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Electrical properties of amorphous Ni-P alloys produced by ion implantation

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The resistivity temperature dependence of room-temperature-implanted $Ni_{1-x}P_x$ alloys was measured at P concentrations between $x=0.14$ and $x=0.27$, and compared to that of evaporated and electrodeposited alloys. The results are discussed in the light of previously reported channeling experiments on the same alloys. It is found that the implanted amorphous $Ni_{1-x}P_x$ systems are identical to their counterparts prepared by conventional techniques.

I. INTRODUCTION

Ion implantation is known[1,2] to be a suitable technique to produce room-temperature-stable amorphous alloys. But, while the physical properties of amorphous systems prepared by quenching or electrodeposition techniques are extensively investigated, very little is known about their implanted counterparts. Recent resistivity,[3] channeling,[3,4] and hyperfine interaction[5] experiments on implanted Ni-P alloys have provided interesting information on the amorphization mechanism as well as on the local structure of the disordered layer. This paper presents a rather complete study of the conduction properties of this system.

The temperature dependence of the resistivity of room-temperature-implanted Ni-P films was studied versus the P-implanted dose, i.e., the film composition. We show that above a certain P concentration, related to the amorphization threshold evidenced in channeling experiments,[3,4] the value of the resistivity and its temperature dependence are the same for a given P concentration as those obtained in the case of evaporated or electrodeposited Ni-P alloys. To our knowledge, no comparison of this kind has previously been reported.

II. EXPERIMENTAL

Nickel films were prepared[6] by evaporation of pure Ni on quartz substrates in a vacuum better than 10^{-7} Torr. The thickness of the films (400 – 500 Å) was measured before implantation by Rutherford backscattering (RBS) experiments using the 380-keV $^4He^{2+}$ beam of the implanter. Film resistivity ratios between room temperature and 77 K before implantation are typically 1.7.

Four films were implanted at room-temperature with P^+ ions delivered by the implanter[7] of the Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse-Orsay at energies of 50 – 75 keV depending on the film thickness. Doses were varied from 5×10^{16} atom cm^{-2} to 1.5×10^{17} atom cm^{-2}, with dose rates lower than 2 μA cm^{-2} to avoid target heating. The vacuum during implantation was always better than 10^{-7} Torr. The thickness of the films and the energy of the P beam were chosen in order to obtain $Ni_{1-x}P_x$ alloys as homogeneous as possible over the whole film thickness, using the theoretical range and range-straggling calculations of Winterbon[8] and the results of our previous experiments[3–5] on the Ni-P system. The composition of the films and their homogeneity were measured after implantation by RBS experiments using a 1.8-MeV $^4He^+$ beam provided by the Van de Graaff accelerator[9] of the Groupe de Physique des Solides, Ecole Normale Supérieure Paris VII. The energy resolution was 12 keV, corresponding to a depth resolution of about 140 Å.

Figure 1 shows a typical RBS spectrum after P implantation. It exhibits two peaks arising from the backscattering of α particles on P and Ni atoms, respectively. The best way to determine the mean composition of thin homogeneous films is to measure the ratio of the areas of the two peaks. But in our case, this would lead to rather large errors due to the partial overlap between the P peak and the background due to the quartz substrate and to the (small) contribution of a P-implantation profile tail in this substrate. The mean compositions given in Table I were then deduced simply from the ratio of the heights of the two peaks; they agree well with the less precise values obtained from the ratio of the peak areas after taking the above remarks into account. The shape and width of the P peaks testify that the P-

