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Zero-phonon line associated with the midgap level *EL*2 in GaAs: Correlation with the $\mathrm{As_{Ga}}$ antisite defect

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The defect which brings about the zero-phonon line (ZPL) in the intracenter absorption spectra of the midgap level *EL*2 in GaAs (ZPL defect) is identified as the neutral charge state of the As antisite defect from the anticorrelative spectral dependency of the ZPL in optical absorption (OA) and the photo-EPR signal of $\mathrm{As_{Ga}^{+}}$. This result gives definite evidence that *EL*2 and the As antisite are the same defect. The ZPL and its phonon replicas were also observed in the photocurrent (PC) spectra. The spectral dependency of the ZPL enhancement and quenching in PC exhibited an anticorrelative change with those in OA. The origin of this anticorrelative change was due to the contribution of carriers trapped in the shallow levels to PC.

The dominant deep donor level in GaAs crystals, grown from the melt or from the vapor phase, is the electron trap *EL*2. It is the center which plays an important role in the compensation mechanism of undoped semi-insulating GaAs utilized for integrated circuits. The questions as to whether or not and how *EL*2 is related to the As antisite defect, $\mathrm{As_{Ga}}$, have generated a great deal of interest. However, in spite of extensive investigations involving a wide variety of measurements, the identity has been a matter of controversy.

The first experimental evidence of the existence of As antisite defects in melt-grown $\mathrm{As_{Ga}}$ was given a few years ago by submillimeter wavelength electron-paramagnetic-resonance (EPR) experiments.[1] After that, the $\mathrm{As_{Ga}}$ antisite EPR signals were observed in neutron-irradiated,[2] electron-irradiated,[3] plastically deformed[4] samples, and in as-grown GaAs (Ref. 5) by a conventional *X*- or *K*-band EPR spectrometer. The strong argument for the association of the $\mathrm{As_{Ga}}$ antisite defect with the *EL*2 defect has been given recently by photo-EPR measurements.[6,7] It has been shown that the *EL*2 defect and the $\mathrm{As_{Ga}}$ antisite defect have practically identical optical and photoelectronic properties; the result is that the *EL*2 defect can be identified with the $\mathrm{As_{Ga}}$. However, this contrasts with conclusions based on measurements of the $\mathrm{As_{Ga}}$-induced magnetic circular dichroism (MCD), according to which *EL*2 is most likely not the $\mathrm{As_{Ga}}$ antisite defect.[8,9] The main intention of this Rapid Communication is to give an answer to this conflict.

Recently, it has been observed that the optical absorption attributed to *EL*2 contains a band of intracenter transitions with a zero-phonon line (ZPL) and transverse-acoustic-phonon replicas.[10] This ZPL has been found to split under uniaxial stress depending on the direction of the stress and the light propagation.[11] The static crystal-field theory permits an interpretation of the observed splitting to be $A_1 \rightarrow T_2$ transitions. The lack of measurable magnetic field effects on the ZPL was taken to imply that the transitions take place between ground and excited states which are spin singlet. Therefore, these states were identified as $^1A_1$ and $^1T_2$, respectively. This result was in excellent agreement with the theoretical prediction of the As antisite levels, i.e., the $^1A_1$ ground state in the energy gap, and the excited $^1T_2$ state resonant with the conduction band.[12,13]

However, there has been no direct evidence, to our knowledge, on the correlation between the ZPL and the As antisite defect $\mathrm{As_{Ga}}$. In this Rapid Communication, we report on new experimental results on the identification of the ZPL defect as the neutral charge state of As antisite defect ($\mathrm{As_{Ga}^{0}}$) and therefore we can more correctly identify the *EL*2 defect as the As antisite. Also, it is shown that the ZPL is observed in PC spectra and exhibits opposite enhancement and quenching characteristics from the ZPL observed in OA.

GaAs crystals used in this study were grown by liquid encapsulated Czochralski (LEC) technique,[14] and cut into $3\times3\times20\text{-mm}^3$ samples. For the measurements of the ZPL, the sample was placed in a cold finger of a variable-temperature (8–300 K) optical cryostat. The measurements of the OA of the sample were performed along the 20-mm-long direction. At the same time, photocurrent measurements were carried out on the same sample with indium electrodes made on parts of the side walls of the sample. The ZPL in OA was detected by scanning the chopped monochromatic light (monitoring light) around the position of the ZPL at 1.04 eV and using lock-in detection method.

