Observation of Vacancy Charge States in $Cd_{0.2}Hg_{0.8}Te$ by Positron Annihilation

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Positron trapping at charged vacancies V_{Hg}^{0}, V_{Hg}^{1-}, and V_{Hg}^{2-}, in $Cd_{0.2}Hg_{0.8}Te$ has been investigated. Doppler measurements reveal the temperature dependence of the trapping rates and provide evidence for the predicted existence of Rydberg precursor states. This first direct observation of the vacancy charge states yielded energies of 18 meV and 41 meV for the singly and doubly ionized states, respectively.

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In semiconductors vacancies may act as either acceptors or donors and they often dominate the electrical properties. The vacancies may exist in various charged states and although it is appreciated that these will change with temperature as the position of the Fermi level moves, it is desirable that direct observations should establish the ionization energies in specific semiconductors. Until recently only electrical measurements have been available but these are not ideal; Hall measurements respond to free carriers resulting from the ionization of both vacancies and impurities.

For some years positron annihilation spectroscopy has been applied to semiconductors [1–3]. Both lifetime and Doppler broadening investigations have revealed the capacity of lattice vacancies to trap positrons, but the interpretation of results has been handicapped by the fact that, unlike metals, in semiconductors vacancies are likely to be charged. This has serious consequences for the trapping rates. Fortunately, a theoretical paper [4] has lately demonstrated the role of charges on vacancies in influencing the positron trapping rates hence pointing the way forward.

In this Letter we report measurements which offer a dual significance; they supply the evidence to support the temperature dependence proposed in the trapping theory of Puska, Corbel, and Nieminen [4] and they allow the first direct determination of the vacancy ionization energies as a rising temperature alters the charge state from neutral, to singly, and then doubly negative.

In metals, vacancies appear as deep potential wells in which positrons may be trapped, the energy released in the trapping process being absorbed by electron-hole pair creation. In semiconductors the existence of a band gap may preclude this process with the positron energy being absorbed by less efficient phonon scattering, although in some cases localized states in the band gap induced by the defects themselves may offer an intermediate step in the energy loss. Although positive defects will repel positrons, negatively charged defects will attract positrons strongly due to the long range Coulomb potential. In their model, Puska, Corbel, and Nieminen [4] proposed a two-process capture mechanism for the low temperature regime. A delocalized positron is first captured into a precursor Rydberg state from which a direct transition to the ground state may occur prior to the annihilation. A crucial feature of this model is the prospect of detrapping from the shallow Rydberg state resulting in a temperature dependence of the trapping rate for negatively charged defects. In addition the magnitude of the trapping rate will be related to the defect charge. Evidence for the temperature dependence has been reported: Makinen *et al.* [5] found a much enhanced trapping rate for silicon vacancies at low temperatures.

Cadmium mercury telluride ($Cd_xHg_{1-x}Te$) is a semiconductor that is a widely used infrared detector material with an energy gap and hence a spectral response determined by x. As grown, the material is p type due to the large concentration ($\sim 10^{17}$ cm^{-3}) of mercury vacancies which act as acceptors. The energy levels that are induced in the band gap by a vacancy will determine its degree of ionization as the Fermi level is varied. Hence a mercury vacancy may exist as V_{Hg}^{0}, V_{Hg}^{1-}, or V_{Hg}^{2-} depending on the temperature. However, the position of these energy levels has not been assessed directly.

Elizarov, Bogoboyashchii, and Berchenko [6], using infrared absorption, have suggested that Hg vacancies are singly negatively ionized at 77 K, but doubly above 200 K; however, Hall measurements by Vydyanath [7] indicated that vacancies remained doubly ionized over the whole range 77–300 K. Work has been reported employing positron annihilation spectroscopy to bulk CdHgTe but temperature-dependent trapping rates were not invoked [8–10]. A beam measurement has also been made [11].

