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Three-dimensional Observation of Metallic Nanoparticles Formed in Insulators by Ion Implantation

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Metallic nanoparticles formed in ceramic (sapphire) and polymer (polyimide) substrates by ion implantation have been observed using a new scanning transmission electron microscope (STEM) that has been developed for the three-dimensional observation of nanostructures. The implanted specimens were processed as 100-300 nm diameter cylinders that were 1-2 μm long, which included the implanted layer, produced using a focused ion beam (FIB) fabrication system. STEM observations at 300kV were performed by rotating the specimens around the axis of the cylinder. Ni atoms implanted in sapphire at a high energy formed particles aligned with the surface plane without requiring an annealing stage. The Cu particles in sapphire assumed a disc-shape arranged parallel to the surface, located in a highly damaged layer due to the anisotropy in diffusion. On the other hand, crystalline spherical particles 5-10 nm in diameter were observed near the surface, and in deeper layers. The Cu particles formed in polyimide were uniformly dispersed at depths between 10 and 70 nm from the surface. A fine structure in the particles was observed in dark-field mode.

Key words: nanoparticle, ion implantation, sapphire, polyimide, 3D-EM

1. INTRODUCTION

Metallic nanoparticles formed in insulating materials have great potential for application in novel devices because of their peculiar characteristics, such as their optical nonlinearity [1] and magnetic properties [2]. Ion implantation is one of the most useful methods to fabricate nanoparticles in the surface layer of materials [3]. We have previously studied the structures of such particles and the electrical properties of implanted layers [4,5]. Characterizing and controlling the distribution, the shape, the growth direction, and the crystal structure of the particles is important in designing new devices.

Recently, a new electron microscope, the 3D-EM, has been developed for the three-dimensional (3D) observation of nanostructures. It was constructed by a joint research team composed of members from RIKEN, the Japan Atomic Energy Research Institute (JAERI), Nagoya University, Kogakuin University, and Hitachi Ltd. [6]. The instrument is based on a Hitachi HF-3000 300 kV FE-TEM/STEM and is equipped with an accurate eucentric sample stage, an automatic focusing system, and a sample-position correction system. It can also carry out electron energy loss spectroscopy (EELS). The system was designed to obtain images easily and quickly by rotating a sample over a wide angle range. The system has been shown to be useful for the characterization of defects in semiconductor devices. In this study, we have observed the shape and the distribution of metallic nanoparticles formed in insulators using the 3D-EM.

2. EXPERIMENTAL

2.1 Nanoparticle formation

The (110) and (001) surfaces of single crystal α-Al_2O_3 (sapphire) specimens were implanted with 3 MeV Ni ions at a fluence of 1.6×10^{18} cm^{-2} using a tandem accelerator in Tokyo University, and 380 keV Cu ions at a fluence of 2.7×10^{17} cm^{-2} using an electrostatic accelerator in JAERI. The maximum concentration of implanted elements was greater than 20%. During implantation, the specimens were tilted 5° from the perpendicular axis. The current density used was 1-2 $\mu A/cm^2$, the experimental pressure was 1×10^{-5} Pa, and the experimental temperature on the rear surface of the specimens was around 380 K for Ni implantation, and 350 K for Cu implantation. The mean ion ranges, calculated by TRIM code [7], were 1.2 μm for Ni, and 160 nm for Cu. Thermal annealing was carried out on Cu implanted specimens at 1073 K for 1 h in vacuum (pressure of 5×10^{-6} torr).

A 15-μm thick Kapton film produced by Toray-DuPont was implanted with Cu ions using the low-current accelerator at RIKEN under an acceleration voltage of 100 kV. The fluence was 5×10^{16} cm^{-2}, and the current density was kept to 0.1 μAcm^{-2} and the pressure below 1 x 10^{-5} Pa. During irradiation, the temperature on the rear side of the specimens was below the glass transition temperature of polyimide (T_g = 632 K), so that no change in film quality due to the high temperature was expected. The mean ion range for the implanted ions was calculated to be 80 nm by TRIM code.