In Fig. 1, we present the optical absorption and the photocurrent spectrum around the ZPL obtained at 8.5 K on the same semi-insulating GaAs sample. The ZPL and its two phonon replicas are shown in both the spectra. The ZPL defect can be assigned to one unique center because the half width of the ZPL is less than 1 meV. Up to five (sometimes six) replicas could be observed in the spectra. All of them appear at similar intervals of about 11 meV.

In order to investigate the spectral dependency of the ZPL enhancement and quenching, the sample was simultaneously illuminated by a second light which changes the electron occupancy of the ZPL defect. The intensity of the second light was about five times stronger than that of the monitoring light, but the light intensities were kept at a level sufficiently low to prevent transition of the normal *EL*2 state to its metastable state.[15] This was judged by the comparison of consecutive absorption spectra.

The intensity of the ZPL observed in OA as a function of the wavelength of the second light is shown in Fig. 2(a). The dashed line indicates the magnitude of the ZPL without the light illumination of the second light. This signal level shows the ZPL intensity obtained immediately after illuminating the monitoring light on the sample so as not to change the population in the level associated with the ZPL defects from that in the dark. The ZPL in OA is enhanced

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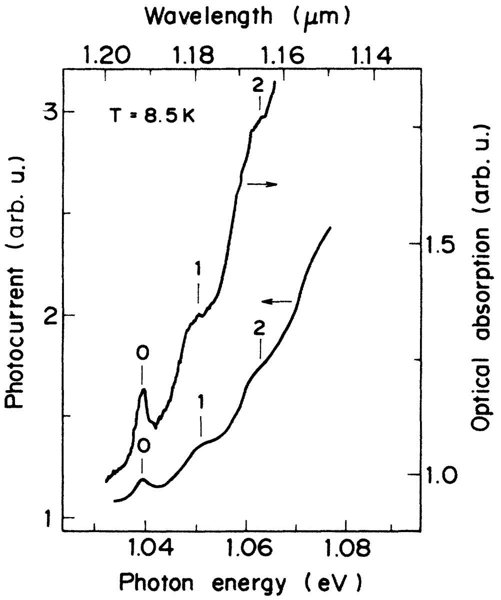

FIG. 1. Fine structures observed in optical absorption and photocurrent spectra which show ZPL and its phonon replicas.

by the second light illumination with wavelengths ranging from 1.1–1.6 μm and quenched for the range of 1.1 μm to the absorption edge (~ 0.82 μm).

The photo-EPR measurements with the same sample as used in the ZPL measurements were carried out, prior to the OA and PC measurements, without the indium electrodes, with a JEOL *X*-band spectrometer at 9.15 GHz, using the 100-KHz field modulation. The sample was immersed in liquid helium in a quartz Dewar and then placed into the microwave cavity. The sample was illuminated with monochromatic light through a hole of the microwave cavity.

The magnitude of the $\mathrm{As}_{\mathrm{Ga}}^{+}$ EPR signal as a function of the light wavelength is shown in Fig. 2(b). The signal level before the light illumination is indicated by a dashed line. The $\mathrm{As}_{\mathrm{Ga}}^{+}$ signal is changed by the light illumination. The enhancement of the signal is observed in the wavelengths ranging from the absorption edge to 1.1 μm and quenched in the region of 1.1–1.6 μm. These photoresponses of the $\mathrm{As}_{\mathrm{Ga}}^{+}$ signal are successfully interpreted by assuming that the As antisite defect has photoionization cross sections identical to those of $EL2$ and, therefore, the $\mathrm{As}_{\mathrm{Ga}}$ antisite and $EL2$ are the same defect.[6,7] According to this assumption, the photoenhancement of the $\mathrm{As}_{\mathrm{Ga}}^{+}$ signal occurs by photoionization of the neutral $\mathrm{As}_{\mathrm{Ga}}^{0}$ center into the singly ionized center $\mathrm{As}_{\mathrm{Ga}}^{+}$ (EPR sensitive charge state). Similarly, the photoquenching of the $\mathrm{As}_{\mathrm{Ga}}^{+}$ EPR signal is caused by the conversion of the singly ionized $\mathrm{As}_{\mathrm{Ga}}^{+}$ center into the neutral charge state $\mathrm{As}_{\mathrm{Ga}}^{0}$ (EPR nonsensitive charge state). The enhancement of the $\mathrm{As}_{\mathrm{Ga}}^{+}$ signal in the range of the absorption edge to 1.1 μm is due to the dominant ionization process of $EL2$ (namely $\mathrm{As}_{\mathrm{Ga}}^{0}$), because the photoionization cross section for electrons from $EL2$ to the conduction band, σ_n^0, becomes predominant compared with that for holes from $EL2$ to the valence band, σ_p^0, for this wavelength region.[7] The quenching of the EPR signal around 1.3 μm is due to the electron filling in the $EL2$ centers by the electron transition from the valence band to $EL2$.

