Negative-ion implanter for powders and its application to nanometer-sized metal particle formation in the surface of glass beads

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We have developed a negative-ion implanter for uniform implantation into each powder surface without particle scattering. It consists of a plasma sputter-type negative-ion source, a mass separator, an acceleration tube, a lens, $X-Y$ deflectors, a 90° deflector, and a Faraday cup with an agitator. The electrostatic 90° deflector bends a horizontal beam to a vertical direction and leads it into the Faraday cup. The agitator is an electromagnetic vibrator at a frequency of 120 Hz, which mixes particles for whole surface treatment and uniform implantation. In this implanter, we obtained no scattering implantation for spherical oxide beads with diameters ranging from 5 to 1000 μm in an agitated state, and also obtained a good uniformity of implanted atoms among beads. For an application of the negative ion implantation into powders, copper ions were implanted into soda-lime glass beads and plates at conditions of 50 and 30 keV, respectively, with 1×10^{17} ions/cm^2. In linear optical properties, both implanted samples show a clear absorption at a photon energy of 2.2 eV due to resonance absorption of copper surface plasmon. In addition, the implanted glass plate shows the large third-order nonlinear susceptibility, $\chi^{(3)}=1.3\times10^{-7}$ esu. These results suggest the existence of copper nanometer-sized particles in glass. © *2000 American Institute of Physics.* [S0034-6748(00)67502-0]

I. INTRODUCTION

The use of negative ions as implant particles in ion implantation provides an advantage of almost ‘‘charge-up free’’ phenomena for substrates of insulator and isolated electrodes.[1–4] Therefore, the negative-ion implantation is expected to be a useful method for surface modification of powders. Powders have been used in many fields such as catalysis industry and medical treatments. Surface treatment of powder particles by ion implantation is desired to have more effective and newly functional properties.[5–9] However, materials of the powder in most cases are insulators such as oxides. In the conventional ion implantation with positive ions, a charging problem is inevitable that causes particle scattering and miss-control of implantation. In addition, agitation of powders is required for implantation into the whole surface of each particle. This agitation makes the scattering at a charging voltage lower than that for stationary state due to decrease in the van der Waals force between particles.[10]

To solve this scattering problem, we developed negative-ion implanter for powders with an agitator. The nonscattering implantation by using negative ions was already reported.[11–13] In this article, we describe the negative-ion implanter for powders and its features, and also show an application of negative-ion implantation to forming copper nanometer-sized particle in powder surface.

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II. NEGATIVE-ION IMPLANTATION FOR POWDER SURFACE

A. Negative-ion implanter for powder

Figure 1 shows a schematic configuration of a developed negative-ion implanter. The implanter consists of a rf-plasma-sputter-type negative-ion source,[14,15] a mass-separator, an acceleration column, a Q lens and two set of deflectors for $X-Y$, a chamber for silicon substrate (chamber 1), an electrostatic 90° deflector, and a chamber for powder (chamber 2). The source is a rf-plasma-sputter-type heavy negative ion source with a sputtering target of an outer diameter of 34 mm with a spherically concave surface, which can deliver an ion current in mA-class. This implanter can accelerate ions up to 125 keV by the acceleration column. The $X-Y$ deflectors are for elimination of neutral beam and for scanning ion beam. Figure 2 shows an enlarged configuration around Chamber 2. The electrostatic 90° deflector bends a horizontal beam to a vertical direction and leads it into the Faraday cup. In the center of the bottom plate of Faraday cup, an agitator of electromagnetic vibrator was placed. It can mix powder particles for implantation into whole surface of each particle and uniform implantation by vibrating the holder at a frequency of 120 Hz with an amplitude of 0.5 mm. Detail features of the negative-ion implantation by using this implanter were already reported.[13] Therefore, we described here only a brief summary of them.

