S5-1

Fabrication and Control of Nanoparticle-based Optical Materials by High-flux Negative-ion Implantation

大電流負イオン注入によるナノ粒子・光学材料の生成と制御

N. Kishimoto, N. Umeda*O.A. Plaksin** and Y. Takeda
岸本直樹，梅田直樹*，O.A. Plaksin**，武田良彦

Nanomaterials Laboratory, National Institute for Materials Science,
3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan
物質･材料研究機構ナノマテリアル研究所，〒305-0003 つくば市桜3-13
**VBL, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-0067, Japan*
横浜国立大学VBL，〒240-0067 横浜市保土ヶ谷区常盤台79-5
***SSC RF - A. I. Leypunsky Institute of Physics and Power Engineering, Obninsk, Russia*

A high-flux negative-ion implanter, with a plasma-sputter-type ion source, has been applied to create nanoparticle-based nonlinear optical materials. Usage of negative ions alleviates surface charging of insulators and provides merits of not only efficient atom injection but also kinetic precipitation control by widely changing ion flux. Negative metal ions of 60 keV were implanted into insulators, up to 100 μA/cm^2, fixing a total fluence of 3.0×10^{16} ions/cm^2. Spherical nanocrystals formed within a narrow region near the projectile range. The high-flux implantation is subjected to enhanced diffusion and atomic release of implants. At an optimum flux, the high flux may cause self-organized 2D distribution of nanoparticles.

1. Introduction

High-flux ions have been demanded primarily to expedite ion implantation in semiconductor industry or to develop high-power technologies, such as fusion reactors and pulsed power devices. Another demand of high flux has emerged for fabrication of metal nanoparticles in insulators, since the required fluence (e.g., 1-10 at%) is much larger than that for shallow-impurity doping into semiconductors (e.g., 10^{-1}-100 at.ppm). Although ion implantation methods have a superb merit to introduce metal atoms immiscible in insulators, surface charging for insulating substrates is of concern, especially for low energy/high flux.

Extensive work for insulators has been carried out with positive ions to modify optical properties [1-3], especially to obtain ultrafast nonlinear optical susceptibility associated with metal nanoparticles. However, the surface voltage may reach the acceleration voltage or the breakdown voltage of insulators, though radiation-induced conductivity practically dissipates the surface charge to some extent. Occasionally, usage of positive ions gave extremely large flux dependence in optical properties [1], where surface charging may play a significant role.

Contrarily, usage of negative ions suppresses surface charging down to several volts [4], balancing with secondary electron emission from the substrate surface. Up to now, negative-ion implantation has been applied for powder- and polymeric materials. We have applied high-flux negative-ion implantation to insulators and fabricated nanoparticles in insulators [5, 6].

In this paper, we describe the high-flux negative-ion implantation technique and report kinetic features of nanoparticle fabrication processes induced by high flux.

2. High-flux Negative-ion Implanter

Negative ions are generated by a Cs-assisted heavy-ion source of plasma-sputter type, with a cusp magnetic field [7], as is illustrated in Fig. 1.

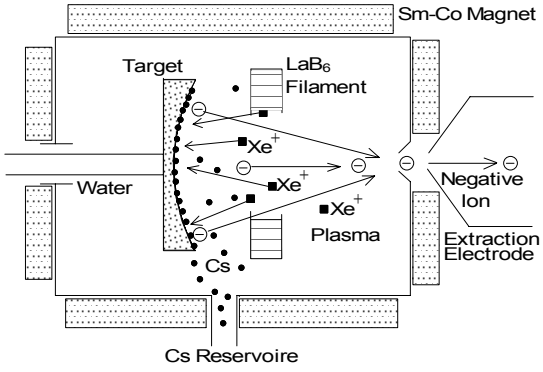

Fig.1. Negative heavy-ion source of plasma-sputter type with multi-cusp magnetic fields.

