PHYSICAL REVIEW B VOLUME 33, NUMBER 5 1 MARCH 1986

Brief Reports

Influence of point defects on the lattice-site occupation of nonsoluble atoms implanted in vanadium

A. Azzam* and O. Meyer

Kernforschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik,
Postfach 3640, D-7500 Karlsruhe, Federal Republic of Germany

(Received 25 June 1985)

In situ channeling analysis showed that the temperature-dependent lattice occupancy for highly nonsoluble systems with rather high positive heat of solution (produced by ion implantation) is governed by the formation of impurity-vacancy complexes. The trapping probability of vacancies as well as the stability of the clusters against annihilation with mobile self-interstitial atoms are correlated with the calculated heat of solution indicating that these processes are governed by thermodynamic driving forces in the dynamic collision cascade. It is concluded that impurity-vacancy recombination and multivacancy trapping processes are the most important mechanisms which determine the lattice-site occupation of implanted ions in metals.

A question of fundamental interest in ion implantation metallurgy is concerned with the lattice position the implanted ion will occupy after it comes to rest in about 10^{-13} s (Ref. 1) after a series of binary collisions. At the end of the trajectory there is a high probability that the ion undergoes a replacement collision[2] and thus reaches a substitutional lattice site. In nonlinear cascade regions, however, where a collective motion of all atoms prevails, the lattice-site occupation mechanism could be the result of an ultrafast quenching process from a liquidlike region.[3] The recombination of implanted atoms with vacancies in the cascade is a very important process for substitutional lattice-site occupation, as vacancies are always potential minima. The interaction with more than one vacancy can lead to foreign-atom–vacancy cluster formation. Xe-vacancy clusters, for example, have been studied by Mössbauer spectroscopy after implantation of radioactive ^{133}Cs in Mo, W, and Ta at room temperature.[4] The formation of In-vacancy complexes in the prompt cascade regime by trapping of mobile vacancies was found after implantation of ^{119}Sn in Fe.[5] The structure of impurity-vacancy clusters after low-temperature irradiation and annealing of solid solutions with oversized atoms in Al has been studied using the channeling technique.[6]

The numerous experimental results on lattice-site determinations for implanted metallic alloys have been summarized and discussed recently.[7] From this summary it is seen that heavy elements from groups IIIa to VIIa of the periodic system usually reveal a high substitutional component in Cu, Ni, Fe, and V, while those of groups Ia, IIa, IIIb, and some rare-earth elements are almost nonsubstitutional after implantation at room temperature.

Implantation and lattice-site analysis in vanadium showed that highly nonsoluble elements (La,Ba,Cs) revealed a temperature-dependent substitutional fraction, while the soluble elements, for example Bi, did not.[8] It was assumed further[9] that those elements with high positive heat of solution (ΔH_{sol}) would have rather high trapping probability for vacancies in order to reduce this H_{sol}. A comparison between the substitutional fraction for the systems *V*La, *V*Ba, *V*Cs, and *V*Bi with the calculated heat of solution after Miedema[10] shows that the nonsubstitutional component $(1-f_s)$ for systems with high ΔH_{sol} could be attributed to the trapping of vacancies and formation of impurity-vacancy clusters in the collision cascade as well as in the delayed regime. In this work we study briefly the system *V*Ba which has a rather high heat of solution (ΔH_{sol}) and the system *V*Ce which has an intermediate (ΔH_{sol}) to prove the existence of these clusters and to get information about their stability by performing post-irradiation and annealing experiments.

Experimental details of sample preparation and analyses have been described previously.[8] The application of channeling measurements in lattice location studies is well documented in the literature (e.g., Ref. 11). For more details on the analysis of impurity–point-defect complexes, see Ref. 6. Briefly, the backscattered He-ion yield is registered as a function of the angle between the incident He beam and the low-index crystal directions of the single crystal. From the normalized angular yield curves for the host and the impurity atoms, the lattice-site location can be determined. As an example, a typical random and a $\langle 111\rangle$-aligned backscattering energy spectrum for a V single crystal implanted *in situ* with 0.08 at.% Ce at 5 K is shown in Fig. 1. He ions backscattered from Ce atoms are well separated in energy from those backscattered from V atoms. The substitutional fraction can be determined by $f_s = (1-\chi^s_{\min})/(1-\chi^h_{\min})$, where $\chi_{\min}$ is the ratio of the aligned to random scattering yield for

