In Situ Channeling Study of Ni-P Amorphous Phase Formation

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The nature and dose dependence of the disorder produced by 125-keV P implantation in Ni single crystals was studied via *in situ* channeling experiments using the 380-keV ^{4}He beam of the implanter. At 90 K, disordering (and presumably amorphization) occurs around the depth of the maximum in the implanted P concentrations; at 300 K, it occurs mainly at the surface and progresses inwards until the P projected range and peak in deposited energy profile are reached. In both cases, the lattice is randomized at a local P concentration of ~0.20.

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As the number of newly prepared noncrystalline metallic alloys increases, the available information[1] on the structural and electronic properties of this intriguing class of solids broadens. Since one is dealing with metastable systems, it has often been necessary to develop preparation techniques—such as splat cooling, vapor quenching, or electrodeposition—which carry the originally demixed components into the alloy state via paths that bypass thermodynamic equilibrium, and which remain sufficiently far from the latter at all times to avert crystallization. As in the case of their crystalline counterparts, the formation and stability criteria[1] for amorphous alloys are prime targets of investigation.

Ion implantation and irradiation disordering have been shown to produce amorphous metallic alloys in several cases.[2-7] For example, P implantation into Ni at room temperature—as studied[3,4] by transmission electron microscopy (TEM)—led to an amorphous system at P concentrations above ~15–20%. In such a case, the amorphization process clearly involves both the atomic displacement (via collision cascades) mechanism and the interatomic interaction between the implanted and host atoms. The transition towards a metastable glass had not been previously studied and was expected to differ from the situation prevailing in the better-known electrodeposited or splat-cooled glasses. Ion implantation at temperatures below point-defect mobility could *a priori* be thought to lead the system farther from equilibrium than other techniques. However, the largely unknown mechanisms by which the ion's deposited energy density is dissipated may well bring the system back towards equilibrium. Information on the amorphization process itself is clearly warranted, as well as information on the relation between (or the relative importance of) radiation damage and "chemical" interactions (i.e., bonding effects) in producing the amorphous phase.

We report a channeling study of the amorphization process in P-implanted Ni. *In situ* experiments performed at 90 and 300 K both show that amorphization occurs when the local P concentration reaches ~20%, and *not* before. However, the mechanisms are entirely different: At 90 K amorphization occurs at the P implantation depth, while at 300 K the amorphous layer is formed at the surface and grows inside, as the P dose increases, at a constant local P concentration. The latter result is discussed in terms of radiation-induced diffusion.

Two electrochemically polished (100) Ni single crystals were implanted with 125-keV ^{31}P ions. In the first series of experiments the implantation and channeling experiments were performed at room temperature and in the second series the sample was both implanted and studied *in situ* via channeling at 90 K. The beam current density was lower than 1.5 μA cm^{-2} in order to minimize target heating. The maximum implantation dose in both cases was 1.5×10^{17} atoms cm^{-2}. All the experiments reported here were performed on the Centre de Spectrometrie Nucléaire et de Spectrométrie de Masse, Orsay, ion implanter equipped with a low-temperature sample-holder goniometric chamber.[8] The implantations were carried out in a random direction and the sample was analyzed at various steps of the implantation with 380-keV ^{4}He^{++} ions delivered by the implanter itself. Random- and [100]-aligned backscattering spectra were registered. The energy resolution was about 10 keV, corresponding to a depth resolution of ~80 Å, i.e., small with respect to the calculated implantation range R_P of P ions (540 Å).

When the sample is implanted at room temperature (Fig. 1), the main results observed on the [100]-aligned spectra are (i) the increase of the surface peak with implantation dose; (ii) the fact that the surface peak is markedly broader than the resolution when the implanted dose is 10^{17} P cm^{-2}, indicating that disorder extends from the surface to a few hundred angstroms inside the crystal; and (iii) the fact that when the implanted dose reaches 1.5×10^{17} P cm^{-2}, the aligned spectrum reaches the random level over an energy window corresponding to the first 700 Å of the crystal.

