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Infrared absorption of deep defects in molecular-beam-epitaxial GaAs layers grown at 200 °C: Observation of an *EL* 2-like defect

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Infrared optical absorption and Hall-effect techniques were employed to study deep defects in As-rich molecular-beam-epitaxial GaAs layers grown at very low temperature (200 °C). A large ir absorption band was observed between 0.55 eV and the band edge. This band is composed of photoquenchable and photounquenchable components. Photoquenching, thermal recovery from the metastable state, and ir absorption properties of the quenchable defect, of estimated concentration $\sim 3\times10^{18}$ cm^{-3}, are identical to those of *EL* 2. On the other hand, the unquenchable defect, of estimated concentration $\sim 3\times10^{19}$ cm^{-3}, resembles the isolated As_{Ga} antisite observed in neutron-irradiated GaAs. Both defects' concentrations, which show different isothermal annealing behavior, are reduced by about an order of magnitude upon thermal annealing of 600 °C for 10 min. This reduction is accompanied by an increase of sample resistivity by a few orders of magnitude.

It has been demonstrated[1] that As-rich molecular-beam-epitaxial (MBE) GaAs buffer layers grown at very low temperatures (as low as 200 °C) can substantially reduce backgating, sidegating, and light sensitivity in metal-semiconductor field-effect transistor and metal-oxide-semiconductor field-effect transistor devices. Unlike MBE GaAs materials grown at substrate temperatures of about 600 °C, the low-temperature materials contain deep defects[2,3] with concentrations as high as mid 10^{19} cm^{-3}. It is expected that the study of these defects will shed new light on the atomic structure of the famous *EL* 2 defect observed in semi-insulating (SI) GaAs and its relationship to the isolated As_{Ga} antisite defect.

In this Rapid Communication we report the infrared absorption of two deep defects in MBE GaAs layers grown at low substrate temperature (200°C). One of these defects behaves like *EL* 2, but does not possess a zero-phonon line (ZPL), while the other defect resembles the isolated As_{Ga} antisite observed in neutron-irradiated GaAs materials. The resistivity of these layers increases dramatically as a function of thermal annealing, and they basically become semi-insulating. Thermal-annealing results indicate that the quenchable and unquenchable components represent two distinctive defects. Based on the photoquenching, thermal recovery from the metastable state, and ir absorption properties, we speculate that the quenchable component (*EL* 2-like defect) of the ir absorption spectrum is an As_{Ga}-related defect (most likely to be more complex than a simple point defect) and the unquenchable component is the isolated As_{Ga} antisite defect.

The MBE layers were grown in a Varian 360 system under normal, As-stabilized conditions, at a growth rate of 0.8 μm/h. The beam equivalent As-to-Ga pressure ratio was about 20. The substrate was SI GaAs grown by the liquid-encapsulated Czochralski (LEC) technique. The substrate's temperature was maintained at 200 °C during MBE growth. The layers were either 5 or 20 μm thick and x-ray-diffraction results indicated that they were single crystal. Several samples were cut for ir absorption and Hall-effect measurements. Infrared-absorption measurements were made with a Cary 2300 spectrophotometer. Its probing light was weak enough that no observable photoquenching occurred during a long sample exposure time in the beam. A closed-cycle refrigerator was used to cool the samples in the dark to 9 K. The samples were quenched with either white light or 1.1-eV monochromatic light. Indium contacts were soldered onto the corners of the samples for Hall–van der Pauw measurements. Some of the samples were annealed under a GaAs proximity wafer at temperatures from 250 °C to 600 °C in a flowing inert gas.

