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Photoresponse of the FR3 electron-spin-resonance signal in GaAs

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The photoresponse of the FR3 electron-spin-resonance (ESR) signal in GaAs has been studied. Excitation and quenching of the FR3 ESR is shown to result from the optically induced charge exchange between the FR3 center and the $\mathrm{As_{Ga}}$ antisite. The FR3 ESR can be persistently excited with photons in the range $1.0\ \mathrm{eV} < h\nu < 1.3\ \mathrm{eV}$. It is demonstrated that this behavior is a direct consequence of the metastability of the $\mathrm{As_{Ga}}$ antisite. Conclusive evidence for the acceptor nature of the FR3 center is presented, the corresponding level lying between $E_v + 0.03$ eV and $E_v + 0.52$ eV.

The near intrinsic resistivity of "undoped" semi-insulating liquid-encapsulated Czochralski-grown (LEC) pBN GaAs (pulled from a pyrolytic BN crucible) results from a close compensation between donors and acceptors which are present in the material in the 10^{15}–$10^{16}\ \mathrm{cm^{-3}}$ range. There is a general consensus[1–4] that the dominant donor species involved is the $\mathrm{As_{Ga}}$ antisite related EL2 mid-gap donor. The situation is less clear for the acceptors involved in compensation. One group has found[3,4] that their data for material grown from near-stoichiometric melts can be explained with carbon being the only significant acceptor. However, other authors find high concentrations of unidentified deep hole traps[5] and evidence for a boron related acceptor.[6] In addition several groups have reported a total of four new electron-spin-resonance (ESR) spectra[7–16] in undoped LEC GaAs corresponding to four different defects all of which are electrically active and have acceptorlike properties. All the new ESR spectra can have astonishingly high intensities indicative of high defect concentrations. It thus appears that carbon is not the only significant acceptor in many undoped semi-insulating (SI) LEC GaAs materials.

In this work we present the first detailed photo-ESR study of the so-called FR3 ESR signal in GaAs. This signal is omnipresent in semi-insulating LEC material[13–16] and is observed only after optical excitation. Its chemical origin is not well established but we have ascribed it tentatively to a trigonal $\mathrm{Ga_{As}}$-$\mathrm{B_{Ga}}$ antisite complex.[14] It is shown here that the photoexcitation of the FR3 signal is due to an indirect process in which a hole from the ionized $\mathrm{As_{Ga}}$ antisite, $\mathrm{As_{Ga}^{+}}$, is transferred to the diamagnetic compensated FR3 center via the valence band.

Conversely photoquenching of the FR3 signal also results from an indirect process in which an electron from the neutral $\mathrm{As_{Ga}^{0}}$ donor is transferred to the paramagnetic FR3 center via the conduction band. Metastable effects are observed for the FR3 signal in the sense that photoquenching is no longer possible once it has been excited with photons in the range $1.0\ \mathrm{eV} < h\nu < 1.3$ eV for long illumination times (> 10 min). It is concluded that this behavior is not a property of the FR3 center itself but is a direct consequence of the metastability of the $\mathrm{As_{Ga}}$ center. Finally we present conclusive evidence that the FR3 acceptor level lies between the shallow acceptor levels ($E_v + 0.03$ eV) and the iron acceptor level ($E_v + 0.52$ eV) i.e., that the FR3 center is a deep acceptor.

The ESR studies were performed at 35 GHz with the sample and cavity immersed in liquid He as described elsewhere.[14] Most measurements were done with a sample (No. 1 here) cut from a standard slice of undoped SI GaAs which was pulled from a pBN crucible by the LEC technique. From previous ESR studies at 9 GHz, samples from the same slice are known to contain about 1×10^{16} $\mathrm{cm^{-3}}$ $\mathrm{As_{Ga}^{+}}$ centers in the dark. Local vibrational mode and Raman measurements on these samples reveal carbon and zinc as residual acceptors each in a concentration of about $1\times10^{15}\ \mathrm{cm^{-3}}$ only (see sample No. 3 in Table I of Ref. 17). Two additional LEC pBN GaAs samples were measured to investigate the dark equilibrium charge state of the FR3 center when the Fermi level E_F lies below mid-gap. One sample (No. 2 here) was deliberately iron doped with E_F pinned to the iron acceptor level. The other sample (No. 3 here) was undoped but grown from a Ga-rich melt. It is lightly p-type and has a relatively high carbon concentration, $1.3\times10^{16}\ \mathrm{cm^{-3}}$ (see sample No. 1 in Table I of Ref. 17). The position of E_F with respect to the band edges is not well defined in this material. Optical absorption measurements[18] indicate spatial inhomogeneities and fluctuations of E_F between the shallow acceptors and the mid-gap position. What is of relevance here is that this sample contains regions where E_F is close to the shallow acceptor levels.

