

Yellow luminescence in *n*-type GaN epitaxial films

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Photoluminescence, resonant Raman scattering, and photoconductivity measurements have been employed to study the yellow emission in undoped *n*-type and a set of Se-doped GaN epitaxial films. It is best described by a transition from the conduction-band edge to a deep acceptor. Unlike the donors and acceptors used in most previous studies that substitute Ga sites, Se atoms can replace N sites. With this unique fact, we identify that the origin of the yellow emission involves the nitrogen antisite. In addition, it is found that persistent photoconductivity can be observed after the yellow band excitation. We further suggest that the nitrogen antisite exhibits a metastable behavior similar to the arsenic antisite in GaAs. [S0163-1829(97)07735-7]

I. INTRODUCTION

Gallium nitride is a promising material for the construction of short-wavelength light-emitting devices, such as light-emitting diodes and laser diodes.¹⁻⁴ In spite of the progress in growth methods, there are still substantial physical properties that remain without a definite answer. One of them concerns the origin of the yellow luminescence in GaN epitaxial thin films. Two mechanisms of the yellow luminescence have been proposed in the literature. In the first one, the luminescence is due to a transition from the conduction band or a shallow donor state to a deep localized state.⁵ The second mechanism assumes a transition from a deep gap state to a shallow acceptor.⁶ Many intrinsic and extrinsic defects have been suggested as the nature of the deep center such as Ga vacancy,^{7,8} N vacancy,⁶ Ga interstitial,⁹ and carbon impurity.⁵ To contribute to the clarification of the situation, we performed several different experiments on undoped and a set of Se-doped GaN epilayers, including photoluminescence, resonant Raman scattering, and photoconductivity. All experiments are in line with the transition from the conduction band or a shallow donor state to a deep localized state to be responsible for the yellow emission. The uniqueness of the Se-doped films is that the Se atoms substitute N sites, while the dopants including donors and acceptors used in most previous studies replace Ga sites. With the studies on Se-doped samples, we attribute the origin of the deep state to the nitrogen antisite. In addition, persistent photoconductivity has been observed after the GaN films were excited by the photon with energy exceeding yellow radiation. This behavior further suggests that the nitrogen antisite has a metastable property similar to the arsenic antisite in GaAs.

II. SAMPLE PREPARATION

The GaN films used for this study were grown by low-pressure metal-organic chemical-vapor deposition. Optical

grade polished (0001)-orientation (*c*-face) sapphires were used as substrates and were cleaned in organic solvents and a hot 3:1 H₂SO₄:H₂PO₃ solution. Triethylgallium (TEGa) and ammonia (NH₃) were used as the Ga and N sources, respectively, and ultrahigh-purity H₂ was used as the carrier gas. The H₂Se was used as the Se source and diluted in H₂ to 50 ppm. Before film growth, substrates were exposed to a H₂/NH₃ ambient in order to remove the surface damaged layer and native oxide. A thin GaN buffer layer (~500 Å) was deposited at 525 °C before the epitaxial GaN growth at 1000 °C. The flow rates of NH₃, TEGa, and H₂ were 1500 SCCM (SCCM denotes cubic centimeter per minute at STP), 8.3 μmole/min, and 1000 SCCM, respectively. The flow rate of H₂Se was varied from 0 to 20 SCCM. The growth rate of undoped GaN film was about 7200 Å/h at 1000 °C. The thickness and morphology were characterized by scanning electron microscopy (SEM) as shown in our previous report.¹⁰ The surface of the films was free from cracks or pits. The typical thickness is about 2 μm. A Hall-effect measurement was performed at room temperature by the van der Pauw method. The undoped GaN film has an electron concentration of about 10¹⁷ cm⁻³ and a mobility of 360 cm²/V s. These values are typical for almost all high-quality undoped GaN samples available to date. For the flow rates of the H₂Se diluted gas of 1, 5, 10, and 20 SCCM, the carrier concentrations are 1.6×10¹⁷, 1.2×10¹⁸, 1.7×10¹⁸, and 1.4×10¹⁸ cm⁻³, respectively. The carrier concentration increases as the flow rate of H₂Se rises and it remains relatively constant up to 20 SCCM. The Se content in the GaN films is examined by means of secondary-ion-mass spectroscopy and x-ray wavelength dispersion spectroscopy.^{10,11} Although the free-carrier concentration becomes saturated due to the creation of surface defects when the flow rate of H₂Se is more than 10 SCCM, the Se atomic percentage increases as the flow rate of H₂Se increases.¹⁰ Details of the sample deposition and structural characterization have been described in our previous report.¹⁰

