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Formation of Self-Orientated Nanocrystals in an Amorphous Alloy under Focused-Ion-Beam Irradiation

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Ga concentration and in-depth distribution of the orientated nano-crystals (NCs) formed from a Ni-P amorphous alloy under focused ion beam (FIB) irradiation with an ion source of Ga have been investigated. After the amorphous alloys were irradiated using an incident angle of the FIB irradiation from 0 to 90 degrees, the crystallographic features and the Ga concentration were confirmed by transmission electron microscopic observation and Energy dispersive X-ray spectroscopy, respectively. More than 70 degrees incident angle irradiation does not contribute to crystallization. The result of refering to the Ga concentration of 70 degrees irradiation revealed more than 5.7 at% Ga concentration interfered with the formation of the NCs. On the other hand, at less than 20 degrees irradiation, the NCs were confirmed with no Ga adoption. The in-depth distribution of the NCs was revealed by a pair of stereo-micrographs taken by tilt ± 12 degrees and calculating the location of the NCs in the thickness direction. The formed NCs were uniformly distributed in the thickness direction over approximately 17 nm. It is, thus, confirmed that all the NCs do not have a free surface on the irradiated specimen judging from the grain size of the NCs approximately 5 to 10 nm.
Key words: orientated nanocrystals, Ni-P amorphous, focused ion beam irradiation

1. INTRODUCTION

Nano-crystals (NCs) have been intensively investigated because they have possibilities to improve physical properties of materials. In general, it is defined that the grain size of the NCs is less than 100 nm. Decrease in the grain size contributes to a remarkable increase in the volume fraction of grain boundaries in materials. This is one of the reasons attracting much attention. In some fields such as mechanical, magnetic, catalytic materials [1-3] and so on, improvements have been developed.

Several methods have been proposed to gain aimed NCs. These include deposition on substrates [4], ion implantation [5], recrystallization following severe plastic deformation [6] and crystallization from the amorphous state [1]. When materials are chosen and the physical properties are designed, it is well known that grain size, composition, distribution and crystal orientation are very important issues. It is, however, difficult to obtain crystallographically orientated crystals with grain sizes less than 100 nm.

In our previous research, we focused on an amorphous alloy in thermally meta-stable state and non-equilibrium. It is, thus, expected that crystallization from amorphous alloys will occur not by thermal diffusion but by other external fields. Focused ion beam (FIB) was, then, applied to a Ni-P amorphous alloy and the self-orientated NCs were obtained [7]. Furthermore, it was revealed that the orientation of the NCs was strongly dependent on the incident angle of the FIB irradiation [8].

The formation mechanism of NCs has not been clear. Judging from previous research, Ga ions are considered to play an important role in the formation of orientated NCs. The higher the incident angle, the more Ga ions, as well as, irradiation damage may be adopted in the matrix. The Ga concentration was confirmed by energy dispersive X-ray spectroscopy (EDXS). The effect of FIB incident angle on the Ga concentration has not, however, been identified. The in-depth profile of the NCs has not also been clarified, thus stereo transmission electron microscopy (TEM) micrographic observation was carried out to know the through thickness distribution of the formed NCs in this study.

2. EXPERIMENTAL

The material used in this study was a Ni-11.5wt%P amorphous alloy thin film with a thickness of 12 μm prepared by electroless deposition on an Al-Mg based substrate. The amorphous layer was separated from the substrate using a NaOH aqueous solution. The amorphous alloy was mechanically cut into a circular disk with a diameter of 3 mm. Electro polishing was, then, performed in a HCl_4-CH_3COOH (1:9) mixed solution at 273 K. After the specimen was cut into a semi-circular disk, FIB micro-fabrication was carried out at room temperature. The FIB apparatus was a HITACHI FB2000-A operating at 30 keV with a liquid metal ion source of Ga^+. The beam current was decreased from 3.53 to 0.08 nA with decreasing the specimen thickness. The estimated dose-rate for the final FIB micro-fabrication was 6.2×10^{13} ions/cm^2s. The minimum probe size of the FIB was approximately a few tens of nanometers. The TEM apparatus used was a Philips CM200 operating at 200 keV equipped with EDXS. For selected area electron diffraction (SAED) analysis, the same selected area aperture with a diameter of 200 nm was employed throughout the study.