Figure 1 shows the ESR spectrum of sample No. 1 for three different orientations of the external magnetic field. Apart from weak signals in the $g \approx 2$ region ($H \approx 12.4$ kG) it displays only the lines of the FR3 signal. In semi-insulating material it is observed exclusively after optical excitation of the sample as has been noted previously[14] for a representative set of ten SI LEC materials. As can be seen from Fig. 2(b) the low-energy onset of photoexcitation is at 0.8 eV, i.e., near mid-gap. Two qualitatively different types of excitation occur depending on the illumination time and photon energy chosen. Short-time illumination (up to ≈ 1 min) excites the FR3 signal such that it can be subsequently quenched optically. This reversible excitation band is peaked at 0.9 eV [see Fig. 2(b)]. It is difficult to measure the reversible excitation for photon energies above 1.0 eV because of competing

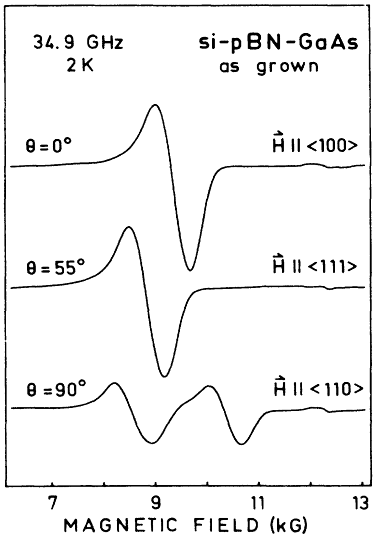

FIG. 1. ESR spectra of the FR3 signal in undoped SI GaAs following optical excitation.

quenching. Long-time illumination (longer than 10 min) in the range 1.0 eV $< h\nu <$ 1.3 eV leads to a persistent excitation of the FR3 signal, i.e., it can no longer be quenched with light in the range 0.6 eV to 1.5 eV. The signal can be removed only if the sample is warmed up. The persistent excitation band in Fig. 2(b) is centered around 1.18 eV. All data points in this figure were obtained under identical initial conditions (zero signal intensity before illumination). This is true also for the FR3 quenching curve in Fig. 2(a), where the initial conditions were set by applying 0.9 eV excitation light for 30 s. Subsequently the quenching light was applied for a period of 1.5 s. The quenching efficiency q plotted in Fig. 2(a) is therefore defined as $(I_{0.9\,\mathrm{eV}} - I_{h\nu})/I_{0.9\,\mathrm{eV}}$ where $I_{0.9\,\mathrm{eV}}$ and $I_{h\nu}$ are the FR3 signal intensities before and after quenching. It is difficult to measure the quenching efficiency below 1.0 eV since there is overlap with the 0.9 eV excitation band. However, it seems that the quenching curve extrapolates to a threshold near 0.8 eV.

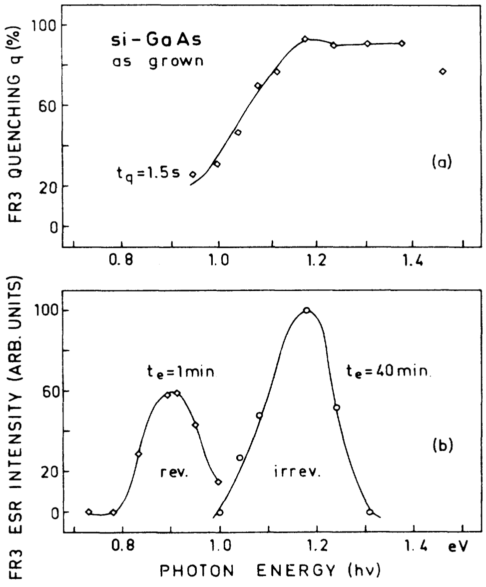

FIG. 2. Spectral dependencies of the FR3 ESR signal; (a) quenching and (b) enhancement in undoped semi-insulating GaAs.