A range of four CdHgTe samples have been prepared with $x=0.2$ by the cast, recrystallize, anneal process using the purest materials—e.g., the measured Na in the CdHgTe was $\sim 5\times 10^{15}$ cm^{-3} [12]. This is a three stage process in which initially the elements Cd, Hg, and Te, in proportions to give the required x value, are reacted at high temperature in an evacuated, sealed ampoule and then cooled rapidly to prevent segregation of the constituents. The polycrystalline ingot so formed, still in the ampoule, is then reheated to near the melting point where grain growth occurs during which two or three major grains grow at the expense of smaller ones. These single crystal regions are very uniform in composition but possess a high concentration of Hg vacancies due to loss of

Hg to the vapor space in the ampoule. The third stage of the process involves taking slices cut from major grains and annealing them to yield required electrical properties. Slices of 1 mm were cut and placed in sealed evacuated silica ampoules containing reservoirs, before being inserted into temperature-controlled furnaces. The samples A, B, and C with hole concentrations C_v, indicated by Hall measurements at 77 K, of 3×10^{18}, 5×10^{16}, and 2×10^{16} cm^{-3}, and sample D with 10^{14} cm^{-3} [7], were prepared with reservoirs of powdered CdTe, vacuum, Hg, and Hg at 600, 300, 410, and 220 °C for duration 5 min, 1 d, 2 h, and 10 d, with quench into cold water, air cool, quench, and air cool, respectively.

To study the behavior of positrons as a function of temperature a traditional sandwich geometry was used of two pieces of CdHgTe ($10\times10\times1$ mm^3) embracing a 20 μCi ^{22}NaCl source. The Doppler broadening of the annihilation 511 keV photons was recorded with a stabilized germanium detector. The conventional line-height parameter S [10], defined as the ratio of the contents of a central 15 channels to the whole photopeak centered at channel 5000, was calculated for spectra obtained in 1 h periods. A rise in S indicates enhanced trapping.

Figure 1 shows the results for samples A, B, C, and D. As expected the highest concentration yields a high S, implying a narrower spectra line, i.e., less Doppler broadening due to a higher fraction of positrons being trapped. But it is the variation with temperature that interests us. Sample C is the most extraordinary with a clear maximum at 125 K. We suggest the decline in S at the higher temperatures is due to the postulated detrapping from precursor states [4], but the decline at lower temperatures is a consequence of a countervailing reduction in trapping due to the vacancies losing their negative charges.

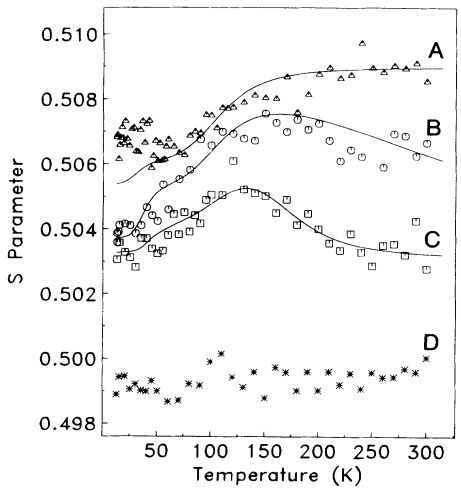

FIG. 1. The Doppler line-height parameter S observed for samples A, B, C, and D with different vacancy concentrations as a function of temperature.

