Disassociation of Cadmium-Vacancy Complexes within the Displacement Spike

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Cadmium-vacancy complexes are formed in Al single crystals after implantation of Cd ions at 293 K. Postirradiation of these implants with H^+ and Kr^+ ions even at 5 K leads to an increase of the substitutional component (f_s) of Cd in Al. The increase of f_s is attributed to disassociation of neighboring Cd-vacancy pairs and serves as a quantitative measure for unstable pair recombination in the relaxation phase of the collision cascade. Our data support the results of molecular-dynamics calculations.

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Numerous techniques have been applied to identify small impurity defect complexes. The ion-channeling technique is a convenient technique to study the trapping of vacancies or self-interstitial atoms (SIA's) by substitutional solute atoms in metals.[1] By use of this technique, the formation of In-vacancy complexes has been observed for homogeneous solid solutions of Al-0.02-at.% In after irradiation with 1-MeV He^+ ions at 35 K and additional annealing above 200 K where the vacancies become mobile. Then the solute atoms are displaced from their substitutional sites and are shifted to interstitial sites of high or low symmetry depending on the different complex configurations formed by the trapping of one or more vacancies. The number of displaced In atoms can easily be registered with use of the channeling technique. It was further observed that the displaced fraction of In atoms in Al[1] as well as in Ni[2] and Cu[3] could be strongly reduced by subsequent irradiation with He^+ ions at 70 K. As the SIA's are mobile in Al, Ni, and Cu above about 40 K but vacancies are not, it is generally believed that the trapped vacancies are annihilated by absorption of mobile SIA's. The impurity atoms then will shift back to their original substitutional lattice sites.

Previously we have shown that the increase of the substitutional fraction of Cd in Al can also be produced by irradiation at 5 K.[4] Thus the decrease of the number of Cd-vacancy complexes is not only due to the annihilation of the trapped vacancies by absorption of mobile SIA's but is a recovery process which occurs within the lifetime of the collision cascade. In the following study we show that the recovery process is independent of the cascade density, the mean transferred energy in a single event, and the damage production efficiency. We conclude that the most probable recovery process is the disassociation of displaced Cd atoms from neighboring vacancies by the spontaneous recombination of unstable Frenkel pairs.

Sample preparation and details of the experimental setup have been described previously.[4] The single crystals are mounted on a liquid-helium- (4.2 K) cooled two-axis goniometer[5] which is coupled to a 350-keV ion implanter for implantation and postirradiation and to a 2.0-MeV Van de Graaff accelerator for analysis. In order to avoid sample heating, the power dissipated during postirradiations and channeling measurements was limited to 50 mW, far below the cooling power of the goniometer (2 W at 5 K). The energies of the ions used for postirradiation were chosen so that they penetrate the implanted region. The application of channeling measurements to material analysis[6] and the analysis of impurity-point defect complexes[1] are well documented in the literature. The substitutional fraction (f_s) was determined by[6] $f_s = (1-\chi_i^{\min})/(1-\chi_h^{\min})$, where $\chi_i^{\min}$ and $\chi_h^{\min}$ are the normalized minimum yields for the impurity and the host, respectively. The yields were measured in the energy windows as indicated in Fig. 2. The modified Kinchin-Pease formula[7] $D = (0.8\phi F_D) \times 7(2E_D N)$, with the atomic density (N) of the host and a threshold displacement energy (E_D) of 18 eV,[8] has been used to convert the employed ion fluences (ϕ) to a "displacements per atom" scale (D). The program[9] TRIM2 been used to determine the energy density deposited into nuclear collisions (F_D) above E_D in the depth where the impurity atoms are located.

After implantation of 200-keV Cd^+ in Al at 77 K, a f_s value of 0.94 is observed. In Fig. 1 the angular yield curves for Al and Cd are shown which match nearly perfectly after implantation at 77 K.

In an annealing process the Cd atoms are displaced from the substitutional sites at about 220 K (see Fig. 1) in a temperature region where the vacancies become mobile (stage III) and are trapped by the Cd atoms. The narrowing of the angular yield curves of Cd during the annealing process is a strong indication that Cd-vacancy complexes are formed.[10] At 293 K the Cd atoms are shifted to interstitial sites of low symmetry which are difficult to analyze by channeling. The angular yield curve closely resembles that of a random distribution of Cd atoms (see Fig. 1).

