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Cd$_{0.2}$Hg$_{0.8}$Te

LETTER TO THE EDITOR

A study of vacancy-type defects by positron-lifetime measurements in a II–VI semiconductor: $Cd_{0.2}Hg_{0.8}Te$

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Abstract. Positron lifetime measurements in $Cd_{0.2}Hg_{0.8}Te$ give direct evidence of the presence of monovacancies in samples annealed under Hg atmosphere. A single lifetime of $\tau = 309$ ps is detected and attributed to a monovacancy. It is proposed to be the doubly ionised mercury vacancy. Measurements in the 15–300 K temperature range show no charge state transition.

When n-type $Cd_{0.2}Hg_{0.8}Te$ single crystals are annealed at high temperature in various Hg atmospheres and quenched at room temperature, they present an n–p conversion. Vydyanath [1] suggests that this phenomenon is due to the formation of doubly ionised Hg vacancies during annealing. The hole concentration in these samples decreases as the Hg pressure of annealing increases, and he proposes a thermodynamic model for the formation of these defects where the defect concentration is proportional to the hole concentration and a function of Hg pressure and annealing temperature.

A good method for determining whether there are vacancy-type defects in crystals is the measurement of positron lifetime. Indeed, when positrons are trapped in a low-electron-density region such as a vacancy, their lifetime is increased. Positron annihilation has been widely used for the last twenty years to study thermodynamic properties of vacancy-type defects in metals [2]. This method can be applied to semi-conductors and native defects have recently been studied in GaAs [3] and $Cd_xHg_{1-x}Te$ [4, 5].

In this paper, we present positron-lifetime measurements in $Cd_{0.2}Hg_{0.8}Te$ crystals. In p-type annealed samples, evidence is given of the presence of monovacancies at 300 K. The measured lifetime in the vacancies is $\tau_d = 309 \pm 1$ ps and remains constant in the 15–300 K temperature range. We attribute it to V_{Hg}^{2-}.

The $Cd_{0.2}Hg_{0.8}Te$ starting materials were single crystals grown by the Travelling Heater Method [6] in Te solvent and annealed for two weeks in a Hg atmosphere at 250 °C. Crystals thus obtained are n-type with a carrier concentration of 1.5×10^{15} cm^{-3} and are used as reference samples (SAMP0). To prepare p-type crystals, we anneal four pairs of them (called SAMP1, SAMP2, SAMP3, SAMP4) at 410 °C under Hg pressure varying from 2×10^{-2} to 1 atmosphere. The Hg pressures are lower than the saturated pressure around the sample, 2 atm at 410 °C as deduced from [7], which ensures the creation of

Table 1. Characteristics of the annealed $Cd_{0.2}Hg_{0.8}Te$ single crystals and positron-lifetime measured at room temperature; T_A is the temperature of annealing; P_{Hg} is the mercury partial pressure during annealing; the experimental carrier concentration is deduced from Hall measurements at 77 K; the theoretical carrier concentration is deduced from Vydyanath's thermodynamic model [1], the average positron lifetime is noted (s) when corresponding to a single lifetime.

Crystal	T_A (°C)	P_{Hg} (atm)	Type	Experimental carrier concentration measured at 77 K (cm^{-3})	Theoretical carrier concentration at 77 K (cm^{-3})	Average positron lifetime at 300 K (ps)
SAMP0	410	—	n	$(1.5 \pm 0.1)\,10^{15}$	—	286 ± 2 (s)
SAMP1	410	1	p	$(2.0 \pm 0.2)\,10^{16}$	$1.6\,10^{16}$	306 ± 1
SAMP2	410	0.37	p	$(3.5 \pm 0.3)\,10^{16}$	$4.3\,10^{16}$	309 ± 1 (s)
SAMP3	410	0.12	p	$(6.5 \pm 0.5)\,10^{16}$	$1.3\,10^{17}$	309 ± 1 (s)
SAMP4	410	2×10^{-2}	p	$(1.5 \pm 0.1)\,10^{17}$	$6.3\,10^{17}$	309 ± 1 (s)

Hg vacancies. According to the relationship between the Hg pressure of annealing and the hole concentration proposed by Vydyanath in [1], the hole concentrations in these samples are expected to vary from 10^{16} to $10^{17}\,cm^{-3}$. The characteristics of annealings are summarised in table 1 for each pair. The annealings were performed by using a temperature-gradient oven. Each pair of samples was placed at one end of a celled quartz tube and a drop of Hg at the other end. The length of the tube was adjusted to keep the drop of Hg at the temperature corresponding to the desired Hg pressure.

To measure the carrier concentrations in the crystals, Hall-effect measurements were carried out on each sample using the Van der Pauw method [8] in a magnetic field of 7930 gauss. We plotted the Hall coefficient R_H as a function of temperature in the 10–160 K (see figure 1). We consider, as in Vydyanath's study [1], that the acceptors are completely ionised around 77 K. For a given pair, the R_H values obtained at 77 K do not differ by more than 8%. We can therefore consider the two samples of a pair to be equivalent and originating from a $Cd_{0.2}Hg_{0.8}Te$ crystal characterised by its hole concentration at 77 K. In figure 2, the obtained experimental values of the hole concentrations are plotted together with the theoretical curves deduced from Vydyanath's model [1]. The hole concentration increases as the Hg pressure decreases in substantial agreement with his thermodynamic model, which suggests that the hole concentration in our crystals is proportional to the V_{Hg}^{2-} vacancy concentration.