Unusual FR3 signal transients occur for illuminations between 1.0 and 1.3 eV and this effect is shown in Fig. 3. When the signal is excited with 0.9 eV light it saturates after ≈ 20 s. Part of the signal decays if the excitation light is switched off. If the sample is then illuminated with light in the range 1.0 eV $< h\nu <$ 1.3 eV, e.g., with $h\nu = 1.18$ eV as in Fig. 3, the FR3 signal is quenched completely within a few seconds but reappears after a long illumination time. Now the signal no longer can be quenched optically. Thus we observe a nonmonotonic signal transient in which the ESR signal is first quenched and then reexcited by the same light.

All the results reported so far were obtained with the undoped SI sample No. 1. The iron-doped sample No. 2 also exhibits the FR3 signal but again only after optical excitation. However, the Ga-rich p-type material No. 3 shows the FR3 resonance already in the dark.

From this last observation we can draw an important conclusion: When the Fermi level E_F drops from the iron acceptor level to the shallow acceptor levels, the FR3 center changes its charge state from diamagnetic, compensated to paramagnetic, uncompensated. In other words, the FR3 center is associated with an acceptor level which lies between $E_v + 0.03$ eV and $E_v + 0.52$ eV. Thus FR3 is not a mid-gap defect despite the fact that the excitation threshold in Fig. 2(b) is near 0.8 eV.

According to the foregoing paragraph it is evident that the photoresponse of the FR3 signal does not result from photoionization processes at the FR3 center itself. Rather photoionization of a mid-gap defect and subsequent trapping of carriers at the FR3 center is involved. The obvious candidate for this mid-gap defect is the As$_{\mathrm{Ga}}$ antisite since sample No. 1 is known to contain $\approx 1\times10^{16}$ cm^{-3} As$_{\mathrm{Ga}}^{+}$ centers in the dark and at least as many As$_{\mathrm{Ga}}^{0}$ centers. It

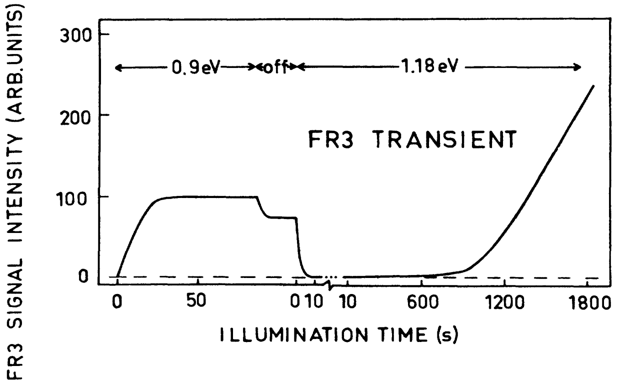

FIG. 3. The $h\nu = 1.18$ eV FR3 ESR signal transient in semi-insulating GaAs following excitation with $h\nu = 0.9$ eV.

is shown in the following that the photoresponse of the FR3 signal can be consistently traced back to the optical properties of $\mathrm{As}_{\mathrm{Ga}}$, which are well known from previous studies.[8,19]

Comparison of the FR3 excitation curve, Fig. 2(b), with the $\mathrm{As}_{\mathrm{Ga}}^{+}$ quenching curve, Fig. 2(b) in Ref. 19, reveals striking similarities. Both curves exhibit two bands peaked near 0.9 and 1.18 eV, respectively. Within the lower one photoinduced ESR intensity changes are optically reversible. Within the upper one such changes are optically irreversible. Thus the spectral shape of FR3 excitations reflects the quenching properties of $\mathrm{As}_{\mathrm{Ga}}^{+}$. This fact suggests the model sketched in Fig. 4, where σ_n^0 and σ_p^0 are the electron and hole photoionization cross sections of the $\mathrm{As}_{\mathrm{Ga}}$/EL2 mid-gap level and σ_*^0 is the cross section for the transition from the normal to the metastable state. In this figure we have neglected the second level of $\mathrm{As}_{\mathrm{Ga}}$/EL2 since its optical response appears to be very weak.[20] In semi-insulating material with the Fermi-level E_F at mid-gap both $\mathrm{As}_{\mathrm{Ga}}^{0}$ and $\mathrm{As}_{\mathrm{Ga}}^{+}$ coexist and an $\mathrm{As}_{\mathrm{Ga}}^{+}$ ESR signal is observable in the dark. On the other hand, no FR3 signal is observable in the dark since E_F is above the FR3 level and all centers are in the diamagnetic compensated state $\mathrm{FR3}_{\mathrm{dia}}$. Photoneutralization of $\mathrm{As}_{\mathrm{Ga}}^{+}$ with $h\nu > 0.75$ eV, process σ_p^0 in Fig. 4, now provides a source of free holes which when trapped at $\mathrm{FR3}_{\mathrm{dia}}$ excite the FR3 ESR signal. This mechanism explains the virtual identical curves for $\mathrm{As}_{\mathrm{Ga}}^{+}$ quenching and FR3 excitation.