The geometrical relation between the FIB direction and the specimen is schematically illustrated in Fig. 1. An (x-y-z) Cartesian coordinate system fixed to the specimens was employed. In this system, the y-axis and the z-axis were set parallel to the projected ion beam direction on the irradiated surface and the surface normal of the specimen, respectively. The incidence angle (θ) is defined as the angle between the FIB direction and the tangent to the specimen surface, i.e. reducing (θ) means moving to grazing incidences. The incident FIB angle (θ) on the specimen surface was changed from 0 to 90 degrees.

To investigate the Ga concentration for the specimens irradiated at the incident angle from 0 to 90 degrees every 10 degrees, the EDXS was done.

A pair of stereo micrographs was taken by tilt of ± 12 degrees for the specimen (θ) = 35 degrees irradiation to reveal the through thickness distribution of the NCs in the irradiated area.

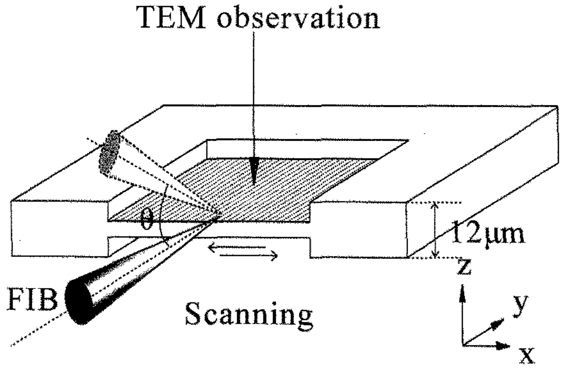

Figure 1 Schematic drawing of ion beam fabrication procedure. The y-axis and z-axis were set parallel to the projected FIB direction and the surface normal of the irradiated plane, respectively. The hatched area is the irradiated plane.

3. RESULTS & DISCUSSION

Figure 2-(a) shows a SAED pattern from the irradiated plane obtained at (θ) = 0 degree with the incident electron beam set parallel to the irradiated plane normal. In the SAED pattern, the clear 6 diffraction spots in addition to halo rings from the amorphous matrix correspond to a <111> incident electron diffraction pattern of f.c.c.-Ni. The analysis of the SAED pattern confirms that the y direction is approximately parallel to <110> of the f.c.c.-Ni within an accuracy of 2 degrees. Figure 2-(b) shows a dark field electron micrograph (DFEM) taken using a reflection marked in the SAED pattern. In the irradiated plane, crystallographically orientated NCs with grain size approximately 5 to 10 nm formed.

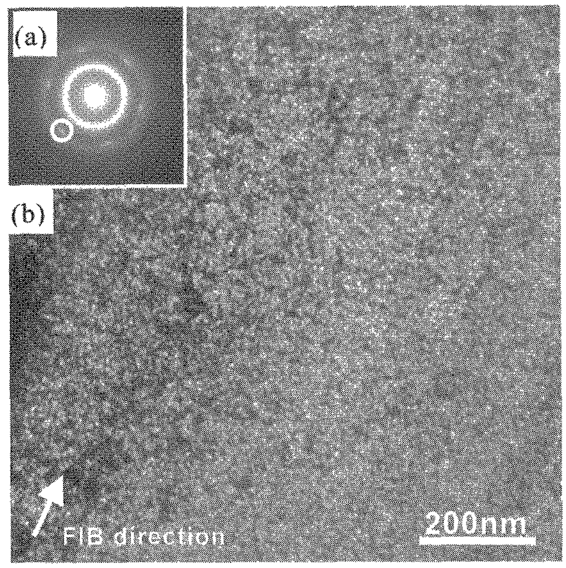

Figure 2 (a) SAED pattern from the irradiated plane for (θ) = 0 degree irradiation, and (b) DFEM of the irradiated plane.

Up to 60 degrees of the incident angle, the formation of the NCs has been confirmed [8]. Figure 3-(a) shows a SAED pattern of 70 degrees irradiation. Clear diffraction spots are not visible in Fig. 3-(a) without halo rings. One of possibilities is the disappearance of the reflections from the crystals behind the halo ring. Figure 3-(b) was taken using a point of the distance of {220} spots of the f.c.c-Ni. The crystallization was not confirmed at the angle. At more than 70 degrees, the NCs were not visible.

