Photoenhancement and photoquenching of the 0.68-eV *EL*2 photoluminescence emission in GaAs grown by molecular-beam epitaxy at low temperatures

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We report the photoenhancement and photoquenching of the 0.68-eV *EL*2 photoluminescence emission in low-temperature GaAs grown at 200–350 °C. *EL*2 exists in both a quenchable and unquenchable configuration. For the layer grown at 200 °C, *EL*2 is exclusively in the unquenchable configuration. The concentration of *EL*2 in the unquenchable configuration decreases with increasing growth temperature. The quenchable and unquenchable configurations can be explained by a model of the isolated As_{Ga} under relaxed and strained conditions, respectively. The stress present in low-temperature layers is responsible for the unrelaxed condition and consequently for the lack of quenchability. The photoenhancement is attributed to the hole photoionization of $(As_{Ga})^+$ and to the presence of a high concentration of the compensating V_{Ga}.

Molecular-beam epitaxy (MBE) GaAs is normally grown at substrate temperature (T_G) between 580 and 600 °C. However, low-temperature (LT) GaAs grown at $T_G < 500$ °C has recently attracted much attention because of the unique material properties and excellent device performance. The most outstanding characteristic of LT MBE GaAs is its nonstoichiometry[1] with up to 1 at. % excess As for the material grown at 200 °C. The excess As is incorporated as about 10^{20} cm^{-3} As_{Ga} centers in 200 °C as-grown materials and primarily as $\sim 10^{17}$ cm^{-3} As precipitates[2] after annealing such material for 10 min at 600 °C. Thus, assessment of LT materials must address the excess As and the associated intrinsic defects: As_{Ga}, V_{Ga}, As_i, and associated pair defects. The As_{Ga} center is known as *EL*2 itself[3,4] or as a component[5] of *EL*2 as a defect complex. Perhaps the most prominent property of *EL*2 in the usual GaAs is its photoinduced metastability: at low temperatures, illumination with light at energies of 0.8–1.5 eV makes the *EL*2 level disappear, and the defect is transformed from its normal state *EL*2-*N* to the metastable state *EL*2-*M*. The metastable state is electrically as well as optically inactive[6] in the ambient condition. The transformation from the metastable to normal state is achieved by (i) a pure thermal process due to heating the sample above 140 or above 50 K, respectively,[7,8] for semi-insulating and *n*-type materials, and (ii) optically assisted thermal recovery[9] above 60 K as well as pure optical recovery[10] under the ambient condition, and the pure optical recovery caused by the capture[11] of a photocreated hole on the negatively charged state $(EL2\text{-}M)^-$ under hydrostatic pressure.

The quenching due to metastability of *EL*2, as observed in the usual GaAs, was also reported[12–15] for LT GaAs. Quenchable and unquenchable configurations of *EL*2 are found for the LT layer.[12,13] The transition to the metastable state takes place in a much broader energy range, and the maximum efficiency is substantially shifted[13,14] to a higher energy of 1.4 eV for a 220 °C as-grown layer[14] compared to the value of 1.18 eV in the usual GaAs. The term "usual GaAs" denotes material grown by the liquid-encapsulated Czochralski (LEC) or Bridgman methods. However, thermal recovery of the quenched configuration of *EL*2 occurs at ~130 K for LT materials,[15] which is the typical recovery temperature for the usual GaAs. Current measurements[15] on LT layers grown at 200 °C and annealed at 550 °C showed a larger reduction of the current after light illumination ($h\nu \lesssim 1.12$ eV) compared to that of as-grown or annealed layers at $\lesssim 350$ °C.

In the present work, we report the metastability associated with 0.68-eV *EL*2 photoluminescence (PL) emission present in LT MBE GaAs grown at 200, 230, 250, 300, and 350 °C. The 0.68-eV PL band present in the usual GaAs quenches[16] over the energy of 0.8–1.5 eV. For the present LT GaAs, we find both quenching and enhancement of the 0.68-eV *EL*2 PL intensity, which depends on the growth temperature of the LT layers.

