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LASER-SURFACE MELTING AND THERMAL ANNEALING

MASTER

E. N. Kaufmann
L. Buene
M. L. McDonald
J. Kotthaus
K. Freitag
C. W. Draper
R. Vianden

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Hafnium-Implanted Nickel Studied with TDPAC and RBS/Channeling
Before and After Laser-Surface Melting and Thermal Annealing

E. N. Kaufmann*

Lawrence Livermore National Laboratory^x, University of California
Livermore, CA, 94550

and

L. Buene⁺ and M. L. McDonald

Bell Laboratories, Murray Hill, NJ, 07974, USA

and

J. Kotthaus, K. Freitag and R. Vianden

Institut für Strahlen- und Kernphysik der Universität Bonn
D-53 Bonn, Federal Republic of Germany

and

C. W. Draper

Western Electric Engineering Research Center
Princeton, NJ, 08540, USA

ABSTRACT

The Hf implanted Ni system has been studied by the time-differential perturbed angular correlation (TDPAC) technique and by Rutherford backscattering (RBS)/channeling. Low fluence implants were thermally annealed in vacuum at increasing temperature in order to study the evolution of substitutional and defect-associated solutes using TDPAC. Both detrapping and precipitation (or segregation) effects have been observed. Higher fluence implants were studied by both TDPAC and RBS/channeling in as-implanted as well as laser-surface-melted regimes.

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+ Resident visitor at Bell Laboratories. Supported in part by Royal Norwegian Council for Scientific and Industrial Research. Present Address: VERITAS, 1322 Høvik Norway.

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1. Introduction

The NiHf system had been studied by the time-differential perturbed angular correlation (TDPAC) method by several groups with somewhat conflicting results. Using the same method, Gerdau et al.^{1,2)} performed a systematic study of alloys of several Hf concentrations prepared by electron-beam melting and succeeded in eliminating most of the discrepancies. They found that at solute levels up to 0.5 at.%, a substitutional alloy could be prepared and that at higher levels, various intermetallic compounds were formed. They also noted from the spread in magnetic hyperfine field at the Hf sites that the presence of Hf, even in low concentrations, produces significant distortion of the Ni lattice. Finally, they observed that at temperatures above $\sim 325^{\circ}\text{C}$, time-dependent effects appeared in the Hf-Ni interaction.

Some of the early work for which questions arose dealt with specimens prepared by ion implantation. To characterize that work, Kaufmann et al.³⁾ performed RBS/channeling studies on Ni single crystals implanted with 2×10^{14} Hf/cm² (~ 0.2 at.%) before and after thermal annealing. They found that only $\sim 50\%$ of the implanted Hf resided in substitutional sites, the remainder in regions of disorder. Upon annealing above 550°C , Hf precipitation occurred with an indication of Hf movement toward the Ni surface.

One question left unresolved was the definitive correlation between magnetic field sites (secondary sites having been implied in some work) and the substitutional/disordered components found by channeling. In the work reported below, we show that the so-called substitutional component, as defined by ion-beam channeling, probably includes two Hf sites; one truly substitutional and one defect associated.

A parallel question concerning the way in which an impurity, such as Hf, is incorporated into a metastable supersaturated solid-solution in a host, such as Ni, by means of rapid solidification has arisen more recently. Since the NiHf system had already been extensively investigated by both TDPAC and

RBS/channeling and its equilibrium phase diagram shows an appropriate size-limited terminal solubility at the Ni-rich end, this system seemed ideal to study whether defect-association not visible in channeling experiments may occur on rapid solidification. The particular advantages of TDPAC for this study were discussed by Kaufmann⁴⁾ and the specific utility of Hf and Ni as well as preliminary results on as-implanted and laser-surface-melted (LSM) samples were reported by Buene et al.⁵⁾

Since that original proposal, two related works have appeared. Pleiter and Prasad⁶⁾ used TDPAC to study the In-implanted Al system before and after LSM. They found only nonunique lattice disorder in as-implanted cases but identified unique In-defect complexes after LSM as those also seen in radiation damage experiments. The Eu-implanted Ni system was studied before and after LSM by Battaglin et al.⁷⁾ using only the RBS/channeling method. They deduced Eu-defect association after melting from the absence of the expected metastable substitutional alloy. Neither of these studies was designed to distinguish between the trapping of defects at solute atoms at the instant of incorporation into the solid and the subsequent trapping of quenched-in mobile defects.

We report below a similar attempt using both experimental methods on the NiHf system, in the hope that the combined data would constrain the possible interpretations to only one or a few unique possibilities.

