treatment After Ion Implantation

The heat treatment of ion-implanted ceramics results in damage recovery, the recrystallization of noncrystalloid layers, solution, deposition and compound formation. Figure 4 shows backscattering channeling spector in isochronous heat treatment in air of sapphire after implanting 523-K Ni^+ ions into it. As can be seen from this figure, Ni atoms, as implanted, have maximum concentration at a depth (range) of 0.12 μm from the surface and show Gaussian distribution. The crystallinity of the substrate is largely disturbed near the above-mentioned depth, but it shows no sign of noncrystallization. An hour's heat treatment at 1473 K of this specimen permitted the substrate's crystallinity to almost recover and Ni to deposit near that depth. X-ray diffraction finds that Ni has deposited through the matching of (111) surface with sapphire's (0001) surface[18]. The same treatment at 1673 K of the specimen permitted $NiAl_2O_4$ to deposit with (111) surface matching with (0001) surface in this case, too[18]. It is considered that at 1473 K, Ni coagulates due to insufficient supply of oxygen from the atmosphere to deposit as Ni particles. Implanting Cr^+ ions into sapphire and their heat treatment in air result in a state in which Cr substitutes for and dissolves the Al lattice position. Heat treatment of the same in a vacuum also permits Cr to deposit. In this way, combining ion implantation and heat treatment after implantation results in diversified surface layer structures.

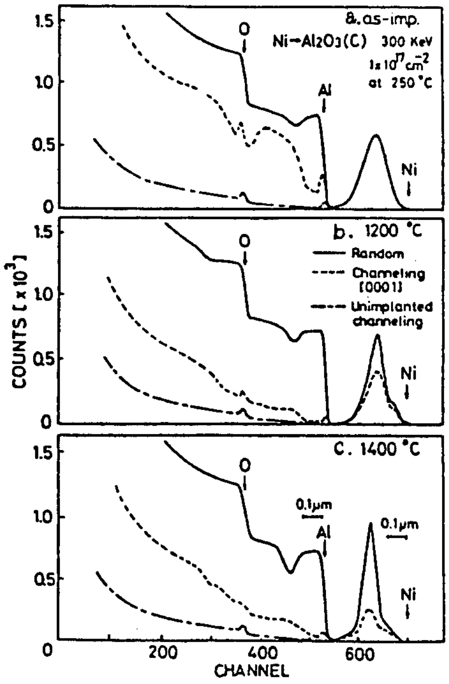


Figure 4. Backscattering Channeling Spector of Sapphire Heat Treated in Air After Its Implantation of 300-keV Ni^+ Ions

III. Mechanical Properties

1. Hardness

It is not easy to precisely evaluate the hardness of an ion-implanted layer as the thickness of a layer modified through ion implantation is not more than several hundred nm. Measuring hardness by a micropenetrometer, however, reflects a structural change in an ion-implanted layer in a relatively sensitive manner. Because of this meter a great number of examples have been reported. Figure 5 shows the dependency of the hardness on implanting quantities with 300-keV Ni^+ ion-implanted sapphire[7]. With 100-K implantation, as stated above, Dc, a minimum implanting quantity to cause noncrystallization, can be expressed as:

$$Dc\ (100\ K) = 2 \times 10^{15}\ Ni/cm^2.$$

In this case, as can be seen from Figure 5, the hardness as well as dosage increases for $D < Dc$, while for $D > Dc$, namely, in a state of noncrystalloid, the hardness shows about six-tenths the value before implantation. With 300-K implantation, Dc can be expressed as:

$$Dc\ (300\ K) = {\sim}2 \times 10^{17}\ pieces/cm^2.$$

In this case too, the hardness as well as dosage increases for $D < Dc$, while for $D > Dc$, the hardness becomes about six-tenths the value before implantation. The factors to increase hardness through implantation are:

(1) hardening caused by radiation defects and (2) hardening caused by solution or deposition. An attempt is being made[19] to evaluate the hardness by assessing the contribution of these two factors separately.