2.2 Sample processing

The surface layer of the implanted specimens was cut using an FIB system (Hitachi FB-2000A) and a wedge-shaped piece was took out using a micro-sampling system employing a tungsten needle manipulator. Then, the piece was transferred to the top of a pin-shaped sample holder, and fixed using a beam-assisted tungsten deposition system. The surface of the sample piece was removed, leaving a cylinder 100 – 300 nm in diameter for the rotating STEM observations, as shown in Fig.1. The rotating axis was parallel to the main cylinder axis. We could observe the specimen without any of the obstacles and change in thickness that is a problem when rotating planar samples in conventional cross-section observations.

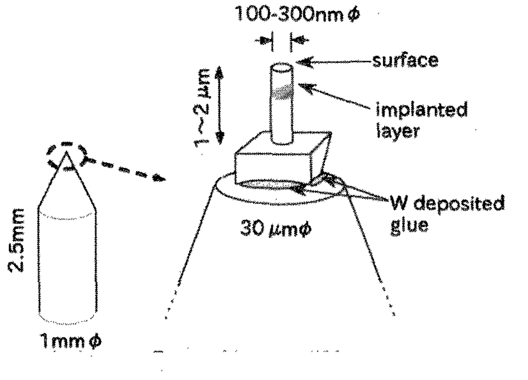

Fig.1 The pin-shaped sample holder and cylindrical sample prepared using an FIB and a micro-sampling system.

2.3 Observations

The cylindrical specimens were observed under bright-field (BF) and high-angle annular-dark-field (HAADF) STEM mode at 300 keV. The sample rotating range was 180°, and images were taken in 3° steps. The observations were performed using an electron current of 30μA under a pressure below 3 x 10^{-6} Pa. The reconstruction of the 3D images by tomography or topography was not developed in this study, because of the non-linearity in the electron intensity from crystalline samples.

3. RESULTS AND DISCUSSION

3.1 Nanoparticles in sapphire

Figure 2 shows a BF-STEM image of the 3 MeV Ni implanted specimen. The depth of implanted layer is 1.3 μm from the surface, which agrees well with the calculated value. The detailed view is shown in Fig.3. The implanted Ni atoms form nanoparticles around 5 to 10 nm in diameter aligned along the (110) plane. This result agrees with the electrical resistivity measurements, which indicate that the implanted Ni atoms form particles without requiring any post-implantation thermal annealing [4]. A rotating observation showed that the particles were widely distributed in a plane, rather than aligned in a string-like manner. Although the mechanism of the formation and the arrangement of the particles is still not clear, we presume that excess impurities will tend to collect in fissures along the (110) plane formed by internal stress.

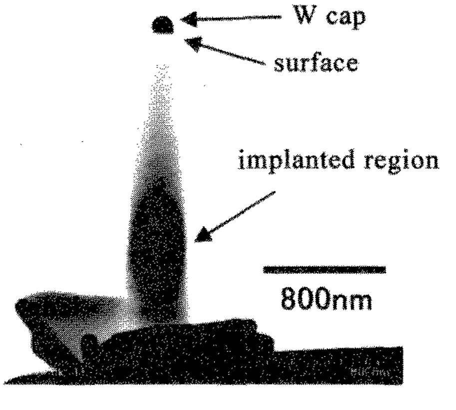

Fig.2 A cylindrical sample fabricated from 3 MeV Ni implanted sapphire (BF-STEM image).

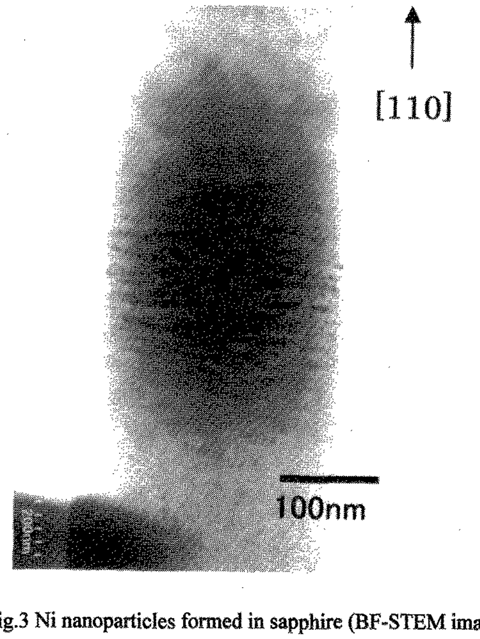

Fig.3 Ni nanoparticles formed in sapphire (BF-STEM image).

