Indium-Hg vacancy interactions in $Hg_{1-x}Cd_xTe$ measured by perturbed angular correlation

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The interaction of mercury vacancies with dopant indium atoms in $Hg_{0.79}Cd_{0.21}Te$ was studied using the perturbed $\gamma\gamma$ angular correlation (PAC) technique. Two dominant PAC signals, characterized by quadrupole interaction strengths $v_{Q1} = 83$ MHz and $v_{Q2} = 91$ MHz and asymmetry parameters $\eta_1 = \eta_2 = 0.08$, were observed and attributed to one or more In-V_{Hg} complexes. The complexes appeared after annealing doped samples at $T \geqslant 350$ °C in vacuum and quenching. The fraction of In atoms associated with vacancies was increased further by annealing at 80 °C for > 10 h. The In-vacancy complexes vanished on annealing in a Hg-saturated atmosphere.

The II-VI narrow band-gap semiconductor $Hg_{1-x}Cd_xTe$ ($x = 0.2$) is technologically important for its use as an infrared detector in the 8–12 μm wavelength range. In its as-grown state, (Hg,Cd)Te is often p type due to the large concentration of mercury vacancies. When these vacancies are removed by a low-temperature anneal in Hg-saturated conditions, the material becomes n type because of unknown residual impurities.[1]

Indium is a common donor dopant in (Hg,Cd)Te. Implantation of In produces an n-type layer and causes a large amount of damage which inhibits carrier mobility.[2] The junction depth is dominated by a tail in the carrier concentration that does not coincide with the implanted region.[3] If the In is diffused in under vacuum, Hg vacancies are introduced. The interaction between In atoms and Hg vacancies has been inferred from electrical measurements,[4] but In-vacancy complexes have not been identified.

Using the perturbed $\gamma\gamma$ angular correlation (PAC) technique, we have made the first atomic-scale measurements of the trapping of Hg vacancies by In atoms in (Hg,Cd)Te. PAC has been used in the past to measure defect structure in metals,[5] and in semiconductors such as Si[6,7] and CdTe[8,9] by measuring the hyperfine interaction between the nuclear moment of a probe atom and the local electric field gradient (EFG) caused by the defect structure. This method allows us to measure the short-range interaction between the isotope ^{111}In and point defects in (Hg,Cd)Te.

For this experiment, bulk, randomly oriented single-crystal samples of $Hg_{1-x}Cd_xTe$ ($x = 0.21$) were provided by H. F. Schaake of Texas Instruments. The samples were grown by melting, quenching, annealing at 660 °C, at 550 °C in vacuum, and finally at 270 °C in Hg vapor. The first anneal was done for grain growth, the second to reduce the dislocation concentration, and the third to remove native Hg vacancies and to convert to n type. These samples were cleaned with a 0.5% Br/methanol solution to remove surface impurities and native oxide. They were then immediately sealed in cleaned evacuated quartz tubes in which a solution of about 10 μCi (10^{11} nuclei) of [111]InCl$_3$:HCl had been dried. The samples were then annealed at 350 °C for 6 h or 400 °C for 30 min to diffuse in the In. The samples were further prepared by various an-

neals in vacuum or Hg atmosphere followed by water quenches or slow cools. One sample was crushed to permit polycrystalline PAC analysis.

The PAC experiment consists of measuring the time-dependent anisotropy between the gamma ray, γ_1, which populates the $I = 5/2$ state in [111]Cd (the isotope to which ^{111}In decays by electron capture) and a second gamma ray, γ_2, emitted by the transition to the ground state. This is done by measuring the number of coincidence counts between NaI detectors at 90° to each other using a standard slow-fast coincidence technique. The number of coincidence counts $I(\Theta,t)$ of γ_1 and γ_2 observed at detectors separated by an angle Θ is directly related to the angular correlation function $W(\Theta,t)$ by[5]

$$I(\Theta,t) = I_0 e^{-t/\tau} W(\Theta,t). \qquad (1)$$

Here, τ is the lifetime of the intermediate state (120 ns) and $W(\Theta,t)$ is defined by