The Cd-vacancy complexes are disassociated by postirradiation even at 5 K by use of H^+ and Kr^+ ions. The recovery of substitutional Cd by Kr^+ postirradiation is demonstrated in Fig. 2 where the random spectrum from an Al single crystal implanted with 1.0 at.% Cd is shown

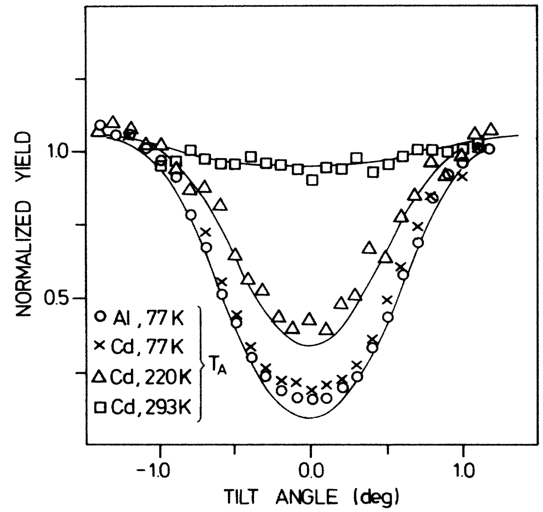

FIG. 1. Angular scans through the ⟨110⟩ axial direction of an aluminum single crystal implanted with 8×10^{15} Cd^+ at 77 K (≙1.2 at.% Cd). The implantation was performed at 77 K. The analyses were done at $T_A = 77$ K (circles and crosses), 220 K (triangles), and 293 K (squares) (Ref. 10).

together with three ⟨110⟩ aligned spectra. The decrease of the Cd peak area of the aligned spectra with increasing Kr^+ ion fluence clearly demonstrates the increase of the substitutional component of Cd in Al. The increases of f_s at 5 and 77 K as a function of the ion fluences are shown in Figs. 3(a) and 3(b) for H^+ and Kr^+, respectively. It is obvious that the results do not depend on the substrate temperature, indicating that the annihilation of trapped vacancies by long-range migrating SIA's is not necessary for the improvement of f_s. The substitutional fraction is proportional to $\ln\phi$ (ϕ = fluence). This dependence is obeyed up to nearly complete recovery [see Fig. 3(b)]. The complete recovery indicates that the probability for vacancy trapping is small within the lifetime of the cascade.

The 100% substitutionality obtained after implantation at 5 K shows that stable Cd-vacancy complexes do not form in Al and that the substitutional lattice site is the site of lowest energy. Previously it was noted that f_s vs ϕ is independent of the Cd concentration in the range between 0.1 to 1.4 at.%.[4] This range has been extended up to 10 at.% Cd revealing the same result. The fact of complete recovery even at high Cd concentration is a further hint that Cd precipitation does not occur after implantation at 293 K or during annealing to 293 K as it is known that precipitates will not dissolve completely by recoil dissolution[11] and that the precipitate size would influence the recovery process. The fact that the increase of f_s with ϕ does not depend on the Cd-vacancy complex concentration again indicates that the recovery process is not due to the absorption of SIA's within the lifetime of the cascade which, if we assume a constant capture radius, would cause such a dependence.

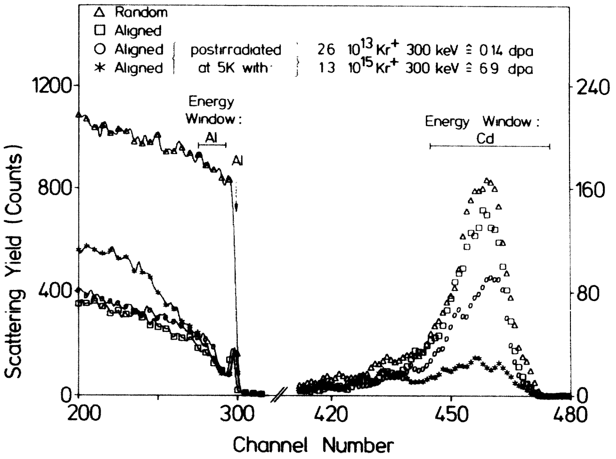

FIG. 2. Random and ⟨110⟩ aligned backscattering spectra from a 200-keV Cd^+ implanted and 300-keV Kr^+ postirradiated aluminum single crystal. Implantation (at 293 K), postirradiations, and analysis (at 5 K) were performed *in situ*. "dpa" stands for displacements per atom.