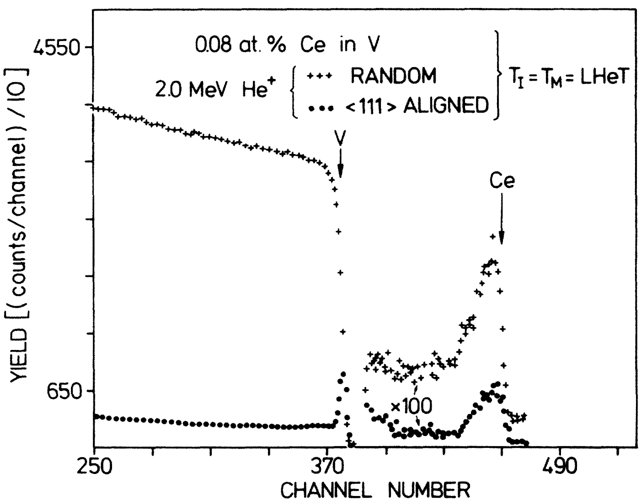

FIG. 1. Random and ⟨111⟩-aligned spectra from a Ce$^+$-implanted vanadium single crystal. Implantation and analysis are performed at 5 K.

the solute ($\chi_{\min}^{s}$) and for the host ($\chi_{\min}^{h}$). From Fig. 1, a substitutional fraction of 0.73 ±0.05 can thus be determined. The angular yield curves for the Ce and the V atoms reveal the same critical angle, indicating that the Ce atoms occupy substitutional lattice positions without relaxation.

The substitutional fractions, as determined previously for the systems *V*Bi, *V*La, and *V*Ba, together with the present results for *V*Ce after implantation of 0.1 to 0.2 at.% of foreign atoms at substrate temperatures T_I of 5, 77, and 300 K are summarized in Fig. 2. The following results are noted: (a) The substitutional fraction for *V*Bi is 1, independent of the lattice temperature. This f_s value is larger than the value of 0.3 obtained from the replacement collision theory indicating that recombination of the foreign atom with a vacancy in the cascade is the fate of any soluble or nearly soluble ion in a metal, resulting in a high substitutionality.[8] (b) The substitutional fraction for the systems *V*Ce, *V*La, and *V*Ba depends on the implanted species with $f_s = 0.73$, 0.59, and 0.45, respectively; however, it is independent of the lattice temperature for temperatures below 100 K, indicating that the interaction with self-interstitial atoms (SIA's), which are mobile between 6 and 50 K,[12] does not play an important role for the lattice-site occupation mechanism. (c) A system-dependent decrease of f_s is noted after implantation at 300 K. Stage III for vacancy motion in V lies between 200 and 300 K (Ref. 12) and vacancy-impurity interactions, which would lead to a decrease of f_s, are quite probable during implantation at 300 K.

The following post-irradiation and annealing experiments have been performed for the systems *V*Ce and *V*Ba after implantation at RT, as well as at liquid-nitrogen temperature (LN$_2$T), to prove that the nonsubstitutional components $(1-f_s)$ are the result of the impurity-vacancy complex formation.

In order to annihilate the Ce-vacancy clusters if formed after implantation at 300 K, post-irradiation experiments with He ions at LN$_2$T are performed. The irradiation with light ions at LN$_2$T is an efficient procedure to produce single vacancies and mobile SIA's which could annihilate the impurity-vacancy clusters. The results of these experiments are summarized in Table I and are illustrated in Fig. 3. After implantation of Ce with different concentrations at 300 K, the substitutional fraction ranges from 0.2 to 0.46 and the critical angle $\psi_{1/2}$ for Ce atoms is smaller than that for V [Fig. 3(a)] indicating that the Ce atoms are displaced from their substitutional lattice site. These RT-implanted *V*Ce systems are post-irradiated with He ions at 77 K. The substitutional fraction increases with increasing He fluence and reaches a maximum saturation value of 0.73 [Fig. 3(b)] in agreement with the value for the *V*Ce system as-implanted at 77 K [Fig. 3(c)]. The increase of the substitutional component is attributed to the existence of Ce-vacancy complexes, which are partly annihilated by absorbing the self-interstitial atoms. From the difference of the critical angles for Ce and V in Fig. 3(b), it can be concluded that Ce atoms are still displaced by about 0.12 Å, which means that Ce-multivacancy complexes are annihilated to Ce-divacancy complexes. If the post-irradiated system is warmed up to RT, the substitutional fraction decreases, due to the trapping of vacancies which become mobile.[12]

A nonsubstitutional component $1-f_s$ of about 0.27 is noted after low-temperature implantation, as well as after post-irradiation of the *V*Ce system. Further post-irradiation experiments on low-temperature implants did not lead to an

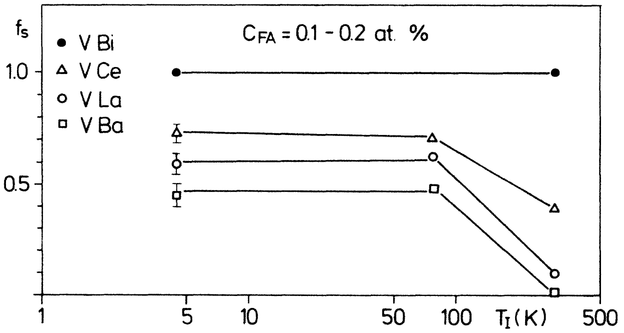

FIG. 2. Substitutional fraction of several ions in vanadium as a function of the substrate temperature during implantation and analysis. C_{FA} is the concentration of foreign atoms.

