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Ion-beam irradiation of Cu and a Cu-Ni alloy single-crystal specimens: Proposed atom movement mechanism

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Rutherford backscattering and channeling measurements have been applied to study deep radiation damage and depth profile of implanted Au atoms in pure Cu and Cu-1 at. % Ni alloy single-crystal specimens, which were irradiated off axis at room temperature by 300 keV Au^+ ions to a dose of 2×10^{16} ions/cm^2. The damage range and depth range of the implanted Au atoms in the specimens of pure Cu were strikingly deeper than those in the specimens of Cu-1 at. % Ni alloys, respectively. An atom movement mechanism in solids under ion beam irradiation is proposed as the origin of the observed result.

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Interaction of energetic ion beams with solids and materials property change induced under ion-beam irradiation have long been attracting attention from both points of view of its basic understanding and application. In order to understand the phenomena, a large number of works[1] have already been performed both theoretically and experimentally. However, the process of the interaction and the material property change induced under ion-beam irradiation has not yet been fully understood and still remains as a field of fundamental scientific problems, although material modification by ion-beam irradiation has widely been applied in various engineering fields.

Because the interaction process occurs in a very short time in order of pico seconds,[2] it can not be followed with present experimental techniques. Thus, computer simulation has been rather extensively applied as a superior way after the pioneering investigation by Gibson and coworkers.[3] In order to gain the detailed insight into the irradiation induced phenomena, it has become especially important to obtain findings experimentally and compare them with results obtained by computer simulation.

In this article, the authors report the results of an experimental study of both damage range and depth profile of Au atoms implanted in single crystal specimens of pure Cu and Cu-1 at. % Ni alloys.

2-mm thick slices were cut from 2-cm diameter single-crystal pure Cu and Cu-1 at. % Ni alloy rods with surfaces parallel to (110) plane. The slices were mechanically polished and then electro-polished in a solution of H_3PO_4(40%), CH_3OH(40%), and H_2O(20%) for about 60 min at 3-V, 300 mA. Then, in order to eliminate the lattice defects, the slices were annealed in vacuum with a Zr platelet in a sealed quartz tube at 600 °C for 48 h, which were followed by slow cooling to room temperature at a rate of about 1 °C per min. The Zr platelet was used for the purpose to reduce the oxidation of the surfaces of the slices during annealing in the sealed quartz tube. The specimens for Au^+ ion implantation were finally prepared by being electro-polished again in the above-mentioned solution for the purpose of eliminating the probable surface oxide films. After these specimens were transferred into an ion implantation chamber, Au^+ ions with 300 keV were implanted into the specimens to a dose of 2×10^{16} ions/cm^2 at a dose rate of about 1×10^{12} ions·cm^{-2}·s^{-1} at room temperature. The implantation was made at an angle of 8° from the surface normal to minimize ion channeling.

Rutherford backscattering and channeling measurements were made with a well collimated 2.5 MeV He^+ ion beam obtained from Tandetron accelerator at the Institute for Materials Research, Tohoku University. The yields of backscattered He^+ ions were measured using silicon surface-barrier detector mounted at an angle of 170° to the incident beam direction. The energy resolution of the detection system was about 18 keV (full width at half maximum) (FWHM).

Typical Rutherford backscattering energy spectra corresponding to aligned and random incidences from both unimplanted and implanted pure Cu and Cu-1 at. % Ni alloy specimens are shown in Figs. 1 and 2, respectively. In these figures, spectra corresponding to random incidence from both pure Cu and Cu-1 at. % Ni alloy specimens unimplanted are not shown, because they are the same as the corresponding spectra from pure Cu and Cu-1 at. % Ni alloy specimens

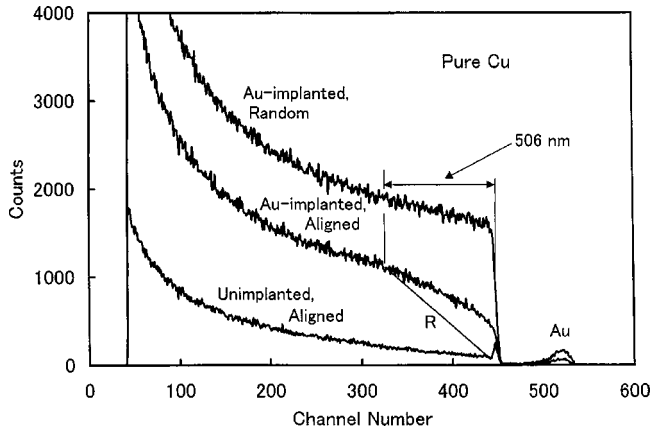

FIG. 1. Rutherford backscattering energy spectra corresponding to an aligned and random incidence from unimplanted and Au-implanted pure Cu specimens.

