Intrinsic defects in GaN. II. Electronically enhanced migration of interstitial Ga observed by optical detection of electron paramagnetic resonance

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Optical excitation at 1.7 K with 364-nm laser light produces partial annealing recovery of the damage produced in GaN by 2.5-MeV electron irradiation *in situ* at 4.2 K. Observed is a reduction in the irradiation-produced 0.95-eV photoluminescence (PL) band, recovery in the visible luminescence, and conversion between the two electron-paramagnetic-resonance (ODEPR) signals L5 and L6 associated with interstitial Ga. This is interpreted as resulting from electronically excited migration of the interstitial Ga allowing it to convert between lattice sites near the Ga vacancy from which it was ejected. The relative rates of conversion between the two sites are found to vary between different samples and upon electron irradiation fluence.

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I. INTRODUCTION

The gradual deterioration of devices such as laser diodes during their operation is a major concern for the optoelectronic industry. One very important and scientifically interesting source for such deterioration is recombination-enhanced migration,[1] i.e., the fact that the injection of free carriers into the semiconducting material in question can lead to an enhanced migration of intrinsic defects, which causes a change in the electronic and optical properties of the material. As mentioned in the preceding paper[2] (hereafter referred to as A), gallium nitride (GaN) is of considerable importance for optoelectronic applications. Therefore, any evidence of electronically enhanced migration of intrinsic defects in this material would be highly interesting.

In paper A the observation was reported of two distinct configurations for interstitial Ga in GaN by optical detection of electron paramagnetic resonance (ODEPR) after 2.5-MeV electron irradiation *in situ* at 4.2 K. Their ODEPR signals, labeled L5 and L6, were observed in a broad photoluminescence (PL) band centered at 0.95 eV which was also produced by the irradiation. Although their spin-Hamiltonian parameters are very similar and their spectral lines strongly overlap, it was possible to separate their relative contributions because L5 is a negative signal (a spin-dependent process competing with the PL) and L6 is a positive signal (a feeding process for the PL). Immediately after the electron irradiation, only L5 was observed, but, in one sample, L6 was observed to emerge weakly even at the first annealing stage at 60 K, and there was evidence that its emergence was substantially enhanced when the annealing was performed under optical excitation. Evidence of differences for the relative concentration of L6 depending upon the sample and the original electron irradiation dose was also briefly cited.

In A, two tentative models were presented for the origin of the L5 and L6 ODEPR spectra. In one, they were identified as arising from Ga_i^{2+} in the two available interstitial sites in the wurtzite lattice, *T* and *O*,[3] respectively. In the other, they were identified with Ga_i^{2+} in two different *T* sites (or, possibly *O* sites, see note added in proof, paper A), with L6 arising from the interstitial in a site closer to the Ga vacancy from which it was ejected. In either case, if correct, this implies diffusional motion of the interstitial at these cryogenic temperatures, either via a jump between the *O* and *T* sites, which corresponds to one-half of a full diffusion jump, or via a full diffusion jump between *T* (or *O*) sites.

Normal thermally activated long-range motion of the interstitial, with its subsequent trapping by other defects, has been found to require several hours at room temperature.[2,4] This strongly suggests that motion at as low a temperature as 60 K must be the result of some other process. In particular, it suggests that optical excitation is playing a central role.

In the present paper, we explore more carefully the L5 $\rightleftarrows$ L6 conversion process and the role of optical excitation.

II. EXPERIMENTAL DETAILS

As in A, the ODEPR experiments were performed at $\sim$1.7 K in a 20-GHz EPR spectrometer capable of 2.5-MeV electron irradiation *in situ* at 4.2 K. The details of the spectrometer and its modification for ODEPR studies are described there. The samples studied were taken from three different $\sim$500 μm thick undoped (*n*-type) free standing platelets grown by hydride vapor phase epitaxy (HVPE) at NEC, labeled VPE2-155, VPE2-180, and VPE2-331, which are also described in A. For the study of the optically induced L5 $\rightleftarrows$ L6 conversion rates, the PL was excited with $\sim$100 mW/cm^2 of the 364-nm line from an argon-ion laser ($\sim$25 mW emanating from the fiber which expands to an area of $\sim$1/4 cm^2 at the sample position). The 364-nm line was chosen because it corresponds to a photon energy just below the band gap of wurtzite GaN at 1.7 K, and therefore penetrates the sample while still exciting free carriers (from defect- and impurity-related levels in the gap). For the ODEPR measurements, some were performed at that elevated excitation level to monitor the L5 $\rightleftarrows$ L6 conversion during the excitation, others at levels up to a