TABLE I. Influence of post-irradiation at LN$_2$T on the substitutional fraction of the system *V*Ce produced by implantation at RT.

Ce (at.%)	Fluence (He atoms)/cm^2)	f_s (±0.05)
0.08	0	0.2
	2×10^{15}	0.64
	5×10^{15}	0.71
	1.8×10^{16}	0.73
0.17	0	0.36
	2×10^{16}	0.56
0.3	0	0.46
	2×10^{16}	0.58

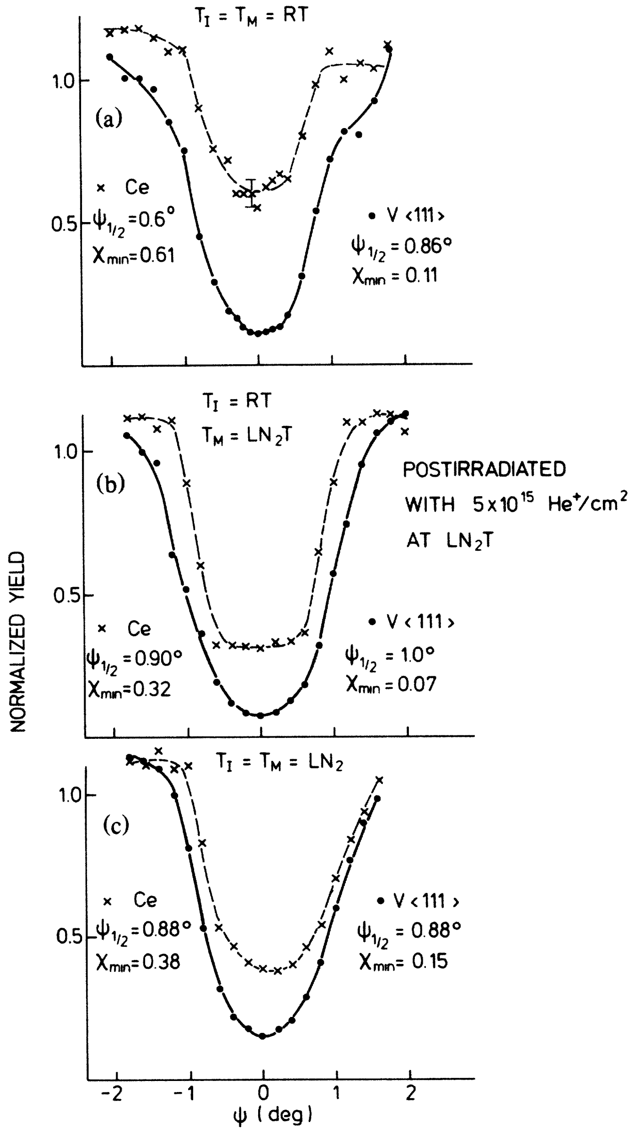

FIG. 3. Angular yield curves through the ⟨111⟩ axial direction from Ce$^+$-implanted V single crystals. (a) as-implanted at RT; (b) implanted at RT and post-irradiated with 5×10^{15} (He$^+$ ions)/cm^2, 200 keV at LN_2T; and (c) as-implanted at LN_2T.

increase of f_s, indicating that the Ce atoms are either trapped in vacancy-rich cores of the displacement spike or Ce precipitations are formed in the prompt cascade regime. Precipitate formation is not probable as firstly, the average mean distance between foreign atoms is about 30 Å and diffusion is negligible at 5 K, and secondly, the fraction of nonsubstitutional atoms does not depend on the concentration between 0.04 and 0.3 at. %, which is otherwise expected for precipitate formation. As this component is proportional to the number of collision cascades, the formation of rather stable Ce-multivacancy complexes in the prompt cascade regime seems to be the only probable explanation for the nonsubstitutional component.

Similar post-irradiation experiments at LN_2T have been performed for the *V*Ba system. Here, no change of f_s was observed, indicating that Ba-vacancy complexes are rather stable and have a small capture radius for SIA. In order to prove that the nonsubstitutional component is also due to Ba-vacancy complexes, the following annealing and post-irradiation experiments are performed. After implantation of Ba into V at 77 K, the substitutional fraction is 0.45. Upon warming up to room temperature, f_s decreases from 0.45 to 0.35. The trapping of vacancies during warm-up is demonstrated in Fig. 4(b). As such an effect was not observed for the *V*Ce system, it is concluded that Ba has a larger capture radius than Ce for vacancies.