Comparison of the FR3 quenching curve, Fig. 2(a), with the $\mathrm{As}_{\mathrm{Ga}}^{+}$ enhancement curve, Fig. 2(a) in Ref. 19, again reveals similarities in their spectral shapes. This suggests that free electrons created during photoionization of $\mathrm{As}_{\mathrm{Ga}}^{0}$, process σ_n^0 in Fig. 4, become trapped at the paramagnetic FR3 center and thus quench its ESR signal. Provided that the illumination times are short (< 10 s), excitation and quenching of the FR3 ESR can be repeated many times. On this time scale only the processes σ_n^0 and σ_p^0 in Fig. 4 are efficient. Thus the ESR intensity changes result simply from the reversible photoinduced charge exchange between the centers $\mathrm{As}_{\mathrm{Ga}}$ and FR3.

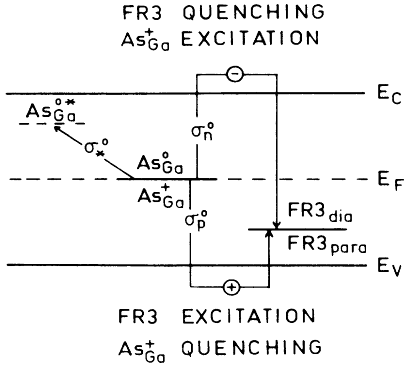

FIG. 4. Level scheme of $\mathrm{As}_{\mathrm{Ga}}$ and the FR3 center in semi-insulating GaAs. The second $\mathrm{As}_{\mathrm{Ga}}$ level at $E_c - 1.0$ eV has been omitted for clarity. The position of the FR3 level, $\mathrm{FR3}_{\mathrm{dia}}/\mathrm{FR3}_{\mathrm{para}}$, is uncertain between $E_v + 0.03$ eV and $E_v + 0.52$ eV. Photoneutralization of $\mathrm{As}_{\mathrm{Ga}}^{+}$, process σ_p^0, leads to the quenching of the $\mathrm{As}_{\mathrm{Ga}}^{+}$ ESR and the excitation of the FR3 ESR if the hole is trapped by $\mathrm{FR3}_{\mathrm{dia}}$. Process σ_n^0 transforms $\mathrm{As}_{\mathrm{Ga}}^{0}$ into $\mathrm{As}_{\mathrm{Ga}}^{+}$ and thus excites the $\mathrm{As}_{\mathrm{Ga}}^{+}$ ESR signal. If the electron in the conduction band is trapped by $\mathrm{FR3}_{\mathrm{para}}$, the FR3 ESR is quenched. In analogy to EL2, the transformation of $\mathrm{As}_{\mathrm{Ga}}^{0}$ into its metastable state $\mathrm{As}_{\mathrm{Ga}}^{0*}$, process σ_*^0, is responsible for the nonmonotonic $\mathrm{As}_{\mathrm{Ga}}^{+}$ and FR3 ESR transients.

The situation is more complicated when long time illumination within the 1.18 eV FR3 excitation band is applied as is obvious from the observation of nonmonotonic FR3 signal transients, see the $h\nu = 1.18$ eV transient in Fig. 3. We will now show that this effect as well as the persistent excitation of the FR3 resonance are a direct consequence of the metastability of the $\mathrm{As}_{\mathrm{Ga}}$/EL2 center. In doing so we make use of the fact that the EL2 mid-gap level and the $\mathrm{As}_{\mathrm{Ga}}^{+}$ ESR involve the same defect.[20]

