*EL*2 Deep Donor State in Semi-Insulating GaAs Revealed by Frequency Dependent Positron Mobility Measurements

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(Received 19 April 1994)

Positron mobility measurements carried out on semi-insulating GaAs, using the Doppler shift in annihilation radiation technique, show a sharp transition from a high mobility value $\sim 120\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$ to a lower value $\sim 45\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$ just below room temperature. The temperature of the transition is found to be dependent on the frequency of the applied AC bias. We show that this effect is an artifact due to the thermal ionization of the *EL*2 deep donor state, which in its ionized state forms a positive space charge that causes the positron to experience large electric fields. This observation suggests a new positron annihilation-based deep-level transient technique applicable to semi-insulating materials.

PACS numbers: 61.72.Vv, 71.60.+z, 78.70.Bj

In recent years, point defects in GaAs have been the subject of a number of informative studies using vacancy sensitive positron annihilation techniques [1–3]. The measurement of the positron diffusivity in GaAs has also shown that ionized acceptors may be detected, as these shallow traps trap positrons in hydrogeniclike orbits in a similar way to holes, albeit at higher temperatures due to the larger positron effective mass [4]. In this Letter we report on measurements made on the positron mobility in semi-insulating GaAs, using the Doppler-shifted annihilation radiation technique proposed by Bergersen and McMullen [5] and later developed by Mills *et al.* [6,7]. In addition to phonon and shallow trap limiting processes, we find an interesting frequency dependence for the observed positron mobility just below room temperature, and this we show to have its origins in the ionization of the compensating *EL*2 native deep donor state.

In this study, the samples used were undoped liquid encapsulated Czochralski grown semi-insulating GaAs(100) obtained from ICI Wafer Technology Limited. The resistivity of the material was quoted as $10^8\ \Omega$ cm, and the thickness was 0.5 mm. The free carrier, *EL*2 and carbon concentrations were quoted as 6×10^7, 1.5×10^{16}, and $9 \pm 6 \times 10^{14}\ \mathrm{cm^{-3}}$, respectively. Two samples were cut to the size of 1 cm × 1 cm and the electric contact formed by evaporating an Au circular disc of thickness 100 nm and diameter 7 mm on both sides of each sample. The source of positrons, 20 μCi of ^{22}NaCl deposited on and sandwiched between 3 μm thick Ni foil, was sandwiched between the two prepared samples.

The experimental apparatus used for making the positron mobility measurements was similar to that developed by Mills *et al.* [7] and has been described by us in a previous paper reporting a preliminary set of measurements on GaAs [8]. The essential features of the apparatus were, however, as follows. A triangular voltage wave with peak amplitudes of ±200 V and its compliment were applied to the two outer contacts of the sample sandwich structure, while the central contacts were earthed via the Ni source. The electric field in the samples was thus made to vary linearly in time (assuming the samples to be either simple Ohmic or dielectric in nature). Frequencies of 0.25, 1, and 5 Hz were used for the applied bias. The sample structure was mounted on a cold finger inside a conventional liquid nitrogen cryostat, and a high purity (HP) Ge detector with its axis along the direction of the applied electric field was used to detect the Doppler-shifted annihilation photons. After amplification, the 511 keV annihilation peak pulses were bisected using two single-channel analyzers (SCAs) and the count rates in the lower and upper widows (N_A and N_B, respectively) were monitored as a function of the phase of the applied voltage, using a synchronized 1024 channel multichannel scalar (MCS). The sequential red and blue shifting of the annihilation line due to the electric-field drift of the positron was detected over the duration of a measurement (~72 h), by the small fractional changes ΔN_A and ΔN_B that occur in N_A and N_B as a result of the applied bias. A stabilizer unit kept the count rates N_A and N_B equal over times greater than 100 s. The positron drift velocity at any phase of the applied bias was obtained using the expression [7]

$$v_+ = \tfrac{1}{2}\alpha[\Delta N_A/\langle N_A\rangle - \Delta N_B/\langle N_B\rangle], \qquad (1)$$

where $\langle N_A\rangle$ and $\langle N_B\rangle$ are the mean count rates of N_A and N_B, and α is a calibration constant, which for our setup was $2.1 \times 10^8\ \mathrm{cm\,s^{-1}}$. The v_+ data calculated by (1) were augmented by a detector averaged $\cos(\theta)$ factor 1.08 and by a source correction factor of 1.15.

