Helium implanted <u>Al</u>Hf as studied by ^{181}Ta TDPAC

R GOVINDARAJ*, K P GOPINATHAN[†] **and B VISWANATHAN**

Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India
[†]Department of Physics, Cochin University of Science and Technology, Cochin 682 022, India

Abstract. Time differential perturbed angular correlation (TDPAC) measurement on <u>Al</u>Hf reference sample has shown that a fraction 0·88 of probe nuclei are defect free and are occupying the substitutional sites in fcc Al matrix, and the remaining are associated with Hf solute clusters. Measurements on helium implanted sample indicate the binding of helium associated defects by Hf solute clusters. Isochronal annealing measurements indicate the dissociation of the helium implantation induced defects from Hf solute clusters for annealing treatments beyond 650 K. On comparison of the present results with that reported in <u>Cu</u>Hf subjected to identical helium implantation, it is inferred that the Hf solute clusters in <u>Al</u>Hf bind less strongly the helium associated defects than in <u>Cu</u>Hf.

Keywords. TDPAC; electric field gradient; Hf solute clusters; helium-vacancy complex; defect recovery.

1. Introduction

In recent years a considerable effort has been directed to the behaviour of helium in metals as helium is produced by (n, a) reaction in nuclear materials. Helium atoms are insoluble in metals and are strongly attracted by vacancies. Implantation of helium ions in metals leads to the formation of He–V complexes and helium atoms stabilized vacancy clusters (Wilson *et al* 1981; Ullmaier 1983). In the post-irradiation annealing studies, rearrangement of He–V complexes leading to the nucleation and growth of helium bubbles has been reported (Wilson *et al* 1981). As helium atoms are strongly bound to open volume defects, an attractive interaction between the latter and impurities present in a sample would lead to the formation of He–V complexes as bound to impurities (Amarendra *et al* 1992a). Therefore impurities play an important role in either accelerating (Van siclen and Wright 1992) or decelerating (Amarendra *et al* 1992b) the growth of helium bubbles in materials.

The hyperfine interaction of such impurities, meaning the interaction between the nuclear moments of (the concerned isomeric state of) the impurities and electromagnetic fields at their sites in a sample (Recknagel *et al* 1983), provides a powerful method for studying the behaviour of helium in metals (Rinneberg *et al* 1978). The hyperfine interaction induced perturbation of angular correlation of g rays emitted in cascade (separated by the isomeric state of interest) by suitable radioactive probe atoms introduced in the sample, has been established as a

powerful technique for studying defects in solids (Gary *et al* 1990). The experimental hyperfine interaction parameters enable us to identify the defects that are bound to probe nuclei and their geometry.

The interaction between vacancies and impurities becomes complicated while some of the latter are present as small aggregates in addition to isolated atoms. In general, open volume defects such as vacancies for example are trapped more strongly by impurity atom clusters than that of a single oversized impurity atom in the matrix. The trapping of defects by impurity atom clusters also becomes significant if the concentration of the impurities is appreciable. The clustering of impurity atoms (solutes) in certain samples subjected to non-equilibrium treatments, has been reported in the literature (Wichert 1993). The evolution of vacancies within precipitates is also quite important in metallic alloy systems (Belaidi *et al* 1992). Hf solute clusters are found to bind strongly the helium associated defect complexes in homogeneous helium implanted <u>Cu</u>Hf by the combined time differential perturbed angular correlation (TDPAC) and positron lifetime measurements carried out by us (Govindaraj *et al* 1999).

This paper examines the interaction between helium and isolated and/or clusters of Hf atoms in a homogeneously helium implanted <u>Al</u>Hf by time differential perturbed angular correlation technique.

2. Experimental

Al of purity 99·999% and Hf of purity 98·5%, with a composition of 0·5 wt% of Hf were prepared by arc-

*Author for correspondence

melting and homogenized. Samples of dimension 1 cm × 0·1 cm × 635 μm were made from the melt. The thickness of the samples were chosen to be 635 μm to match with the range of 40 MeV α particles as deduced by transmission of ion in matter (TRIM) code (Biersack and Haggmark 1980).