To perform the positron-lifetime experiments, we use a pair of identical crystals between which the positron source is sandwiched.

To conduct our experiments, we use a positron-lifetime spectrometer based on a fast–fast coincidence system with a resolution of 275 ps. We record about 2×10^6 annihilations to obtain the positron-lifetime distribution. The distribution of the positron lifetimes was recorded as a function of temperature from 15 K to 300 K by using a closed-cycle He cryocooler. Before measuring the samples, we etched their surfaces chemically with a 5% bromine methanol solution.

The positron-lifetime spectrum $n(t)$ in a crystal is generally well described by a sum of exponentials. We analysed the experimental spectra with a fitting program [9] to determine the number of exponential components (1, 2, or more), their intensity I_i
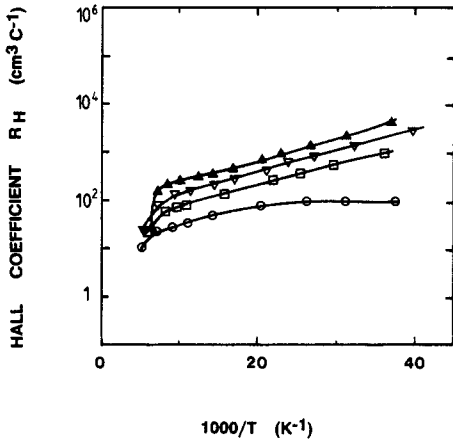
Figure 1. Hall coefficient R_H as a function of temperature in the single $Cd_{0.2}Hg_{0.8}Te$ crystals annealed at 410 °C under mercury partial pressure of 1 ($\blacktriangle$), 0.37 ($\triangledown$), 0.12 ($\square$) and 2.0×10^{-2} ($\circ$) atm. The corresponding hole concentrations measured at 77 K are (in cm^{-3}): 2.0×10^{16} ($\blacktriangle$), 3.5×10^{16} ($\triangledown$), 6.5×10^{16} ($\square$), 1.5×10^{17} ($\circ$).
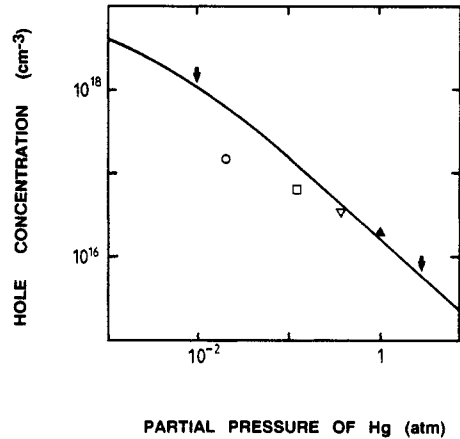

Figure 2. Hole concentration measured at 77 K as a function of the partial pressure of Hg under which the $Cd_{0.2}Hg_{0.8}Te$ crystals have been annealed at 410 °C. The full curve corresponds to the values calculated in Vydyanath's model [1]. Arrows represent the limits of the equilibrium diagram.
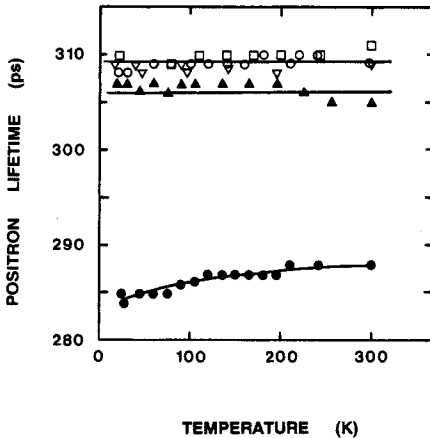

Figure 3. Positron average lifetime as a function of temperature for the reference n-type $Cd_{0.2}Hg_{0.8}Te$ sample ($\bullet$) and for the p-$Cd_{0.2}Hg_{0.8}Te$ annealed at 410 °C under various partial pressures of mercury. Hole concentration measured at 77 K (in cm^{-3}): 2.0×10^{16} ($\blacktriangle$), 3.5×10^{16} ($\triangledown$), 6.5×10^{16} ($\square$), 1.5×10^{17} ($\circ$).

($\Sigma_i I_i = 1$), and their time constant τ_i. In our experiments, only one or two lifetimes were resolved in the spectra.

In the n-type starting crystal (SAMP0), we detect a single lifetime of 286 ± 2 ps at 300 K. The lifetime decreases slightly by only 2 or 3 ps as the temperature decreases from 300 K to 15 K as seen in figure 3.