The ir absorption spectra of a 5-μm-thick sample are shown in Fig. 1 for different annealing temperatures. In this figure we have plotted spectra before (solid lines) and after (dashed lines) photoquenching. The difference spectrum (quenchable defect) obtained from the spectra taken

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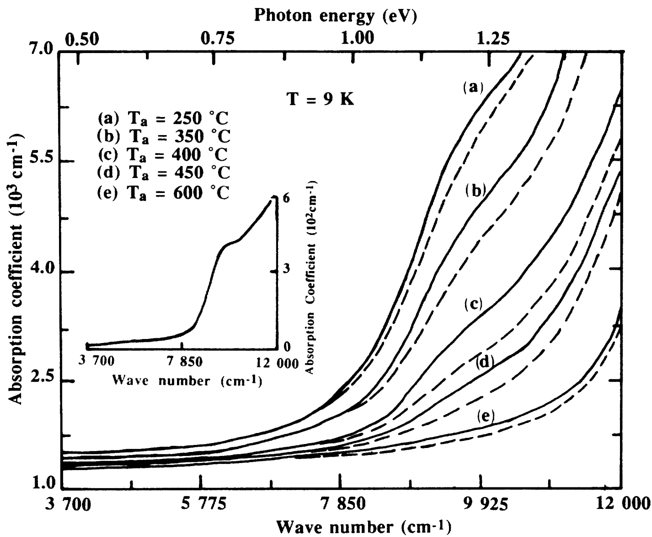

FIG. 1. Infrared-absorption spectra taken before (——) and after (---) photoquenching the sample with 1.1-eV monochromatic light after cooling in the dark to 9 K for different annealing temperatures. The MBE layers were 5 μm thick and grown on LEC GaAs substrates which were maintained at 200 °C during growth. The annealing time was 10 min at each temperature. Absorption due to the substrate was not subtracted. The inset is the spectrum of the quenchable component ($EL2$-like defect) obtained after thermal annealing at 450 °C.

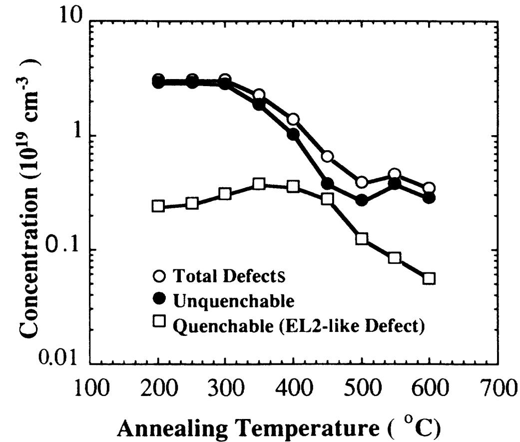

FIG. 2. The concentrations of total defects, $EL2$-like defect, and unquenchable defect as a function of annealing temperature. The annealing time was 10 min at each temperature.

before and after quenching is similar to the well-known $EL2$ spectrum with a broad absorption peak located around 1.18 eV (see the inset of Fig. 1). However, a ZPL was not observed at any annealing temperature. The concentrations of both quenchable and unquenchable (dashed spectra in Fig. 1) defects were estimated from Martin's calibration[4] after subtracting the background absorption coefficient measured at 0.55 eV from the absorption coefficient obtained at 1.18 eV. The spectra in Fig. 1 show a threshold at ~0.55 eV for lower annealing temperatures $T_a \leq 400$ °C, which increases to ~0.75 eV for higher $T_a \geq 400$ °C. This suggests that some centers shallower than $E_c - 0.75$ eV, where E_c is the bottom of the conduction band, may be present in the as-grown materials, but are destroyed upon annealing. The substrate was 0.5 mm thick and a separate measurement showed that the absorbance due to its own $EL2$ is below the detection limits of the spectrophotometer.

The concentration of total defects, quenchable (QD) and unquenchable (UQD), are plotted in Fig. 2. It is clear from this figure that UQD is thermally unstable at $T_a \geq 350$ °C, while the QD concentration [QD] is increased in the T_a range of 200–400 °C and then QD becomes unstable at $T_a \geq 450$ °C. The increase of [QD] between 200 and 400 °C may suggest that the atomic structure of QD is further formed during annealing. An alternative explanation for the rise of [QD] is that the very large absorption due to UQD in the as-grown and the lower-temperature annealed samples (see the dashed spectra in Fig. 1) in the spectral region $h\nu \geq 1.0$ eV did not allow enough transmitted light for QD to be completely quenched.

