PHYSICAL REVIEW B VOLUME 34, NUMBER 7 1 OCTOBER 1986

Channeling study of amorphous phase formation in Ni_3B by ion implantation

A. Benyagoub, J. C. Pivin, F. Pons, and L. Thomé
Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse, Bôite Postale No. 1, 91406 Orsay, France

(Received 2 April 1986)

The amorphous phase formation in Ni_3B single crystals bombarded at 90 K with $^{83}Kr^+$, $^{58}Ni^+$, $^{11}B^+$, and $^1H^+$ ions is studied via *in situ* Rutherford backscattering and channeling experiments. It is found that no threshold value of the density of deposited energy per incident ion exists for amorphization and that, contrary to what was expected from previous experiments on ion-bombarded metallic compounds, the amorphization kinetics does not depend on the mass of the incident ions but is an almost linear function of the number of atoms displaced in the atomic collision cascades.

While ion implantation has been commonly used in the past to produce amorphous metallic alloys,[1-5] the mechanisms by which the amorphous layer is built under implantation have only recently been investigated.[6-8] The study of the amorphization kinetics (i.e., the variation of the fraction of amorphous volume with the implantation fluence) has shown that the decisive parameter governing amorphization was the chemical effect due to the presence of the implanted atoms, the role of the damage cascades being only to randomly shake up the implanted layer in order to allow the system to choose its equilibrium configuration. Thus at sufficiently low temperature (where the implanted species is not mobile in the host metal), the amorphization curve presents a sigmoidal shape due to the fact that an impurity concentration threshold exists above which amorphization starts abruptly by the formation of amorphous clusters in the region where the local concentration of implanted atoms exceeds a given value. It was then of major interest to complete such a study by investigating the effect of the damage cascades alone in experiments where the chemical nature of the sample is not modified by the ion bombardment. This can be done by irradiating crystalline metallic alloys having an amorphous counterpart with inert ions.

It is believed from amorphization experiments on irradiated semiconductors that, depending on the energy density deposited by the ion beam (hence on the mass of the irradiating ion), two different processes can occur in the crystalline-to-amorphous transition induced by ion irradiation:[9-12] amorphization by defect accumulation above a critical defect density in the linear cascade regime (light ions); direct ion impact amorphization in the displacement spike regime (heavy ions). It is clear that the amorphization kinetics must present a sigmoidal shape in the former case and a linear variation in the latter. Transmission electron microscopy (TEM) and resistivity experiments on various irradiated intermetallic compounds[13-18] do not show conclusively the validity of such a description in the case of metals. It is moreover often assumed that, even at low temperature, a minimal value of the density of deposited energy is required for amorphization.

The purpose of the present work is to show that a metallic compound presenting an amorphous counterpart, Ni_3B, can be amorphized by irradiation with ions of medium energy whatever their mass (even with hydrogen) and that, at sufficiently low temperature (90 K), the amorphization kinetics is a linear function of the number of displacement per atom (DPA) produced by the irradiating ions. Amorphization was monitored by *in situ* Rutherford backscattering (RBS) and channeling experiments.

Pure Ni_3B single crystals were grown in the [100] direction by C. B. Finch, using the Czochralski method.[19] They were cut with an electrolytical saw in order to minimize deformations, annealed 1 h at 450 °C in vacuum and electrolytically polished. Irradiations were performed at 90 K on the Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse-Orsay ion implanter[20] in a random direction with ions of different masses: $^{83}Kr^+$, $^{58}Ni^+$, $^{11}B^+$, and $^1H^+$ which do not change (except H) the chemical nature of the alloy. Ion dose rates were always kept lower than 0.5 $\mu A\,cm^{-2}$ in order to prevent target heating. The ion energies were chosen (see Table I) to obtain comparable ion and defect depth distributions. Table I gives the values of the ion (R_p) and defect (R_d) projected ranges calculated with the TRIM program[21] for the different irradiation conditions. RBS spectra were recorded *in situ* at the implantation temperature in the [100] and in a random direction using the 380-keV $^4He^{2+}$ beam delivered by the implanter itself. The energy resolution is about 10 keV, corresponding to a depth resolution of ~80 Å.

TABLE I. Irradiation parameters: R_p and R_d are, respectively, the ion projected range and the maximum damage depth calculated with TRIM (Ref. 21).