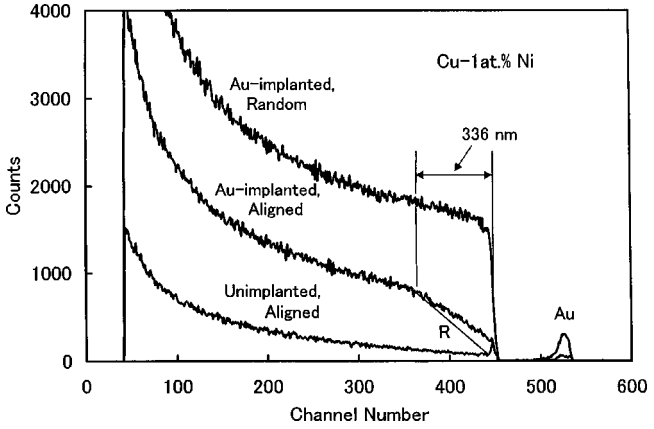

FIG. 2. Rutherford backscattering energy spectra corresponding to aligned and random incidence from unimplanted and Au-implanted Cu-1 at. % Ni alloy specimens.

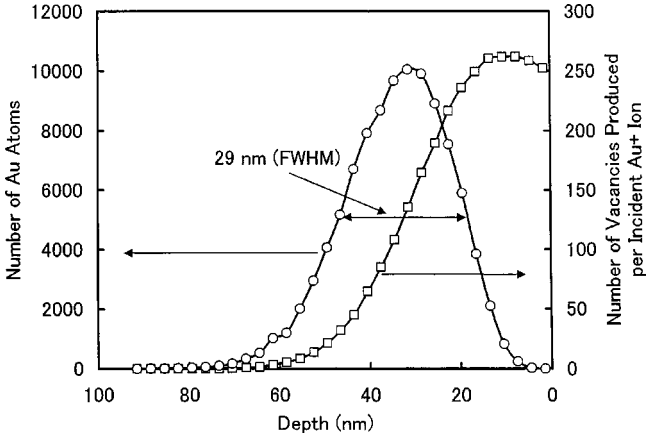

FIG. 3. Depth profiles simulated of implanted Au atoms and of vacancies produced per incident Au^+ ion.

implanted except the small peaks from implanted Au atoms on the higher energy side of the high-energy edge of the Cu spectra.

It can be seen that the aligned spectra from both pure Cu and Cu-1 at. % Ni alloy specimens unimplanted are essentially the same and the normalized minimum yields of aligned spectra of back-scattered He^+ ions at the surfaces were less than 0.04, which indicates a high perfection of the specimen crystals.[4,5] As far as the profiles of these aligned spectra are concerned, no indications of lattice disorder or imperfections in the crystals are observed in both pure Cu and Cu-1 at. % Ni alloy specimens unimplanted.

As is seen in Figs. 1 and 2, backscattering energy spectra corresponding to aligned incidence from both pure Cu and Cu-1 at. % Ni alloy specimens show damaged profiles after implantation of Au^+ ions. In Figs. 1 and 2, the depths of the damaged regions are indicated. In order to characterize the damaged regions, damage depth is defined as the distance on horizontal axis between the position of the half height of the random edge and the point of inflexion on the aligned spectra from implanted specimens.[4–6] It should be noted that the damage depth in the pure Cu specimen is significantly deeper than that in the Cu-1 at. % Ni alloy specimen. In Figs. 1 and 2, the depth scales are obtained using the tabulated values of the stopping power for ^4He in different elements by Ziegler.[7]

Applying the linear approximation to the random fraction of the analyzing beam,[4–6] the areas of the yields between the lines labeled *R* and the profiles of backscattered energy spectra in Figs. 1 and 2 are due to the scattering of channeled ions from scattering centers caused by damage and are taken as proportional to the total concentration of the scattering centers.[4–6] Thus, the larger area of the yield in pure Cu specimen than that in Cu-1 at. % Ni alloy specimen indicates the larger defect concentration in the pure Cu specimen than that in the Cu-1 at. % Ni alloy specimen.