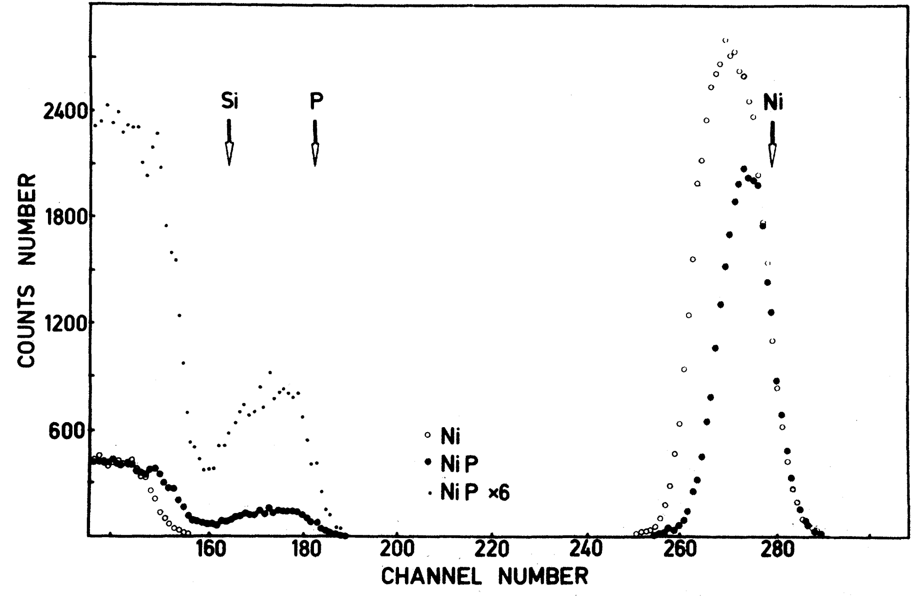

FIG. 1. RBS spectra on a Ni film before (open circles) and after (full circles) implantation at room temperature of 8.3×10^{16} atoms P/cm^2. Analyzing particles: 1.8-MeV ^{4}He ions. Energy calibration: 3.04 keV/channel.

concentration homogeneity over the whole sample thickness was typically 10% for all our samples, as already observed[3–5] on other experiments on implanted Ni-P systems. Comparison of the RBS spectra obtained on unimplanted and implanted films (see Fig. 1) also allows a determination of the average Ni-sputtering coefficient by P ions: $S=2.1\pm0.2$. The P-sputtering coefficient by P ions is more difficult to determine, due to the uncertainty of about 5% in the implanted dose. The analysis of the P peak shows that up to a dose of 9×10^{16} atom cm^{-2} there is no measurable sputtering of P atoms within our experimental uncertainties, and that for higher doses the P-sputtering coefficient may be estimated at 1.0 ± 0.5 assuming a P surface concentration $x\sim0.20$. The above values clearly indicate preferential sputtering for the host atoms. This point is obviously important for studies on the implanted Ni-P system.

The resistivity measurements were performed between 4.2 K and room temperature using a standard four-point probe technique. Temperature measurements were carried out using a calibrated carbon (100 Ω Allen-Bradley) resistor from 4.2 K up to 30–40 K and a calibrated 100 Ω platinum resistor from 30–40 K up to room temperature.

TABLE I. Sample and resistivity data.

Film[a] composition	ρ (293 K) ($\mu\Omega$ cm)	$\beta\times10^4$ [b] (K^{-1})	T_m (K)	$\alpha\times10^3$ [c]
$Ni_{0.86}P_{0.14}$	83.1(8.3)	4.4(1)	12	−0.44(5)
$Ni_{0.81}P_{0.19}$	111(11)	1.8(1)	14.5	−0.62(5)
$Ni_{0.77}P_{0.23}$	151(15)	0.23(1)	17.5	−0.80(5)
$Ni_{0.73}P_{0.27}$	164(16)	−1.3(1)		−1.04(5)

[a] The error in the given film composition extracted from RBS experiments (see text) is ±0.01.

[b] $\beta=\frac{1}{\rho}\frac{d\rho}{dT}\Big|_{T=293\text{ K}}$.

[c] $\alpha=\frac{1}{\rho}\frac{d\rho}{dLnT}\Big|_{T=4.2\text{ K}}$.

The heating rate was typically 60 K/h. Uncertainties in film dimensions are the main contribution to the error (of the order of 10%) on the absolute magnitude of the resisitivities.

III. RESULTS

The resistivity temperature dependence between 4.2 K and room temperature for the implanted Ni-P films is shown in Fig. 2. It is clear that: (i) The overall slope of the curves decreases when the P concentration increases and becomes negative for the highest concentration; (ii) the variation is linear at high temperatures, i.e., above ~ 150 K (slope β) for the four samples; (iii) there is a resistivity minimum (T_m) around 15 K for those alloys whose resistivity slope is positive at high temperature. An analysis of the low-temperature part (below T_m) of the resistivity variation reveals a logarithmic temperature dependence (slope α) as evidenced in Fig. 3. Table I summarizes the parameters obtained from the data in Figs. 2 and 3.

IV. DISCUSSION

As found in a previous experiment,[3] the resisitivity values of the $Ni_{1-x}P_x$ implanted films are in the range 80—160 $\mu\Omega$ cm, characteristic of amorphous metallic alloys. Figure 4 compares the values reported in Table I with those obtained by Cote[10] and Bouchet[11] on electrodeposited and evaporated Ni-P alloys, respectively. In spite of the differences in preparation techniques, the overall resistivity composition dependence is the same for the different samples. This dependence has been ascribed mainly[10] to the increase of the Fermi momentum k_F with alloying. According to the extended Ziman theory,[12] as $2k_F$ approaches k_p (the position of the first maximum in the structure factor) an increase of the resistivity is expected with a gradual transition of $d\rho/dT$ from positive to negative values.