The samples were thermal neutron irradiated at CIRUS reactor, Bhabha Atomic Research Centre, Mumbai, to a fluence of 2×10^{22} n/m², to produce ^{181}Ta probe nuclei by the reaction ^{180}Hf (n, γ) ^{181}Hf → $^{\beta-181}$Ta. The TDPAC of the 133–482 keV γ–γ cascade of ^{181}Ta was measured by a three-detector twin fast-slow coincidence setup using NaI(Tl) detectors. The prompt time resolution of the setup measured with a ^{60}Co source was 2·2 ns FWHM when gated for the above cascade of ^{181}Ta (Govindaraj and Gopinathan 1996). The common movable detector was gated for the START (133 keV) γ-ray while the other two detectors fixed at 90° and 180° with respect to the START detector, detected the STOP (482 keV) γ-ray. The START detector was moved at periodic intervals between 90° and 180° with respect to either of the STOP detector and the delayed time resolution spectra were obtained in the form of the count rate as a function of the time elapsed between the emission of 133 and 482 keV γ-rays. Hence for each position of the START detector two time spectra $W(90°, t)$ and $W(180°, t)$ were recorded simultaneously.

From the delayed time resolution spectra $W(90°, t)$ and $W(180°, t)$, the normalized anisotropy function $R(t)$ was calculated as

$$R(t) = A_2 G_2(t) = 2 \frac{[W(180°, t) - W(90°, t)]}{[W(180°, t) + 2W(90°, t)]}. \tag{1}$$

The normalized anisotropy $R(t)$ spectra were least squares fitted to the function (Vianden 1983),

$$R(t) = A_2 \sum_{i=0}^{n} f_i G_2^i(t), \tag{2}$$

where A_2 is the effective anisotropy parameter which is – 0·2 for the isomeric state of interest and for the present detector geometry (Frauenfelder and Steffen 1982). The value of n is determined by the number of resolved frequency components in the fourier spectra of $R(t)$ spectrum. The function $G_2^i(t)$ is given by

$$G_2^i(t) = \sum_{m=0}^{3} a_m^i \exp[-d_i k_m(h_i)w_{Qi}t] \cos[k_m(h_i)w_{Qi}t], \tag{3}$$

where,

$$\sum_{i=0}^{n} f_i = 1, k_0 = 0, k_1(h_i) + k_2(h_i) = k_3(h_i),$$

and

$$\sum_{m=0}^{3} a_m^i(h_i) = 1.$$

The spin value of the isomeric state of ^{181}Ta is 5/2 leading to

$$n_{Qi} = eQV_{zz}^i/h = 10w_{Qi}/3p, \tag{4}$$

where V_{zz} is the principal component of the electric field gradient (EFG) tensor. When the EFG is not axially symmetric, the asymmetry parameter $h = (V_{xx}-V_{yy})/V_{zz}(|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|)$ is extracted from the fit of the measured $R(t)$ to (2). The values of k_m depend on h. Therefore the EFG tensor is completely determined by the frequency n_Q and the asymmetry parameter h. A non-vanishing value of d (i.e. the width of the Lorentzian distribution of quadrupole frequency) implies either a significant concentration of defects and/or impurities in the material under study, or a disordered arrangement of atoms in the probe surroundings.

TDPAC measurements carried out on the reference sample indicate that $0·12 \pm 0·02$ fraction of probe nuclei experiences a Lorentzian distribution of quadrupole frequencies with a mean at 290 ± 5 MHz, an asymmetry parameter of $0·12 \pm 0·04$ and a relative width of $0·22 \pm 0·12$. The corresponding data analysed $R(t)$ spectrum of probe nuclei is shown in figure 1a. The above quadrupole parameters match with that of probe nuclei in Hf matrix as reported in the literature (Berthier *et al* 1970; Vianden 1983). Therefore it is interpreted that these quadrupole parameters are due to the association of probe atoms with coherent Hf solute clusters. The presence of Hf solute clusters in the sample has been confirmed by transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDAX) measurements as shown in figures 2a and b, respectively.

A pair of AlHf samples was homogeneously implanted with helium using a 40 MeV alpha particle beam from a Cyclotron to a dose of 100 atom parts per million (appm). The homogeneous helium implantation of the sample was done by attenuating the alpha particles of 40 MeV energy by Al foils of different thicknesses mounted on a rotating wheel. The thickness of Al foils were so chosen to result in overlapping helium profiles throughout the thickness of the sample (Amarendra 1992a). The helium implanted samples were subsequently thermal neutron irradiated as mentioned earlier to obtain ^{181}Ta, the TDPAC probe nuclei.

TDPAC measurements were conducted at room temperature in the as implanted sample and following each step of an isochronal annealing treatment from 323 to 873 K in steps of 50 K. Annealing treatments of the sample were done at a pressure of 10^{-6} torr. The data analysed $R(t)$ spectra corresponding the helium implanted sample subjected to isochronal annealing treatments are shown in figure 1.