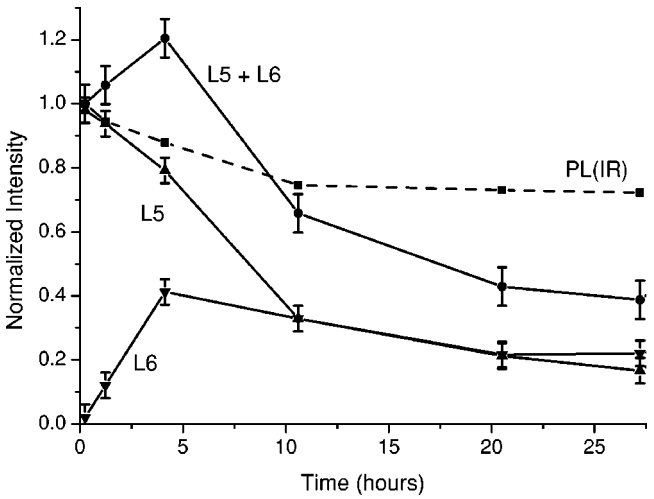

FIG. 1. Intensities of the ODEPR signals and the total IR luminescence vs time of 100-mW/cm^2 excitation at 1.7 K by 364-nm laser light for sample VPE2-331d immediately after 2.5-MeV electron irradiation at 4.2 K to a fluence of 6×10^{16} e/cm^2.

factor of 10 lower, as was normally done in A, to minimize conversion during the ODEPR measurements. (Due to the slow conversion rate that is observed to occur under full excitation, a detailed quantitative study of the its dependence upon excitation power was not performed, other than to demonstrate that the rate scales roughly proportional to the power.) In each case, the intensities of the ODEPR signals were corrected for their measured dependence upon excitation level.

For the analysis of the intensities of the L5 and L6 spectra in each ODEPR spectrum, the stronger high-field hyperfine lines measured with $\mathbf{B}\perp\hat{\mathbf{c}}$ were used (see Fig. 4 in A). Each spectrum was corrected according to its measured magnetic-field calibration and for small deviations in the microwave frequency from 19.910 GHz, the value selected for the comparisons. After having subtracted an appropriate linear background, the spectrum was then least-squares fitted to

$$aG(\mathrm{L5})+bG(\mathrm{L6}), \tag{1}$$

where G(L5) and G(L6) are each a pair of Gaussian lines (for the two Ga isotopes) which were determined to best represent the high-field hyperfine lines of the L5 and L6 spectra measured at 19.910 GHz, which are shown in Figs. 4(a) and 4(c), respectively, of A. The intensities, widths, and magnetic-field positions of the Gaussian components were kept constant, with the relative intensities of the two isotopic components being locked to the natural abundance ratio (^{69}Ga/^{71}Ga$=60.1/39.9$). The a and b parameters resulting from the fit provided in this manner our estimates of the L5 and L6 intensities, respectively, in each spectrum.

III. RESULTS

To separate the role of optical excitation from that of thermal annealing, we first study the effect of prolonged optical excitation at 1.7 K, before any thermal annealing step. The results are shown in Fig. 1 for sample VPE2-331d, after 2.5-MeV electron irradiation at 4.2 K to a fluence of 6×10^{16} e/cm^2. We see that conversion does indeed take place under optical excitation alone at 1.7 K.[5] The L6 intensity grows in monotonically from zero, saturating at L6/L5 ≈1. At the same time, the sum of L5 and L6 is decreasing, as is the shallow effective-mass donor signal (not shown) and the total luminescence in the IR. (In the ODEPR experiment, the total IR luminescence between 1000 and 1800 nm, the long-wavelength limit of the Ge detector, is collected. The total luminescence, monitored by the dc output of the detector during the experiment, underestimates the recovery because the decrease in the 0.95-eV band is accompanied by a recovery of the V^{3+} luminescence band originally present.[2] This will become evident in additional experiments to be described below.) On the other hand, the visible PL (not shown), initially reduced by the irradiation to $\sim31\%$ of its as-grown value, has recovered to $\sim70\%$ of its as-grown value at the end of the optical excitation. In order to estimate the rates of the annealing and conversion, we have fitted the sum L5+L6 (omitting the initial small increase) and the ratio L6/L5 to appropriate exponential functions. The resulting characteristic decay times are (17 ± 4) h for the annealing and (3.8 ± 0.5) h for the conversion.

The fact that the IR intensity decreases, accompanied by a major recovery in the visible PL, by itself clearly reveals that optically induced recovery of some kind is taking place, strongly suggesting that defect motion must be occurring. The apparently correlated L5 $\rightarrow$ L6 conversion strongly suggests that the mobile species is the Ga interstitial.