2. Experimental Procedure

High purity <110> Ni single crystals were lapped, electropolished and implanted with the radioisotope, ¹⁸¹Hf, using the University of Bonn radio-implanter. The fluence is estimated at $\sim 5 \times 10^{13}/\text{cm}^2$ at an energy of 80keV. Such samples were used directly for TDPAC measurements as a function of vacuum-thermal annealing. Samples to be used in LSM tests were previously implanted with either $1.4 \times 10^{16}/\text{cm}^2$ or $4.4 \times 10^{16}/\text{cm}^2$ of stable ¹⁸⁰Hf at Bell Laboratories. These were studied by TDPAC and

RBS/channeling before and after LSM in air by a Q-switched Nd:YAG laser at Western Electric-ERC. The laser beam, focussed to $\sim 35\mu\text{m}$ and pulsed at 11kHz with a pulse width of $\sim 150\text{ns}$ and peak power density of $\sim 100\text{MW}/\text{cm}^2$, was raster-scanned over the implanted sample area. The same system had been used to study Ni crystals previously.⁸⁾

TDPAC studies described here were carried out in Bonn using a standard NaI(Tl)-detector system to observe the cascade gamma-rays through the 482keV excited level of ^{181}Ta , the daughter nucleus of the ^{181}Hf decay. The usual slow-fast coincidence electronics provided the time-dependent gamma-ray coincidence spectra. The basis of the TDPAC method is described in several texts^{9,10)} and use of the ^{181}Ta cascade has been previously reported.^{11,12)} Measurement after thermal annealing at various temperatures were conducted with the NiHf samples in an external polarizing magnetic field. Those performed on LSM samples used no external field.

RBS/channeling measurements were performed with the 1.8 MeV $^4\text{He}^+$ beam of the Bell Laboratories 2MV Van de Graaff accelerator using the same techniques described elsewhere.^{8,10)}

3. Results, Analysis and Interpretation

3.1 Thermal Annealing

The perturbation factor derived from the time-dependent coincidence data for the as-implanted low-fluence sample is shown in Figure 1. Two frequency components are clearly seen in these data. In addition, the oscillations are not centered about a zero value indicating the presence of interactions at some Hf sites which are not of a unique-aligned magnetic character. The solid curve in the figure resulted from a fit to two unique magnetic sites plus a third component representing sites where a strong and nonunique static interaction is present such that, for those sites, the angular correlation anisotropy rapidly decays to a "hard-core" value. The fitting function also

allowed for a distribution of field values for each unique site to account for effects of distant lattice disorder and impurities. The unperturbed anisotropy was known from liquid-source measurements. After annealing at 380°C, one of the unique sites is absent leaving a single frequency as shown in the data of Figure 2. Upon annealing at 720°C, no well defined unique site remains as seen in Figure 3. In Table I, the thermal annealing fit results are summarized.

One sees from the data that initially about two-thirds of the Hf resides in highly nonunique environments ("hard-core"). This is somewhat greater but still consistent with early channeling results.³⁾ A slight recovery of this fraction is seen at intermediate annealing temperatures where Gerdau et al.¹⁾ found the onset of time-dependent behavior. Also at this temperature, site 2 begins to vanish and the population of site 1 is enhanced. Finally at 720°C, no unique site is observed, which is in agreement with the so-called precipitation reported in Ref. 3. Site occupancy fractions are displayed graphically in Figure 4.

The frequency at site 1 agrees with that known to be the substitutional value from alloy studies.¹⁾ Thus site 2 represents a unique defect-trapping configuration not previously reported. The data do not support the presence of a strong electric quadrupole interaction at site 2 implying that the defect geometry is not highly asymmetric. A weak quadrupole field cannot be ruled out, however. Also, because the fraction of solute in site 2 is from 1/3 to 1/2 that in substitutional sites, the channeling work of Ref. 3 should have observed a unique second site were it such that the Hf atom is displaced into lattice interstices. Various defect trapping configurations at implanted impurities in fcc metals have been identified and a summary of results was published by Pleiter and Hohenemser.¹³⁾ A trapped trivacancy is the most

likely configuration for our case in so far as our TDPAC data is concerned. It has been noted ¹⁴⁾ that this defect is very sensitive to implant fluence which may explain the failure of Ref. 3 to observe it in channeling. A similar attempt to identify this type of defect in In-implanted Ni by Arends et al. ¹⁵⁾ also failed. The temperature at which detrapping occurs agrees with the onset of stage B in quenched Ni ¹⁶⁾ attributed to the annealing of small voids and dislocation loops and to the time-dependent region seen by Gerdau. ¹⁾

At the highest temperature, no unique site is seen with TDPAC and RBS/channeling ³⁾ showing nonsubstitutionality and migration toward the surface (but not into an oxide layer). This behavior is not expected when the Hf concentration is below the solubility limit in Ni. The evidence points to the interruption of simple substitutional diffusion of Hf into the bulk by some sort of trapping effect which operates when the Hf becomes mobile. Perhaps the sinks for Hf are extended defects or clusters which have not annealed or possible internal oxidation due to residual oxygen present during annealing.