3. Results and discussion

Data analysis of $R(t)$ spectrum in the helium implanted sample indicates the presence of two defect associated fractions with the following hyperfine interaction parameters viz. $n_{Q1} = 370 \pm 15$ MHz, $f_1 = 0.05 \pm 0.01$, $d_1 = 0.42 \pm 0.05$, $h_1 = 0.3 \pm 0.15$, $n_{Q2} = 1060 \pm 25$ MHz, $f_2 = 0.08 \pm 0.01$, $d_2 = 0.18 \pm 0.04$ and $h_2 = 0.36 \pm 0.04$. The defect associated fractions in the helium implanted sample sums to almost equivalent to that of the reference sample. Furt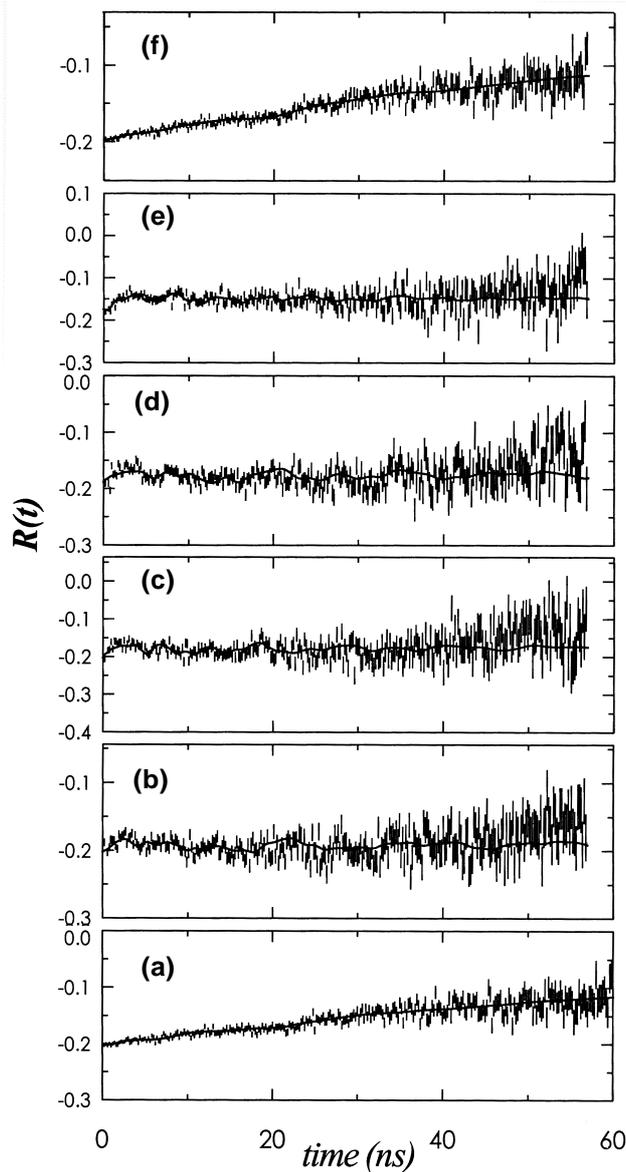her on comparison with the results obtained in the reference sample it can be observed that the quadrupole parameters as experienced by probe nuclei in the helium implanted sample are entirely different. The above observations indicate an efficient trapping of helium implantation induced defects by probe atoms associated with solute clusters. The following discussion involves the identification of defects associated with the fractions of probe nuclei leading to the observed variations of quadrupole interaction parameters with annealing treatments of the sample.