A subsequent 6-h anneal in the dark at 240 K produced little change in the amplitudes of the individual ODEPR signals or the PL intensities.

Next, to further separate the role of thermal annealing from that of optical excitation, we reverse the procedure on a freshly electron-irradiated sample by quickly annealing 30 min at 200 K after only a brief ODEPR characterization before the anneal, and then studying the effect of subsequent optical excitation at 1.7 K. The result is shown in Fig. 2 for sample VPE2-331e after irradiation to a fluence of 1.6×10^{17} e/cm^2 at 4.2 K. Here we see that the L6/L5 ratio increases significantly even during the initial characterization prior to the 200-K anneal, having already reached ~0.6 by the time of the first measurement after the 200-K anneal. It continues to rise, however, after the anneal with a rate roughly comparable to that in Fig. 1, settling down, in this case to the much larger value of ~2.4. From this it is clear that the anneal alone is not a significant source for the conversion, but that optical excitation appears to be required. Shown also is the result of a 240-min anneal at 270 K, which removes L6 preferentially. Under continued optical excitation after the 270-K anneal (not shown), L6 reemerges at the expense of L5 but with the L6/L5 ratio at that point approaching only ~1.

In the figure, we show also the combined L5+L6 ODEPR amplitude, and the 0.95-eV PL intensity as measured directly from its spectral dependence at several points during the measurements. Here, the substantial optically induced annealing of the 0.95-eV PL band is clearly evident: at the end of the illumination and 270-K anneal only $\sim6\%$

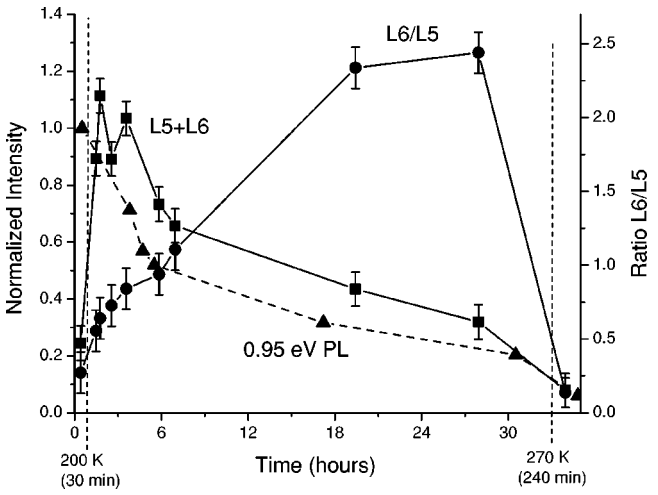

FIG. 2. Intensities of the interstitial-Ga ODEPR signals and the 0.95-eV PL band vs time of 100-mW/cm^2 excitation at 1.7 K by 364-nm laser light for sample VPE2-331e after a 30-min, 200-K anneal. The sample was first irradiated by 2.5-MeV electrons at 4.2 K to a fluence of 1.6×10^{17} e/cm^2, and briefly characterized before the anneal.

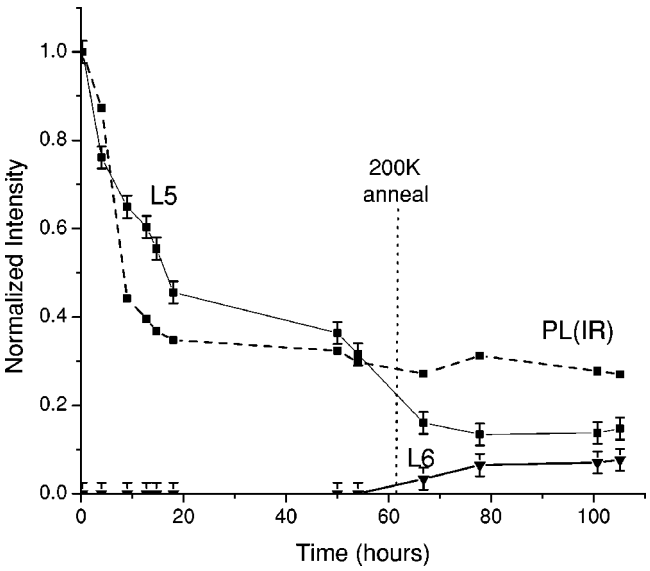

FIG. 3. Intensities of the ODEPR signals and the total IR luminescence vs time of 100-mW/cm^2 excitation at 1.7 K by 364-nm laser light for sample VPE2-180f. After irradiation by 2.5-MeV electrons at 4.2 K to a fluence of 5×10^{16} e/cm^2, the sample was first subjected to prolonged excitation and then further excitation after a 30-min, 200-K anneal.

remains. Since ~50% of the total IR intensity monitored in the ODEPR studies remains at this point, similar to that observed for VPE331d in Fig. 1, this shows the important contribution of V^{3+} and its recovery to the total IR luminescence.