Irradiating ion	Ion energy (keV)	R_p (nm)	R_d (nm)
^1H	5	42	25
^{11}B	40	57	40
^{58}Ni	190	49	27
^{83}Kr	260	52	30

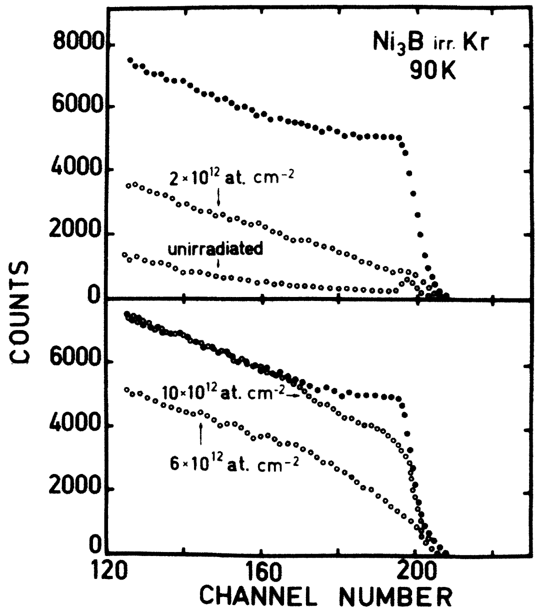

FIG. 1. Aligned (open circles) and random (solid circles) RBS spectra recorded on a Ni_3B single crystal irradiated at 90 K with 360-keV ^{83}Kr ions. Analyzing particles: 380-keV ^4He ions; energy calibration: 1.3 keV/channel.

Figure 1 presents RBS spectra recorded on the Ni_3B crystal irradiated with increasing fluences of Kr^+ ions. The corresponding aligned backscattering yields, normalized to the random yields, are shown in Fig. 2 as a function of depth in the crystal. From that figure, it is clear that, contrary to what was observed in the case of low-temperature implantation experiments[6–8] where a disorder peak was present at the implantation depth, the damage profile is rather flat from the surface to a depth higher than R_d in agreement with the defect distribution calculated by TRIM.[21] This similarity between the experimental damage profiles extracted from the channeling data and the theoretical defect distributions is also observed in the case of Ni, B, and H irradiations. The detailed analysis of the damage profile (which has been measured with a better accuracy on samples irradiated with the final fluences using a 2-MeV $^4He^+$ analyzing beam) is the topic of a forthcoming paper and we will restrict the present discussion to the comparison of the evolution with the irradiation fluences of the dechanneling yield at the maximum damage depth R_d (i.e., in a region where the damage distribution is rather flat in a depth window corresponding to our experimental resolution).

It has been shown in Refs. 22 and 23 that the value of the amorphous fraction α at the maximum disorder depth can be extracted from a precise analysis of the dechanneling curves (Fig. 2) by assuming that irradiation leads to the formation of amorphous zones which produce a direct backscattering of the channeled analyzing ions.[24] The amorphous nature of the disordered alloy is demonstrated (even for H irradiation) by additional grazing x-ray diffraction experiments on the samples irradiated at the final fluence (i.e., when the disorder is total in the surface layer). Figure 3 presents the evolution of the amorphous fraction at R_d (determined with the procedure developed in Refs. 22 and 23) with the number of DPA (calculated using the TRIM program[21]) produced by irradiation with Kr, Ni, and B ions. It is worth noting that it was impossible to extract the value of α in the case of the H irradiation, due to the fact that H implantation creates a hydride which causes an additional dechanneling for the analyzing ions. However, when the total H fluence was reached, the crystal was annealed at room temperature and H was seen to desorb out of the sample; the remaining alloy was then a pure amorphous Ni_3B alloy.

Figure 3 shows that the amorphization kinetics varies nearly linearly with the number of DPA (with an exponential saturation at high fluences, more pronounced in the case of B irradiation), whatever the irradiating ion mass. The fits (solid lines) were done by assuming that amorphization results from the coalescence of amorphous clusters formed in the core of overlapping damage cascades (Gibbons' model[9]) and growing under subsequent ion impacts.[22] The overlap number (number of times that a damage cascade has to shake up a given volume of the target to amorphize this volume) extracted from the fit is 1 (2 is also possible) in the case of irradiation with Kr ions