The MBE layers were grown in a Varian Gen-II system under As_4 using a nonindium-bonded substrate holder. Growth temperatures were 200, 230, 250, 300, 350, and 400 °C and were determined by a noncontacting thermocouple. The thickness of the layers was ~2 μm. Details of the growth are explained elsewhere.[17] PL measurements were made using a variable-temperature Janis optical Dewar. The 5145-Å line of an Ar-ion laser was used as an excitation source with an intensity of 10^{-1}–10 W/cm^2. PL spectra were obtained with Spex monochromators of focal length $f = 0.5$ and 1.29 m and were detected with a C31034 photomultiplier tube, a liquid-nitrogen-cooled Ge, and a liquid-nitrogen-cooled InAs detector. The light from a focal length $f=\frac{1}{4}$ m Bausch-Lomb monochromator connected to a 40-W iodine-tungsten lamp was used for transforming the $EL2$-N to the $EL2$-M state at 2 K. Exposure time was 30 min for each wavelength. Thermal recovery from the $EL2$-M state to the $EL2$-N state was affected by heating the sample at 200 °C for 20 min. The same flux of 4×10^{16} photon/cm^2 sec was used for the entire energy region of 0.8–1.5 eV. Heat treatments were performed at 300–600 °C for 10 min in a conventional furnace purged with flowing N_2. A GaAs wafer was placed on top of the LT layer during heat treatments in order to inhibit As loss. Structural characterization of the layers was performed using a double-crystal x-ray diffractometer, mounted onto a water-cooled generator equipped with a Cu target. Nondispersive, surface-symmetric rocking curves were measured using the (004) reflection.

The type of deep-center PL emission in LT GaAs depends mostly on the growth temperature, but also on the As_4/Ga beam equivalent pressure (BEP) ratio. The as-grown 200 °C grown layers show two PL bands at approximately 0.68 and 1.1 eV. The 0.68- and 1.1-eV emissions are more prominent in wafers grown with BEP ratios of 16 and 26, respectively. The 230, 250, and 300 °C grown layers show only one dominant PL emission at 0.68 eV. With increasing growth temperature the 0.68- and 1.1-eV bands are quenched. The 400 °C grown layers show only one emission, peaking approximately at 0.8 eV. However, the 350 °C grown layers generally show only one type of emission, either at 0.68 or 0.8 eV. The 0.8-eV emission is attributed to the associated pair center of As_i-V_{Ga}. Details of the assignment will be published elsewhere.[18] The 0.68-eV emission can be attributed to a transition from the $(EL2\text{-}N)^0$ state to the valence band based on the results of previous work[19–21] with GaAs grown by the LEC or Bridgman methods. Samples having only the 0.68-eV $EL2$ emission present in the LT layers grown at 200, 230, 250, 300, and 350 °C were chosen for the present study of metastability. Figure 1 shows the $EL2$ PL spectra obtained at 2 K from the layers grown at 200 and 350 °C. The PL spectra are identical except for a larger value (147 meV) of full width at half maximum (FWHM) for the 200 °C grown layer compared to that of the 350 °C grown layer (110 meV). The values of FWHM for 230, 250, and 300 °C grown layers lie between those of 200 and 350 °C grown layers. The increasing FWHM with decrease of growth temperature can be attributed to the larger inherent stress at lower temperatures. In fact, the FWHM of the 350 °C grown layer is the same as that[19–21] of LEC semi-insulating GaAs.

Figure 2(a) shows the metastability efficiency M vs photon energy E used to transform $EL2$-N to the $EL2$-M configuration for layers grown at $T_G=300$ and 350 °C. M is defined as $(I_N-I_M)/I_N$, where I_N and I_M are the PL intensity of the 0.68-eV $EL2$ emission before and after illuminating with a metastability-inducing photon. Positive and negative signs of M indicate quenching and enhancement of the $EL2$ emission intensity, respectively. The M-vs-E curves for the two growth temperatures show the same shape over all the quenching wavelength.

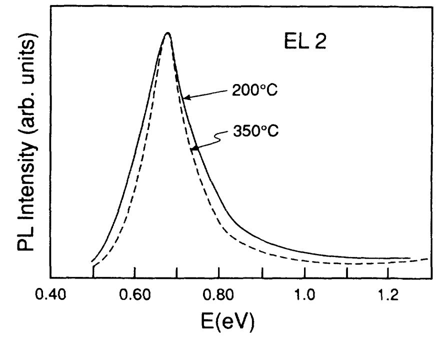

FIG. 1. Photoluminescence spectra of the 0.68-eV $EL2$ emission present in the layers grown at 200 and 350 °C.