Thermal electrons from a LaB_6 filament ignite a Xe plasma, which is confined by the cusp magnetic field and powerfully sputters the solid target electrically biased at 200-800V. Concurrently, Cs coverage on the target surface enhances negative

ion production. The concave target contributes to increase the beam brightness. The intense negative ions are extracted from the plasma by two extraction electrodes, being accelerated up to 60 keV. The ion source provides us with a well-oriented and intense negative beam. Although space-charge effects tend to become significant with increasing the flux to a mA-level, the total Cu-fluxt of 3 mA was attained at the specimen position, after an efficient transport system including a variable permanent quadrupole-magnet triplet.

3. Material Kinetics by High-Flux Negative Ions

3.1 Beam-surface interactions with negative Ions

Employment of negative ions excludes surface-charge-related instability in ion implantation and we, therefore, can extract material kinetics induced by high flux.

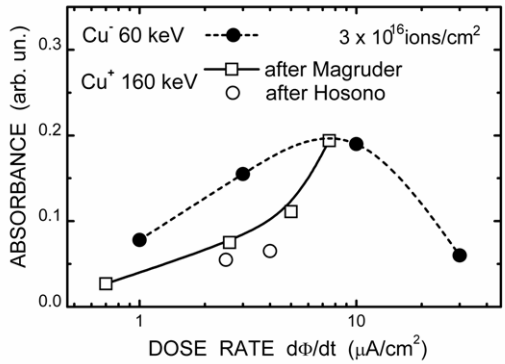

Fig. 2. Flux-dependence of optical absorbance at surface plasmon for Cu-implanted a-SiO_2. Data after Magruder et al [1] and Hosono et al [2,3] are also given for comparison.

Optical absorption of Cu^--implanted a-SiO_2 is greatly dependent on ion flux. Fig. 2 shows absorbance of a surface-plasmon peak at 2.2 eV. The absorbance has a maximum around 10 μA/cm^2, where the surface-plasmon peak becomes prominent. The convex variation results from the Cu retention and implies that beam-surface interactions play a significant role and that the optimum flux exists for modification. The result of negative ions can be compared to the data of positive Cu ions by Magruder et al [1] and Hosono et al [2,3]. The difference means that negative ions are twice as effective as the positive ions and that repulsion of surface charging is alleviated by use of the negative ions. The rapid increase of absorbance is caused by a decrease in surface repulsion effects.

On the other hand, the absorbance decreases beyond the peak flux, where the Cu retention decreases. It is due to sublimation/sputtering processes enhanced by high flux.

3.2. Nanoparticle self-organization by high flux

High flux enhances not only spontaneous precipitation but also atomic rearrangement of nanoparticles along the depth, depending on material species. The a-SiO_2 shows significant atomic rearrangement depending on ion flux, while spinel $MgO{\cdot}2.4(Al_2O_3)$ has less precipitation tendency and more stable atomic distribution.

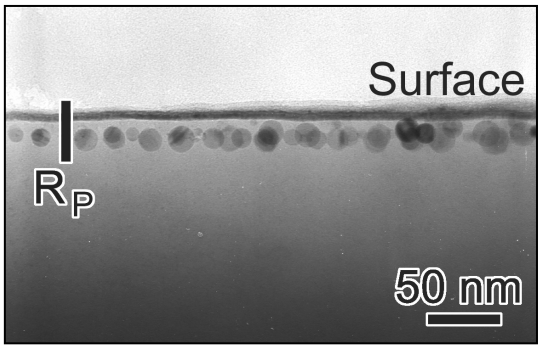

Fig. 3 Cross-sectional TEM images of a-SiO_2 implanted with 60 keV Cu^- at 45 μA/cm^2 to 3×10^{16} ions/cm^2.

Fig 3 shows a cross-sectional TEM image of an a-SiO_2 implanted with 60 keV Cu^- at a critical high flux. Right before losing implants at the higher fluxes, spherical nanoparticles are spontaneously aligned at a certain depth, as a 2D distribution. The 2D nanocrystals are fabricated by high flux without post-implantation annealing. The nanostructure formation is regarded as a *self-organization* induced by high flux. The depth position is much shallower than the projected range, indicating significant atomic rearrangement.

The dynamic in-beam processes are likely caused by electronic excitation at high fluxes and are applicable for controlling nanoparticle structures

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