In Fig. 3, a depth profile of vacancy concentration obtained by the simulation using the Monte Carlo particle transport code TRIM85 (Ref. 8) is shown as a measure of theoretically expected damage profile. In the simulation, 25 eV was assumed as the displacement energy[2,8] and the number of Au^+ ions assumed was 100 000. It can be seen that the damaged region in the pure Cu specimen observed by channeling experiment extends up to about 10 times deeper than that expected from the simulation. In Fig. 3, a depth profile simulated of implanted Au atoms in Cu is also shown.

Enlarged Rutherford backscattering spectra from impurity Au atoms corresponding to aligned and random incidence from Au-implanted pure Cu and Cu-1 at. % Ni alloy specimens are shown in Figs. 4 and 5, respectively. Comparing the Figs. 4 and 5, it can be seen that the depth profiles of Au atoms in the pure Cu specimen in Fig. 4 are markedly broader than those in the specimens of Cu-1 at. % Ni alloys in Fig. 5, the profiles of which are also broader than that of the simulated one in Fig. 3.

Comparing the random spectra in Figs. 4 and 5, it can be seen that the peak concentration of Au atoms in the Cu-1 at. % Ni alloy specimen is about two times higher than that in the pure Cu specimen. It should be noted that the vertical scales are different between the figures. Comparing the peak height of the random and aligned spectra in each of the Figs. 4 and 5, it can roughly be estimated that about one half of the implanted Au atoms occupy substitutional sites in the pure

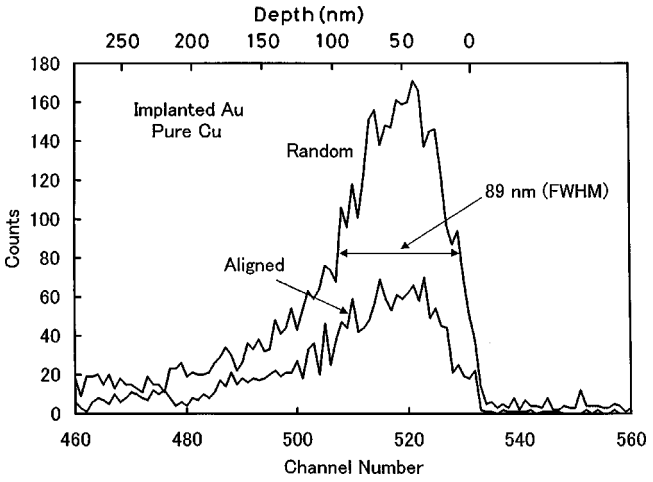

FIG. 4. Enlarged Rutherford backscattering energy spectra corresponding to aligned and random incidence from implanted Au atoms in pure Cu specimen.

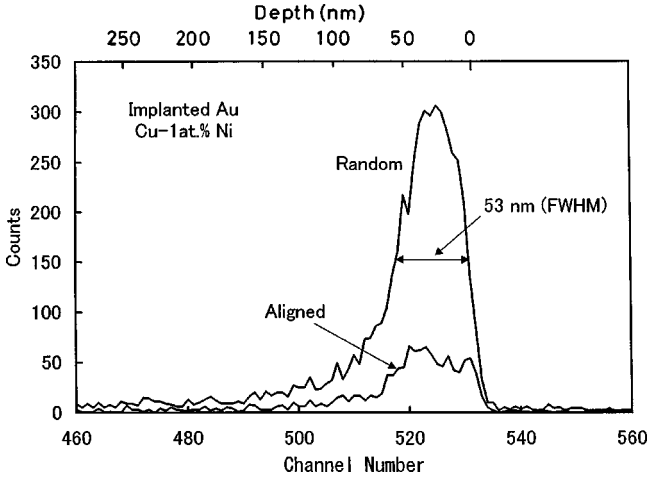

FIG. 5. Enlarged Rutherford backscattering energy spectra corresponding to aligned and random incidence from implanted Au atoms in Cu-1 at. % Ni alloy specimen.