The maximum of the quenching efficiency is approximately at 1.18 eV, which is the same as that usually observed[16] for LEC GaAs. Also, the entire quenching energy region is almost the same as that observed in LEC GaAs. Figure 2(b) shows the M-vs-E relation for 250 and 200 °C grown layers. For the 250 °C grown layer, photoquenching and photoenhancement occur, respectively, for photon energies of ~1.0–1.35 and ~1.35–1.55 eV. The M-vs-E relation for the 230 °C grown layer shows almost the same inverted S shape as for the 250 °C grown layer. However, the maximum and minimum values of

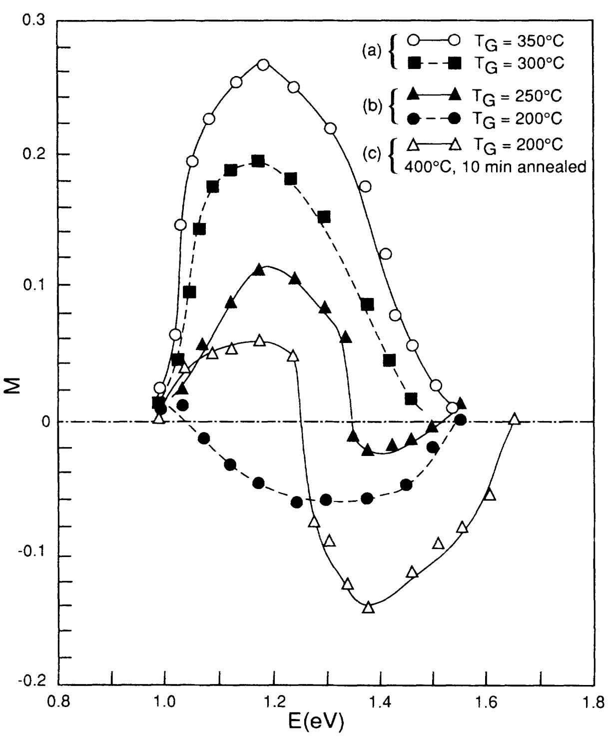

FIG. 2. (a) M-vs-E relation for the layers grown at 300 and 350 °C. M is defined as (I_N-I_M/I_N), where I_N and I_M are the PL intensity of the 0.68-eV $EL2$ emission before and after illuminating with a metastability-inducing photon. E is the energy of the photon. (b) M-vs-E relation for the layers grown at 200 and 250 °C. (c) M-vs-E relation for the layer grown at 200 °C and heat treated for 10 min at 400 °C.

M are 0.07 at 1.18 eV and -0.05 at 1.38 eV, respectively. For the 200 °C grown layer, only photoenhancement occurs. Figure 3 shows the UQ-vs-T_G relation for 200, 230, 250, 300, and 350 °C grown layers, where the parameter UQ is defined as $UQ=1-M$. $UQ<1$ and $UQ>1$ thus indicate quenching and enhancement, respectively. Even though the amount of the quenching and enhancement depends on the intensity of the transforming photon and duration of the illumination time, Fig. 3 clearly shows that the unquenching configuration of $EL2$ increases with decrease of growth temperature, and that all the $EL2$ is in an unquenchable configuration for the 200 °C grown layer. The lack of quenchability will be explained below. The enhancement will be discussed later.

The lattice constant of the LT layers has been determined in order to understand the lack of quenchability in terms of the inherent stress present in the LT layers due to the lattice expansion. The determined values of $[\Delta a/a_0]^{\perp}$ are 9.5×10^{-4} and 3.9×10^{-4}, respectively, for 200 and 250 °C grown layers, where a_0 is the lattice constant of substrate material. These values are similar to those determined by Kaminska and Weber,[13] but smaller than those measured by Wie *et al.*[22] This discrepancy may be from uncertainties of determining the growth temperature. We do not find any significant change of the lattice constant for the layers grown at 300 and 350 °C. The built-in biaxial stress due to the lattice expansion present in the LT layers is determined by using the obtained values of $[\Delta a/a_0]^{\perp}$ and the relation, $\epsilon_{zz}=2S_{12}X$, between the strain perpendicular to the growth layer and stress X in the layer. Here S_{12} is the elastic compliance constant of GaAs. The determined values of X are 1.3 and 0.53 kbar, respectively, for 200 and 250 °C grown layers. These values are not enough to cause the acceptorlike level[11,23] of the $EL2$-M configuration to enter into the band gap. Without a larger pressure than 3 kbar, the acceptorlike level is resonant with the conduction band and therefore unoccupied. The presence of the acceptorlike level inside the band gap is a key configuration for the photorecovery from the metastable to the normal configuration.[11,23] We do not consider that any other recovery processes described earlier[7-11,23] can explain the present unquenchable configuration.