To understand the reason for the much larger L6/L5 ratio obtained in Fig. 2, a third sample VPE2-331h was irradiated to $6\times10^{16}e$/cm^2 and also quickly annealed to 200 K. In that case the optically induced conversion after the anneal saturated at ~1, i.e., similar to VPE2-331d with the same irradiation dose (as shown in Fig. 1). This strongly suggests that in a given sample, the saturation value for L6/L5 is determined primarily by the irradiation dose, being greater for the larger dose, and not by the annealing temperature before which the optical conversion is performed.

The effect of optical excitation on several samples from the VPE2-155 platelet was also studied and for them the behavior was roughly similar to that seen for the VPE2-331 samples. For example, prolonged excitation after 200-K anneal of sample VPE2-155Ae, which was first irradiated at 4.2 K by 1.3×10^{17} e/cm^2, leads to a saturation value of L6/L5 ~2.1.

However, samples from VPE2-180 were observed to behave differently. In A, early results from sample VPE2-180b were described where L6 first emerged only weakly after an anneal in the dark at 60 K, followed by a larger but still weak increase after a second 60-K anneal under optical excitation. No evidence of L6 was observed prior to that even though there were prolonged periods of optical excitation during the ODEPR studies prior to the first anneal. To probe this further, we have repeated the study for a second sample VPE2-180f from the same platelet and irradiated to the same approximate fluence, 5×10^{16} e/cm^2. The results are seen in Fig. 3. As appeared to be the case in A for VPE2-180b, no conversion is indeed observed at 1.7 K prior to anneal. At the same time, however, substantial recovery is clearly taking place, as evidenced by the loss of the L5 and IR intensities and recovery of the visible PL (not shown) at a rate comparable to that for VPE2-331d in Fig. 1. This clearly suggests that the same optically stimulated defect migration is indeed taking place in the VPE2-180 materials, but for some reason L6 is not observed to emerge. L6 does emerge after the 200-K anneal, but, similar to VPE2-180b in A, its intensity is weak with a saturation ratio L6/L5~0.5.

IV. DISCUSSION

In all of the samples studied so far, optical excitation at 1.7 K produces a steady decrease in the irradiation-produced 0.95-eV PL band accompanied by a corresponding recovery of the visible luminescence. It follows that annealing must be taking place, implying, in turn, that optically enhanced defect migration of some kind is occurring. In all samples, immediately after the irradiation, interstitial Ga is observed only in the configuration giving rise to the ODEPR signal L5, and its intensity similarly decreases with optical excitation. In most of the samples studied (VPE2-155 and VPE2-331), L6 emerges as L5 decreases approaching a fixed ratio of L6/L5, as both continue to decrease. With the identification in paper A of L6 as arising from a different lattice configuration of interstitial Ga, this supplies strong evidence that interstitial Ga is the mobile species. The annealing, which occurs at a rate approximately four to six times slower than that of the conversion, presumably arises when the interstitial Ga after having made several jumps recombines with its accompanying vacancy or migrates away to ultimately be trapped by other defects or impurities in the material.

As pointed out in the Introduction, two tentative models were presented in A for the origin of L5 and L6. In one, they were identified as arising from Ga_i^{2+} in the two available interstitial sites in the wurtzite lattice, *T* and *O*,[3] respectively. In the other, they were identified with Ga_i^{2+} in two different *T* sites (or possibly *O* sites, see note added in proof, paper A), with L6 arising from the interstitial in a site closer to the Ga vacancy from which it was ejected. In either case, if correct, conversion between the two sites implies diffusional motion of the interstitial, either via a jump between the *O* and *T* sites, which corresponds to one-half of a full diffusion jump, or via a full diffusion jump between *T* (or *O*) sites. The convergence toward a fixed L6/L5 ratio suggests that the conversion could be occurring in both directions, L5 $\rightleftarrows$ L6, the final ''equilibrium'' ratio being determined by the two rate processes.