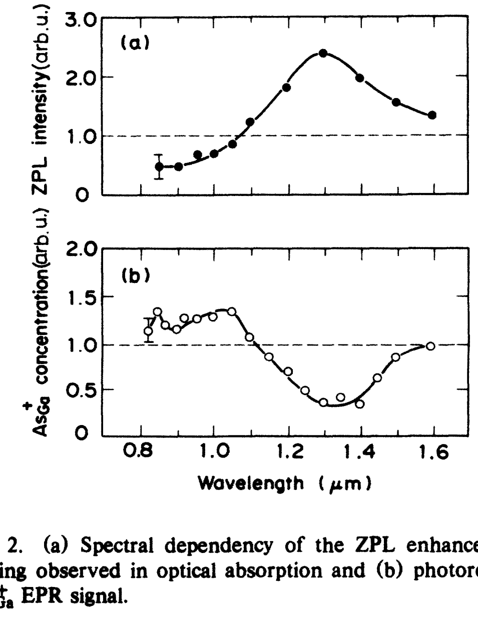

FIG. 2. (a) Spectral dependency of the ZPL enhancement and quenching observed in optical absorption and (b) photoresponse of the $\mathrm{As}_{\mathrm{Ga}}^{+}$ EPR signal.

As we compare the photoresponse of the ZPL in OA [Fig. 2(a)] with that of the $\mathrm{As}_{\mathrm{Ga}}^{+}$ EPR signal [Fig. 2(b)], a clear complementary spectral change is recognized between them. Similar complementary spectral changes between the ZPL intensity and the $\mathrm{As}_{\mathrm{Ga}}^{+}$ EPR signal were observed for several samples measured so far. This behavior can be well understood by considering that only the singly ionized charge state of the As antisite ($\mathrm{As}_{\mathrm{Ga}}^{+}$) is EPR sensitive, whereas only its neutral charge state ($\mathrm{As}_{\mathrm{Ga}}^{0}$) can contribute in the intracenter transition. Consequently, the complementary spectral change of the $\mathrm{As}_{\mathrm{Ga}}^{+}$ signal and the ZPL observed in OA gives definite evidence for the direct identification of the ZPL defect as the neutral charge state of $\mathrm{As}_{\mathrm{Ga}}$ ($\mathrm{As}_{\mathrm{Ga}}^{0}$).

The identification of $EL2$ as being the $\mathrm{As}_{\mathrm{Ga}}$ antisite defect is in conflict with the conclusions based on MCD measurements by Meyer and co-workers.[8,9] They observed (a) that the concentration of $\mathrm{As}_{\mathrm{Ga}}$ determined from EPR signal intensity is different from (about two times larger than) the concentration of $EL2$ determined from the intracenter absorption,[8] and (b) that the $EL2$ absorption can be quenched completely, while the MCD signal of $\mathrm{As}_{\mathrm{Ga}}$ remains practically unchanged.[9] From these experimental results, they questioned the association of $EL2$ with the $\mathrm{As}_{\mathrm{Ga}}$ antisite defect. Arguments (a) and (b) could be used decisively against the association of $EL2$ with $\mathrm{As}_{\mathrm{Ga}}$, if it were not for the fact that the two techniques, i.e., optical absorption and magnetic resonance techniques (EPR or MCD), probe different charge states. Magnetic resonance techniques detect the singly ionized state $\mathrm{As}_{\mathrm{Ga}}^{+}$, which is paramagnetic and not the neutral state $\mathrm{As}_{\mathrm{Ga}}^{0}$. This ionized state does not directly participate in the the transition to the metastable state. It is therefore apparent that the photoquenching characteristics of EPR and MCD signals originating from $\mathrm{As}_{\mathrm{Ga}}^{+}$ must be different from the photoquenching characteristics of $EL2$ in which a neutral $\mathrm{As}_{\mathrm{Ga}}$ defect is involved. Therefore, the conclusion based on the experimental results of MCD, that the $EL2$ is not related to $\mathrm{As}_{\mathrm{Ga}}$, appears very doubtful.[16,17] In fact, in usual photo-EPR experiments, apparently different persistent quenching behavior was observed for the $\mathrm{As}_{\mathrm{Ga}}^{+}$ EPR signal and the microwave photoconductivity intensity which exhibits quenching characteristics similar to optical absorption and photocapacitance.[18] Furthermore, the integrated MCD absorption curve of $\mathrm{As_{Ga}}$ is remarkably similar to the optical-hole ionization cross section, σ_p^0, of the $EL2$ level, as noted by Kaufmann.[16]

After removal of the excitation light, the $\mathrm{As_{Ga}^+}$ EPR signal persists for a long time. This indicates that the electrons and/or holes excited from the $\mathrm{As_{Ga}}$ ($EL2$) centers to the conduction and the valence band are captured on other traps than $\mathrm{As_{Ga}}$ ($EL2$) centers. The results of thermal-stimulated-curent (TSC) measurements discussed below confirm this view.