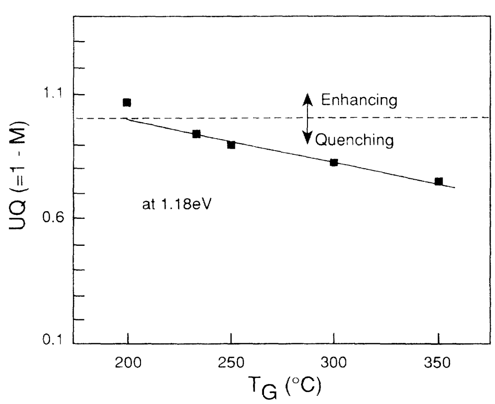

FIG. 3. UQ $(=1-M)$-vs-T_G relation, where T_G is the growth temperature of the layer.

We invoke that (a) $EL2$ exists in both quenchable and unquenchable configurations depending on the situation, (b) the increase of unquenchable $EL2$ with decrease of growth temperature is due to the increase of stress due to the lattice expansion, and (c) the quenchable and unquenchable configurations are due to the isolated As_{Ga} under relaxed and strained conditions, respectively. Jost *et al.*[24] observed only the presence of the unquenchable configuration of $EL2$ for a LT GaAs layer grown at 200 °C using electron spin resonance. However, Manasreh *et al.*[12] reported the presence of both quenchable and unquenchable configurations of $EL2$ from a 20-μm-thick LT layer grown at 200 °C, using near-infrared absorption. The unquenchable configuration of $EL2$ can also be found from $EL2$ created by electron,[25] high-energy proton,[26] and neutron[27] irradiation on LEC or Bridgman-grown GaAs. The unquenchable $EL2$ configuration has been attributed to isolated As_{Ga} (Refs. 25–27) by some workers. From Fig. 3, we know that all the $EL2$ is in the unquenchable configuration for the 200 °C grown LT layer and that the unquenchable configuration increases with the decrease of growth temperature. However, the present observation of the unquenchable configuration for the 200 °C grown LT layer is in direct contrast with the work[12] by Manasreh *et al.*, where the 200 °C layer shows both quenchable and unquenchable configurations of $EL2$. This can be explained easily with the present model. Manasreh *et al.*[12] used a rather thicker layer of $\sim$20 μm compared to the thickness of 2 μm for the present experiment. It is known[28] that LT layers grown near 200 °C are generally of very high crystal quality, possibly up to $\sim$3 μm thickness and become polycrystalline beyond $\sim$3 μm. The polycrystalline layer can be considered as the built-in stress being relaxed. So, the thick layer has relaxed and strained portions of the layer, which can be attributable to the quenchable and unquenchable configurations of $EL2$ for the thicker layer. Also, the x-ray diffraction measurements show that the stress due to the biaxial compression increases with the decrease of growth temperature. Note that we attribute the increase of the unquenchable configuration to the increase of stress. Thus, the quenchable configuration is dominant in relatively stress-free materials such as LEC or Bridgman-grown GaAs. Also, we believe that the unquenchable $EL2$ configuration present in electron-, high-energy proton-, and neutron-irradiated samples[25-27] comes from the stress built during the irradiation. From Fig. 3, we can also expect that LT GaAs grown below 200 °C does not show any quenching for the 0.68-eV PL band. One support for our model comes from Fig. 2(c), where the M-vs-E relation is depicted over an energy range of $\sim$1.0–1.6 eV for a 200 °C grown layer, which was heat treated at 400 °C for 10 min. The M-vs-E relation differs from that of the as-grown 200 °C layer which is shown in Fig. 2(b), but is similar to that of the 250 °C grown layer. Heat treatment causes a decrease of the lattice constant of a LT layer, and the lattice constant reaches[22] the usual value after heat treating at $\sim$600 °C. In fact, the double-crystal x-ray diffraction measurement gives $[\Delta a/a_0]^{\perp} = 5.7\times10^{-4}$, which is slightly larger than that of the 250 °C grown layer as seen in Fig. 2(b).