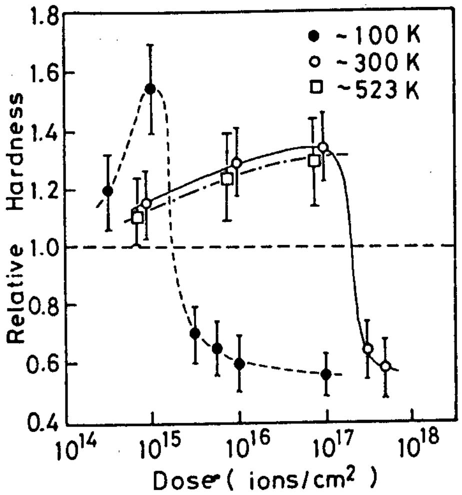


Figure 5. Dependency on Its Dose of 300-keV Ni^+ Ion-Implanted Sapphire's Hardness

2. Fracture Toughness

As a means of measuring K_{1c}, ceramics' fracture toughness, with ease, the microintender press-in fracture method is available. Evaluating K_{1c} of implanted materials using this method often finds an increase of tens of percent. Figure 6 shows a change in 300-keV Ni^+ ion-implanted sapphire's K_{1c} depending on its dosage. It shows the results for different implanting temperatures and for using Vickers intender loads of 50 g and 100 g. The figure shows that K_{1c} increases through implantation under any condition and that low temperature implantation is more effective to increase K_{1c}. As factors to increase K_{1c}, the following can be considered: (1) toughness of implanted layers being higher than that of unimplanted layers and (2) an effect by surface compressive stress induced by implantation.

3. Residual Stress

Ion implantation permits a large quantity of inter-lattice atoms and empty holes to be introduced into a substrate surface layer to expand it in general. Since this expansion is restricted by the substrate, a compressive stress occurs in the surface layer. Introducing impurity atoms through ion implantation will cause the surface layer to expand. This residual stress seems to have a great effect on the above-mentioned fracture toughness and on the effect of ion implantation on flexural strength which will be discussed later. Therefore, to modify mechanical properties, it is extremely important to understand residual stress which is induced by implantation. Figure 7 shows the dependency on dosage of integrated stress (residual stress integrated vertically) of 300-keV Ni^+ ion-implanted sapphire which was measured by a cantilever method[7]. Assuming that a compressive stress layer is within an ion range (130 nm), it is found that residual compressive stress induced by implantation is 2 GPa maximum for 300-K implantation and 9 GPa for 100-K implantation. From Figure 7, it can also be seen that there is a great difference in compressive stresses to be induced for the same dosage depending on implanting temperatures and that compressive stress is maximum right under the minimum dose (Dc) where non-crystallization occurs.

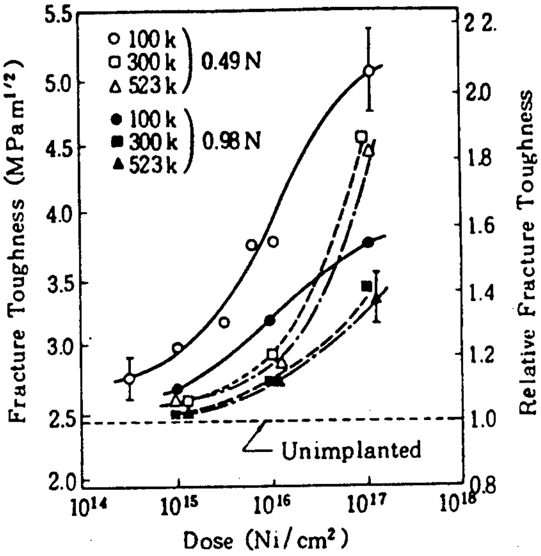


Figure 6. Dependency on Its Dose of 300-keV Ni^+ Ion-Implanted Sapphire's Fracture Toughness Values

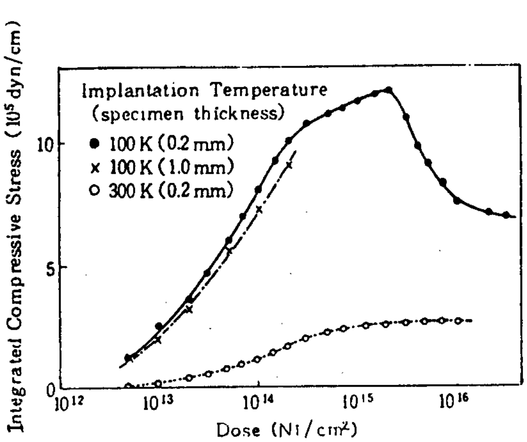


Figure 7. Dependency on Dosage of Integrated Stress of 300-keV Ni^+ Ion-Implanted Sapphire Surface Layer