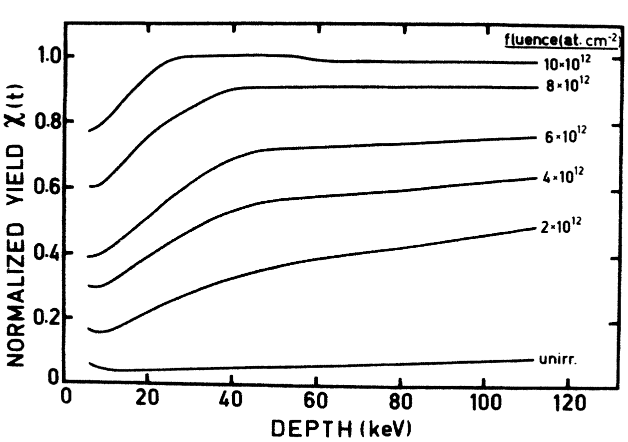

FIG. 2. Depth dependence of the [100]-aligned RBS yields, normalized to the random yields, for 90 K Kr-irradiated Ni_3B single crystal. Krypton energy: 360 keV; analyzing particles: 380-keV ^4He ions.

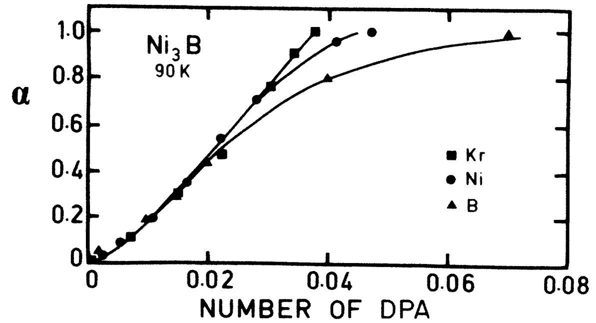

FIG. 3. Evolution of the amorphous fraction α with the number of displaced atoms by the irradiating ions at the maximum disorder depth for Ni_3B irradiated at 90 K. The solid lines are the best fit to experimental data using a modified Gibbons' model for amorphization.

and 2 in the case of irradiation with Ni and B ions; the transverse area of the amorphous zones (as defined in the Gibbons' model[9]) formed by the bombarding ions varies from 2.4×10^{-13} cm^2 (radius ~30 Å) for Kr irradiation to 1.5×10^{-14} cm^2 (radius ~7 Å) for B irradiation. These values agree rather well with the results of resistivity and channeling experiments on NiAl irradiated at 80 K with 360-keV Xe ions,[17,25] where direct ion impact amorphization was observed and a comparable size of the amorphous clusters derived from the kinetics. However, they are in sharp contrast with the results of electron microscopy experiments on NiTi irradiated at 300 K with 2.5-MeV Ni ions,[16] where an overlap number of the order of 13 was needed to fit the sigmoidal shape of the amorphization kinetics. Additional channeling experiments on Ni_3B single crystals irradiated at room temperature with Ni ions have shown[26] that the latter discrepancy is not due to irradiation temperature effects. This difference could then be explained by the fact that the degree of amorphicity measured probably depends on the observation technique used. For instance, TEM may not detect the early stages of amorphization, while resistivity and channeling may sense disordered configurations not truly representative of the amorphous state. An example is provided by the comparison between TEM and channeling results obtained on Ni-P and Pd-Si ion-implanted systems,[6,27,28] which has however demonstrated that the latter technique is a more sensitive indicator of partial amorphization.

From the results given above, it is possible to calculate the number of DPA created in a volume of the Ni_3B target of size comparable to that of the amorphous clusters formed during irradiation located at the maximum damage depth. Such a calculation leads to a value of ~0.03, independent of the irradiating ion mass.

In conclusion, we have shown that (i) a metallic compound having an amorphous counterpart can be amorphized with ions of mass as low as hydrogen when irradiated at sufficiently low temperature; (ii) the amorphization kinetics (expressed versus the number of DPA) is nearly independent of the irradiating ion mass; (iii) a small volume of the target is amorphized as soon as the number of DPA in this volume exceeds a given threshold value.

We wish to thank C. B. Finch for providing us the Ni_3B single crystals and F. Lalu and F. Réthoré for their assistance during implantation. We are also grateful to A. Audouard, H. Bernas, C. Cohen, and A. V. Drigo for valuable discussions and comments.

---

[1] R. Andrew, W. A. Grant, P. J. Grundy, J. S. Williams, and L. T. Chadderton, Nature **262**, 380 (1976).

[2] A. Ali, W. A. Grant, and P. J. Grundy, Philos. Mag. B **37**, 353 (1978).

[3] G. Linker, Nucl. Instrum. Meth. **182/183**, 501 (1981).