Positron mobilities were calculated by first computing v_+ for each MCS channel and by then carrying out a straight line fit to this data plotted against the applied electric field, the latter being taken as V/d, where V and d are the applied voltage and sample thickness, respectively [8]. The data so obtained, plotted over the temperature range 120 to 320 K, are shown in Fig. 1 for the three different frequencies of the applied voltage. Two striking features of the data are the largely temperature independent mobility from 120 to 250 K, and the frequency dependent increase in the mobility that occurs above ~250 K. The

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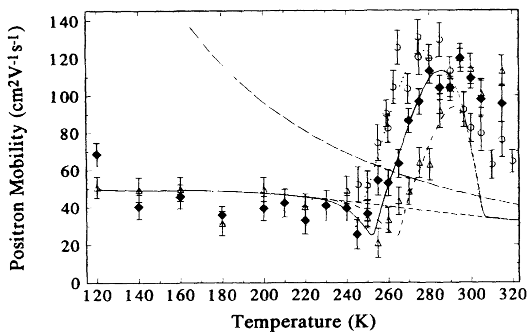

FIG. 1. The temperature dependence of the positron mobility in semi-insulating GaAs, assuming the electric field in the sample is uniform, for the three ramping frequencies 0.25 Hz (○), 1 Hz (♦), and 5 Hz (△). The long dashed curve shows the theoretically predicted acoustic plus polar optic phonon limited mobility, while the short dashed curve shows the shallow trapped plus phonon limited mobility. Model fits to the 0.25, 1, and 5 Hz data are given by the dotted, solid, and dot-dashed curves, respectively.

former can be readily explained on the shallow trapping model [8], while the latter is the important effect that is primarily the object of this Letter. Ignorance of this frequency dependence of the mobility signal was the main cause behind our report of some uncertainty in the room-temperature value of the mobility [8,9]. In Fig. 2 we show the frequency dependence explicitly by changing the frequency and by monitoring the mobility at the fixed temperature of 275 K. It can be seen that the observed positron mobility decreases as the frequency increases.

In elemental semiconductors, the positron propagates through the crystal lattice in much the same way as an electron or hole, scattering mainly from acoustic phonons [6,9,10], the mobility being well described by the Bardeen-Shockley theory [11]. For GaAs, however, a recent study has shown that positron diffusion is as much limited by polar optic phonon scattering as it is by acoustic phonons [9]. In Fig. 1 we show the theoretically predicted low-field mobility μ_+, derived assuming both acoustic phonon (A) and polar optic phonon (PO) scattering [i.e., taking $\mu_+^{-1} = \mu_+^{-1}(\mathrm{A}) + \mu_+^{-1}(\mathrm{PO})$]. The acoustic phonon limited

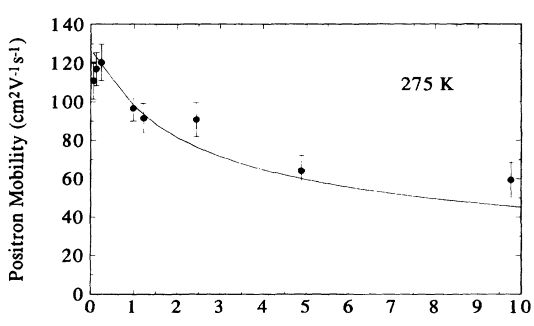

FIG. 2. The observed ramping frequency dependence of the positron mobility in semi-insulating GaAs at 275 K. The solid curve shows the fit given by the nonuniform electric-field transient model described in the text.

mobility has been obtained using the Bardeen-Shockley theory with a positron deformation potential and effective mass of -5.87 eV and 1.3 m_e, respectively [9]. Although there is no universal relaxation time available to describe polar optic phonon scattering, a value for temperatures below 350 K may be defined [12], in which we have taken the optical phonon energy as 35.3 meV, and the high- and low-frequency dielectric constants as 12.85 and 10.89, respectively [13]. From Fig. 1 it is evident that the phonon-scattering limited mobility alone cannot describe the data.