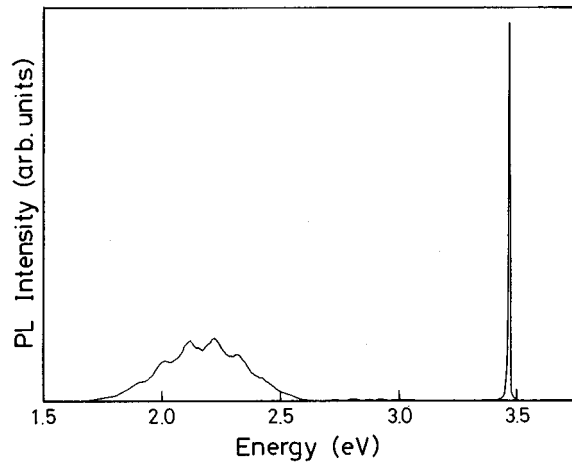


FIG. 1. Photoluminescence spectrum of an undoped GaN epilayer taken at 10 K. The spectrum was taken using a He-Cd laser excitation source at 325 nm.

III. RESULTS AND DISCUSSION

A typical photoluminescence spectrum of the undoped GaN epilayer sample taken at 10 K is shown in Fig. 1. The spectrum was excited by a He-Cd laser working at 325 nm, dispersed by a Spex 1-m double-grating spectrometer, and detected by a cooled GaAs photomultiplier. A detail description of the setup of photoluminescence measurements has been published elsewhere.¹² The photoluminescence spectrum contains a strong near-band-edge exciton luminescence line having a full width at half maximum of less than 10 meV, which is comparable with that of the high-quality GaN film to date.^{6,11,13} In addition, a broad deep-level emission located at yellow region modulated by the Fabry-Pérot interference fringes is observed. The appearance of the interference confirms the smooth surface of the film as seen by SEM. As described before, the origin of this broad yellow emission is still rather controversial. In the following sections, we will present our measurements of resonant Raman scattering, photoconductivity, and photoluminescence to clarify our understanding of the yellow emission.

A. Resonant Raman scattering

For the Raman excitation, six emission lines of a mixed Ar⁺/Kr⁺ ion laser were separately directed at an oblique angle of incidence ($\sim 50^\circ$ to the sample normal), in conjunction with different filters. The detection system consists of a multichannel photodiode array and a double monochromator. We used the backscattering geometry with 2-cm^{-1} spectral resolution. All Raman spectra were taken at room temperature. Details of our Raman scattering setup have been described elsewhere.¹⁴ Here we present only the measured results for GaN films.

The Raman spectrum in $Z(YX+YY)\bar{Z}$ for undoped film is shown in Fig. 2. The observed modes do agree with the selection rule of the C_{6v} symmetry for the geometry used here.¹⁵ The strongest line at 567 cm^{-1} is the high-frequency E_2 mode belonging to the hexagonal wurtzite crystal. The 418-cm^{-1} peak is from the A_{1g} mode of sapphire substrate, which serves as a useful reference for other spectral features.

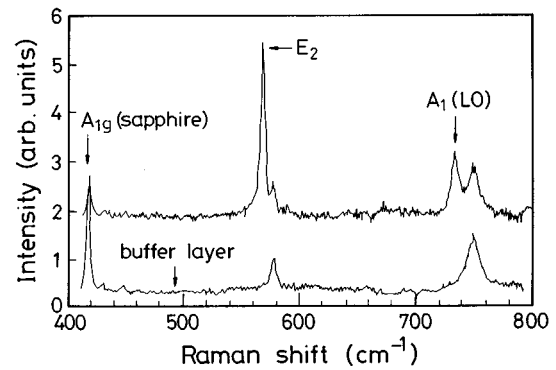


FIG. 2. Raman spectra of the samples without and with a GaN epilayer probed with a 568.2-nm laser at room temperature using the $Z(YX+YY)\bar{Z}$ configuration.