4. Flexural Strength

The strength of ceramics is extremely sensitive to surface conditions such as an existing flaw and residual stress around it, which will permit its strength to be improved through proper surface processing. The effect of ion implantation on strength has been examined with respect to sapphire, Al_2O_3 sintered bodies, SiC sintered bodies and stabilized zirconia single crystal and it has been reported that ion implantation permits a 10-60 percent increase in their strength. Figure 8 shows the results of ion implantation into single crystal Al_2O_3 and an Al_2O_3 sintered body[7], where an increase in flexural strength of up to 60 percent can be seen with single crystal, and about 15 percent at the most with a sintered body. Since improved strength in these examples can be seen irrespective of ion types, it is believed that it resulted mainly from the effect of radiation damage and the aforementioned compressive stress has contributed[3]. Generating compressive stress in a surface layer is an effective way of reinforcing ceramics and compressive stress is generated for reinforced glass using a chemical approach. The greater the compressive stress and compressive stress layer thickness, the greater the degree of reinforcement.

Compressive stress which can be generated through ion implantation is as great as several GPa, while thickness of a compressive stress layer is not more than several hundreds of nanometers, extremely small compared to the size of a flaw which decides the strength of ceramics (probably around 1-100 μm). For this reason, an increase in strength seems to be small compared to the magnitude of induced compressive stress. If ion energy can be increased and the thickness of a compressive stress layer can be made about 10 μm, ion implantation is likely to be a powerful local reinforcement method.

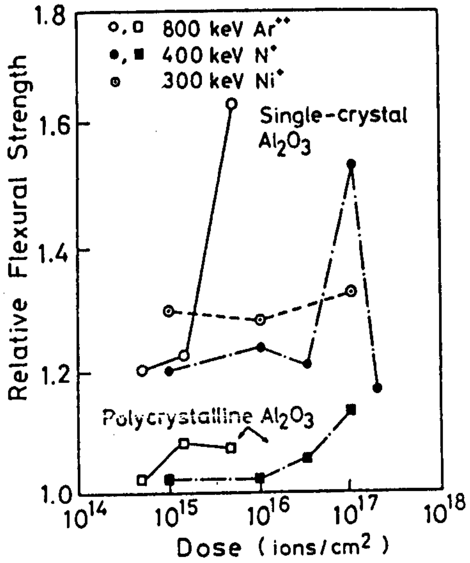


Figure 8. Dependency on Dosage of Flexural Strength of Ion-Implanted Sapphire

5. Frictional and Wear Properties

Being phenomena involving the surface, friction and wear easily reflect the effect of surface modification. It is clear that ion implantation has a great effect on the hardness and toughness of ceramics surface layers, but how are friction and wear reflected? It has been reported that when the surface of a sapphire--its hardness increased by implanting Cr^+ ions--was scratched with a diamond needle: (1) friction coefficient μ increased 20-30 percent, (2) the number of cracks occurring around the scratch flaws decreased, and (3) the quantity of Al_2O_3 removed decreased[19]. It is believed that (1) reflects an increase in hardness and that (2) and (3) are because the occurrence of cracks parallel to the surface is controlled by the compressive stress induced through ion implantation. It has been also reported that scratching the surface which has been made amorphous in the same way reduced wear due to controlled shipping[19]. Sliding a diamond pin with a disc made of sapphire which has been made amorphous through ion implantation with a pin-on-disc testing device resulted in a friction coefficient of 0.04 in the initial sliding, one-sixth the value for an unimplanted disc[19].

Sliding SiC ceramics with a steel is an example showing remarkable improvement in their friction and wear properties. Figure 9 shows that sliding a disc made of a SiC sintered body which has been made amorphous by implanting Ar^+ ions with a SUJ2 steel pin permits: (1) friction coefficient μ to decrease to 0.15 (0.6 with an unimplanted disc), (2) friction coefficient μ to fluctuate less, (3) a smooth sliding state to last up to more than 10^5 times in terms of sliding frequency, and (4) wear of the pin to decrease to about one-fifth that in sliding with an unimplanted disc[20].