3.2 Higher Fluence and Laser-Surface Melting

Three implant fluences were subjected to LSM. The low fluence implant was identical to that described in the previous subsection (ie., only ¹⁸¹Hf was implanted). After LSM, no unique magnetic site was observed and it is believed all the Hf segregated to a surface oxide. The corresponding time-spectra before and after melting were published as Fig. 10 of Ref. 4 and Fig. 1 of Ref. 5, respectively. Data for samples preimplanted with $1.4 \times 10^{16}/\text{cm}^2$ of ¹⁸⁰Hf are shown in Figures 5 and 6, and those for a preimplant fluence of $4.4 \times 10^{16}/\text{cm}^2$ are shown in Figures 7 and 8. These data are identical to those reported in Fig. 2 and 3 of Ref. 5, however the solid curves represent significantly improved fits to the data. The best fits allowed two magnetic sites as well as a component in a broadly distributed electric quadrupole field. The latter possibility served to account for that

fraction which was treated as a "hard-core" component in the previous section. Only the data of Figure 5 required the second unique magnetic site to achieve a good fit. In the fitting process, advantage was taken of the additional information obtained from RBS/channeling measurements on samples implanted at identical fluences. This was done by fixing, in the TDPAC fit, the fraction of Hf in the nonunique quadrupole environment to that found to be nonsubstitutional (in as-implanted samples) or in an oxide layer (in LSM samples). The RBS/channeling energy spectra from which these were derived are shown in Figures 9 and 10.

The presence of an oxide layer containing a significant amount of Hf was verified by comparing LSM of a test sample under air and He gas. This was briefly described in Ref. 5 and completely reported by Draper et al.¹⁷⁾ Parameters resulting from fitting the data of Figs. 5-8 and channeling results are presented in Table II.

In the as-implanted case at the lower fluence (Figure 5), one sees both the substitutional and the previously seen defect-associated sites. The frequencies agree well with those in Table I and the greater distribution widths are undoubtedly due to both implantation induced disorder as well as lattice distortion from nearby Hf solute atoms. It is interesting to note that 75% of the Hf atoms see a unique interaction here (site 1 + site 2) whereas only 33% were in unique sites at the lower fluence (Table I). This is required by constraining the fit to agree with the channeling result. A substitutional fraction from channeling is not necessarily synonymous with a highly unique local environment and an equally good fit after relaxing this constraint does not confirm the presence of site 2. Without additional information, we cannot decide between these alternatives, but it is clear that the channeling substitutional fraction exceeds that seeing a substitutional field.

The as-implanted highest-fluence case (Figure 7) shows a strong, completely nonunique interaction and evidence of a totally disordered surface layer (Figure 10). The peak Hf concentration in the layer is 12 at.%. The fit to distributed electric quadrupole fields could equally well have assumed magnetic fields. Thus, no definitive information can be extracted from the data. After LSM of the sample surfaces, a single unique frequency is recovered in both cases (Figures 6 and 8). Channeling data show epitaxial regrowth (albeit with a considerable defect density) and partitioning of the Hf between retention in an oxide layer and a deep, totally substitutional component (Figures 9 and 10). The frequency and distribution width for the substitutional site in the lower fluence case is consistent with that found by Gerdau et al.¹⁾ in their alloy of 0.5 at.%. The concentration of substitutional Hf in the higher fluence case of 12.3 at.% is nearly five times the maximum equilibrium solubility. The consequent lattice distortion accounts for the broad distribution in the observed magnetic frequency. The field value is some 25% less than that seen at the 0.5 at.% concentration. This is consistent with an extrapolation of the concentration dependence of the magnetic hyperfine field found by Gerdau et al.¹⁾

Even though we have formed a highly supersaturated alloy, no evidence of unique defect trapping during or after solidification has been found. Because good TDPAC fits are obtained which are consistent with channeling data, we also find no evidence for Hf association with the extended defects which are known to be present in the rapidly solidified layer. Each of these points is at variance with the work cited on the AlIn⁶⁾ and NiEu⁷⁾ systems.

