I. 8. PAC Study of Quenched-in Vacancy in Cadmium

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1. Introduction

It has been well established that the resistivity recovery after low temperature irradiation (for instance at 4.2 K) takes place in five stages. From low temperature side these are named as stage I to stage V. The most pronounced ones are stage I and stage III. The stage I has been interpreted as the recombination of self interstitial atoms (SIA) and lattice vacancies where mobile defects are SIA with different activation energies for migration (The close pair recovery). This picture of Stage I proposed by Corbett et al.\textsuperscript{1)} has been widely accepted by most workers. However for the case of Stage III, a controversy exists among investigators. Namely one school has assigned vacancy migration to the stage III and the other school the 2nd type SIA to it.

For the case of Cd, the situation is the same with other metals. Namely Stuttgart group\textsuperscript{2)} has assigned the 2nd type SIA for Cd stage III (100-150 K) and considered the vacancy migrates at higher temperature (for instance at 225 K for Cd). On the contrary, the other groups have assigned the lattice vacancy to the stage III. The cause of the discrepancy is due to the indirect nature of the resistivity measurement which is quite capable of finding a stage but not to determine the specy of the defect causing it.

With applying a perturbed angular correlation (PAC) method with \textsuperscript{111}In as the probe atom, Erlangen group\textsuperscript{3)} has found a defect migrates in stage III to form a defect-probe complex after the radiation damage or quenching from a high temperature. Since only a vacancy is present after the quenching and also the frequency of the defect component is the same after the damage or the quenching, it has been concluded that a vacancy migrates in stage III in Cd after the damage. Here in the PAC work, a merit of the nuclear technique, namely a defect can be identified by the electric field gradient causing the defect component in the spectrum, is fully utilized.

Here in the present experiment, the quenching experiment is repeated for Cd. The purposes of the experiment is; (1) To reproduce Erlangen’s quenching result. (2) To study
the stage III annealing in more details by PAC method. (3) To study the effect of the vacancy concentration on the annealing behavior of stage III as seen by PAC. Since the latter two have not been reported by Erlangen group and several features have been found in the present, the results are reported in the followings.

2. Experimental

Specimens are single crystals with the dimension of 0.2×5×20 mm$^3$ and made from 6-9 ingot. They were irradiated by 25 MeV proton beam to introduce $^{111}$In. The concentration of the probe atom ($^{111}$In) was estimated as less than $10^{-7}$. The specimens were quenched into liquid nitrogen bath after holding for $3\times10^2$ sec at the quenching temperatures in Ar atmosphere between 373 K and the melting point (594 K). Subsequently they were transferred to a measuring cryostat with keeping them in liquid nitrogen and the PAC spectrum was measured by three-detectors set up. After measuring the spectrum in the as quenched state, they were isochronally annealed (5-10 K step with 6×10$^2$ s holding time) between 100 and 200 K. After each annealing the PAC spectrum was measured at 77 K. The annealing was performed in the dewer by lifting it into a furnace. Since single crystals were used in the present, they were set at the exactly the same position relative to the detectors after each annealing procedure. This is because the PAC spectrum for a single crystal strongly depends on the relative orientation among crystal axes and the detectors.4)

3. Results and Discussion

Figure 1 shows an example of the PAC spectrum, $N(\pi)-N(\pi/2)/N(\pi)+N(\pi/2)$, where $N(\pi)$ and $N(\pi/2)$ are the counts of $\gamma_2$ for the stop detectors placed at 180 and 90 degree relative to the start detector for $\gamma_1$, respectively. In the as quenched state, the 50 nsec period precession signal is present showing the $^{111}$In probe atoms are at the substitutional site without trapping the quenched-in vacancy. However as can be seen in Fig. 1, a noticeable change takes place in the spectrum between 125 K and 160 K. This clearly indicates a quenched-in vacancy migrates to $^{111}$In atom giving rise to a new component in the spectra. This can be seen more clearly in Fig. 2 where the Fourier spectra of Fig. 1 are shown. Four components (S14, S28, D1 and D19) are present in Fig. 2, where S14 and S28 are due to the $^{111}$In atoms in the substitutional site (it is well established 3 components with the frequency ratio 1:2:3: are present for I = $5/2$ spin in a symmetric ($\eta=0$) EFG as the case of the present $^{111}$In nucleus in Cd hcp crystal.) Adding to these, D19 takes place after 125 K annealing with the reduction of the substitutional components. This component must be due to a simple complex of $^{111}$In and a vacancy since it has a unique frequency and
also observed in the quenched specimen. This result clearly indicates a vacancy is mobile at 125 K, namely in stage III region, and be trapped to the probe atom $^{111}$In. After the 140 K annealing, the magnitudes of the S14, S28 and D19 are reduced with the growth of D1, of which frequency is quite low indicating the EFG of the defect is weak or almost null. One possibility of such a defect is a cluster of a vacancy around the $^{111}$In atoms. If vacancies condense around the $^{111}$In in the basal plane, the neighboring basal planes collapse to give rise to a stacking fault, which may give rises to a weak EFG. This cluster seems to be not so stable since the substitutional components take place after the 160 K annealing. This annealing behavior is summarized in Fig. 3 where the magnitudes of each lines are plotted as a function of the annealing temperatures. The present experimental results and the interpretation are in accord with those by Erlangen group.$^3$ No observation of the quenching effect by the present author in a previous report is due to the slow quench rate employed there.$^5$