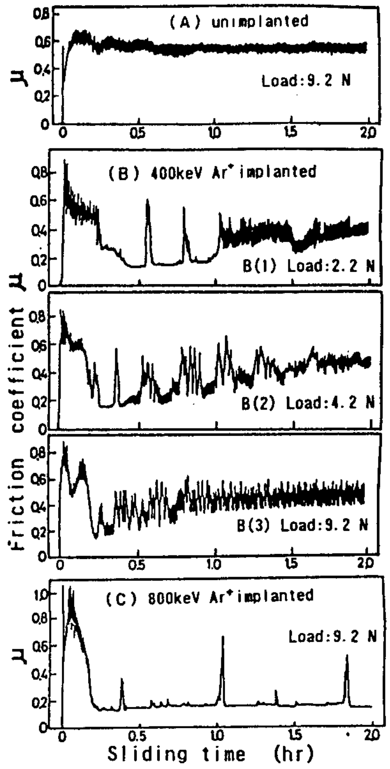


Figure 9. Change in Friction Coefficient Relative to Sliding Time in Sliding SiC Disc With SUJ2 Steel Pin. (A) unimplanted disc; (B) 1 x 10^{16}-piece/cm^2 400 keV Ar^+-implanted disc; (C) 1 x 10^{16}-piece/cm^2 800-keV Ar^+-implanted disc

IV. Surface Modification

1. Junction Between Metal and Ceramics

Ion implantation is also useful as a means of surface modification. The improvement of the adhesive strength of the surface is an example, which involves ion mixing in the surface and utilizing chemical properties of impurity atoms implanted into the surface. The junction using ion implantation of a bulk metal with ceramics involves first coating ceramics with a metal membrane, increasing its adhesive strength through ion implantation and brazing and soldering it with the metal bulk via the metal membrane.

Figure 10 shows a tensile test evaluation of the adhesive strength of a cross-junction body of an Si_3N_4 plate and a cast iron plate which was created by the above method. The junction was obtained by implanting 175-keV N^+ ions into an Si_3N_4 plate coated with a 300-nm Ti membrane, depositing on it 100-nm Fe and soldering it with a cast iron plate using a Pb-Sn soft solder[21]. The interfacial adhesive strength between Ti and Si_3N_4 increases as N^+ ion dosage does, and fracture occurs, not in the Ti/Si_3N_4 interface, but in the soldered portions for dosages of more than 5×10^{16} pieces/cm2.

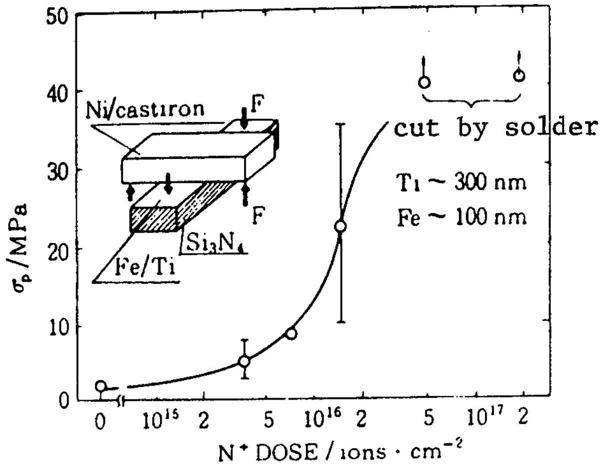


Figure 10. Dependency on N^+ Ion Dosage of Adhesive Strength of Ti Membrane on Si_3N_4 Sintered Body

References

1. S.G. Roberts and T.F. Page, in "Ion Implantation Into Metals," edited by V. Ashworth, W.A. Grant and R.P.M. Procter (Pergamon, New York, 1982) p 135.

2. C.J. McHargue, H. Naramoto, B.R. Appleton, C.W. White and J.M. Williams, Proc. Mater. Res. Soc., 7 (1982) 147.

3. T. Hioki, A. Itoh, S. Noda, H. Doi, J. Kawamoto, and O. Kamigaito, J. Mater. Sci. Lett., 3 (1984) 1099.

4. K.O. Legg, J.K. Cockran, H.F. Solnick-Legg and X.L. Mann, Nucl. Instrum. Methods Phys. Res., B7/8 (1985) 535.

5. C.J. McHargue and C.S. Yust, J. Am. Ceram. Soc., 67 (1984) 117.

6. P.J. Burnett and T.F. Page, J. Mater. Sci., 19 (1984) 3524.

7. T. Hioki, A. Itoh, M. Ohkubo, S. Noda, H. Doi, J. Kawamoto and O. Kamigaito, J. Mater. Sci., 21 (1986) 1328.

8. P.J. Burnett and T.F. Page, Am. Ceram. Soc. Bull., 65 (1986) 1393.

9. T. Hioki, H. Hasegawa, J. Kawamoto, and O, Kamigaito, in "Advances in Ceramics, Science and Technology of Zirconia III," Am. Ceram. Soc., in press.