For a divalent semiconductor the probabilities of vacancies being in states V^{n-} with ionization energies E_n ($n=1,2$) are given by

$$P_2=\frac{g_2\exp[(E_1-E_f)/kT]}{1+g_2\exp[(E_f-E_2)/kT]+g_1^{-1}\exp[(E_1-E_f)/kT]}$$

and

$$P_1=\frac{1}{1+g_2\exp[(E_f-E_2)/kT]+g_1^{-1}\exp[(E_1-E_f)/kT]},$$

with $P_0=1-(P_1+P_2)$ where g_n^{-1} is the spin degeneracy, and the Fermi energy $E_f=kT\ln(N_v/p)$, with p the hole concentration, and the density of states in the valence band $N_v=2(m_v kT/2\pi h^2)^{3/2}$ where m_v is the hole effective mass in the valence band. For CdHgTe we have taken $m_v=0.54m_0$ [6], $g_1^{-1}=3/2$, and $g_2^{-1}=4$ [13]. With a total vacancy concentration $C_v=C_0+C_1+C_2$ and $p=C_1+2C_2$, a cubic equation $x^3+2\alpha x-\alpha(1-\beta)x-\alpha\beta=0$ is obtained [14,15] where $x=p/2C_v$, $\alpha=N_v\times(4g_1^{-1}C_v)^{-1}\exp(-E_1/kT)$ and $\beta=N_v(g_2^{-1}C_v)^{-1}\times\exp(-E_2/kT)$, which allows the probabilities P_0,P_1,P_2 to be calculated for any temperature and used in the fitting for S.

It is assumed that positrons annihilate either in deep traps or in delocalized states, and hence that the two-state trapping model may be applied (e.g., [16]) with $S(T)=(S_f\lambda_f+S_v\kappa)/(\lambda_f+\kappa)$, where S_f and S_v refer to the Doppler parameters that correspond with 100% annihilation in the free and trapped states. λ_f is the annihilation rate from delocalized states, and κ the trapping rate. Although the charge state of a vacancy will not affect S_v [17], the trapping rate will change for different charge states. For the case of negatively charged vacancies the trapping rate will be given by [4]

$$\kappa_n=\frac{\eta_n C_v\kappa_{nR}}{\eta_n C_v+\kappa_{nR}(2\pi m_v kT/h^2)^{3/2}\exp(-E_n/kT)},$$

where $n=1,2$ are the charge states for V_{Hg}^{1-}, V_{Hg}^{2-}, and where κ_{nR} refers to trapping into a precursor Rydberg state and η_n is the rate from the Rydberg state to the final deep trap state. At any temperature the total effective rate will be $\kappa=(\mu_0P_0+\mu_1P_1+\mu_2P_2)C_v$ where μ_n are the specific trapping rates and hence $S(T)=(S_f\lambda_f+S_v\kappa_0+S_v\kappa_1+S_v\kappa_2)/(\lambda_f+\kappa)$.

In fitting the data, λ_f has been taken as 3.63×10^9 s^{-1} [8]. The parameter S_v (≈0.5095) was determined with a sample E with an exceedingly high defect concentration C_v of 5×10^{18} cm^{-3}; and S_f (≈0.4993) was given by the sample D with such a low C_v that the trapping was negligible. Optimum least-squares fits to the data are shown in Fig. 1 for samples A, B, and C. Sample A has a very high concentration and therefore is likely to approach saturation trapping. The large vacancy concentration in this sample reduces the number of allowable Rydberg states and hence a trapping rate is independent of temperature which accounts for the absence of any decrease in S at higher temperatures. At the lowest temperatures, below

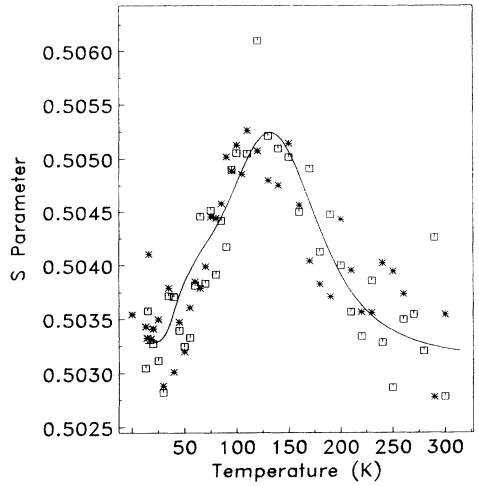

FIG. 2. The Doppler parameter S for two distinct runs of sample C showing the optimum fit to the model. The decline at high temperatures reflects the detrapping of positrons from Rydberg states and the decline at low temperatures indicates the changing charge state of the vacancies.