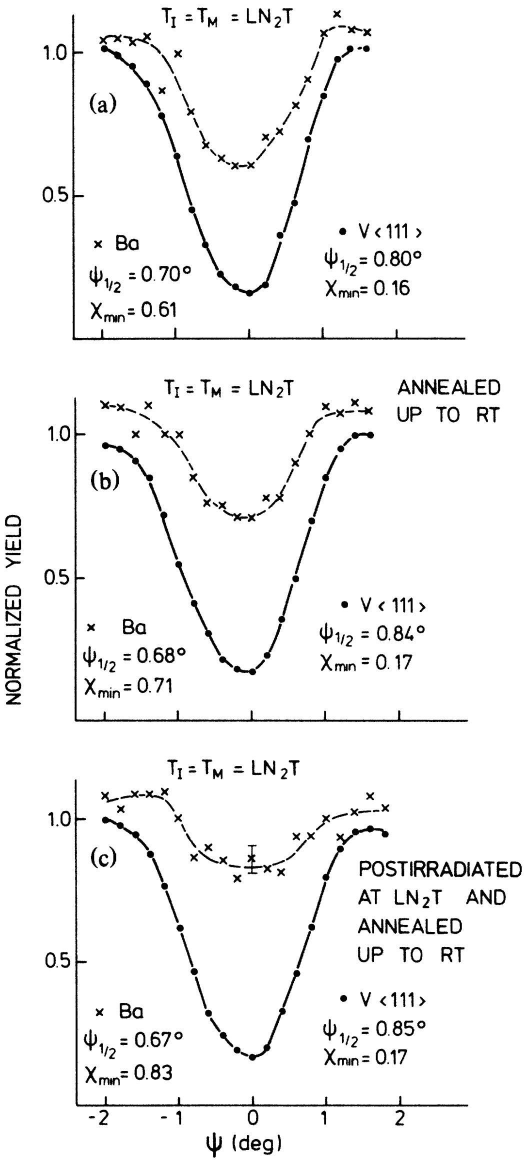

FIG. 4. Angular yield curves through the ⟨111⟩ axial direction from Ba$^+$-implanted V single crystals. (a) as-implanted at LN_2T; (b) implanted at LN_2T, annealed to RT and measured at LN_2T; and (c) implanted at LN_2T, post-irradiated with 1×10^{16} (He$^+$ ions)/cm^2, 200 keV at LN_2T, annealed to RT and measured at LN_2T.

The trapping effect can be enhanced by producing additional single vacancies in a post-irradiation experiment at LN_2T. The angular scan curves shown in Fig. 4(a) are not affected by post-irradiation at LN_2T, indicating that the capture radius for SIA's is small in contrast to the *V*Ce system.

Warming up to room temperature, however, leads to a strong decrease of f_s from 0.45 to 0.11, as is demonstrated in Fig. 4(c). The fact that under similar post-irradiation conditions f_s of Ba is smaller than that of Ce, again indicates that the capture radius of Ba for vacancies is larger than that of Ce.

In Table II the substitutional fractions of the systems under consideration are correlated to the heat of solution. With increasing ΔH_{sol}, the substitutional fraction decreases in the prompt cascade regime at 5 K, as well as in the delayed regime at 300 K, where the vacancies are mobile. The reduction of f_s for Cs, Ba, La, and Ce, if implanted at 300 K in comparison to the 77 K implant, can be attributed to the formation of impurity-multivacancy complexes. The capture radius of the elements for vacancies increases with increasing ΔH_{sol}, while the capture radius of the complexes for SIA's decreases. These results are in agreement with a previous theoretical discussion[9] stating that a positive heat of solution will enhance solute-vacancy attraction. From all the results discussed above, it is concluded that foreign-atom–vacancy recombination and multivacancy trapping processes, governed by thermodynamic driving forces, are the most important mechanisms which determine the lattice-site occupation of implanted ions in metals.

TABLE II. Substitutional fractions: f_s for various atoms implanted in V single crystals at LN_2T and RT and the heat of solution ΔH_{sol} for these implanted systems as calculated using Miedema's theory (Ref. 10).

Ion	ΔH_{sol} (kJ/mole)	f_s (77 K)	f_s (RT)
Bi	57	1.0	1.0
Ce	90	0.73	0.4
La	118	0.58	0.1
Ba	336	0.45	0.0
Cs	686	0.4	0.0

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[*] On leave from Nuclear Physics Department, Nuclear Research Center, Atomic Energy Establishment, Cairo, Egypt.

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