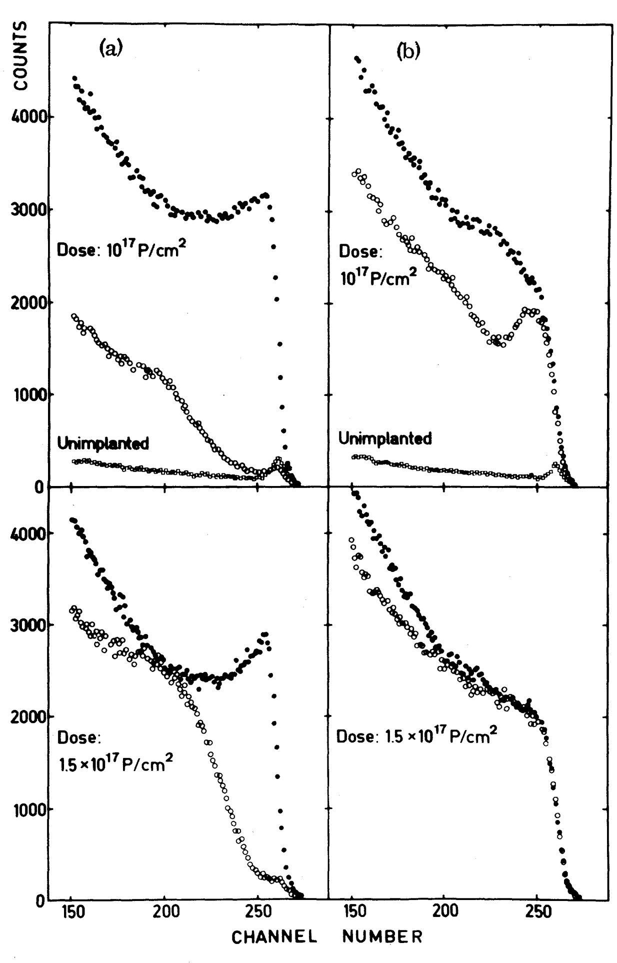

FIG. 1. Random (closed circles) and [100]-aligned (open circles) Rutherford backscattering spectra on Ni crystal implanted at (a) 90 and (b) 300 K with 10^{17} P cm^{-2} (upper) and 1.5×10^{17} P cm^{-2} (lower). Analyzing particles: 380-keV ^{4}He ions. Energy calibration: 1.02 keV/channel. The [100]-aligned RBS spectrum before implantation is shown for comparison.

The [100]-aligned backscattering yield, normalized to the random yield, was calculated as a function of depth for various doses and is shown in Fig. 2. The height of the surface peak increases continuously with the implantation dose, reaching the random level at 1.5×10^{17} P cm^{-2}. The latter result does not exclude that some crystallographic order could remain in the surface layer. However, if this were the case, the aligned backscattering yield would depend on the energy of the probing beam.[9] This was observed in our recent experiments on O-implanted Ni.[10] We therefore performed channeling experiments on the 1.5×10^{17}-P-cm^{-2} implanted sample using a 1.8-MeV ^{4}He beam provided by the Van de Graaff accelerator of the Groupe de Physique des Solides, Ecole Normale Supérieure Paris VII. The surface-layer-aligned yield was again found to reach the random level. The absence of any probing-beam energy dependence shows that this layer is either amorphous or polycrystalline with no preferred orientation. The P profile was obtained by computer analysis (to be published elsewhere), comparing the random spectrum at 1.8

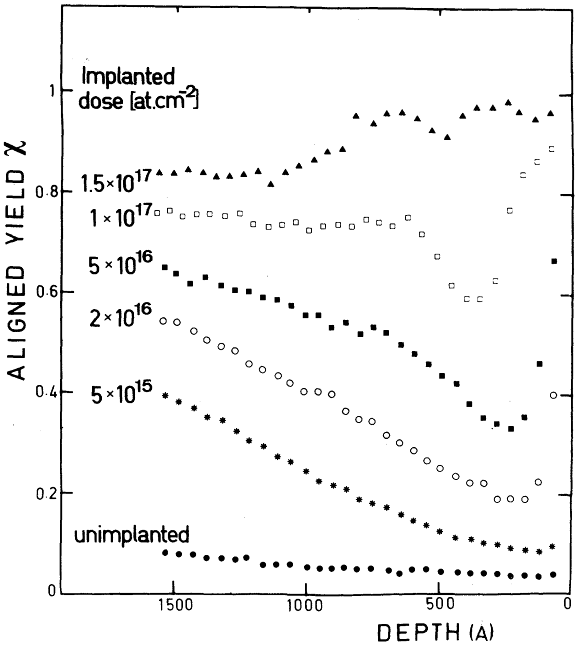

FIG. 2. Depth dependence of [100]-aligned spectra minimum yield at room temperature for P-implanted Ni. Analyzing particles: 380-keV ^{4}He ions.

MeV corresponding to the implanted crystal to the random spectrum of an unimplanted polycrystalline Ni foil. The phosphorus appears to be uniformly distributed over the first 700 Å with a concentration of (25 ± 3) at.%. Multiple scattering of the probing beam in the disordered surface layer accounts for the increase in the aligned yield corresponding to the deeper region of the crystal in the low-energy aligned spectra. A quantitative analysis of the surface peak integral at various steps of the implantation shows that its increase is proportional to the P implantation dose and that about 4–5 Ni atoms are displaced in the surface region for each implanted P atom. The straightforward interpretation of this result is that the implanted P atoms migrate towards the surface where they form a disordered alloy with a stoichiometry corresponding to the eutectic composition $Ni_{0.8}P_{0.2}$. The channeling experiment by itself cannot conclude as to whether the disordered layer is amorphous or polycrystalline. However, resistivity,[11] hyperfine interaction,[12] and TEM[3,4] experiments on room-temperature P-implanted Ni have unequivocally demonstrated that an amorphous alloy is produced. We therefore conclude that our channeling experiments provide information on the amorphization process.