The four p-annealed crystals present drastically longer lifetimes (see table 1). In SAMP1, where the hole concentration is 2×10^{16} cm^{-3} at 77 K, the average lifetime value is 306 ± 1 ps, stable in the 15–300 K temperature range (see figure 3). Two components, independent of temperature, can be resolved in the spectra. The longer one has a value of $\tau = 309 \pm 1$ ps with an intensity of $97 \pm 1\%$. In the other crystals where the hole

concentration is higher than 3.5×10^{16} cm^{-3}, only one lifetime is resolved in the spectra. The value is the same in these three crystals: $\tau = 309 \pm 1$ ps. This lifetime is stable in the 15–300 K temperature range (see figure 3).

The lifetime of the positron in a given state is inversely proportional to the electronic density seen by the positron in this state. In a crystal such as $Cd_{0.2}Hg_{0.8}Te$, the positron can annihilate from a delocalised state with a characteristic bulk lifetime τ_b corresponding to the 'perfect' crystal, or from a localised state trapped in defects (as vacancies) with a characteristic lifetime τ_d. If the positron trapping occurs in vacancy-type defects, the measured lifetime is longer than the delocalised positron lifetime: $\tau_b < \tau_d$, because a vacancy defect corresponds to a deficit of electrons.

The value of the bulk lifetime in $Cd_{0.2}Hg_{0.8}Te$ is not currently well established. The value of 265 ps has been attributed to the bulk lifetime in [10] while this value is 275 ps in [4] and more recently 282 ps in [11]. The last value has been deduced from *in situ* positron-lifetime measurements under Hg atmosphere. The lifetime of 286 ps is the shortest single lifetime measured in our crystals. It is stable in the 15–300 K temperature range and very close in value to 282 ps [11]. We attribute it to annihilations in the bulk and therefore reach the conclusion that positrons do not detect vacancy-type defects in the reference n-type crystal. In the four p-type annealed crystals where a longer lifetime of $\tau = 309$ ps is observed, the presence of vacancy-type defects is unquestionable. The lifetime of 309 ps is a reasonable value for monovacancies as predicted theoretically [12]. We have also found that heavy-ion irradiations carried out on $Cd_xHg_{1-x}Te$ crystals give rise to lifetimes in this range along the ion tracks. We can therefore conclude that the p-type annealed crystals contain monovacancy-type defects. Table 1 clearly shows that the positron lifetime is the same in the three crystals where the hole concentration is greater than 3.5×10^{16} cm^{-3} (SAMP2, SAMP3 and SAMP4). This means that positrons annihilate only in vacancies (or monovacancy-type defects) and not in the bulk when the vacancy concentration reaches a concentration corresponding to about 3.5×10^{16} cm^{-3} holes.

The monovacancy-type defect characterised by $\tau_d = 309$ ps is neutral or negative because the positrons which are positively charged can be trapped only in neutral or negative vacancies. Assuming that the vacancies detected by positrons are the ones described in [1], i.e. doubly ionised mercury vacancies, we attribute the lifetime of 309 ps to the doubly ionised mercury vacancy V_{Hg}^{2-}. Recent experimental works [11] have also attributed the lifetime of 310 ps to V_{Hg}^{2-} vacancies. According to Vydyanath's model, the V_{Hg}^{2-} concentration is two times lower than the hole concentration at 77 K where the acceptors are considered to be completely ionised. Knowing that, we can estimate from table 1 that the vacancy concentration above which positrons are completely trapped in vacancies is about 1.7×10^{16} cm^{-3}. The positron trapping coefficient per vacancy can be estimated by applying the positron trapping model [2] in the sample SAMP1 which contains 10^{16} cm^{-3} V_{Hg}^{2-} vacancies according to the present model and where positrons annihilate from either bulk or V_{Hg}^{2-}. With the bulk value of 286 ps and the vacancy lifetime of 309 ps, we calculate from the average lifetime of 306 ps in this sample a positron trapping rate in the vacancies of $(2.3 \pm 0.8) \times 10^{10}$ ns^{-1}. This trapping rate corresponds to $(1 \pm 0.1) \times 10^{16}$ cm^{-3} vacancies, which yields to a positron specific trapping rate of $(2 \pm 1) \times 10^{-6}$ cm^3 s^{-1} (or $(7 \pm 3) \times 10^{16}$ s^{-1}). This value is higher by an order of magnitude than the one calculated in [10]. The origin of this discrepancy is not yet understood. To match the value calculated in [10], we have to assume that in our samples defects other than vacancies appear in the carrier balance and electrically compensate the vacancies. Experiments are in progress to check the compensation of our crystals. On the other hand, this high value for the positron trapping coefficient can be understood

because of the negative charge of the vacancies and the narrow gap of $Cd_{0.2}Hg_{0.8}Te$ [13]. The stability of the lifetime signal for the four samples in the 15–300 K temperature range indicates that positrons do not detect any change of charge state in these Hg monovacancies.

Positron-annihilation measurements detect monovacancies in $Cd_{0.2}Hg_{0.8}Te$ samples annealed under mercury atmosphere. These monovacancies are proposed to be doubly ionised mercury vacancies V_{Hg}^{2-} with a characteristic lifetime of 309 ± 1 ps. A defect concentration of about 1.7×10^{16} cm^{-3} is sufficient to trap all positrons.

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