Cu specimen, while about three fourths of Au atoms occupy substitutional sites in the Cu-1 at. % Ni alloy specimen.[4–6,9]

In metals and alloys, thermally activated diffusion of atoms may be generally negligible at room temperature.[10] It is well known, on the other hand, that migration of impurities can be enhanced by many orders of magnitude during ion implantation.[11] The phenomena are usually called irradiation enhanced diffusion and have been explained as a result of the generation and the migration of excess vacancies and interstitial atoms caused by the collision cascades created by the implanted ions.[11] In case of crystalline materials, in addition to the above-mentioned generation and migration mechanism, there are two well-known atom movement mechanisms during irradiation, namely, channeling and ''dynamic crowdion'' or replacement collision sequence, both of which were originally proposed by Stark[12] and Seeger,[13] respectively, and predicted later in computer simulations.[3,14]

It is difficult, however, to understand the observed differences of the depth profiles of damage and implanted Au atoms between pure Cu and Cu-1 at. % Ni alloy specimens as the result of the differences of the generation of excess vacancies and interstitial atoms and/or as the result of the differences of properties of replacement collision sequence or channeling, because the specimens of pure Cu and Cu-1 at. % Ni alloys are to be essentially the same collisionally, since Cu and Ni atoms have almost equal mass and the impurity concentration of Ni is relatively low, though it has been revealed that the presence of the solute atoms sometimes plays significant roles on phases of cascade development.[15,16] Thus, the differences of the depth profiles of damage and those of implanted Au atoms between pure Cu and Cu-1 at. % Ni alloy specimens are forced to be ascribed to differences in noncollisional transport properties of atoms between the specimens. It is, however, also difficult to explain these differences by the differences of migration properties of simple point defects of interstitials and/or vacancies, because, as approved usually, at room temperature, vacancies are not mobile in both the specimens and, though interstitials are mobile, the difference of the migration energy for interstitials should be insignificant between the specimens. In this connection, it should be noted that the self-interstitial migration energy of Cu is 0.117 eV (Refs. 17 and 18) and the dissociation energy of self-interstitial Cu atoms trapped by substitutional Ni solute atoms is smaller than 0.15 eV.[19]

The fact that the damage depth of crystalline materials subjected to ion beam irradiation sometimes exceeds the ion projected range by more than an order of magnitude seems to be firstly mentioned by Linker *et al.*[20] Similar results for copper were firstly obtained by Sood and Dearnaley[21] and later by other workers,[22,23] by whom the phenomena had also been experimentally studied for various specimens. As the origin of the deep radiation damage, dislocation movement was proposed by Friedland and Alberts.[23] Formation of dislocation structure in the near-surface region far exceeding the ion projected range was as actual fact observed by several workers by applying transmission electron microscopy.[24,25]

The above-mentioned result of the differences of the depth profiles of damages between pure Cu and Cu-1 at. % Ni alloy specimens supports the dislocation movement mechanism as an origin of the deep radiation damage. The reasons are as follows. Molecular dynamic simulation predicted that local melting occurs and persists for several ps (Ref. 2) in energetic displacement cascades. The occurrence of local melting is not surprising, because energy densities in cascades are typically of the order of 1–10 eV/atom for ultrashort time intervals ($<$0.1 ps) between collisions.[26] Some experimental results also indicated that during ion irradiation local melting actually occurs in energetic displacement cascades.[27] Therefore, it is feasible to expect strong time-dependent stress field gradient near the cascades. In this field, dislocations may be created and propagated into the bulk resulting in deep radiation damage. Dislocation loops could act as sources for dislocation multiplication.[28] The elastic limit of homogeneous copper alloy containing 1 at. % Ni is about seven times higher than that of pure Cu.[29] Then the generation and the propagation of dislocations are made more difficult in Cu-1 at. % Ni alloy than in pure Cu. This fact, therefore, can cause the differences of depth and defect concentration of the damaged regions between the two types of the specimens.

On the other hand, in 1952, Buffington and Cohen[30] reported the phenomenon of strain-enhanced diffusion in metals. Since then there had been a number of experimental and theoretical papers devoted to the strain-enhanced diffusion. Based on the comprehensive and detailed studies, the origin of the strain-enhanced diffusion was accounted for by Cohen *et al.*[31] by the presence of moving dislocations which provide high-diffusivity path for tracer atoms.