[4] L. Mendoza-Zélis, L. Thomé, L. Brossard, J. Chaumont, K. Królas, and H. Bernas, Phys. Rev. B **26**, 1306 (1982); L. Thomé, A. Traverse, and H. Bernas, *ibid.* **28**, 6523 (1983).

[5] B. Rauschenbach and K. Hohmuth, Phys. Status Solidi **172**, 667 (1982).

[6] C. Cohen, A. V. Drigo, H. Bernas, J. Chaumont, K. Królas, and L. Thomé, Phys. Rev. Lett. **48**, 1193 (1982); C. Cohen, A. Benyagoub, H. Bernas, J. Chaumont, L. Thomé, M. Berti, and A. V. Drigo, Phys. Rev. B **31**, 5 (1985).

[7] G. Linker, Mater. Sci. Engin. **69**, 105 (1985).

[8] L. Thomé, F. Pons, J. C. Pivin, and C. Cohen, Nucl. Instrum. Meth. B **15**, 269 (1986).

[9] J. F. Gibbons, Proc. IEEE **60**, 1062 (1972).

[10] J. R. Dennis and E. B. Hall, J. Appl. Phys. **49**, 1119 (1978).

[11] G. Carter and R. Webb, Radiat. Eff. Lett. **43**, 19 (1979).

[12] D. A. Thompson, Radiat. Eff. **56**, 105 (1981).

[13] L. M. Howe and M. H. Rainville, J. Nucl. Mater. **68**, 215 (1977).

[14] P. Moine, J. P. Rivière, N. Junqua, and J. Delafond, *Metastable Materials Formation by Ion Implantation,* edited by S. T. Picraux and W. J. Choyke (North-Holland, New York, 1982), p. 243; P. Moiné, J. P. Rivière, M. O. Ruault, J. Chaumont, A. Pelton, and R. Sinclair, Nucl. Instrum. Meth. B **7/8**, 20 (1985).

[15] A. E. Berkowitz, W. G. Johnston, A. Mogro-Campero, J. L. Walter, and H. Bakhru, in *Metastable Materials Formation by Ion Implantation,* Ref. 14, p. 195.

[16] J. L. Brimhall, H. E. Kissinger, and L. A. Charlot, Radiat. Eff. **77**, 273 (1983); J. L. Brimhall, H. E. Kissinger, and A. R. Pelton, *Ion Implantation and Ion Beam Processing of Materials,* edited by G. K. Hubler, C. R. Clayton, O. W. Holland, and C. W. White (North-Holland, New York, 1984), p. 163.

[17] C. Jaouen, J. P. Rivière, R. J. Gaboriaud, and J. Delafond, *Amorphous Metals and Non-Equilibrium Processing,* edited by M. Von Allmen (Les Editions de Physique, Paris, 1984), p. 117.

[18] A. Schmid and P. Ziemann, Nucl. Instrum. Meth. B **7/8**, 581 (1985).

[19] C. B. Finch, O. B. Cavin, and P. F. Becher, J. Cryst. Growth **67**, 556 (1984).

[20] J. Chaumont, F. Lalu, M. Salomé, A. M. Lamoise, and H. Bernas, Nucl. Instrum. Methods **199**, 193 (1981).

[21] J. P. Biersack and L. G. Haggmark, Nucl. Instrum. Methods **168**, 257 (1980).

[22] A. Benyagoub, Doctorat d'Etat thesis, University of Orsay, 1986.

[23] L. Thomé, *Proceedings of the International Workshop on Solid State Reactions After Ion Implantation Detected by Nuclear Methods, Göttingen, 1986,* edited by K. P. Lieb and M. Uhrmacher (Universität Göttingen, Göttingen, 1986).

[24] This analysis procedure is more accurate than that developed in Ref. 6, particularly in the case where the peak due to the direct backscattering of the He ions is not very pronounced.

[25] L. Thomé, J. Delafond, C. Jaouen, and J. P. Rivière, Proceedings of the International Conference on Ion Beam Modification of Materials, Catania, 1986 [Nucl. Instrum. Meth. (to be published)].

[26] L. Thomé, J. C. Pivin, F. Pons, and A. Benyagoub, Proceedings of the International Conference on Ion Beam Modification of Materials, Ref. 25.

[27] A. Benyagoub, H. Bernas, M. Berti, J. Chaumont, C. Cohen, A. V. Drigo, and L. Thomé (unpublished).

[28] M. Schack, Docteur Ingénieur Thesis, University of Orsay (1984).