Below room temperature, the positron, like the hole, becomes progressively subject to shallow trapping on negative impurity sites in the crystal [4], causing the observed mobility to be significantly lower than that predicted from phonon loss and effectively independent of temperature in the range 100–220 K [8]. To account for positron shallow trapping on ionized acceptors, we have included in μ_+ the factor $[1 + \{(\delta/k_{st}) + (\lambda/k_{st})\}^{-1}]^{-1}$ [8], where $\delta/k_{st} = A(kT)^{+3/2}\exp(-E_{st}/kT)$, in which δ is the detrapping rate, k_{st} is the trapping rate, λ is the annihilation rate ($= 4.35\ \mathrm{ns}^{-1}$), E_{st} is the shallow trap binding energy ($= 43$ meV [4]), and $A = C_{st}^{-1}(m^*/2\pi\hbar)^{3/2}$, C_{st} being the concentration of shallow traps [4]. When treated as fitting parameters, A and λ/k_{st} values of 3000 $\mathrm{eV}^{-3/2}$ and 0.25 are found, respectively. While these values are in good agreement with values obtained by Saarinen *et al.* for their undoped GaAs samples [4], and thus lead us to believe that the shallow trapping phenomenon is both occurring and dominant in this lower temperature range, they do indicate a shallow trap concentration ($10^{18}\ \mathrm{cm}^{-3}$ based on A or $8 \times 10^{17}\ \mathrm{cm}^{-3}$ based on λ/k_{st} and a trapping coefficient $\cong 10^{15}\ \mathrm{s}^{-1}$ [14]), higher than the ionized acceptor concentration of $\cong 10^{15}\ \mathrm{cm}^{-3}$. This anomaly is beyond the scope of this Letter, but could possibly be explained if the dominant shallow trap is $\mathrm{Ga_{As}}^-$, [4,14], providing this center was being compensated by a related shallow donor state of nearly equal concentration.

While the combined effects of phonon scattering and shallow trapping explain the low-temperature data, they cannot produce the observed mobility frequency dependence just below room temperature. In the following discussion this effect is shown to be an artifact due to a nonuniform intense electric field adjacent to the positron injecting contact, that arises from ionized deep donors.

It is well known that the Fermi level at a metal-semiconductor contact pins at some position within the band gap [15]. For Au on GaAs the Fermi level pins ~0.9 eV below the conduction band, irrespective of whether the material is n or p type [15]. It is thus reasonable to assume the same pinning to occur for Au on semi-insulating material. Such a barrier will, when the contact is under reverse bias, severely restrict electron flow into the sample. The carrier concentration in our samples indicates that the Fermi level in the bulk will be only 0.09 eV above the midgap position and 0.2 eV above the $EL2$ level (0.825 eV below the conduction band)

[16]. The $EL2$ donor levels will thus be almost totally occupied with electrons and neutrally charged. The small remnant charge of $EL2^+$ will be largely balanced by the concentration of ionized shallow acceptors. When the positron injection contact is either zero or forward biased, apart from a thin $EL2^+$ space-charge region formed from Fermi-level mismatch at the interface, the same situation prevails in the region of the contact as in the bulk, namely a dynamic equilibrium between electron capture by $EL2^+$ and electron emission from $EL2^0$. However, on reverse biasing the positron injecting Schottky contact, and within a charge relaxation time of $\varepsilon/\sigma \sim 10^{-6}$ s, free carriers are effectively depleted from the sample as a result of blocking contacts for electrons and holes. The absence of electrons in the conduction band reduces the electron capture process to close to zero, leaving the $EL2^0$ centers free to emit electrons to the conduction band at the rate [17]

$$g = \sigma v N_C \exp[-(E_C - E_T)/k_B T], \quad (2)$$

where σ is the $EL2^+$ electron capture cross section, v is the mean electron thermal velocity $(3k_B T/m^*)^{1/2}$, N_C is the conduction-band effective density of states, and $E_C - E_T$ is the energy difference between the deep level and the conduction band.