In the 380 keV Cu implanted specimens, no particles were observed without carrying out post-implantation annealing. Figure 4 shows BF-STEM images taken by rotating a cylinder of a sample that was Cu-implanted and then annealed. The implantation was performed perpendicular to the (001) plane. Large precipitates were observed at a depth from 130 to 150 nm, which were composed of irregular plate-shaped particles, with some precipitates being connected to each other. These observations indicate that the diffusion speed in the (001) plane direction at a depth that is a little shallower than mean ion range is much faster than that in the perpendicular direction due to the high level of damage induced by the displacement collisions. The moire patterns shown in Fig.5 indicate that particles were composed of single crystals.

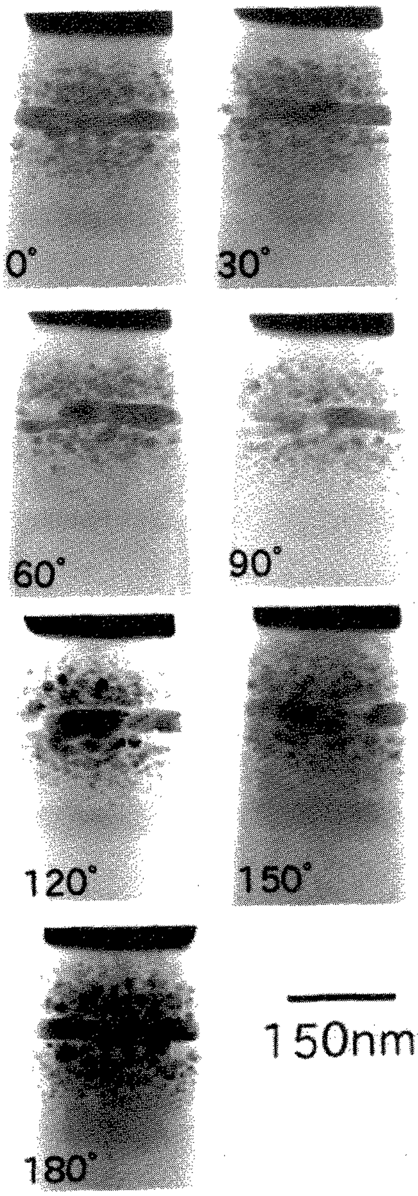

Fig.4 A rotation series of a cylinder sample implanted with 380 keV Cu at a fluence of 2.7 x 10^{17} cm^{-2} followed by thermal annealing (BF-STEM image).

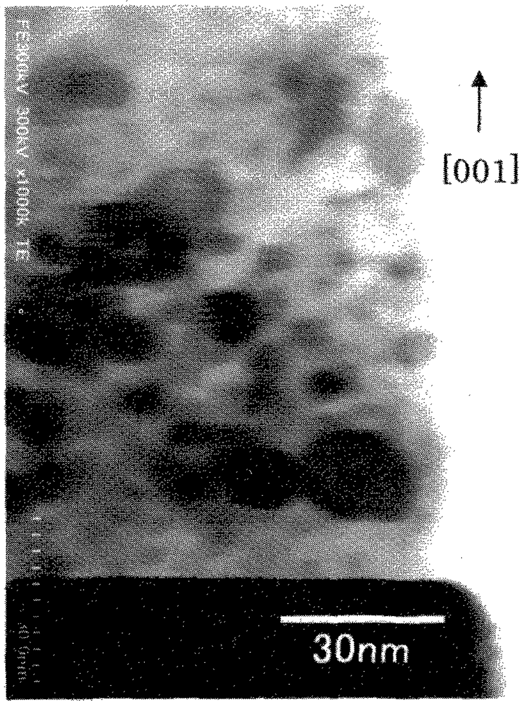

Fig.5 Moire patterns of Cu nanoparticles formed at depths from 30 to 120 nm from the surface.