The $h\nu = 1.18$ eV photocapacitance transient (see Fig. 1 in Ref. 21) and the ESR transient (see Fig. 1 in Ref. 19) of $\mathrm{As}_{\mathrm{Ga}}$/EL2 are nonmonotonic. These transients are fully equivalent since at each instant their magnitude is proportional to the $(\mathrm{As}_{\mathrm{Ga}}/\mathrm{EL2})^{+}$ concentration. The fast initial increase results from ionization of neutral $\mathrm{As}_{\mathrm{Ga}}$/EL2, process σ_n^0 in Fig. 4, and occurs at a rate that is proportional to $\sigma_n^0 + \sigma_p^0$.[21] The subsequent slowly decreasing part of the transients is related to the transformation of the $\mathrm{As}_{\mathrm{Ga}}$/EL2 center into its metastable state.[21] This transformation occurs only for the neutral center[22] and is characterized by the optical cross section σ_*^0 in Fig. 4. Within the decreasing part of the $\mathrm{As}_{\mathrm{Ga}}$/EL2 transients the simultaneous action of σ_*^0, σ_n^0, and σ_p^0 leads to a net photoneutralization of singly ionized $\mathrm{As}_{\mathrm{Ga}}$/EL2 centers at a rate[21] that is proportional to $\sigma_*^0 \sigma_p^0/(\sigma_n^0 + \sigma_p^0)$. After a long illumination time practically all centers have been transformed into the electrically and optically inactive metastable state $(\mathrm{As}_{\mathrm{Ga}}^{0}/\mathrm{EL2}^{0})^{*}$. The mid-gap level in Fig. 4 has ceased to exist and during the whole transformation process free holes have been produced in the valence band, their net concentration being equal to the maximum concentration of $(\mathrm{As}_{\mathrm{Ga}}/\mathrm{EL2})^{+}$ at the maximum of the transients.

It is now quite transparent what causes the nonmonotonic $h\nu = 1.18$ eV FR3 signal transient in Fig. 3 if one notes that it is complementary to the $(\mathrm{As}_{\mathrm{Ga}}/\mathrm{EL2})^{+}$ transients. Trapping of electrons, supplied by $\mathrm{As}_{\mathrm{Ga}}^{0}$, at the paramagnetic FR3 center rapidly quenches the FR3 ESR. The net production of free holes during persistent $(\mathrm{As}_{\mathrm{Ga}}/\mathrm{EL2})^{+}$ quenching which become trapped at the now diamagnetic FR3 center restores its ESR signal under prolonged illumination. It is also clear why the FR3 signal is persistently excited once $\mathrm{As}_{\mathrm{Ga}}^{+}$ has been persistently quenched. Since all $\mathrm{As}_{\mathrm{Ga}}$/EL2 centers have been transformed into metastable $(\mathrm{As}_{\mathrm{Ga}}^{0}/\mathrm{EL2}^{0})^{*}$, normal $(\mathrm{As}_{\mathrm{Ga}}/\mathrm{EL2})^{0}$ centers are no longer available as a source of electrons to be trapped at $\mathrm{FR3}_{\mathrm{para}}$. Thus the optical properties of the FR3 center reflect those of $\mathrm{As}_{\mathrm{Ga}}$/EL2.

The last statement must be slightly restricted. A glance at Fig. 2(a) shows that the FR3 quenching efficiency q indeed looks very similar to the $\sigma_n^0(h\nu)$ shape of $\mathrm{EL2}^0$ below $h\nu \approx 1.3$ eV. However, q does not increase steeply above 1.3 eV as $\sigma_n^0(h\nu)$ does. Instead q has dropped clearly for the highest energy data point. We interpret this as evidence that the FR3 center itself becomes optically active for sufficiently high photon energy. An electron from the compensated center FR3$_{\rm dia}$ can then be excited to the conduction band and can be trapped at $\mathrm{As}_{\mathrm{Ga}}^{+}$. This process, being just the reverse of the FR3 quenching process in Fig. 4, excites the FR3 ESR and thus reduces the quenching efficiency in Fig. 2(a).

One can suspect that electron excitation from compensated deep acceptors also occurs in junction photocapacitance measurements on EL2.[23] If such effects are not separated from real EL2 effects the interpretation of photocapacitance data may be obscured. In this connection it is interesting to note that the normal EL2 photocapacitance behavior is observed in Bridgman-grown GaAs (Ref. 23) where the concentration of the FR3 center is negligible.[14]

Photoneutralization of residual shallow acceptors, carbon and zinc, in semi-insulating GaAs has been recently observed in Raman scattering[24] and far-infrared absorption measurements[25] and $(\mathrm{As}_{\mathrm{Ga}}/\mathrm{EL2})^{+}$ was assumed to be the source of the holes bound to the shallow acceptors. The analogy with the results for the deep FR3 acceptor confirms this view.

We have already noted that the SI sample No. 1 studied here contains only $\approx 2\times10^{15}$ cm^{-3} shallow acceptors but $\approx 1\times10^{16}$ cm^{-3} $\mathrm{As}_{\mathrm{Ga}}^{+}$ centers in the dark. This underlines the fact that deeper acceptors must be present in typical LEC GaAs. The FR3 center is certainly one important candidate.

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