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Defects and positron states in $Hg_{1-x}Cd_xTe$ semiconductors

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Abstract. Single crystals of $Hg_{1-x}Cd_xTe$ ($x = 0.35$, 0.27 and 0.20) were studied by positron annihilation in a temperature range from −150 to 500 °C. It was found that, when samples were heated from 20 to 500 °C, the positron mean lifetime $\bar{\tau}$ and Doppler broadening lineshape parameter S always show a 'V'-type behaviour with a minimum at around 250 °C. We attributed this behaviour to the annealing and creation of Hg vacancies. The formation enthalpy of V_{Hg}^{2-} was estimated to be 0.71 eV. The values of the positron lifetimes in the bulk state and in the V_{Hg}^{2-} trapped state were obtained as 282 ps and 310 ps, respectively. The specific positron-trapping rate μ of V_{Hg}^{2-} was estimated to be $(5 \pm 1) \times 10^{14}\ s^{-1}$.

1. Introduction

Positron annihilation studies on semiconductor defects have produced many results. Much work has concentrated on Si, Ge and III–V compounds and a preliminary understanding of the behaviour of positrons in these semiconductors has been reached [1]. However, there is still an absence of data on II–VI compounds, particular on the mercury cadmium telluride (MCT) system, which is one of the most important infrared detector materials.

It is well known that MCT is very difficult to grow and the material contains a large number of defects. The defects in MCT play an important role in determining its properties, but the nature of these defects is not thoroughly understood [2, 3]. Since positron annihilation is a powerful tool for revealing the defect structures of semiconductors, it is worth investigating the thermodynamics of defect processes in MCT by positron annihilation.

2. Experimental details

Three as-grown single-crystal samples of $Hg_{1-x}Cd_xTe$ ($x = 0.35$, 0.26 and 0.20) were examined using positron lifetime and Doppler broadening measurements. Before the measurements were made, the surfaces of all the samples were polished and etched in a 0.5% bromine–methanol solution. The other experimental details are as follows.

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For sample 1 ($Hg_{0.65}Cd_{0.35}Te$), the sample holder was kept in a closed vacuum chamber, which was pre-pumped to 10^{-5} Torr. The sample was heated to each pre-set temperature and soaked for 20 min; it was then cooled to room temperature for *in situ* resistance and positron measurements. After being heated to 327 °C, sample 1 was partly destroyed.

In the experiment on sample 1, defect annealing and vacancy creation were observed (see § 3 for details). In order to check whether these effects are general and whether positron trapping has any temperature dependence, we carried out two more experiments—one in a lower-temperature range (sample 2) and the other in a higher-temperature range (sample 3).

Positron measurements were carried out on sample 2 ($Hg_{0.73}Cd_{0.27}Te$), at the same temperatures as the annealing temperatures (from −151 to 170 °C) in a vacuum of 10^{-5} Torr. It took 1 h to record each spectrum and 30 min to change the temperature.

Sample 3 ($Hg_{0.80}Cd_{0.20}Te$) and some mercury were placed in a specially designed furnace. The two heaters were separately controlled so that the desired combination of sample temperature and mercury temperature could be obtained. At each sample temperature (20–500 °C) the mercury temperature (30–350 °C) (higher so as to obtain a mercury partial pressure) was changed step by step. Positron measurements were made following each step. The recording time for each spectrum was 1 h. The sample temperature was changed every 15 h on average.

3. Results and discussion

Figure 1 shows the results for sample 1. The curves of positron lifetime, Doppler broadening and conductivity have a V shape. Two opposite mechanisms which affect the concentration of positron traps have to be assumed. One is defect annealing, which is dominant below 260 °C, and the other is defect creation, which is dominant at temperatures above 260 °C. A longer mean lifetime and a higher S mean more defects in the samples. Thus it is reasonable to assume that in as-grown samples or in samples being heated at around 310 °C there are more defects than in samples being annealed at around 260 °C.

The variation in conductivity shows the same tendency as the variation in positron annihilation parameters, which gives a hint as to the type of defect. From Hall measurements it was concluded that, in undoped MCT, doubly charged Hg vacancies V_{Hg}^{2-} are responsible for the hole concentration [4]. Therefore it is reasonable to assume that the defects affecting positron annihilation are the same as those affecting conductivity, namely V_{Hg}^{2-}.

Figure 2 shows that the defects in as-grown samples can be greatly reduced by annealing the samples at 150–170 °C for a sufficiently long time and there is no sign that positron trapping is temperature dependent in MCT from −150 to 170 °C.