The variation of the hyperfine interaction parameters with isochronal annealing temperature is shown in figures 3 and 4. Following the annealing step at 323 K the value of n_{Q1} is found to increase to 470 ± 15 MHz with $f_1 = 0.1 \pm 0.04$, $h_1 = 0.26 \pm 0.04$ and $d_1 = 0.44 \pm 0.04$. For annealing treatments up to 573 K there has been a steady decrease of n_{Q1} which later saturates at a frequency of 294 ± 12 MHz.
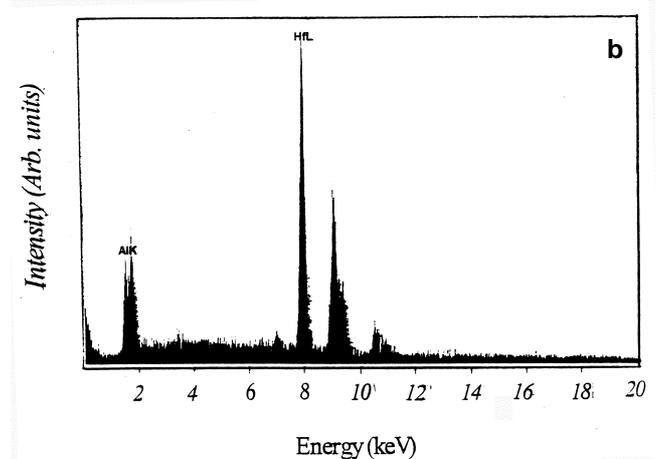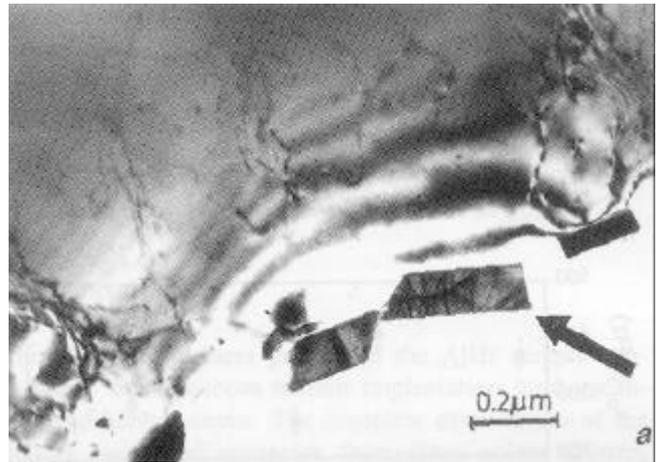

Figure 1. The experimental $R(t)$ vs t (TDPAC) spectra at room temperature in the reference and helium implanted AlHf samples subjected to the following annealing treatments. The continuous curve in each spectrum is the one calculated using the fitted values of the parameters. (**a**) Reference sample, (**b**) as helium implanted, (**c**) $T_a = 323$ K, (**d**) $T_a = 423$ K, (**e**) $T_a = 523$ K and (**f**) $T_a = 723$ K.

Figure 2. **a.** TEM micrograph showing the presence of Hf precipitates. One such precipitate is marked in the figure and **b.** EDAX spectrum corresponding to the precipitates as shown in figure 2a, identified as that of hafnium.

Helium implantation results in a large concentration of vacancies produced in the sample. The vacancy clusters trapped by substitutional Hf atoms result in the cubic charge configuration leading to the zero electric field gradient (EFG) at the sites of the probe nuclei. Therefore the fraction $(1 - f_1 - f_2)$ might include the probe atoms associated with vacancy clusters in cubic charge configuration (Gary *et al* 1990) in addition to the substitutional and defect free fraction.

The defects associated with the fraction f_1 of the probe nuclei during the different annealing stages is identified based on the following arguments.

(I) The defect associated with the fraction f_1 of probe nuclei is not a monovacancy or a di-vacancy, as the probe nuclei trapping these defects are characterized by a zero asymmetry parameter. The probe atom trapping a mono-vacancy (di-vacancy) will be axially symmetric along $\langle 110 \rangle$ ($\langle 100 \rangle$) direction (Gary *et al* 1990).

(II) Also as the vacancy migration stage sets in pure Al at around 200 K, it is quite likely that the vacancies exist in the AlHf sample as clusters trapped by Hf atoms instead of a mono or a di-vacancy at room temperature. Positron lifetime measurements carried out by us on quenched pure Al and AlHf samples indicate the presence of voids and vacancy clusters, respectively (Govindaraj 1998). The

trapping of vacancies by hafnium impurities arrests the growth of voids in the as quenched AlHf sample. Therefore only the vacancy clusters as trapped by hafnium impurities are present in the as quenched sample. Hence it is more likely that Hf impurities are associated with vacancy clusters instead of mono or di-vacancies in the helium implanted sample.

(III) The helium implantation mainly results in the formation of isolated He–V complexes and large vacancy clusters stabilized by helium atoms. The trapping of vacancies by probe atoms associated with Hf solute clusters that are present in the initial condition of the sample, has resulted in the formation of the fraction f_1 of probe nuclei experiencing the observed quadrupole parameters. The trapping of vacancies by more than one Hf atom as seen in the present case is supported by the finite, non-zero value of the asymmetry parameter h_1. The quadrupole frequency (n_{Q1}) and the asymmetry parameter (h_1) of the fraction f_1 remains almost constant with respect to annealing temperature between the interval 325 and 475 K.