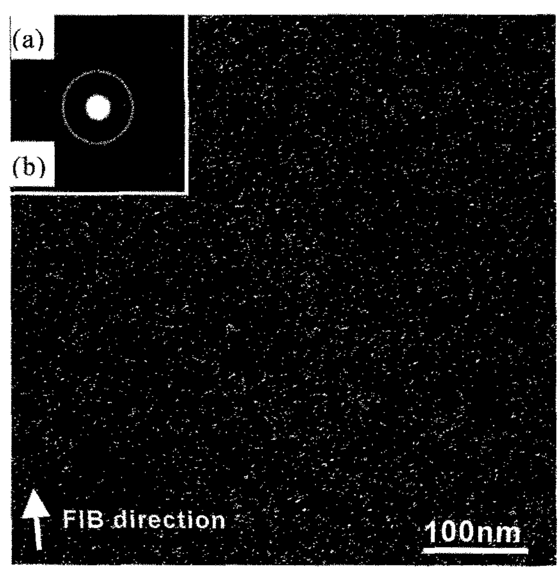

Figure 3 (a) SAED pattern from the irradiated plane for (θ) = 70 degree irradiation, and (b) DFEM of the irradiated plane.

EDXS analysis for the respective values of (θ) revealed that the concentration of Ga increased with increasing the incident angle (θ). The Ga concentration at the incident angle, (θ) = 0, 30, 60, 70 are 0, 1.5, 2.9 and 5.7 at%, respectively. When the crystallographic features obtained by TEM observation are compared to these results, more than 5.7 at% Ga concentration was found not to contribute to the formation of the NCs. On the other hand, at less than 20 degrees, it was revealed that the NCs formed by the Ga even though it wasn't included in the matrix. The NCs are, thus, considered to be formed not by ion implantation, but by collision between the atoms as a trigger. Further investigation is, however, required into the formation mechanisms of NCs by FIB irradiation.

The through thickness distribution of the NCs was investigated. To take a pair of stereo-micrographs, the specimen was tilted in the TEM by ± 12 degrees for the specimen of (θ) = 35 degrees irradiation. From the micrographs, the NCs were revealed to be uniformly distributed in the thickness direction. As a result of calculating the distribution from the stereo micrographs, the NCs are distributed approximately over 17 nm in the thickness direction. As the grain size of the NCs is approximately 5 to 10 nm, the NCs do not have on a free surface.

4. CONCLUSIONS

In the present study, we have investigated Ga concentration and in-depth distribution of the orientated NCs formed from a Ni-P amorphous alloy by the FIB irradiation with an ion source of Ga. Energy dispersive X-ray spectroscopy and transmission electron microscopic observation reveals that the Ga concentration increases with increasing the incident angle of the FIB and more than 5.7 at% Ga concentration does not contribute to the formation of the NCs. Furthermore, for the low incident angle of the FIB irradiation, the NCs formed with little Ga ions in the matrix. The NCs are, thus, considered to be formed not by ion implantation, but by collision between the atoms as a trigger. The in-depth distribution of the NCs was revealed by a pair of stereo-micrographs taken by tilt of ± 12 degrees and measuring the location of the NCs in thickness direction from the stereo-micrographs. The NCs are uniformly distributed in the thickness direction over approximately 17 nm.

REFERENCES

[1] A. Inoue, Y. Yokohama, and T. Masumoto, *Mater. Sci. Eng., A* **181**, 2 (1994).
[2] A. M. Tonejc, N. Ramsak, A. Prodan, A. Tonejc, A. Khalladi, S. Surinach, and M. D. Baro, *Nanostruct. Mater.* **12**, 677 (1999).
[3] M. L. Trudeau, J. Y. Huot, R. Shultz, D. Dussault A. Van Neste, and G. L'Esperance, *Physical Rev. B* **45**, 4626, (1992)
[4] K. Sato, B. Bian, T. Hanada and Y. Hirotsu *Scripta Mater.* **44**, 1389, (2001).
[5] C.A. Walsh, J.Yuan and L. M. Brown, *Phil. Mag. A*, **80**, 1507 (2000).
[6] D. H. Shin, I.Kim and K. T. Park, *Acta Mater.*, **49**, 1285 (2001).
[7] R. Tarumi, K. Takashima and Y. Higo, *Appl. Phys. Lett.*,**81**, 4610 (2002).
[8] R. Tarumi, K. Takashima and Y. Higo, to be published.

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