Additional support for our model comes from theoretical work[4] on the transformation of $EL2$ to the metastable state. Dabrowski and Scheffler's model[4] of $EL2$ shows that $EL2$ is the isolated As_{Ga} and that the metastable state configuration is the $V_{Ga}As_i$ pair structural transition from the normal state As_{Ga}. The unrelaxed isolated As_{Ga} center has a deep a_1 level in the band gap and a t_2 resonant state at the bottom of the conduction band. The t_2 state consists of degenerate $2a$ and $1e$ states. With the displacement of the arsenic atom, the t_2 state splits into $2a$ and $1e$ states. The driving mechanism causing the displacement along the [111] direction is the Jahn-Teller effect under the relaxed situation with the nearest neighbor. The splitting of the $2a$ and $1e$ states is a precursor for the transformation to the metastable state. We suggest that the internal strain field present in LT GaAs possibly reduces the probability of a [111] direction displacement. Thus, the metastable transformation probability would be reduced. In this model, the quenchable and unquenchable $EL2$ configurations are As_{Ga} in relaxed and strained environments, respectively.

Now, we turn our attention to the enhancement observed in the layers grown at 200, 230, and 250 °C. The enhancement shows a broad feature peaking at 1.2–1.4 eV over the photon range of 1.0–1.55 eV for the 200 °C grown layer, whereas the enhancement for the 250 °C grown layer is over the photon energy range of 1.3–1.55 eV with a sharp peak at ~1.38 eV, while the quenching is dominant over other photon energies. The enhancement of the 0.8-eV PL intensity indicates an increase of $(EL2\text{-}N)^0$ since the 0.68-eV emission is due to the transition from $(EL2\text{-}N)^0$ to the valence band. An immediate first-step process is by hole photoionization to the $(EL2\text{-}N)^+$ state. The capture cross section σ_p for hole photoionization to $(EL2\text{-}N)^+$ was determined experimentally.[29] However, a recent theoretical calculation[30] by Baraff and Schluter finds that the experimental values[29] do not represent the real σ_p and shows that σ_p is almost flat in the energies of 0.9–1.4 eV. This indicates that the hole photoionization to the $(EL2\text{-}N)^+$ alone cannot explain the enhancement peak observed from the 250 °C grown layer. So we invoke the presence of a two-step process for increasing $(EL2\text{-}N)^0$ where (i) the conduction-band electrons are produced by the electron photoionization of compensating acceptors and (ii) the conduction-band electrons transform the $(EL2\text{-}N)^+$ to $(EL2\text{-}N)^0$. The compensating acceptors should be of intrinsic origin, considering the large number of $(EL2\text{-}N)^0 \sim 3\times10^{19}$ cm^{-3} (Ref. 12) for a 200 °C grown layer. Isolated V_{Ga} centers of $\sim 5\times10^{18}$ cm^{-3} are observed to be present in a 250 °C grown layer.[31] Even for a 300 °C grown layer, a large number of V_{Ga} are shown to be present using slow positron annihilation.[32] Theoretical calculation[33] places the energy levels of ${V_{Ga}}^{0/-}$, ${V_{Ga}}^{-1/-2}$, and ${V_{Ga}}^{-2/-3}$ at 0.168, 0.283, and 0.436 eV above the valence band. We believe the ~1.38-eV enhancement maximum from the 250 °C grown layer [Fig. 2(b)] is related to the ${V_{Ga}}^{0/-}$ level. So, the contribution from the process, $(EL2\text{-}N)^+ + h\nu \rightarrow (EL2\text{-}N)^0 + \text{hole}$, is relatively small for the 250 °C grown layer compared to the two-step process involving ${V_{Ga}}^{0/+}$. The flat enhancement from the 200 °C grown layer can be attributed to the two mechanisms enhancing $(EL2\text{-}N)^0$: (1) the above-mentioned two-step procedure through neutral and negatively ionized V_{Ga} and (ii) the hole photoionization of the $(EL2\text{-}N)^+$ state to the valence band.

In conclusion, the photoenhancement and photoquenching of the 0.68-eV $EL2$ photoluminescence emission were observed from LT GaAs layers grown at 200, 230, 250, 300, and 350 °C. $EL2$ consists of unquenchable and quenchable configurations. The concentration of $EL2$ in the unquenchable configuration increases with decreasing growth temperature. The quenchable and unquenchable configurations can be explained with a model of the As_{Ga} under strained and relaxed conditions. The inherent stress present in LT GaAs due to the lattice expansion causes the strained state and, consequently, the lack of quenchability. The enhancement was attributed to the hole photoionization of $(As_{Ga})^+$ and to the neutral and positively ionized V_{Ga}.

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