(IV) Beyond 475 K there is a decrease in the value of n_{Q1} and h_1 implying the change in the defect configuration to a more symmetric configuration. This is understood to be due to the re-clustering of Hf atoms through the diffusion aided by vacancies. This leads to the reformation of
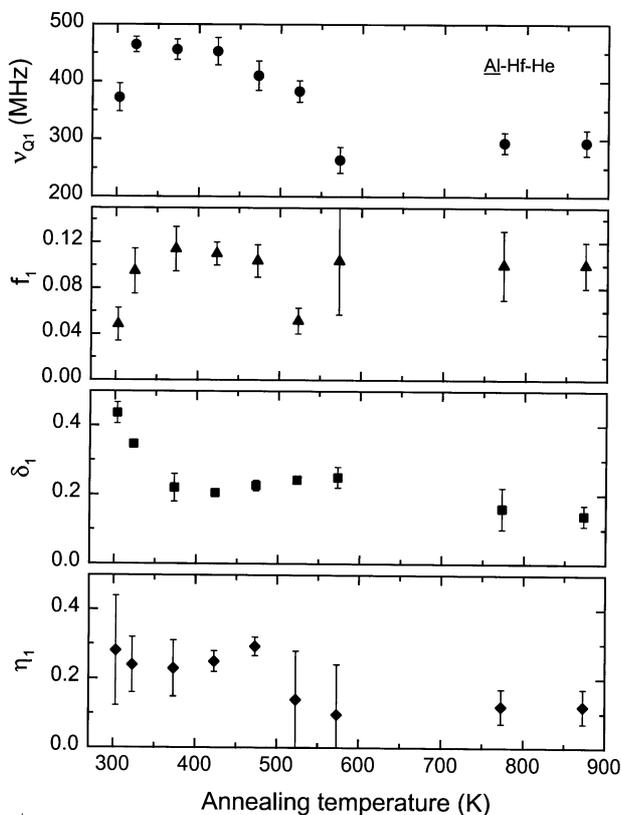

Figure 3. The variation of the quadrupole interaction parameters viz. n_{Q1}, f_1, h_1 and d_1 with annealing temperature.
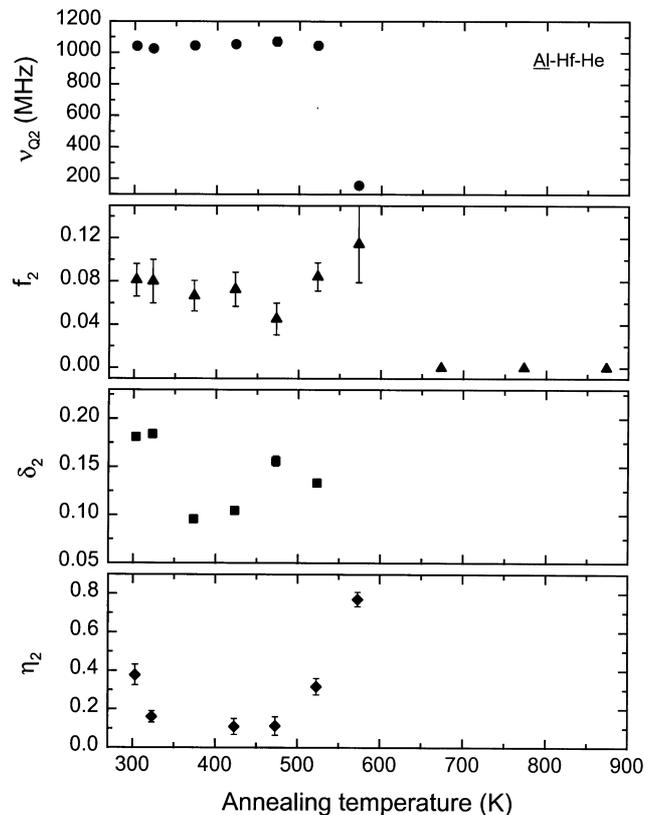
Figure 4. The variation of the quadrupole interaction parameters viz. n_{Q2}, f_2, h_2 and d_2 with annealing temperature.

hafnium atom clusters in *hcp* configuration. This results in the reappearance of the quadrupole frequency $n_{Q1} = 290 \pm 4$ MHz with $h_1 \approx 0.12 \pm 0.04$, having almost the same value of the quadrupole frequency as that of the probe atoms in Hf matrix (Vianden 1983).