Under the reverse biased electron depletion condition, deep levels will tend towards total ionization exponentially; the concentration of charged centers $EL2^+$ being given by [17]

$$s(t) = n_T[1 - \exp(-gt)], \quad (3)$$

where n_T is the deep donor density. Providing the ionization rate is not too low, the space-charge density does not continue to grow at a uniform rate across the sample, but only within a depletion width $w(t)$ from the positron injecting contact given by

$$w(t) = \left\{\frac{2\varepsilon[\phi_{\mathrm{bi}} + V(t) - I(t)R]}{es(t)}\right\}^{1/2}, \quad (4)$$

where ϕ_{bi} is the intrinsic band bending (built in potential) of the contact, $V(t)$ is the applied bias, $I(t)$ is the residual current flowing through the sample, R is the bulk series resistance, and ε is the permittivity of the material [15,18]. According to (4), if the applied bias is fixed or slowly varying, $w(t)$ will collapse onto the positron injecting contact as $s(t)$ increases. Within the same depletion approximation [15,18] the electric field $E(x,t)$ inside our samples, both of width d, for $w > d$ is given by:

$$E(x,t) = V(t)/d + es(t)\left(\tfrac{1}{2}d - x\right)/\varepsilon \qquad 0 < x < d$$

$$= V(t)/d - es(t)\left(\tfrac{1}{2}d + x\right)/\varepsilon \qquad -d < x < 0,$$

and for $w \le d$

$$E(x,t) = I(t)R/d + es(t)(w(t) - x)/\varepsilon \qquad 0 < x < w$$

$$= I(t)R/d + es(t)(w(t) - x - d)/\varepsilon \qquad -d < x < -d + w$$

$$= I(t)R/d \qquad x \ge w, -d + w < x < 0. \quad (5)$$

Our purpose now is to find the mean drift velocity of positrons within a sample having the electric-field profile (5), and for this the positron implantation profile of positrons is taken as $P(x) = (1/x_0)\exp(-x/x_0)$, x_0 being the mean implantation depth [19]. The probability of the positron thermalizing at a position with electric field E is then given by

$$P(E) = \beta e^{-d/2x_0} \cosh\left[\phi \frac{d}{2x_0}\left(1 - \frac{w}{d}\right)^2 + \beta\left(\frac{V}{d} - E\right)\right]$$

$$E(d,t) < E < E(0,t), \quad (6)$$

where $\beta = \varepsilon/esx_0$ with $\phi = 0$ $(w > d)$ and $\phi = 1$ $(w \le d)$. The mean drift velocity is finally given by averaging positron drift velocities over the sample

$$\langle v_+ \rangle = p(E_B)v_+(E_B) + \int_{E(x=0)}^{E(x=d)} P(E)v_+(E)\,dE, \quad (7)$$

where $p(E_B) = \phi e^{-d/2x_0}[\cosh(d/2x_0) - \cosh(d/2x_0 - w/x_0)]$ and $E_B = I(t)R/d$.

Equations (2)–(7) have been implemented numerically to simulate the present case where $V(t)$ takes triangular form. The predicted positron mobility has been calculated from the time averaged value $\langle\langle v_+ \rangle\rangle$, of $\langle v_+ \rangle$ over a period divided by the mean applied linear electric field ($V_0/2d$, where V_0 is the peak voltage). This procedure is equivalent to least squares fitting a straight line through the $\langle v^+ \rangle$ data versus applied linear electric field plot. In (2) the values pertaining to $EL2$ have been taken, namely an electron capture cross section of 1.2×10^{-13} cm^{-2}, $E_C - E_T = 0.825$ eV [16]. In addition, we have taken $N_C = 4.7 \times 10^{17}$ cm^{-3} and $m^* = 0.067\, m_e$ [14]. In (3) n_T has been taken as the $EL2$ concentration which is 1.5×10^{16} cm^{-3}. In (4) ε has been taken as $12.4\varepsilon_0$, ϕ_{bi}, as 0.3 eV [18], and $I(t)$ was obtained from dc experiments at various temperatures. In (5) the bulk resistance R is estimated to be 1.3×10^7 Ω from the sample resistivity and dimensions. In (6) the mean implantation depth x_0 for GaAs is taken as 40 μm [18]. In (7), since we are not aware of any theoretical $v(E)$ relation for polar-optic phonon scattering, the relationship $v_+(E)$ is taken as the full Bardeen-Shockley formula for acoustic phonon scattering [11] with a longitudinal velocity of sound 4.8×10^5 cm s^{-1} [13].