10. S.G. Roberts and T.F. Page, J. Mater. Sci., 21 (1986) 457.

11. C.J. McHargue, M.B. Lewis, J.M. Williams and B.R. Appleton, Mater. Sci. Eng., 69 (1985) 391.

12. P.J. Burnett and T.F. Page, Proc. Mater. Res. Soc., 27 (1984) 401.

13. C.J. McHargue, P.S. Sklad, P. Angelini and M.B. Lewis, Nucl. Instr. Methods, B1 (1984) 246.

14. S. Noda, H. Doi, T. Hioki and O, Kamigaito, J. Mater. Sci. Lett., 4 (1985) 523.

15. J. Lankford, W. Wei and R. Kossowsky, J. Mater. Sci., 22 (1987) 2069.

16. M. Kohzaki, S. Noda, H. Doi and O. Kamigaito, Mater. Lett., 6 (1987) 64.

17. J.F. Ziegler, "New Uses of Ion Accelerators" (Plenam, New York, 1975).

18. M. Ohkubo, T. Hioki and J. Kawamoto, J. Appl. Phys., 60 (1986) 1325.

19. C.J. McHargue, in "Ion Beam Modification of Insulators" (Elsevier, New York, 1987) p 223.

20. Akio Itoh, Tatsumi Hioki and Junichi Kawamoto, manuscripts for lectures at Third Symposium on Surface Layer Modification Through Ion Implantation, p 7, 1987.

21. S. Noda, H. Doi, N. Yamamoto, T. Hioki and O. Kamigaito, J. Mater. Sci. Lett., 5 (1986) 381.

20117/6091 END

10

Foreign Broadcast Information Service (FBIS) and Joint Publications Research Service (JPRS) publications contain political, economic, military, and sociological news, commentary, and other information, as well as scientific and technical data and reports. All information has been obtained from foreign radio and television broadcasts, news agency transmissions, newspapers, books, and periodicals. Items generally are processed from the first or best available source; it should not be inferred that they have been disseminated only in the medium, in the language, or to the area indicated. Items from foreign language sources are translated. Those from English-language sources are transcribed, with the original phrasing and other characteristics retained.

Headlines, editorial reports, and material enclosed in brackets [ ] are supplied by FBIS/JPRS. Processing indicators such as [Text] or [Excerpts] in the first line of each item indicate how the information was processed from the original. Unfamiliar names which are rendered phonetically or transliterated by FBIS/JPRS are enclosed in parentheses. Words or names preceded by a question mark and enclosed in parentheses were not clear from the original source but have been supplied as appropriate to the context. Other unattributed parenthetical notes within the body of an item originate with the source. Times within items are as given by the source.

SUBSCRIPTION/PROCUREMENT INFORMATION

The FBIS DAILY REPORT contains current news and information and is published Monday through Friday in 8 volumes: China, East Europe, Soviet Union, East Asia, Near East & South Asia, Africa (Sub-Sahara), Latin America, and West Europe. Supplements to the DAILY REPORTs may also be available periodically and will be distributed to regular DAILY REPORT subscribers. JPRS publications generally contain less time-sensitive information and are published periodically. Current JPRS publications are listed in *Government Reports Announcements* issued semi-monthly by the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, Virginia 22161 and the *Monthly Catalog of U.S. Government Publications* issued by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

U.S. Government offices may obtain subscriptions to the DAILY REPORTs or JPRS publications (hardcovers or microfiche) at no charge through their sponsoring organizations. DOD consumers are required to submit requests through appropriate command validation channels to DIA, RTS-2C, Washington, D.C. 20301. (Telephone: (202) 373-3771, Autovon: 243-3771.) For additional information or assistance, call FBIS, (703) 527-2368, or write to P.O. Box 2604, Washington, D.C. 20013.

The public may subscribe to either hardcover or microfiche versions of the DAILY REPORTs and JPRS publications through NTIS at the above address or by calling (703) 487-4630. Subscription rates will be provided by NTIS upon request. Subscriptions are available outside the United States from NTIS or appointed foreign dealers. Back issues or single copies of the DAILY REPORTs and JPRS publications are not available. New subscribers should expect a 30-day delay in receipt of the first issue.

Both the DAILY REPORTs and the JPRS publications are on file for public reference at the Library of Congress and at many Federal Depository Libraries. Reference copies may also be seen at many public and university libraries throughout the United States.