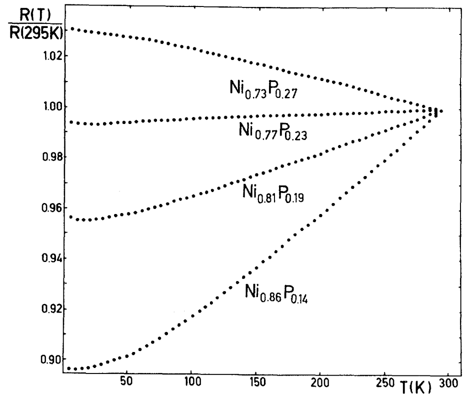

FIG. 2. Resistivity temperature dependence in the range 4.2—293 K for room-temperature-implanted Ni-P films.

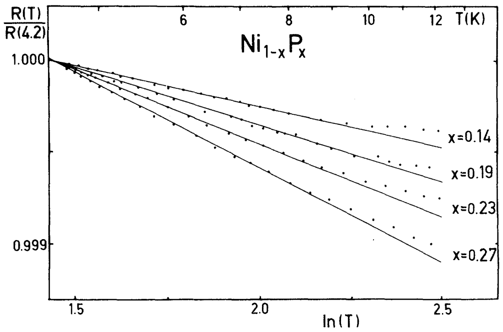

FIG. 3. Resistivity vs ln$T$ in the range 4.2—15 K for room-temperature-implanted Ni-P films.

The temperature coefficients (TCR) of the resistivity β (see Table I) found for $x \geq 0.19$ are typical of amorphous alloys. A change of sign of β occurs at $x \sim 0.24$, i.e., at the same composition as in the case of electrodeposited alloys[10] and as predicted by the extended Ziman theory. The corresponding residual resistivity $\rho_0 \sim 150$ $\mu\Omega$ cm fits well with Ref. 10 and with Mooij's empirical criterion.[13] Figure 5 shows that here again good agreement is obtained between the β values measured for implanted and electrodeposited or evaporated alloys when the eutectic composition is reached. At lower P concentration, a difference exists, particularly in the case of the $Ni_{0.86}P_{0.14}$ sample. This difference could be explained by compositional inhomogeneities in the film, since

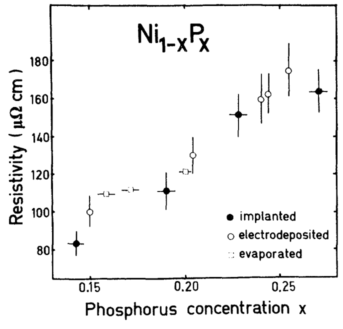

FIG. 4. Resisitivity vs P concentration for Ni-P alloys prepared by different techniques. Implanted: our results; electrodeposited: Ref. 10; evaporated: Ref. 11.

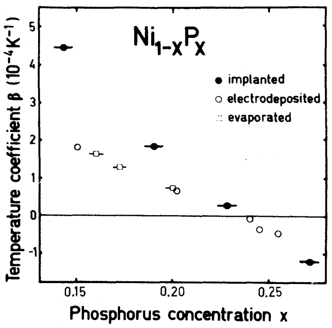

FIG. 5. Temperature coefficient of the resistivity vs P concentration for Ni-P alloys prepared by different techniques. Implanted: our results; electrodeposited: Ref. 10; evaporated: Ref. 11.

the existence of a thin Ni layer (10% of the whole thickness) implanted with only a few percent of phosphorus may increase β by more than a factor of 2 while the resistivity reduction would only be of the order of 20%. However, the experimental conditions discussed above make this hypothesis unlikely. A more reasonable explanation is that for the lower P concentrations the alloy is not completely amorphous, as indicated by transmission electron microscopy[1] and channeling[3,4] experiments which show that a P concentration of 18−20% is required to stabilize the implantation-induced disorder, i.e., to achieve complete amorphization. In fact, this result suggests that the TCR provides a sensitive probe of implanted-sample amorphization. Further tests on other systems such as Pd-Si are warranted to establish this conclusion.

At very low temperatures (below 9 K), a logarithmic decrease of the film resistivity with increasing T is evidenced in all our samples (see Fig. 3). For those films which present a positive β, this leads to a resistivity minimum at $T_m = 12-18$ K. Such a behavior has already been observed in amorphous Ni-P specimen[10,14] as well as in other transition-metal— metalloid amorphous alloys.[14,15] The slopes α of the logarithmic term and the T_m values obtained in our experiments (see Table I) are comparable to those given by these authors. For example, Cochrane *et al.*[14] find $\alpha = -1.00(4) \times 10^{-3}$ and $T_m = 17$ K in the case of an electrodeposited $Ni_{0.75}P_{0.25}$ alloy. Moreover, Table I indicates that α increases nearly linearly with the P content. A similar result has been reported by Tóth[16] and by Stobiecki and Hoffmann[17] on amorphous ferromagnetic Fe-B alloys. The compilation of these results and of the data of Cochrane[15] on $(Fe_{40}Ni_{40})\,B_{20-x}P_x$ alloys shows that α is roughly proportional to the effective number of conduction electrons per atom given by the metalloid impurity.