The model fits we obtain are shown in Figs. 1 and 2. The reasonable fits to our data indicate the basic correctness of our interpretation, namely that the rise in positron mobility just below room temperature is an artifact produced by the enhancement of the mean-electric field experienced by positrons in the samples. As the temperature is increased, the deep levels ionize at a faster rate, and when an appreciable charging occurs within the period of the applied field, electric field enhancement adjacent to the positron injecting contact, and an associated apparent rise in mobility, results. The higher the frequency of the applied field the higher the temperature must be in order for the same amount of charging to occur, and consequently the mobility rise translates to higher temperatures.

At still higher temperatures the apparent mobility begins to decrease. This decrease is attributed to two causes. The first is that the real mobility of the positron is decreasing with temperature due to an increase in phonon scattering. The second is that, when under reverse bias, a significant electron current begins to flow into the space-charge region (through either thermionic emission over the Schottky barrier or through carrier generation through deep levels), and this causes a fraction of $EL2^+$ centers to capture electrons and become $EL2^0$, thus diminishing the magnitude of the space charge. The space charge tries to relax to the dc distribution, but does not have sufficient time to do so. In this respect it is noted that the data taken with the lowest frequency show the greatest drop in mobility as more time is available for the traps to neutralize.

In an electric field, the cross section for trapping decreases while the rate of detrapping increases, and both these effects contribute to fewer positrons annihilating from immobile shallow trapped states. In the above model we have taken the reduced shallow trapping rate as given by Eq. (6) in Ref. [20], with $A = 0.2\ \mathrm{kV}^{-1}\,\mathrm{cm}$. (Since A scales as the positron mobility, this value is in good accord with the value of $0.05\ \mathrm{kV}^{-1}\,\mathrm{cm}$ found for InP[$\mu_+ = 15 \pm 5\ \mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$] [20]). The detrapping rate has been modified by reducing E_{st} by the factor $(eE/4\pi\varepsilon)^{1/2}$. Electric field inhibited shallow trapping is found to be so effective that essentially positron motion is only phonon limited throughout much of the depletion region. Failure to incorporate this phenomenon in the model reduces only the intensity of the modeled mobility peak (by some 60%) and as expected leaves both the shape and position of the mobility rise unalterred.

The model we present does not take into account the fact that some positrons in the depletion region may drift appreciable distances ($\sim 1\ \mu$m) into the contact [18]. To first order, we find that the effect of the positron annihilating at a position of higher electric field is counteracted by the fact that some ($<10\%$) of positrons become immobile in the contact.

In this work we give strong evidence to suggest that an observed increase in positron mobility can result from a region of positive space charge, formed as a result of deep donors ionizing. The evidence is also decisive that in the present case we are observing the ionization of the $EL2$ center, since if $E_C - E_T$ is varied by more than 0.1 eV, good fits to the data cannot be obtained. (We have tried to fit the our data assuming parameters, $E_C - E_T$, σ, and n_T; for other deep levels in GaAs, such as $EL3$, $EL5$, and $EL6$ and have failed.) Both the electron capture cross section σ and concentration n_T that give good fits to the data are those pertaining to $EL2$.

In the present work we have used a radioactive source to implant positrons into the deep donor space-charge region, but this is not the most ideal way to observe the mobility signal reported here. With the use of a low-energy positron beam, $\sim 100\%$ of the positrons could be implanted into the active space-charge region of a single sample to give a much stronger Doppler-shifted signal. Doppler-shifted transients could then be observed after trap filling in much the same way as capacitance transients are observed in conventional DLTS (deep level transient spectroscopy). Here, however, it would be the electric-field strength of the depletion zone being monitored rather than the capacitance. The exciting aspect of this proposal is that this technique would be applicable to semi-insulating materials, whose long charge relaxation times ε/σ render DLTS inapplicable.

The authors are much indebted to the help of Dr. A. P. Mills, Jr. in setting up the Doppler-shift technique. We are grateful to Dr. T. P. Chen and Mr. C. V. Reddy for helpful discussions.

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