The TSC measurements were carried out with the same sample and electrodes as used in the ZPL measurements in PC. Deep-level identification in semi-insulating GaAs is often carried out using TSC measurements.[19,20] A typical experiment consists of first filling the trap states by shining intrinsic light (having higher energies than the band-gap energy) to a cooled sample. Then, as the sample is warmed, the charges are released and swept away by the applied external electric field. The resulting current contains information on trap states in the gap. In our TSC measurements, the sample was cooled at 8.5 K in the dark and then illuminated by extrinsic light (having lower energies than the band-gap energy) to change the occupation of $EL2$ centers. Band-to-band transition is inhibited for the extrinsic light illumination and the electron transitions from the valence band to $EL2$ and from $EL2$ to the conduction band are allowed. After illumination the sample was kept for 1 min in the dark prior to increasing the temperature. Two insets in Fig. 3 show examples of the TSC spectra as a function of temperature for the excitation lights with the wavelengths 0.9 and 1.2 μm, respectively. The heating rate could not be kept constant and varied from ~0.5–0.2 K/sec in the measurements.

Figure 3 shows the peak current of dominant TSC peaks as a function of the excitation wavelength. The peak intensity is not necessarily a measure for the carrier density, but at least the change in the peak intensity gives a measure for the rough estimation of the change in the carrier density. Two dominant n-type TSC peaks (N-1 and N-2) are observed for the excitation wavelengths ranging from the absorption edge to 1.2 μm, while only one dominant p-type TSC peak (P-1) appears for the excitation wavelengths longer than 1.2 μm. The n-type TSC peaks appear when the $\mathrm{As_{Ga}^+}$ EPR signal is enhanced, whereas the p-type TSC peak appears when the $\mathrm{As_{Ga}^+}$ EPR signal is quenched [see Fig. 2(b)]. Therefore, it is reasonable to consider that the n-type TSC peaks are due to the electron excitation from the $\mathrm{As_{Ga}^0}$ centers to the conduction band (σ_n^0), followed by the trapping of the electrons by the ionized shallow donor levels, and the p-type TSC peak is due to the electron transfer from the valence band to the $\mathrm{As_{Ga}^+}$ centers (σ_p^0) followed by the trapping of holes by the ionized acceptor level. The total density of trap states (or accumulated carrier concentrations trapped by the shallow levels) should be the same order as the concentration of the $\mathrm{As_{Ga}}$ (namely, $EL2$) centers, because the large enhancement (~50–500%) of the EPR signal due to the light illumination persists for a long time after cessation of the light illumination. The type of conduction in the TSC peaks was determined by photo-Hall measurements. The conversion of the conduction type in semi-insulating GaAs by the persistent photoquenching[15] has been reported by Lin, Omel'yanovski, and Bube[21] and Peka, Brodovoi, Mishova, and Mirets.[22] However, to our knowledge, there is no report on the conversion of the conduction type in semi-insulating GaAs caused by changing the excitation wavelengths without the persistent photoquenching.

The spectral dependency of the ZPL enhancement and quenching observed in PC is shown in Fig. 4. For the comparison, the spectral dependency of ZPL in OA is also shown. The ZPL in PC is strongly enhanced in the range of the absorption edge to 1.1 μm, in which the ZPL in OA is quenched, and quenched in the range of 1.1–1.6 μm, whereas the ZPL in OA is enhanced in this region. The spectral dependencies of the ZPL enhancement and quenching in PC reveal the anticorrelative change with those in OA. This fact strongly indicates that the different mechanisms contribute in both PC and OA processes. Comparing the photoresponse of the ZPL in PC with the n-type TSC peaks, we can clearly see that there is good correlation between them. Better linear correlation was recognized