According to Hall-effect measurements, the annealed samples are controlled by hopping conduction, with resistivity (ρ) as low as ~15 Ω cm. The reduction of [QD] and [UQD] upon thermal annealing (see Fig. 2) is accompanied by a dramatic increase of ρ. The results are presented in Fig. 3 where ρ is increased by about 5 orders of magnitude after 10-min annealing at 550 °C. This behavior is shown in Ref. 2 to result from the decrease of hopping conductivity in a midgap defect band of concentration larger than 10^{19} cm^{-3}.

To verify that the UQD and QD really have different annealing behavior, an isothermal annealing was performed at 350 °C and is shown in Fig. 4. The UQD decreases in an approximate exponential fashion, while the

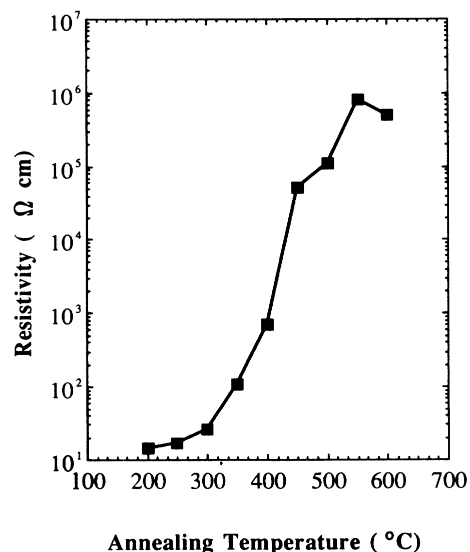

FIG. 3. The resistivity of 5-μm-thick sample as a function of annealing temperature. The annealing time was 10 min at each temperature.

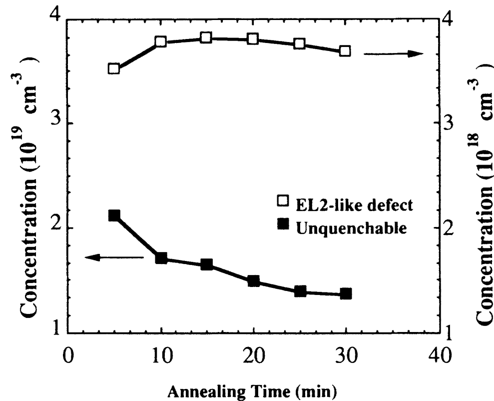

FIG. 4. Isothermal annealing at 350 °C for both the quenchable ($EL2$-like defect) and the unquenchable defect (isolated As_{Ga} antisite).

QD has obviously different behavior. Thus, it appears that two separate defects, with different annealing behavior, exist in our samples. The residual absorption in the low-temperature MBE samples is similar to that observed in the neutron-irradiated GaAs materials.[5] It was argued earlier that the residual absorption in neutron-irradiated material can be correlated with the isolated As_{Ga} antisite,[5] mainly because (1) the isolated As_{Ga} defect introduced artificially by neutron[6,7] as well as electron[8] irradiation does not possess a metastability, and (2) the threshold energy of the residual absorption (~0.75 eV) agrees with the electron paramagnetic resonance results of the isolated As_{Ga} antisite.[9] By invoking the same arguments, the UQD in the low-temperature MBE material can be identified with the isolated As_{Ga} antisite. On the other hand, the photoquenching, thermal recovery from the metastable state, and the ir absorption of the QD are identical to those of $EL2$ observed in LEC GaAs materials. Although still controversial, there is a large body of evidence (see, for example, Refs. 5, 8, and 10–14) which suggests that $EL2$ is a complex defect; if so, it is reasonable to assume that the QD atomic structure is more complex than a simple point defect.