3.2 Nanoparticles in polyimide

Figure 6 shows BF-STEM images of the 100 keV Cu implanted polyimide specimen. The Cu particles had diameters between 10 and 20 nm, and were uniformly dispersed at depths of 10 to 70 nm. The rotating observation results show that the particles do not make contact with each other. The contrast of each particle changed dramatically under rotation, and this implies that the particles have a crystalline structure.

The region from the surface to a depth of around 100 nm is stable against the electron beam because carbonization was already well progressed due to the implantation procedure. On the other hand, the deeper region was degraded by the electron beam, and a decrease in density was observed. The discharged gas will be a source of contamination accumulating on the surface of the cylinder, and this was not seen in the sapphire specimens.

Figure 7 shows an HAADF-STEM image of Cu nanoparticles. The fine structure of each particle was observed as a result of the change in the contrast. The particles are composed of crystalline polyhedra. The results reveal that the mobility of Cu atoms in polyimide under irradiation is quite high.

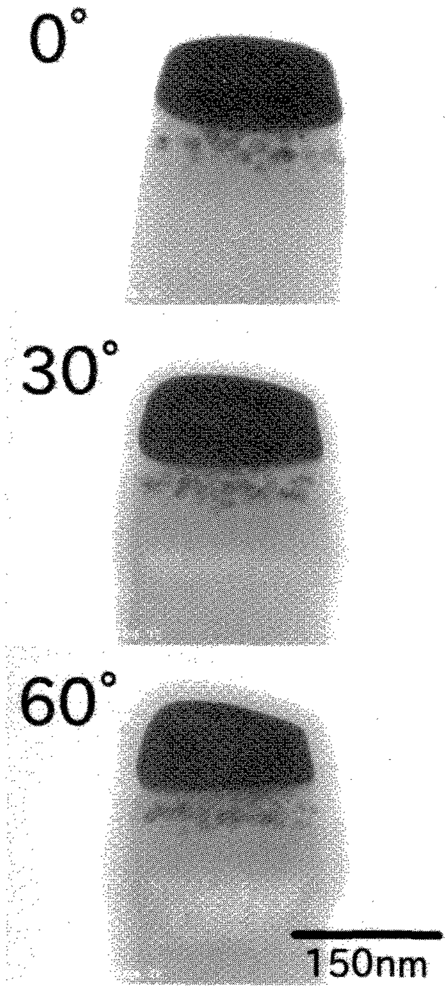

Fig.6 A rotation series of a cylinder sample implanted with 100 keV Cu at a fluence of 5×10^{16} cm^{-2} without any thermal annealing (BF-STEM image).

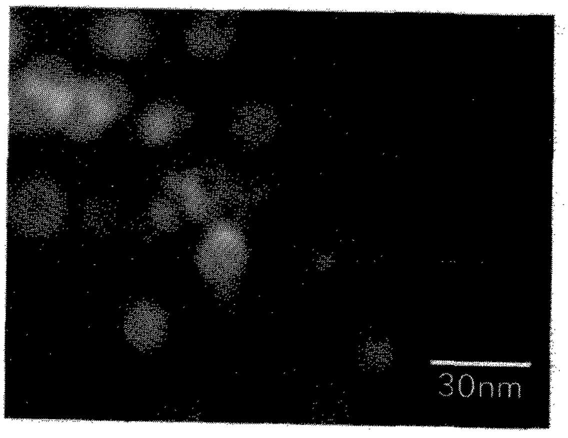

Fig.7 An HAADF-STEM image of Cu nanoparticles formed in a carbonized layer of polyimide.

4. SUMMARY

The distribution and the shape of metallic nanoparticles formed in sapphire and polyimide by ion implantation were observed using 3D-EM. The peculiar distribution of Ni particles and complicated shape of Cu particles in sapphire were elucidated by the rotating observation. Observation with higher magnification focused on a single particle will make the shape of Cu particles in polyimide clearer. The time required for adjusting position and focus was extremely reduced by the newly developed systems. Rotating observation was impossible without the system due to the degradation and the deposition of contamination by electron irradiation especially in the polyimide specimen.

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