The mean positron lifetime τ and Doppler parameter S as functions of temperature (20–500 °C) for a constant mercury pressure p_{Hg} of 2×10^{-2}atm are shown in figure 3. The full results for sample 3 with respect to the effect of mercury pressure will be discussed elsewhere. In addition to the expected V shape behaviour below 320 °C, it was observed that the positron trapping tends to saturate near 500 °C, indicating that most positrons were trapped and annihilated by Hg vacancies. By extrapolating the curve for $\bar{\tau}$ in figure 3, it is easy to obtain lifetime values characteristic of positron annihilation by Hg vacancies and in the bulk; they turn out to be 310 ps for τ_V and 282 ps for τ_b. It was

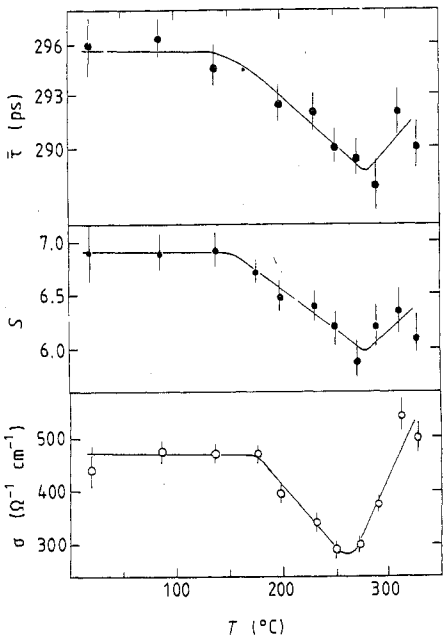

Figure 1. Positron annihilation mean lifetime $\bar{\tau}$, Doppler broadening lineshape parameter S and conductivity σ in $Hg_{0.65}Cd_{0.35}Te$ as functions of temperature.

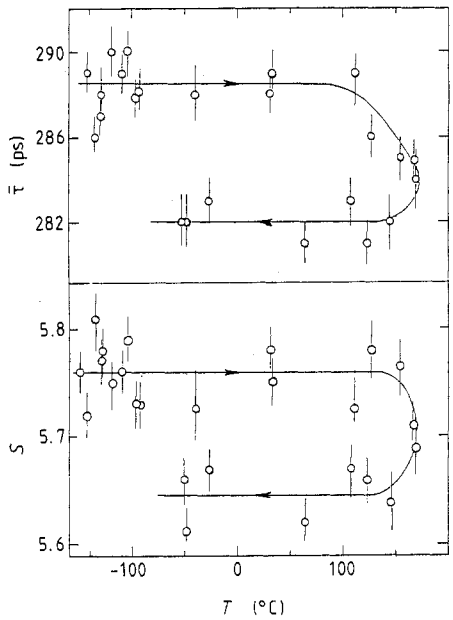

Figure 2. Positron annihilation mean lifetime $\bar{\tau}$ and Doppler broadening lineshape parameter S in $Hg_{0.73}Cd_{0.27}Te$ as functions of temperature.

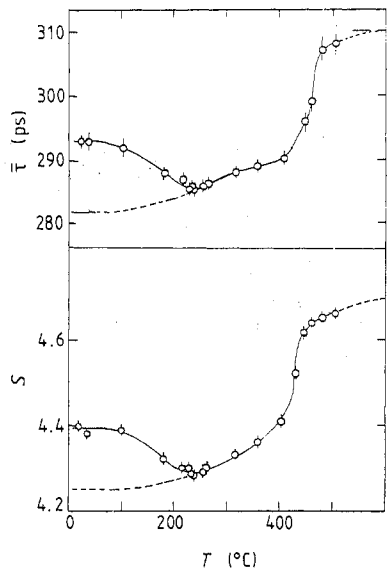

Figure 3. Positron annihilation mean lifetime $\bar{\tau}$ and Doppler broadening lineshape parameter S in $Hg_{0.80}Cd_{0.20}Te$ as functions of temperature. The mercury partial pressure p_{Hg} is 2×10^{-2} atm.