The 736 cm^{-1} corresponds to the $A_1(\text{LO})$ mode. The satellite structure just above the strong E_2 peak at 578 cm^{-1} and the peak at 745 cm^{-1} are the E_2 mode and $A_1(\text{LO})$ mode belonging to the buffer layer, as compared with the bottom spectrum of Fig. 2.

In Fig. 3 we show the relative enhancement of the intensity of the E_2 and $A_1(\text{LO})$ modes as a function of the pumping photon energy. Quite interestingly, we can clearly see that the enhanced factor rises rapidly from about 2.2 eV, shows a peak around $2.4 \pm 0.1\text{ eV}$, and then decreases. From the resonant effect in the Raman scattering, we can deduce the fact that there is a broad electronic transition in GaN epilayer with its energy in the range of yellow radiation. Because the detected E_2 and $A_1(\text{LO})$ signal belongs to the epilayer, we can exclude the possibilities that the observed yellow-band transition comes from buffer layer or interface.

B. Photoconductivity

The above photoluminescence (PL) and Raman scattering does not tell us whether the transition is from the conduction-band edge to a deep localized state or from a deep localized state to the valence-band edge. In order to

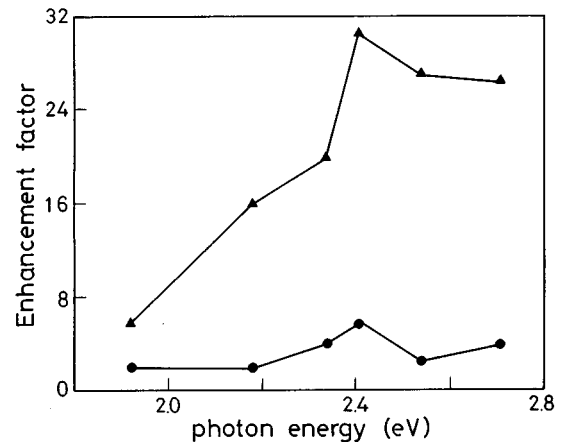


FIG. 3. Enhancement factors of the E_2 mode and $A_1(\text{LO})$ mode as a function of photon energy normalized using a Raman line of the BaF₂ crystal plate, where the triangles and solid dots represent the data for the E_2 and $A_1(\text{LO})$ modes, respectively.

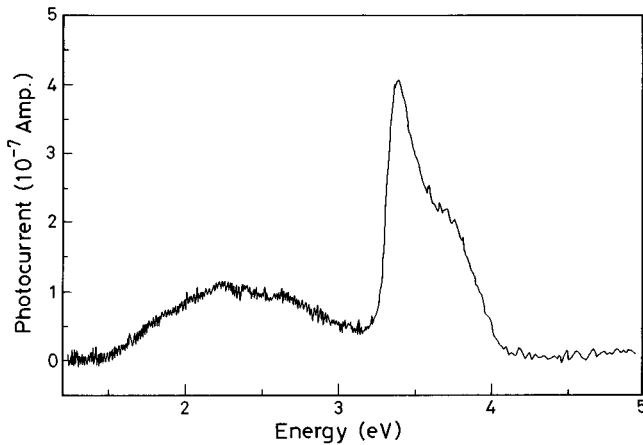


FIG. 4. Photoconductivity spectrum of an undoped GaN sample taken at room temperature.

resolve this question, we perform the photoconductivity measurements. For the photoconductivity measurements, Ohmic contacts were formed by depositing the indium drop to the four corners of the samples and annealing the sample at 400 °C for 10 sec. A tungsten lamp dispersed by a monochromator was used as the photoexcitation light source. The sample was attached to a sample holder and placed inside a closed-cycle He refrigerator, with care to ensure good thermal contact yet electrical isolation. The data obtained under different conditions were taken in such a way that the system was always allowed to relax to equilibrium. A bias of 2.0 V was supplied and the conductivity was measured by a Keithley 236 source measure unit. Details of the photoconductivity measurement were similar to those described previously.¹⁶

Figure 4 illustrates a typical photoconductivity spectrum of GaN film. We can see that in addition to the band-edge peak, a broadband localized at the yellow range is observed. It can be correlated to the yellow emission in the PL spectrum and the resonant transition in Raman scattering. Because the conduction carriers are electrons according to the Hall-effect measurements, the observed photoconduction caused by yellow radiation can be viewed as the excitation of electrons from a localized state to the conduction band. Thus the photoconductivity measurement indicates that there is a deep level located 2.3 eV below the conduction-band edge and the recombination of conduction electrons through this deep level can give the yellow emission.