Taking into account the above-mentioned two phenomena in different fields, namely, the deep radiation damage and the strain-enhanced diffusion, the authors propose the presence of an atom movement (diffusion) mechanism in solids under ion-beam irradiation due to the high-diffusivity path provided by moving dislocations. In this context, the difference of depth profiles of Au atoms implanted between the pure Cu

and the Cu-1 at.% Ni alloy specimens is explained by the difference of the forces resisting dislocation motion between the two types of the specimens.

The detailed mechanism of the atom movement (diffusion) related to moving dislocations under ion-beam irradiation, however, requires further investigation. For the purpose of testing the proposed mechanism, computer simulation would be of eminent importance.

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[1] *Handbook of Modern Ion Beam Materials Analysis*, edited by J. R. Tesmer and M. Nastasi (Materials Research Society, Pittsburg, 1995).
[2] T. Diaz de la Rubia, R. S. Averback, R. Benedek, and W. E. King, Phys. Rev. Lett. **59**, 1930 (1987).
[3] J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. **120**, 1229 (1960).
[4] W. K. Chu, J. W. Mayer, and M-A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978).
[5] D. S. Gemmell, Rev. Mod. Phys. **46**, 129 (1974).
[6] F. H. Eisen, in *Channeling*, edited by D. V. Morgan (John Wiley & Sons, London, 1973).
[7] J. F. Ziegler, *Helium Stopping Powers and Ranges in All Elements* (Pergamon, New York, 1977).
[8] J. F. Ziegler, J. P. Biersack, and U. Littmark, in *The Stopping and Range of Ions in Solids*, edited by J. F. Ziegler (Pergamon Press, New York, 1985).
[9] J. A. Davies, in *Channeling*, edited by D. V. Morgan (John Wiley & Sons, London, 1973).
[10] A. Guinier and R. Jullien, *The Solid State*, translated by W. J. Duffin (Oxford, New York, 1989).
[11] J. Gittus, *Irradiation Effects in Crystalline Solids* (Applied Science Publishers, London, 1978).
[12] J. Stark, Phys. Z. **13**, 973 (1912).
[13] A. Seeger, in *Proceedings of the United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, 1958* (United Nations, Geneva, 1958), Vol. 6, p. 250; *Radiation Damage in Solids* (IAEA, Vienna, 1962), Vol. 1, p. 107.
[14] M. T. Robinson and O. S. Oen, Appl. Phys. Lett. **2**, 30 (1963); Phys. Rev. **132**, 2385 (1963).
[15] H. F. Deng and D. J. Bacon, Phys. Rev. B **53**, 11 376 (1996).
[16] R. Vascon and N. V. Doan, Radiat. Eff. Defects Solids **141**, 375 (1997).
[17] J. W. Cobett, R. B. Smith and R. M. Waker, Phys. Rev. **114**, 1452 and 1460 (1959).
[18] F. W. Young, J. Nucl. Mater. **69/70**, 310 (1978).
[19] H. Wollenberger, J. Nucl. Mater. **69/70**, 362 (1978).
[20] G. Linker, M. Gettings, and O. Meyer, in *Ion Implantation in Semiconductors and Other Metals*, edited by B. L. Crower (Plenum, New York, 1973).
[21] D. K. Sood and G. Dearnaley, J. Vac. Sci. Technol. **12**, 463 (1975).
[22] M. Vos and D. O. Boerma, Nucl. Instrum. Methods Phys. Res. B **15**, 337 (1986).
[23] E. Friedland and H. W. Alberts, Nucl. Instrum. Methods Phys. Res. B **33**, 710 (1988).
[24] L. M. Matthews and C. A. B. Ball, J. Appl. Phys. **61**, 2166 (1987).
[25] Yu. P. Sharkeev, A. N. Didenko, and E. V. Kozlov, Surf. Coat. Technol. **65**, 112 (1994).
[26] P. Sigmund, Appl. Phys. Lett. **25**, 169 (1974); **27**, 52 (1975).
[27] U. Gonser and F. E. Fujita, Phys. Status Solidi B **172**, 13 (1992).
[28] D. A. Jones and J. W. Mitchell, Philos. Mag. **3**, 1 (1958).
[29] T. Suzuki, in *Dislocation Dynamics*, edited by A. R. Rosenfield *et al.* (McGraw-Hill, New York, 1968).
[30] F. S. Buffington and M. Cohen, Trans. Am. Inst. Min., Metall. Pet. Eng. **194**, 859 (1952).
[31] M. Cohen, Trans. Jpn. Inst. Met. **11**, 141 (1970).