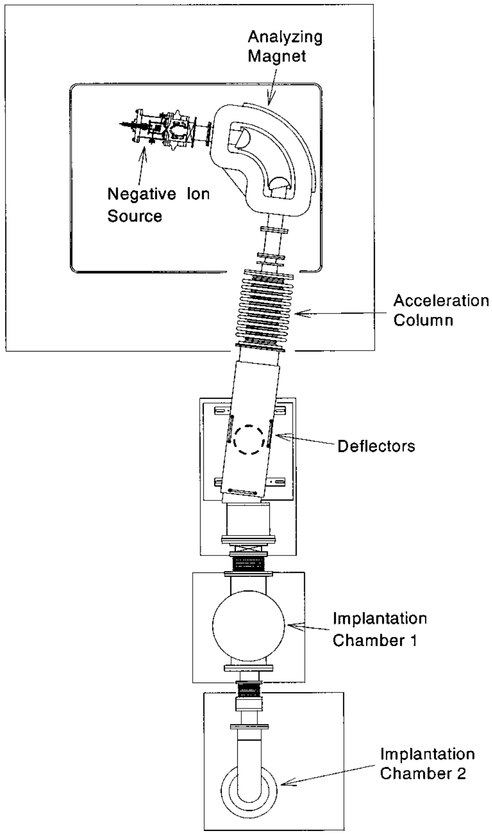

FIG. 1. Schematic configuration of a negative-ion implanter which consists of a plasma-sputter-type negative ion source, a mass separator, an acceleration column, a lens and deflection system, an implantation chamber 1 for flat substrates, a deflector, and an implantation chamber 2 for powder materials

B. Features of negative-ion implantation into powder

1. Nonscattering implantation

In the negative-ion implantation with any ion of C^-, BO^-, and Cu^-, no scattering was observed for all kinds of powder samples in the size range of 5–1000 μm at the vibrated state or at the stationary state. Nonscattering means that charging voltage did not reach the predicted value of several hundreds of volts for scattering. For glass plate, the surface charging voltage was found to be negative, several volts, due to formation of electric double layers.[3,4] Therefore, the charging voltage of the glass powder is considered to be equal to that of glass plate.

2. Evaluation of uniformity

The spherical 605 μm, glass beads were implanted with Cu negative ions of 40 keV at an average surface dose of 1×10^{16} ions/cm^2 during the agitation. Implantation uniformity was evaluated by the atomic ratio of Cu/Na obtained from x-ray photoelectron spectroscopy spectra. The average ratio and standard deviation were 0.24 and 0.026, respectively for ten samples. From this result, good uniformity of implantation was obtained at the vibrating conditions of 120 Hz and 0.5 mm.

3. Depth profile

Depth profiles of Cu atoms for spherical 605 μm glass beads and plane glass implanted with conditions: 70 keV,

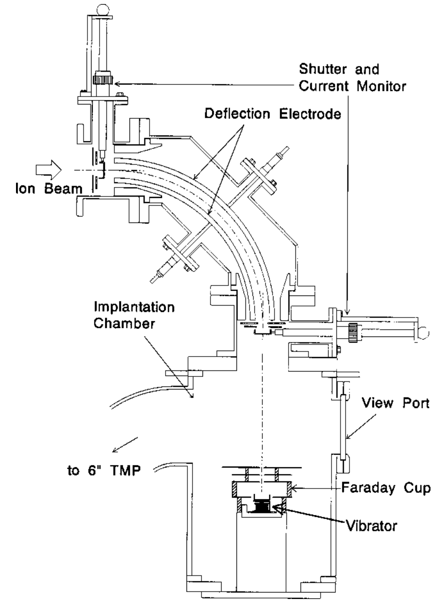

FIG. 2. Enlarged schematic diagram around the implantation chamber 2 for powder.

1.1×10^{16} ions/cm^2 of Cu^- were investigated by secondary ion mass spectroscopy. The peak depths were 40 nm for the bead and 60 nm for the plane glass. For the implantation into spherical beads, the incidence angle of ions depends on the incident point over the spherical surface, and is changed by the bead rotation due to agitation. Therefore, the depth profile can be calculated by a convolution of penetration profiles depending on the incident angle of a spherical surface and a simple profile obtained from the TRIM code for a flat surface at normal incidence.[11] Projected range of ion to spherical surface was about 60% shallower than that in the flat plate, which was in good agreement with the experimental results.

III. APPLICATION TO FORMATION OF NANOSIZED PARTICLES IN BEAD SURFACE

A. Experiment

Cu negative ions were implanted into spherical soda-lime glass beads with an average diameter of 605 μm at an ion energy of 50 keV with an average surface dose of 1.0 $\times10^{17}$ ions/cm^2 during the agitation. The average ion current density was 2 μA/cm^2. They were also implanted into plane soda-lime glass plate at 30 keV with a dose in a range of 3.0×10^{16}–1.0×10^{17} ions/cm^2. Only the glass-plate samples were annealed at 300 and 400 °C for 1 h in an atmosphere of argon gas.