$$W(\Theta,t) = 1 + A_{22}G(t)P_2(\cos \Theta), \qquad (2)$$

where A_{22} is the anisotropy factor determined by the isotope and the detector geometry and $P_2(\cos \Theta)$ is the Legendre polynomial. The time-dependent part is

$$G(t) = f_0 + \sum_k f_k \sum_{n=0}^{3} S_{kn} \cos[g_n(\eta_k)\omega_{k0}t], \qquad (3)$$

where η_k is the asymmetry parameter of the kth electric field gradient (EFG), f_k is the fraction of In probe atoms in the kth EFG, ω_{k0} is the fundamental precession frequency associated with the kth EFG, g_n is a parameter that depends on the asymmetry, and S_{kn} are coefficients dependent upon the orientation and asymmetry of the EFG. The EFG is characterized by the parameters η, representing the asymmetry of the EFG, and $v_Q \equiv eQV_{zz}/h$, the quadrupole interaction strength. Here, V_{zz} is the magnitude of the principal component of the EFG and Q is the nuclear quadrupole moment. For an axially symmetric EFG, the interaction strength is related to the fundamental precession frequency by $\omega_0 = 3\pi v_Q/10$, and $g_1:g_2:g_3$ is 1:2:3.

A ratio $R(t)$ of the counts $I(\Theta,t)$ for detectors at 180° and 90° gives the time-dependent part of the angular correlation:

$$R(t) = A_{22}G(t). \tag{4}$$

This experimentally measured $R(t)$ can be fitted using a least-squares routine to determine the following information: (i) the fraction f_k of In probe atoms having an EFG associated with a specific defect complex, (ii) the quadrupole interaction frequency ν_Q associated with the EFG, (iii) the asymmetry parameter η of the EFG, and (iv) the orientation of the EFG with respect to the axes of a single crystal.

For samples that were doped with ^{111}In by annealing in evacuated quartz capsules at 350 °C for 30 min and cooling slowly in the furnace, no well defined EFGs were observed. The $R(t)$ spectrum decayed slowly with time, indicating that a large fraction of the In atoms were in sites associated with small EFGs. After diffusion, the samples were annealed successively in vacuum for 30 min at 80, 200, 300, 350, and 400 °C and the capsules were quenched in water at 283 K. A PAC spectrum was taken after each of the anneals. As shown in Fig. 1(a), the anneal at 400 °C produced two signals, corresponding to interaction frequencies $\nu_{Q1} = 83$ MHz and $\nu_{Q2} = 91$ MHz, both with asymmetry parameter $\eta = 0.08$. Similar signals were observed after annealing at 350 °C for 6 h in vacuum and water quenching. These signals are attributed to well defined defect complexes containing the ^{111}In probe atoms.

The fraction of probe atoms associated with these defect complexes was increased by further annealing at 80 °C for > 10 h and water quenching [Fig. 1(b)]. The Fourier transform of this spectrum, shown in Fig. 1(c), indicates the presence of two distinct EFGs. As seen from Eq. (3), every EFG has three frequencies associated with it. The presence of two peaks in Fig. 1(c) near 160 MHz suggests that there are two nearly equal fundamental frequencies in the vicinity of 85 MHz. These frequencies are indicated by an asymmetric broadening of the Fourier transform peak near 85 MHz and by the separation of the first harmonics at 160 and 170 MHz. The enhancement of the PAC signals caused by annealing at 80 °C in Fig. 1(b) shows that the vacancies can be rearranged about the In probe atoms without escaping from the vicinity of the In at this temperature. This is consistent with previous measurements which have shown that annealing at this temperature is insufficient to remove radiation damage.[3,10]

The effect of annealing atmosphere on the defect concentration is shown in Fig. 2. The top panel shows the PAC spectrum obtained after a 6 h vacuum anneal at 350 °C (water quenched) followed by a 12 h anneal at 80 °C (water quenched). This spectrum is similar to that in Fig. 1(b). After annealing the same sample in a saturated Hg atmosphere for 6 h at 350 °C and water quenching the PAC signals were not seen (bottom panel). Since this treatment reduces the Hg vacancy concentration, this result implies that the signals are due to In-V_{Hg} complexes.