50 K, we find a rise in S which hints at detrapping from very shallow states and we have therefore omitted results below 50 K from the fittings for sample A.

Figure 2 shows the data for two distinct runs on sample C. The fit is good; it is impossible to fit if the presence of neutral vacancies is ignored. Figure 3 shows the optimum individual specific trapping rates and the relative populations of the V_{Hg}^{0}, V_{Hg}^{1-}, and V_{Hg}^{2-} states as a function of temperature. For samples B and C the ionization energies $E_1=15,18$ meV and $E_2=42,41$ meV were obtained, respectively. For sample A, $E_2=42$ meV and a line is plotted in Fig. 1 with $E_1=14$ meV. However, as noted above, our observations for sample A do not concur with the model below 50 K, but do support theoretical arguments concerning band broadening that suggest neutral vacancies would not exist in cases of very high hole concentrations. In Fig. 3(b), at 300 K, the estimated trapping rate for V_{Hg}^{2-} is $3\times10^{17}\ s^{-1}$; this exceeds two previous estimates, $9\times10^{14}\ s^{-1}$ [8] and $7\times10^{16}\ s^{-1}$ [9], which we note differ themselves remarkably.

Some work on ionization energies of acceptor states in p-type $Cd_xHg_{1-x}Te$ has been reported; deep level transient spectroscopy [18] has indicated two traps, one with an energy level of 43 meV; the Hall effect has yielded 15 [19], 11 [20], and 6 meV [21]. However, these electrical measurements do not distinguish between vacancies and electrically active defects such as impurities; the virtue of positron annihilation spectroscopy is that it reveals vacancies specifically.

In conclusion, the experiments beautifully demonstrate the temperature dependence of the detrapping of positrons from weakly bound Rydberg precursor states that arise due to the action of the long range attractive Coulomb potential in semiconductors. The measurements provide the first direct evidence of the varying vacancy charge states in $Cd_xHg_{1-x}Te$.

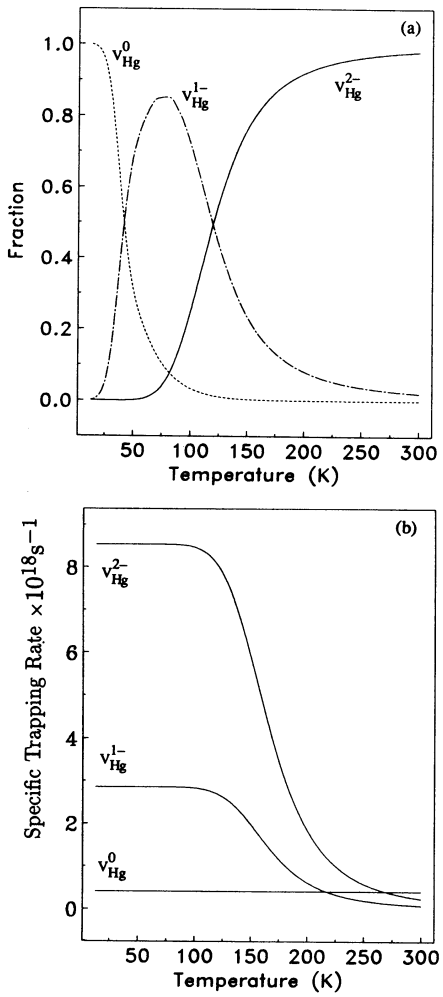

FIG. 3. (a) For sample C the estimated relative fractions of the V_{Hg}^{0}, V_{Hg}^{1-}, and V_{Hg}^{2-} states as a function of temperature. (b) The specific trapping rates indicated by the fit in Fig. 2.

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