The existence of long-range P transport at 300 K is interesting in itself. It contrasts with the situation prevailing in previously studied systems such as Ni-Si,[13,14] probably because of the interstitial nature of P atom in Ni. The diffusion coefficient of P in Ni at room temperature has not been measured, to our knowledge, and is presumably very low, so that P mobility in Ni is certainly radiation enhanced. A similar result was found for O in Ni.[10] The migration towards the surface may be related to several mechanisms,[13,14] e.g., interstitial P diffusion or the formation of a mobile P-vacancy complex. Further studies of this problem are in progress. How the amorphous phase is initiated near the surface is unclear at present: It could be formed directly or via segregation and subsequent amorphization (by the ion beam) of a crystalline Ni-P phase. Once an amorphous layer is formed, our results demonstrate that P migration is stopped at the interface between the crystal and the amorphous layer, inducing the latter's growth.

The situation is strikingly different when the implantation is performed at 90 K, as illustrated in Figs. 1 and 3. In this case, the surface peak remained unchanged even after implantation at 1.5×10^{17} P cm^{-2}. The disorder level was low and saturated between 5×10^{15} and 5×10^{16} P cm^{-2}, demonstrating that as long as the P concentration is low comparatively little disorder is stabilized. It increased markedly at the P implantation depth (540 Å) for an implantation dose of 10^{17} P cm^{-2}. At 1.5×10^{17} P cm^{-2} the aligned yield remains very low in the surface region while the random level is reached at R_P. The sample was then annealed up to room temperature: No change was found in the 380-keV aligned spectrum. A channeling experiment at 1.8 MeV confirmed that—as in the room temperature implantation case—this result was energy independent. The P profile extracted from the high-energy experiments is peaked around R_P with a maximum concentration of (25 ± 5) at.%: In contrast to the case of room-temperature implantation, there is no long-range P motion.

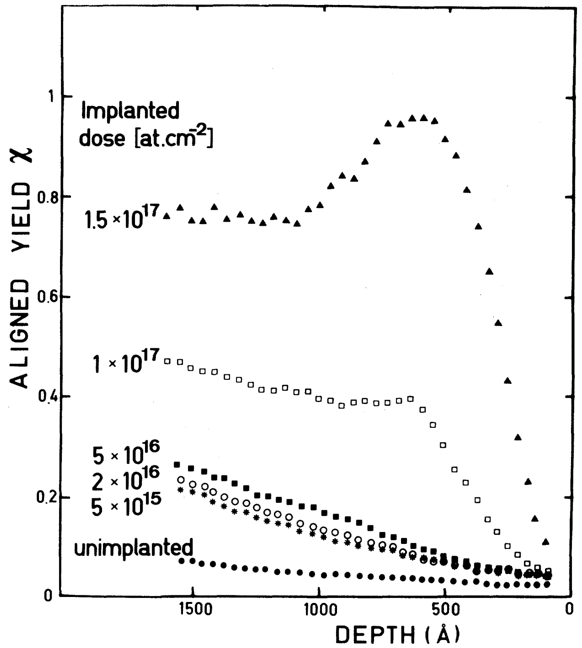

FIG. 3. Depth dependence of [100]-aligned spectra minimum yield at 90 K for P-implanted Ni. Analyzing particles: 380-keV ^{4}He ions.

The absence of any significant disorder in the near-surface region in these experiments contrasts with our observations on the 300-K implanted sample. The sharp enhancement in the disorder level of the implanted layer at and above the 10^{17}-P-cm^{-2} dose range can be related to an average P concentration threshold, around 12 at.%, above which the disorder is stabilized by the P atoms. When the average composition of this layer reaches about $Ni_{0.8}P_{0.2}$, the channeling results strongly indicate that an amorphous layer has been formed. However, the near-surface region has largely preserved its highly ordered single-crystal character, in contrast to previously known cases.[6,7]

Thus we have obtained the following new results: (i) long-range P migration occurs at 300 K but not at 90 K; in both cases (ii) a highly disordered phase is stabilized by the P atoms themselves, and (iii) full disorder is reached when the local P concentration reaches the eutectic composition. Possibly, the last is our most significant result in view of the considerable difference between the amorphous phase formation mechanisms at 300 and 90 K. Studies of the amorphous phase formation will provide information about P migration mechanisms and possible phase segregation in both the crystalline and amorphous phases.

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