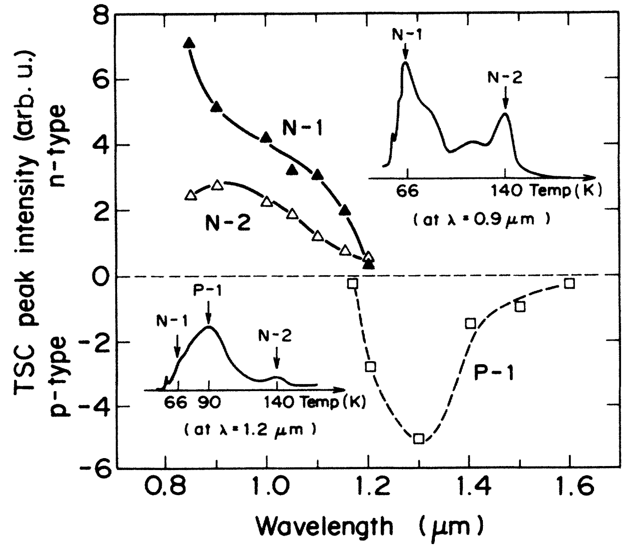

FIG. 3. Dominant TSC peak intensities as a function of the excitation wavelength.

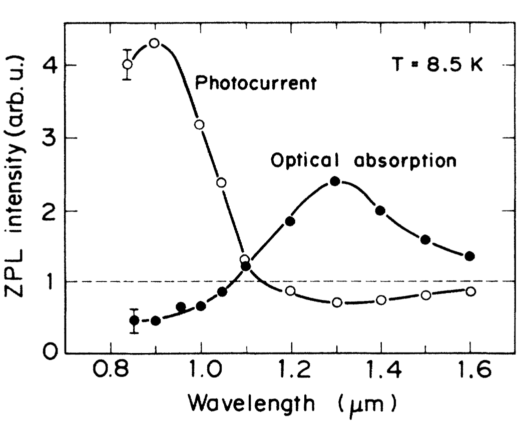

FIG. 4. Spectral dependency of the ZPL enhancement and quenching observed in the photocurrent. For comparison, the spectral dependency of the ZPL observed in optical absorption [shown in Fig. 2(a)] is also shown.

between the integral of the TSC spectra (accumulated carrier density trapped on the defects) and the ZPL intensity in PC. We have also observed, in the course of the persistent photocurrent quenching, that the number of electrons trapped in the n-type shallow levels is quenched in a manner nearly identical to that of the photocurrent quenching behavior. These experimental results suggest that the electrons trapped on the shallow levels observed in the TSC measurements must significantly contriute to the ZPL in PC. Furthermore, a well correlated spectral change of the p-type TSC peak and a new EPR signal, which is called "singlet" in Ref. 7, was also observed. The details will be reported elsewhere.

We have proposed an Auger-type process[23] as a mechanism of the ZPL to be observed in PC, in which the released energy in the intracenter transition of *EL*2 (i.e., the decaying process from the excited state to the ground state of the *EL*2), may lead to ionization of electrons trapped in the shallow levels exhibiting the TSC signals, and thus lead to the generation of free carriers in the conduction band. According to this assumption, the intensity of the ZPL in PC is a function of the number of electrons trapped in the shallow levels and the number of the neutral charge state of $\mathrm{As}_{\mathrm{Ga}}$ ($\mathrm{As}_{\mathrm{Ga}}^0$). We have also observed that the ZPL intensity in PC strongly depends on the scanning direction of the wavelength and is always somewhat enhanced for the scanning from high to low photon energies. This experimental result also indicates that the Auger-type process accompanied by the intracenter transition in *EL*2 much more likely contributes to create free carriers, because the scanning from high to low photon energies first fills the shallow ionized donor levels as observed in the TSC measurements (Fig. 4), and then the intracenter transition induces free carriers in the conduction band from the filled shallow levels by the Auger-type process.

However, alternative mechanisms of the ZPL to be observed in the PC spectrum cannot be discarded. One of the possibilities is the increase of the electron mobility due to filling of the ionized shallow traps by photogenerated carriers from *EL*2, together with the decaying process of the electrons from the excited state of the *EL*2 to the conduction band, because the excited $^1T_2$ state of the $\mathrm{As}_{\mathrm{Ga}}^0$ center is resonant with the conduction band.[12,13] Further studies are necessary to exactly identify its mechanism, but the distinct contribution of the electrons trapped by the shallow donor levels to PC is obvious.

In summary, the ZPL defect associated with the *EL*2 intracenter transition was identified as the neutral charge state of the As antisite defect ($\mathrm{As}_{\mathrm{Ga}}^0$) from the anticorrelative spectral dependency between the ZPL's in OA and the photo-EPR signal of $\mathrm{As}_{\mathrm{Ga}}^+$. Also, this result gives definite evidence that *EL*2 and the As antisite are the same defect. Furthermore, the origin of the anticorrelative change of the photoresponses for the ZPL's observed in OA and PC was due to the contribution of the shallow levels to the photocurrent.

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