The PAC signals were suppressed by annealing in vacuum at 150 °C for 6 h or at 200 °C for 30 min and quenching. Stefanis[3] has annealed In-implanted (Hg,Cd)Te for 1 h in vacuum and observed a change in the conductivity from the as-implanted n type to p type after anneals at 200
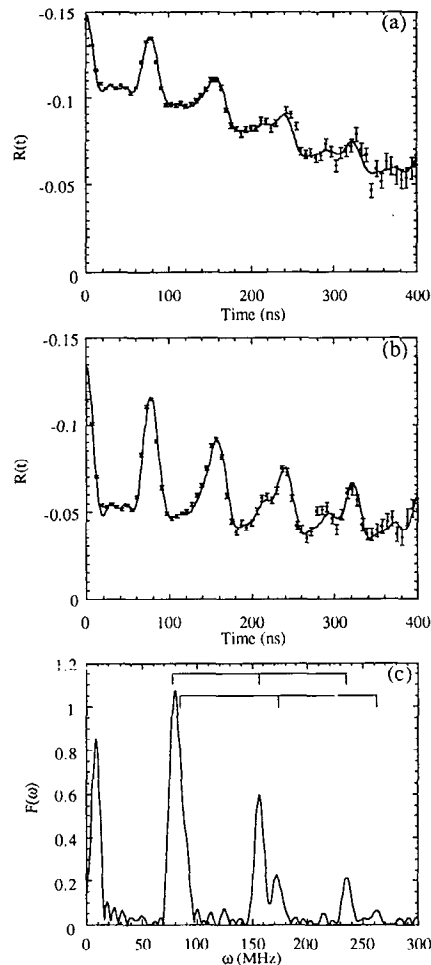

FIG. 1. PAC spectra of ^{111}In in $Hg_{0.79}Cd_{0.21}Te$ at 293 K. (a) Annealed at 400 °C for 30 min in vacuum and water quenched. (b) Subsequently annealed at 80 °C for 10 h in vacuum and water quenched. The solid lines represent least-squares fits of the data. (c) Fourier transform of $R(t)$ spectrum shown in (b).

and 250 °C. Higher temperature anneals were shown to give n-type material which is presumed to be due to the activation of implanted impurities. Similar treatment of Xe-implanted materials show the same switch to p type, but no return to n type on higher anneals as with the In-implanted samples.[3] These data along with the present measurements show that the destruction of Hg vacancy clusters in (Hg,Cd)Te occurs in the temperature range between 150 and 200 °C.