The results for H^+ and Kr^+ ion irradiation at 5 K are compared in Fig. 4 with use of a D scale evaluated as discussed above. The initial slope shows that in the fluence region where single cascades do not yet overlap the fraction of Cd atoms which move to substitutional lattice

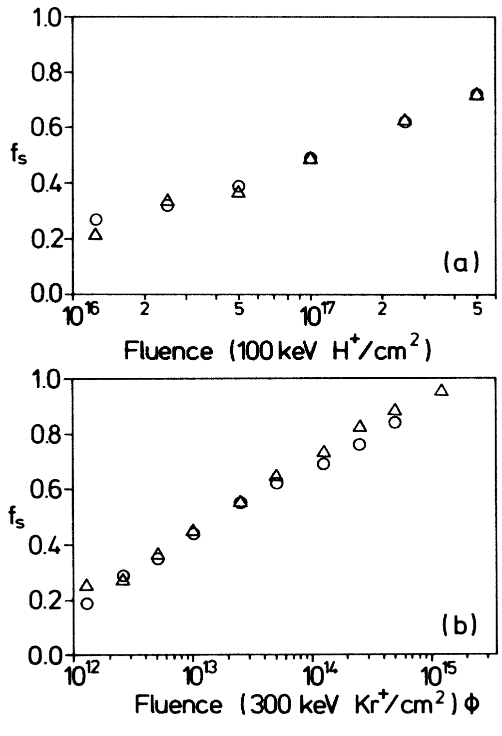

FIG. 3. Increase of the substitutional fraction (f_s) of Cd implanted in aluminum single crystals at 293 K as a result of (a) H^+ and (b) Kr^+ postirradiations at 5 K (triangles) and 77 K (circles).

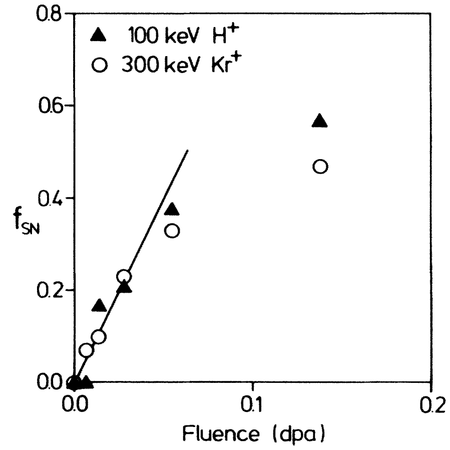

FIG. 4. The normalized substitutional fraction (f_{SN}) of Cd implanted in Al at 293 K vs the employed postirradiation ion fluence in displacements per atom. The postirradiations and analysis were done at 5 K. Also shown is a straight line fitted to the initial slope of the data points.

sites is about a factor of 8 larger than the number of displacements per atom. As the ratio of the recovered Cd-vacancy complexes to the initial number of complexes is independent of the Cd concentration, the cross section for the recovery process is determined. Therefore, we conclude that within a single event the recovery cross section is 8 times larger than the displacement cross section. Further, it is noted that the initial slope is independent of the average cascade density as the mean transferred energy is 0.12 keV for 100-keV H^+ and 2.0 keV for 300-keV Kr^+ irradiation.

The question arises of which processes could contribute to the large cross section for the Cd recovery. The influence of subthreshold collisions is ruled out by the TRIM2 calculations and analytical calculations of the recoil spectra.[12] The ratio of the energy density deposited in nuclear collision to that deposited in subthreshold collisions and in photon production is about 2.2 for H^+ and about 130 for Kr^+ irradiation. As a result of this fact one would expect a far steeper slope for H^+ irradiation in contrast to the observed result.