Several attempts[14,15,18] have been made to account for the resistivity minimum and the logarithmic dependence below this minimum, but there is still considerable controversy regarding the mechanism responsible for it. Kondo scattering and "pseudo-Kondo" scattering from the two-level system presumably existing in amorphous metals have both been invoked. Our data bring no information on the origin of the effect. It is, however, of interest to stress (as in previous work[14,15]) the fact that neither the sample-preparation technique, nor the impurity content, affect α or T_m in $Ni_{1-x}P_x$ and that T_m exists whether the samples are ferromagnetic or not. The effect is hence presumably rather basically related to the existence of sample amorphicity.

V. CONCLUSION

The resistivity experiments reported in this paper show that the conduction properties of room-temperature-implanted amorphous Ni-P alloys are identical to those of amorphous Ni-P alloys made by evaporation or electrodeposition, as soon as the eutectic composition is reached. This result, together with channeling[4] and hyperfine interaction[5] results leads us to conclude that room-temperature implantation produces an amorphous state identical to that obtained by standard quenching or deposition techniques in the concentration range $x = 0.20-0.27$. In Ref. 4, we demonstrated that the buildup of the amorphous layer at room temperature was related to radiation-induced P mobility. The latter process, which provides a driving force towards thermodynamical equilibrium, did not occur at 80 K. It will therefore be of considerable interest to determine whether the results reported in this paper also held after low-temperature P implantation, i.e., when the amorphous system is produced still further from thermodynamical equilibrium.

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[1] A. Ali, W. A. Grant, and P. J. Grundy, Philos. Mag. B37, 353 (1978).

[2] E. Johnson, T. Wohlenberg, W. A. Grant, P. Hansen, and L. T. Chadderton, J. Microsc. (Oxford) 116, 77 (1979).

[3] L. Thomé, L. Mendoza-Zelis, L. Brossard, K. Królas, J. Chaumont, H. Bernas, and C. Cohen, in Proceedings of the International Conference on Amorphous Systems Investigated by Nuclear Methods, Balatonfüred, 1981 [Nucl. Instrum. Methods (in press)].

[4] C. Cohen, A. V. Drigo, H. Bernas, J. Chaumont, K. Królas, and L. Thomé, Phys, Rev. Lett. 48, 1193 (1982).

[5] L. Thomé, P. Heubes, H. Bernas, M. Deicher, and E. Recknagel, in Ref. 3.

[6] A. Traverse, unpublished work.

[7] J. Chaumont, F. Lalu, M. Salomé, A. M. Lamoise, and H. Bernas, in Proceedings of the International Conference on Ion Implantation: Equipment and Techniques, Kingston, 1980 [Nucl. Instrum. Methods 189, 193 (1981)].

[8] K. B. Winterbon, *Ion Implantation Range and Energy Distributions* (Plenum, New York, 1975).

[9] G. Amsel, J. P. Nadai, E. D'Artemare, D. David, E. Girard, and J. Moulin, Nucl. Instrum. Methods 92, 481 (1971).

[10] P. J. Cote, Solid State Commun. 18, 1311 (1976); P. J. Cote and L. V. Meisel, in *Glassy Metals I,* edited by H. J. Güntherodt and H. Beck (Springer, Berlin, 1981).

[11] B. Bouchet, thèse 3ème cycle, Université Pierre et Marie Curie, Paris VI, 1979 (unpublished).

[12] O. Drierach, R. Evans, H. J. Güntherodt, and H. U. Künzi, J. Phys. F 2, 709 (1972)

[13] J. M. Mooij, Phys. Status Solidi A 17, 521 (1973).

[14] R. W. Cochrane, R. Harris, J. O. Ström-Olson, and M. J. Zuckermann, Phys. Rev. Lett. 35, 676 (1975).

[15] R. W. Cochrane, F. T. Hedgcock, B. J. Kästner, and W. B. Muir, J. Phys. (Paris) 39, C6-939 (1978).

[16] J. Tóth, in Proceedings of the International Conference on Soft Magnetic Materials III, Bratislava 1977 (unpublished).

[17] T. Stobiecki and H. Hoffmann, J. Phys. (Paris) 41, C8-485 (1980).

[18] G. S. Grest and S. R. Nagel, Phys. Rev. B 19, 3571 (1979).