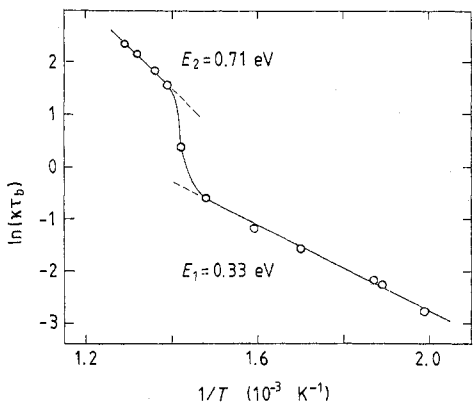

Figure 4. $\ln(\chi\tau_b)$ against $(1/T)$ for $Hg_{0.80}Cd_{0.20}Te$ where T is the temperature in kelvins, τ_b (= 282 ps) is the positron annihilation lifetime in the bulk state in MCT and κ is the positron-trapping rate calculated from equation (1).

noted that the τ_b-value obtained in this way is very close to the minimum lifetime which could be attained by a proper low-temperature anneal, as demonstrated for sample 2 (figure 2). The small τ_V/τ_b ratio of 1.1 means there is strong lattice relaxation around V_{Hg}^{2-}. According to the trapping model [5], the positron-trapping rate can be written as

$$\kappa = (1/\tau_b)[(S - S_b)/(S_V - S)] \tag{1}$$

where S_b and S_V are Doppler parameters characteristic of positron annihilation in the bulk and by Hg vacancies in MCT; these can be obtained by extrapolating the curve for S in figure 3. We know that the positron-trapping rate is proportional to the defect concentration, i.e.

$$\kappa = \mu[V_{Hg}^{2-}] = \mu A \exp(-H_{V^{2-}}/kT) \tag{2}$$

where μ is the specific trapping rate, A is a constant, $H_{V^{2-}}$ is the vacancy formation enthalpy for V_{Hg}^{2-} and T is the absolute temperature. When the data above 240 °C are plotted on an Arrhenius plot (figure 4), it can be seen that the experimental points fall on two straight lines, one with a slope of $E_2 = 0.71$ eV, corresponding to V_{Hg}^{2-} formation, and the other with a slope of $E_1 = 0.33$ eV. From the known facts, it is difficult to determine what the latter defect is. Let us suppose that it is a singly negatively charged Hg vacancy V_{Hg}^{-}; then its formation enthalpy H_{V^-} could be related to the formation enthalpy H_{V^0} of a neutral Hg vacancy V_{Hg}^{0} by

$$H_{V^-} = H_{V^0} - (E_F - E_{V^-}) \tag{3}$$

where E_F is the Fermi energy and E_{V^-} is the energy level of V_{Hg}^{-}. H_{V^0} may be 2.2 eV [3] and seems too high to account for the lower activation energy E_1. Because of the absence of well defined values of defect energy levels in MCT, at the moment we can only say that the energy level difference between V_{Hg}^{2-} and the other type of defect which also acts as a positron trap is $E_2 - E_1 = 0.38$ eV.

From Vydyanath's [4] calculation, the hole concentrations at 400 °C, 460 °C and 500 °C ($p_{Hg} = 2 \times 10^{-2}$ atm) are approximately 0.4×10^{18} cm^{-3}, 2×10^{18} cm^{-3} and 6×10^{18} cm^{-3}, respectively. On the assumption that $[V_{Hg}^{2-}]$ equals half the corresponding hole concentration, the specific positron-trapping rate of V_{Hg}^{2-} can be estimated to be $(5 \pm 1) \times 10^{14}$ s^{-1} on average. If the dominant positron-trapping centre in as-grown samples is V_{Hg}^{2-}, then its concentration roughly equals to the hole concentration at 400 °C in thermal equilibrium ($p_{Hg} = 2 \times 10^{-2}$ atm) as seen in figure 3, namely 2×10^{17} cm^{-3}.

4. Conclusions

(i) In as-grown MCT single crystals, a very high concentration (2×10^{17} cm^{-3}) of vacancy-type defects exists. These defects can be annealed out at a moderate temperature (around 170 °C) for a sufficiently long time (about 1 day).

(ii) In the temperature range 240–500 °C, two types of mercury vacancy may exist: below 430 °C, a defect of formation enthalpy 0.33 eV is dominant; above 430 °C, another defect is dominant, which has a formation enthalpy of 0.71 eV and is assigned to doubly ionised mercury vacancy V_{Hg}^{2-}.

(iii) In $Hg_{1-x}Cd_xTe$ ($x = 0.2$–0.35) crystals, the positron lifetime τ_b in the bulk is 282 ps and the positron lifetime τ_V in the trapped state V_{Hg}^{2-} is 310 ps. The specific trapping rate for V_{Hg}^{2-} is 5×10^{14} s^{-1} (i.e. 20×10^{-9} cm^3 s^{-1}).

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