For evaluation of nanosized particle in glass, we measured linear optical properties of light transmittance and reflectance in a photon energy range of 1.5–4.5 eV for both Cu-implanted bead and plate samples by using a spectrometer (Shimazu, MPS2000). As for nonlinear optical property, only Cu-implanted glass plates were measured for its nonlinear reflectivity by using a Nd:YAG pulse laser. The laser has a wavelength of 532 nm with a pulse width of 7 ns for degenerated four-wave mixing method to obtain the third-order nonlinear susceptibility.

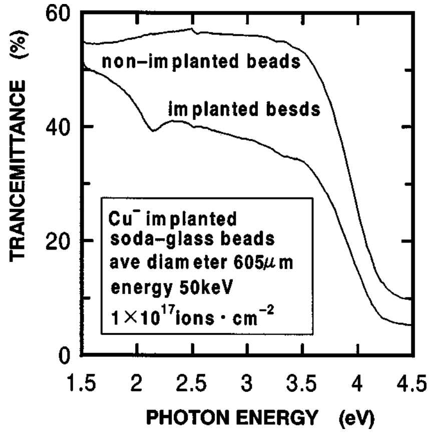

FIG. 3. Transmittance of visible light for 50 keV Cu-implanted and unimplanted soda-lime glass beads as a function of the photon energy.

B. Results and discussion

1. Linear optical properties

Figure 3 shows transmittance of visible light for 50 keV Cu-implanted soda-lime glass beads and unimplanted beads as a function of photon energy. Although the unimplanted beads have no absorption at photon energies below 3.5 eV, the curve for Cu-implanted beads has a relatively large optical absorption at around 2.2 eV.

Figure 4 shows transmittance of light for 30 keV Cu-implanted soda-lime glass plate with the parameter of heat treatment: nonannealed, 300 and 400 °C annealed in Ar gas for 1 h. The clear absorption peak at around 2.2 eV was found in as-implanted (nonannealed) and 300 °C annealed samples, but the peak disappeared after annealing at 400 °C.

The absorption peaks for beads and plate are due to a resonance at 2.2 eV of surface plasmon of copper nanosize particle. As for 400 °C annealed sample, the copper particles were considered to be thermally diffused into the glass plate.

2. Nonlinear optical properties

Figure 5 shows a nonlinear reflectivity measured by the degenerated four-wave mixing method with 532 nm of Nd:YAG laser. From this result, we obtained 1.3×10^{-7} esu of nonlinear third-order susceptibility, which is much larger than the value of $CS_2(10^{-12}\,\text{esu})$. This means that the nanosize copper particles were formed at the surface of the glass plate by ion implantation. As for glass beads, we could not measure the nonlinear reflectivity for the implanted glass beads due to strong scattered light at the spherical surface of beads.

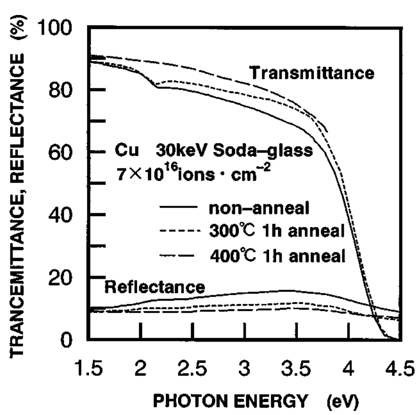

FIG. 4. Transmittance of visible light for 30 keV Cu-implanted soda-lime glass plate as a function of the photon energy with the parameter of heat treatment: nonannealed, 300 and 400 °C annealed in Ar gas for 1 h.

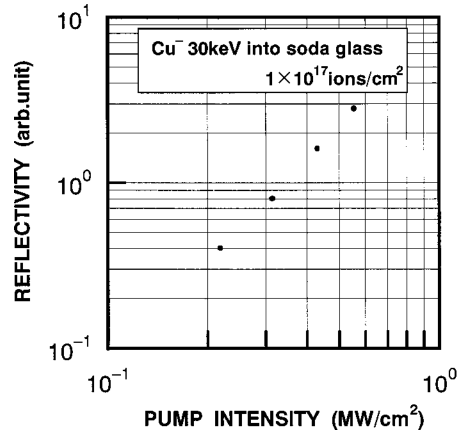

FIG. 5. Relative nonlinear reflectivity for 30 keV Cu-implanted soda-lime glass plate in the degenerated four-wave mixing method with Nd:YAG laser at a wavelength of 532 nm as a function of the pump intensity.

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