(V) The fraction of the probe nuclei f_1 and the corresponding hyperfine interaction parameters remain constant at 0.1 ± 0.03 for annealing treatments beyond 475 K implying the stability of the Hf atom clusters.

Figure 4 shows that the value of n_{Q2} remains varying slightly between 1060 ± 55 MHz and 1120 ± 38 MHz for isochronal annealing treatments up to 523 K. This defect component ceases to exist following the annealing treatment at 673 K.

The fraction f_2 is interpreted to be due to the probe atoms associated with helium atoms.

(i) A high value of n_{Q2} associated with the fraction f_2 of the probe nuclei indicates the formation of helium associated vacancy clusters as trapped by the probe atoms. In general the probe atoms associated with lighter impurity atoms such as hydrogen, helium etc are likely to experience a large quadrupole frequency (Govindaraj 1998).

(ii) The fraction f_2 and the corresponding hyperfine interaction parameters remain almost constant implying the stability of the defects caused by the association of these defects with helium atoms.

(iii) Annealing treatment at 573 K results in the onset of dissociation of the helium atoms as trapped by the Hf impurities leading to the reformation of defect free hafnium clusters. This can be correlated with the formation of the fraction f_1 of probe atoms associated with hafnium solute clusters following the annealing treatment of the sample at 573 K as shown in figure 3.

(iv) Annealing of the sample at 673 K leads to the rearrangement of the hafnium atoms driven by diffusion through the vacancies leading to the formation of the coherent hafnium clusters, resulting in the disappearance of the fraction f_2 of probe nuclei.

The binding energy of He–V complexes in Al is reported to be 4 eV (Pendry 1980). In the present measurement it has been observed that at higher annealing temperatures the He–V complexes trapped by Hf impurities get dissociated. This is expected to result in a significant concentration of the isolated He–V complexes and He stabilized voids which would remain highly stable. Also due to a high value of the binding energy of the He–V complexes, the isolated complexes that are formed in the sample due to helium implantation do not breakup during annealing treatments of the sample even at temperatures close to 673 K. This is known from the results of positron lifetime measurements carried out on helium implanted Al (Jensen and Nieminen 1987). Comparison of the present results with that obtained in helium implanted $\underline{Cu}Hf$ (Govindaraj *et al* 1999) under similar irradiation condi-

tions, indicate the following two important points. Firstly the helium associated fraction f_2 of probe atoms reaches zero beyond 650 K in $\underline{Al}Hf$, whereas the corresponding helium associated fraction in $\underline{Cu}Hf$ exists beyond 900 K. Secondly the value of the quadrupole frequency n_{Q1} reaches 290 ± 4 MHz beyond 650 K in $\underline{Al}Hf$ and 750 K in $\underline{Cu}Hf$.

These can be understood based on the difference in the values of the He–V binding energy in Cu and Al. The value of the binding energy of He–V complexes in Al is reported to be 4 eV (Pendry 1980) while the activation energy of He–V complexes in Al is reported to be around 1.3 ± 0.1 eV (Ullmaier 1983). Whereas in the case of $\underline{Cu}Hf$ the value of the He–V binding energy is reported to be around 2.36 eV (Van Veen 1987) and the value of He–V migration energy is 1.34 eV (Peterson 1978) which is almost the same as that of $\underline{Al}Hf$. As He–V complexes are characterized by a larger binding energy, as compared to the binding energy with Hf solute in $\underline{Al}Hf$, this leads to the detrapping of the helium atom complexes from Hf impurities leading to the disappearance of the helium associated defect complex, characterized by the fraction f_2 of the probe atoms beyond 673 K. The higher stability of He–V complexes as bound to the probe atoms in the helium implanted $\underline{Cu}Hf$ is comprehensible based on the comparable values of the binding energies of He–V complexes and those associated with Hf atoms in $\underline{Cu}Hf$.

4. Conclusions

The Hf solute clusters present in the $\underline{Al}Hf$ sample subjected to homogeneous helium implantation bind vacancies and helium atoms. The complete dissociation of the helium associated vacancies from these solute clusters occurs following the annealing treatment of the sample at 673 K. The above temperature marks the onset of the reformation of Hf solute clusters in the sample. Hf solute clusters are observed to bind the helium associated defects less strongly in $\underline{Al}Hf$ while compared to $\underline{Cu}Hf$ subjected to identical helium implantation.

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