As stated above, it is tempting to associate the QD with $EL2$ because of its quenchable nature. However, two puzzling aspects of this assignment remain: (1) there is no ZPL observed at any annealing temperature, and (2) the QD appears to anneal out at temperatures of about 600 °C. In contrast, the $EL2$ defect observed in standard, SI LEC materials is stable up to 1000 °C (see Refs. 15 and 16) and also possesses a ZPL. Thus, if we postulate that our QD is microscopically equivalent to the LEC $EL2$ defect, then the lack of a ZPL and the lower annealing temperature must be explained. On the other hand, there may be a variety of microscopically *inequivalent* defects which are nevertheless all quenchable. For example, suppose that the ZPL, usually observed at 1.039 eV in LEC materials, and the broad peak (BP) observed at 1.18 eV are really due to two different transitions; then our lack of a ZPL would be more easily explained. In fact, there is some evidence for this assertion. Baj and Dreszer[17] studied $EL2$ under hydrostatic pressure and found that the ZPL and the BP have different hydrostatic pressure coefficients. The ZPL coefficient was noted to follow that of the L minimum of the conduction band[18,19] suggesting that the ZPL is not the no-phonon line of the BP, but rather an internal transition within an effective mass state possessing a T_2-like state associated with the L minimum. This suggestion was also proposed earlier.[20] Therefore, this particular assignment[18,19] of the ZPL, which reflects the symmetry of the L minimum, is in conflict with the T_d point symmetry interpretation as proposed by Kaminska, Skowronski, and Kuszko.[21] The above picture is also in conflict with recent theoretical proposals which identify $EL2$ with the isolated As_{Ga} antisite,[22–24] mainly because these proposals rely on the assumption that the ZPL and the BP observed at 1.18 eV in the ir absorption spectrum belong to the same optical absorption. This issue is as yet unresolved.

The absence of what is called the ZPL in the present samples could possibly be explained by the presence of local electric fields.[25] These electric fields may severely broaden the ZPL, which is narrow and has a very small intensity, while the broad optical transition would not be affected as much. The absence of the ZPL was also reported in neutron-irradiated GaAs samples[5,26] which contain an $EL2$-like defect. The present MBE GaAs layers are grown on LEC GaAs substrates and stress may exist in these layers. However, a uniform stress should not eliminate the ZPL because it should split[21] under uniaxial stress or shift[17] under hydrostatic pressure. Therefore, uniform stress is ruled out as being a reason for the absence of the ZPL. On the other hand, the presence of a *nonuniform* stress could be the cause of the absence of the ZPL. However, thermal annealing should reduce the magnitude of this stress. This assertion is tested in a neutron-irradiated LEC GaAs sample in which $EL2$ is partially decomposed. In this sample, a ZPL was present prior to irradiation and was not observed after irradiation. Upon thermal annealing at 550 °C for 15 min, the ZPL was observed again. Hence, one would expect to observe the ZPL in the low-temperature MBE GaAs materials if it exists after thermal annealing. In fact, we were unable to observe this line even after thermal annealing at 600 °C for 10 min. Based on the above picture, it is doubtful that nonuniform stress is responsible for the absence of the ZPL in our material. It should be noted that the BP in LEC material was observed to shift toward the lower-energy region under hydrostatic pressure.[17] This peak was also shifted in the same direction in neutron-irradiated GaAs samples[26] (the BP was observed at energies as low as 0.83 eV in some samples) where various damage, defects, and stresses are present. On the other hand, the BP was not shifted in the present MBE GaAs layers indicating that the stress is probably minimum in these layers. The above explanation is still tentative because local electric fields may not be the only reason for the absence of the ZPL, but a conclusive picture of why it is not observed has not been reached yet. However, further measurements and analysis are in progress.

In conclusion, we have presented ir absorption of two deep defects in MBE GaAs layers grown at a substrate temperature of 200 °C. The quenchable defect properties

are similar to those of $EL2$ in LEC GaAs materials while the unquenchable component of the ir absorption spectrum is interpreted as being due to photoionization of the isolated As_{Ga} antisite. The concentrations of both defects are reduced by about an order of magnitude after thermal annealing at 600 °C for 10 min. This reduction is accompanied by an increase of resistivity by a few orders of magnitude. One of the remarkable observations of the current investigation is that the concentration of the $EL2$-like defect is about 2 orders of magnitude larger than that of $EL2$ in LEC GaAs materials. The so-called ZPL was not observed in the present samples while the broad peak at 1.18 eV was observed. The consequence of this observation is that the ZPL and the broad peak may not be related and may represent two different transitions in agreement with the recent interpretations of others.[18–20] The absence of the ZPL may also be interpreted as being due to the presence of local electric fields.

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