The ''equilibrium'' L6/L5 ratio appears to depend upon electron irradiation fluence, being greater for larger fluences, but also upon the starting material. To be consistent with reflecting simply the balance between the L5 $\rightleftarrows$ L6 processes, this implies that the various electron- and hole-capture processes involved at the interstitial as well as at competing centers depend upon the different background doping and impurity concentrations originally present in the sample as well as the concentration of the various radiation-produced defects. This is of course reasonable, the effective ''pseudo-Fermi level'' under optical excitation at cryogenic temperatures being strongly dependent upon the various capture cross sections of the defects present. In particular, the optically enhanced recovery observed in the PL for the VPE2-180 samples reveals that the same annealing process is actually occurring for it also. However, to explain in this simple way the failure to see L6 emerge requires that in that sample the L6 $\rightarrow$ L5 rate dominates significantly over that for L5 $\rightarrow$ L6. No obvious important differences in the growth conditions for the different samples are apparent (each undoped with identical 1040 °C growth temperatures and 40 cc/min GaCl flow rates; and with NH_3 flow rates of 1500 cc/min for VPE2-150, 1000 cc/min for VPE2-331, and alternate 1000 and 2000 cc/min layers for VPE2-180), but, of course, the presence of transition element ions detected in the materials[6,7] makes it clear that trace background impurities introduced from the Ga and N sources and elsewhere are not completely under control in the growth process and could therefore vary significantly from sample to sample.

Many questions remain, therefore, about the factors that determine the rates of the various conversion processes, and their interpretation in terms of the detailed microscopic jump processes involved. However, the experimental results presented here appear to have clearly established that they are definitely occurring, i.e., that interstitial Ga can actually move from one lattice configuration to another under optical excitation at 1.7 K.

It is interesting to compare these results to what is known about isolated interstitials in other semiconductors. There are only two other cases where isolated host-atom interstitials have been positively identified by magnetic-resonance studies. They are interstitial Zn in ZnSe,[8–10] and interstitial C in diamond.[11–13] Both have been demonstrated to undergo long-range migration under electronic excitation at cryogenic temperatures. To these we can add the isolated interstitial in silicon,[14] for which there is ample evidence of its efficient long-range motion under ionization conditions at cryogenic temperatures even though it may[15,16] or may not have been observed directly. In the case of interstitial Zn in ZnSe, a detailed study of the process was possible, and the optical conversion between the two interstitial sites in cubic ZnSe was unambiguously demonstrated. In those studies it was also directly established that optical excitation is much more effective for the process than the ionization accompanying the 2.5-MeV electron irradiation utilized to produce the defect. In the present case, the fact that no evidence of L6 is present immediately after the irradiation reveals the same conclusion.

Therefore, in the very few known cases so far, the host metal-atom interstitial in a compound semiconductor and the interstitial host atom in an elemental semiconductor have all been shown to be mobile under electronic excitation at cryogenic temperatures. Apparently for them, a path exists for the energy of electron-hole recombination at the defect to be occasionally converted into the kinetic energy necessary to overcome the energy barrier for their migration. This is an important and unexpected observation, and one which may have serious consequences in terms of degradation mechanisms for devices made from the materials. (In the present case of interstitial Ga in GaN we have not so far established that the rate of the process, requiring several hours of 100-mW excitation at 1.7 K, actually increases significantly as the temperature is raised, as has been observed for the other interstitials.)

V. CONCLUSION

Optical excitation at 1.7 K with 364-nm light has interesting effects on the ODEPR spectra of GaN crystals irradiated *in situ* with 2.5-MeV electrons at 4.2 K. In addition to a partial recovery of the irradiation-produced damage, as demonstrated by a gradual decrease in the irradiation-produced 0.95-eV PL band as well as a gradual recovery of the visible PL as a function of illumination time, we observe a conversion between the ODEPR signals L5 and L6, which have been assigned to two distinct configurations of interstitial Ga. This is best described in terms of diffusional motion of interstitial Ga among lattice sites close to the Ga vacancy from which it was knocked away during the irradiation. The migration must be the result of the electronic excitation provided either by recombination at the interstitial of electron-hole pairs injected into the bulk by the optical excitation, or by direct optical excitation of the interstitial, or a combination of the two. The observed annealing occurs when the interstitial, after having made several jumps, either recombines with its accompanying vacancy or ''escapes'' from it and ultimately becomes trapped by impurities or other defects in the sample.

The fact that the conversion between L5 and L6 converges towards a fixed ratio between their intensities strongly suggests that the interstitial can overcome the barrier for diffusion from both sites. The convergence ratio varies, how-

ever, between different sample types and with the electron irradiation fluence, which indicates that the rates of the conversion processes depend in a complex way on the concentration of irradiation-produced defects as well as the concentration of trace impurities and defects in the as-grown material. Although our experiments do not allow us to understand the details of this, they do show that migration of interstitial Ga in GaN can be induced by electronic excitation—a fact that may have serious implications for deterioration processes in devices made from this technologically important material.

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