Adding to this result, a finer annealing schedule (5K step) reveals that the recovery of S14 takes place in several steps although results are not shown here. Namely the amplitude of S14 decreases between 110 K and 130 K with the growth of D19. Then it increases between 130 and 140 K and again decreases between 140 K and 150 K. After the annealing above 160 K, it gradually recovers to the value before the quenching experiment. D1 starts to grow at 120 K reaching to a maximum at 150 K and then gradually decreases between 150 and 300 K. A trend is observed D1 survives up to higher temperature with the higher vacancy concentration (the higher quenching temperature). This behavior of S14 and D1 is a new observation found in the present.

These results indicate as if there exists two modes of vacancy migration in Cd. Namely one becomes mobile at 110 K thus forming a simple $^{111}$In-vacancy pair. The probability to form the pair is, however, quite small, since the vacancy concentration is much higher than the $^{111}$In concentration and yet a simple pair is formed. This pair is not so stable and dissociates between 130 and 140 K thus giving rise to the S14 increases and D19 decrease. At 140 K the vacancy becomes mobile with a higher migration energy. The concentration of the mobile vacancy is quite high and hence a vacancy cluster are formed around a $^{111}$In atom giving rise to D1. The stability of the cluster (or stacking fault) seems to depend on the size. Namely, with the higher vacancy concentration, a larger cluster is formed and so a higher temperature is needed to anneal out it. Thus D1 survives up to a higher temperature with the higher vacancy concentration.

The presence of two mode vacancy migration is quite reasonable if the anisotropic crystal structure of hcp Cd is taken into account. In a self diffusion experiment of Cd$^9$, the migration energy of vacancy along c-axis has been found smaller than that in the basal
plane. So one can reasonably identify that the vacancy migration along c-axis starts at 110 K (one dimensional diffusion) and then basal plane migration starts at 140 K. At 140 K the mode of the vacancy migration is three dimensional since the one along c-axis should be still active at this temperature. Such a two mode defect migration has been proposed by Seeger et al. for Cd stage III although the defect treated was SIA$^2$ instead of a vacancy as in the present.

The simple pair formation at 110 K despite of the large ratio of the vacancy to $^{111}$In concentration ($V/^{111}$In$=10^{2-3}$) reveals the probability for a vacancy to meet $^{111}$In atom is small if the migration mode is one dimensional. In related with this, the structure of the pair, namely whether the vacancy is trapped to the nearest neighbor site to $^{111}$In atom in the basal plane or to the next nearest site in the next basal planes, is being examined by measuring the amplitude of the D19 line as a function of the crystal orientation.

From the nuclear engineering point of view, the clustering of vacancy around $^{111}$In observed in the present is quite important. Namely the present result directly reveals the impurities formed by a nuclear reaction can act as the center of vacancy clustering (or void formation).

Further work is now in progress together with the cold worked or the damaged specimen, part of which results are reported in a following papers in this volume.

References

Fig. 1. PAC Spectrum for quenched Cd single crystal. Measurement at 77 K after a pulse annealing (10 min.) at the temperature indicated. The quenching temperature is 579 K.

Fig. 2. Fourier spectrum of the PAC spectrum in Fig. 1.
S: $^{111}$In in the substitutional site without vacancy trapping.
S14 (fundamental): S28 (1st harmonic)
D: $^{111}$In in the substitutional site with a vacancy (D19) or vacancy cluster (D1) trapping.
Fig. 3. Annealing spectrum of each components in Fig.2.