A series of measurements was done to determine the influence of measuring temperature on the defect fractions and interaction frequencies. A sample was annealed at 350 °C for 6 h and water quenched, crushed to powder to create a polycrystal, then annealed at 80 °C for 12 h to obtain the maximum defect fractions. The powder sample allows the use of known polycrystalline S_{kn} values [Eq. (3)] to determine the defect fractions more accurately.[5] The PAC spectrum taken at 17 K shows two EFGs with interaction frequencies $\nu_{Q1} = 87$ MHz and $\nu_{Q2} = 94$ MHz and asymmetries of $\eta = 0.08$. Other spectra were taken at various temperatures between 17 and 295 K. The temperature
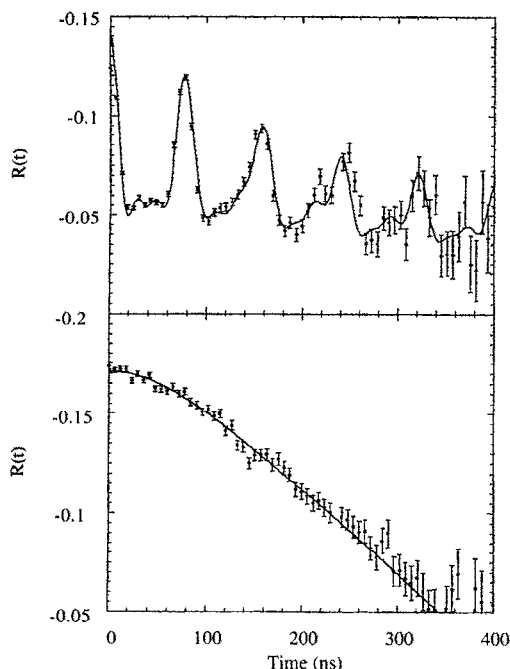
FIG. 2. Effect of annealing atmosphere on defect complexes. The top panel shows a PAC spectrum taken at 293 K from a sample vacuum annealed at 350 °C for 6 h and water quenched, then vacuum annealed at 80 °C for 12 h. The bottom panel shows a spectrum from the same sample subsequently annealed at 350 °C for 6 h in a Hg overpressure. The solid lines represent least-squares fits of the data.
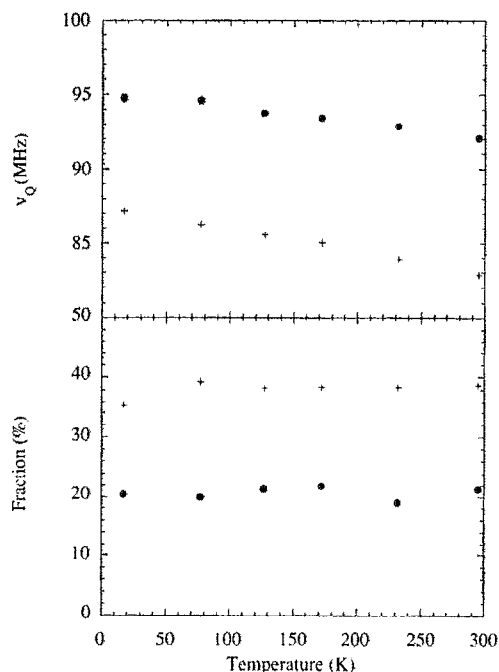
FIG. 3. Temperature dependence of the quadrupole interaction frequencies ν_Q and defect fractions obtained by least-squares fitting of PAC spectra. The crosses represent values for ν_{Q1} and the solid dots represent values for ν_{Q2}.

dependence of the defect fractions f_k and the characteristic frequencies ν_Q are shown in Fig. 3. These data show no observable dependence of the defect fractions on temperature and a small increase in the characteristic frequencies with decreasing temperature. The stability of these defect complexes at room temperature indicates a considerable binding energy ($\geqslant 0.4$ eV).

The determination of the actual structure of the complexes is complicated by the fact that there are few theoretical models to allow accurate calculation of EFGs caused by specific defect structures. As mentioned above, the observed EFGs are related to the concentration of Hg vacancies present in the sample which implies that they are due to In-V_{Hg} complexes. The presence of two separate frequencies can be explained in one of two ways. First, the two EFGs could be related to different complexes or to different charge states of a single complex. Second, the two EFGs could be caused by different local concentrations of Hg and Cd atoms near the In probe atom.

If the 12 next nearest neighbor sites to the substitutional In impurity are occupied by n-Hg atoms and $(12-n)$ Cd atoms, the value of n about a given In atom should be a statistical distribution function of the total Hg to Cd ratio (4:1 for $x = 0.2$). Using this assumption, the fraction of In atoms having n-Hg next nearest neighbors can be calculated. This calculation gives four values of n with fractions greater than 10%. This does not seem to be consistent with the observation of only two EFGs. However, recent Raman[11] and NMR[12] experiments have shown that there is some local order, i.e., there are preferred numbers of Hg

versus Cd atoms around a single Te site. Therefore, the two frequencies observed may be due to certain preferred coordinations. Further experiments will be done to examine these possibilities.

The present experiments provide strong evidence for the existence of stable In-V_{Hg} pairs in $Hg_{0.79}Cd_{0.21}Te$. These are the first atomic scale measurements of such defects in this material; similar defects have been observed by PAC in CdTe[8,9] and (Cd,Zn)Te.[13] This identification of In-vacancy pairs will permit many atomic scale processes to be studied such as vacancy migration, defect clustering, and impurity diffusion.

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