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Table I: Observed frequencies, frequency-distribution widths, and occupancy fractions for thermally annealed NiHf. (Figures in brackets give errors in the last digit)

Temperature	Larmor Frequency (MHz)		Distribution width (%)		Occupancy fractions (%)		
	site 1	site 2	site 1	site 2	site 1	site 2	"hard-core"
(°C)							
Room	531.1 (4)	293.6 (6)	1.1 (2)	1.7 (6)	22.1 (4)	11.2 (4)	66.7 (6)
50	529.6 (7)	293.0 (10)	1.41 (3)	2.4 (7)	21.9 (6)	12.6 (6)	65.6 (11)
100	531.2 (5)	293.8 (5)	0.6 (5)	1.5 (6)	18.4 (5)	15.6 (5)	66.0 (8)
150	539.5 (19)	291.8 (16)	1.3 (6)	2.9 (8)	22.0 (10)	18.5 (10)	59.5 (10)
250	531.0 (4)	293.7 (4)	1.3 (2)	1.5 (5)	28.2 (5)	18.7 (5)	53.1 (9)
330	531.9 (4)	294.7 (6)	1.0 (2)	2.2 (5)	28.5 (5)	14.4 (5)	57.2 (8)
380	532.2 (3)	-	0.9 (2)	-	38.0 (6)	-	62.0 (6)
480	531.8 (3)	-	0.6 (2)	-	42.8 (7)	-	57.2 (7)
680	531.8 (5)	-	0.2 (13)	-	21.2 (7)	-	78.8 (7)
720	530.6 (6)	-	5.0 (50)	-	3.0 (30)	-	97.0 (30)

Table II: Observed frequencies, frequency distribution widths, and occupancy fractions from TDPAC and RBS/channeling measurements (Figures in brackets are errors in the last digit)

TDPAC-Parameter	Hf fluence $1.4 \times 10^{16}/\text{cm}^2$		Hf fluence $4.4 \times 10^{16}/\text{cm}^2$	
	As-implanted	Laser melted	As-implanted	Laser melted
site 1:				
Larmor Frequency (MHz)	520 (5)	511 (3)		371 (8)
Distribution width (%)	8.5 (6)	6.6 (9)		42 (6)
Occupancy fraction (%)	57.4 (3)	62 (fixed)		65 (35)
site 2:				
Larmor frequency (MHz)	297 (15)			260 (12) ^{a)}
Distribution width (%)	18 (4)			0 (16) ^{a)}
Occupancy fraction (%)	17.6 (3)			3(>30) ^{a)}
Quadrupole sites:				
Quadrupole frequency (MHz)	390 (40)	779 (67)	907 (48)	476 (8)
Distribution width (%)	11.4 (23)	44 (5)	43 (3)	18 (3)
Occupancy fraction (%)	25 (fixed)	38 (fixed)	100	32 (fixed)
RBS/channeling				
% substitutional ¹	75	100 ^{b)}	0	100 ^{b)}
% Hf in oxide		38		32
Hf concentration in the metal (at.%)		0.5		2.3

a) The fit is equally good without site 2 in this case.

b) 100% substitutionality refers to the Hf not retained in oxide layer.

Figure Captions

- 1) The experimental magnetic perturbation factor, G_2 , (multiplied by the angular correlation coefficient, A_2) measured in an external polarizing field for a Ni crystal implanted with $\sim 5 \times 10^{13}/\text{cm}^2$ ^{181}Hf in the as-implanted condition. The solid curve is a least-squares fit to the data.
- 2) As in Figure 1, but after annealing the sample at 380°C .
- 3) As in Figure 1, but after annealing the sample at 720°C .
- 4) Occupancy fractions as a function of annealing temperature for site 1 (regular substitutional site), site 2 (defect-associated site), and a component experiencing strong nonunique interactions for which the angular correlation anisotropy is reduced to its "hard-core" value.
- 5) The experimental perturbation factor for the Ni crystal implanted with $1.4 \times 10^{16}/\text{cm}^2$ ^{180}Hf and $\sim 5 \times 10^{13}/\text{cm}^2$ ^{181}Hf in the as-implanted condition.
- 6) As in Figure 5, but after laser-surface melting.
- 7) The experimental perturbation factor for the Ni crystal implanted with $4.4 \times 10^{16}/\text{cm}^2$ ^{180}Hf and $\sim 5 \times 10^{13}/\text{cm}^2$ ^{181}Hf in the as-implanted condition.
- 8) As in figure 7, but after laser-surface melting.
- 9) Rutherford backscattering/channeling energy spectra for the Ni sample implanted with $1.4 \times 10^{16}/\text{cm}^2$ ^{180}Hf , both before and after laser-surface melting. Solid data points correspond to channeling in the $\langle 110 \rangle$ axis of Ni. Open data points refer to random incidence direction of the analyzing $1.8 \text{ MeV } ^4\text{He}^+$ beam.
- 10) As in Figure 9, but for the Ni crystal implanted with $4.4 \times 10^{16}/\text{cm}^2$ ^{180}Hf .

Fig. 1

Fig. 3

Fig. 6

Fig. 7

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