Molecular-dynamics calculations have shown that the energetic cascade development can be divided into collision, relaxation, and cooling phases.[13,14] The maximum number of displaced atoms in the collision phase is usually a factor of 4 to 10 larger than the modified Kinchin-Pease value which is reached at the end of the relaxation phase. The relaxation phase is characterized by an extensive thermal rearrangement and an annihilation of defects. By use of the instantaneous number of Frenkel pairs, the displacement cross section would be similar in size to the cross section for the recovery process. The recovery process could then be described as an unstable-pair-recombination process and would be a measure of it.

The influence of a reduced damage efficiency within the cooling phase can be excluded as the recovery process is independent of the cascade density. Molecular-dynamics calculations[13] and the thermal spike model[12] show the influence of enhanced recombination for dense cascades only. As a result of the fact that spontaneous recombination is faster than defect diffusion it may not be possible to see any influence of the cascade efficiency factor. Replacement collisions also do not contribute to the enhancement of the substitutional fraction.[15]

In summary, the only component which is proportional to the number of displaced atoms and independent of the cascade density and the damage production efficiency is the spontaneous recombination of unstable neighboring Frenkel pairs. The Cd-vacancy complex disassociates within the collision phase of the displacement spike and the Cd atom comes to rest on a substitutional lattice site within the relaxation phase. The substitutionality of Cd is supported by the fact that the *Al*Cd system fulfills the Hume-Rothery conditions and that Cd fits nicely in a substitutional lattice site.[16] Our results show that the instantaneous number of displaced Al atoms within the collision phase is 8 times larger than determined with use of the modified Kinchin-Pease formula. This value supports the results of molecular-dynamics calculations. We believe that our method can be applied for other host crystals.

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[1] M. L. Swanson and L. M. Howe, Nucl. Instrum. Methods Phys. Res. **218**, 613 (1983).

[2] L. M. Howe, M. L. Swanson, and A. F. Quenneville, Nucl. Instrum. Methods Phys. Res. **218**, 663 (1983).

[3] M. L. Swanson, L. M. Howe, A. F. Quenneville, Th. Wichert, and M. Deicher, J. Phys. F **14**, 1603 (1984).

[4] M. K. Kloska and O. Meyer, Nucl. Instrum. Methods Phys. Res., Sect. B **14**, 268 (1986).

[5] R. Kaufmann, J. Geerk, and F. Ratzel, Nucl. Instrum. Methods Phys. Res. **205**, 293 (1983).

[6] L. C. Feldman, J. W. Mayer, and S. T. Picraux, *Materials Analysis by Ion Channeling* (Academic, New York, 1982).

[7] M. J. Norgett, M. T. Robinson, and J. M. Torrens, Nucl. Eng. Des. **33**, 50 (1975).

[8] H. H. Neely and W. Bauer, Phys. Rev. **149**, 535 (1966).

[9] J. P. Biersack and L. G. Haggmark, Nucl. Instrum. Methods **174**, 257 (1980).

[10] The solid lines in Fig. 1 represent Monte Carlo simulation calculations using the following: at 220 K, 80% Cd atoms displaced in the ⟨110⟩ direction with an average amplitude of 0.16 Å, 20% Cd atoms on random sites; at 293 K, 80% Cd atoms ⟨110⟩ displaced with $u_\perp = 0.68$ Å, 20% Cd atoms on random sites.

[11] K. C. Russell, Prog. Mater. Sci. **18**, 265 (1984).

[12] R. S. Averback, J. Nucl. Mater. **108/109**, 33 (1982); R. S. Averback, R. Benedek, and K. L. Merkle, Phys. Rev. B **18**,

4156 (1978).

[13] M. W. Guinan and J. H. Kinney, J. Nucl. Mater. **103/104**, 1319 (1981).

[14] W. E. King and R. Benedek, J. Nucl. Mater. **117**, 26 (1983).

[15] A. Azzam and O. Meyer, Phys. Rev. B **33**, 3499 (1986).

[16] Similar recovery results have been observed for the *Al*In system. Complete recovery, however, cannot be obtained as In implanted into Al at 77 K has an f_s value of 0.83 in close agreement with perturbed-angular-correlation results by F. Pleiter and K. G. Prasad, Hyperfine Interact. **20**, 221 (1984).