A rather interesting feature of the photoresponse in GaN film is the observation of persistent photoconductivity (PPC) as shown in Fig. 5. The conductivity increases gradually after the sample is exposed to light and the light-induced conductivity can persist for a very long period of time after the light is removed, which can extend to more than 10^4 sec. Such PPC behavior has been observed in many important semiconductors.^{17–20} Recently, it has also been detected in Mg-doped *p*-type GaN and attributed to the effects of the metastable behavior of the Mg dopants.²¹ It is found that the decay kinetics of PPC can be described by a stretched exponential function

$$I_{\text{PPC}}(t) = I_{\text{PPC}}(0) \exp[-(t/\tau)^\beta], \quad (1)$$

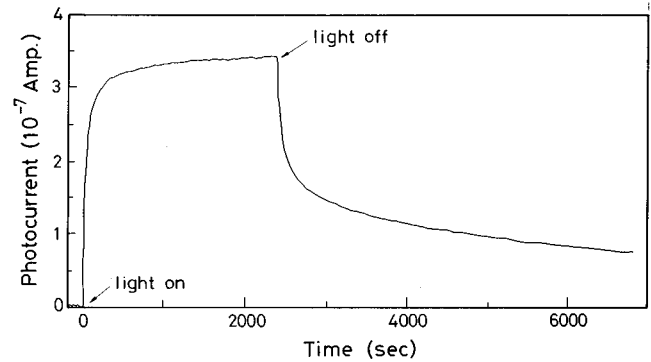


FIG. 5. Typical buildup and decay behavior of persistent photoconductivity in Se-doped *n*-type GaN film at room temperature. The spectrum was excited by a light source at 363 nm, which comes from a tungsten lamp dispersed by a monochromator.

where $I_{\text{PPC}}(0)$ is the PPC buildup level at the moment of light excitation being removed, τ is the PPC decay time constant, and β is the decay exponent. Our measured decay curve as shown in Fig. 5 can be well fitted by Eq. (1) with $\beta=0.29$ and $\tau=1072$ sec, which are on the same order of magnitude as those for Mg-doped GaN.²¹ In addition, the carrier capture barrier ΔE obtained from the temperature dependence of τ ,

$$\tau = \tau_0 \exp[\Delta E/kT], \quad (2)$$

is 132 meV, which is also in good agreement with the Mg-doped GaN. Here the temperature of the measurements is in the range 17–300 K and there are three decades of variation in the time constant τ . Thus we can conclude that the PPC effects observed in Se-doped *n*-type GaN and Mg-doped *p*-type GaN have the same behavior. We therefore suggest that the PPC effect is caused by the intrinsic defect in GaN rather than the dopant impurities. We also found that the PPC effect can be observed for the pumping photon energy down to 2.3 eV, corresponding to the yellow emission. In analogy to the previous studies of the PPC effect,^{16–19} we can deduce that the deep center located at 2.3 eV below the conduction band exhibits metastable behavior. After an electron is excited to the conduction band, the deep center can undergo a large lattice relaxation, which creates an energy barrier to prevent the photoexcited carrier from returning to the origin state; thus the PPC effect occurs. Investigation of PPC effect has led to a fruitful understanding of the carrier relaxation and the metastability of many crystal defects.^{16–19} The PPC effect observed in GaN films certainly warrants further study. Here we concentrate only on the fact that the deep level that causes the yellow emission in GaN has a metastable property, which can induce the PPC effect. A recent report shows that the GaN films without the yellow emission do not contain PPC behavior.²¹ This result provides further evidence to support the strong correlation between the origin of the yellow emission and PPC effect.

C. Photoluminescence

Up to now, we have established that the transition of the yellow emission is from the conduction-band edge to a localized state and the localized state has the properties of

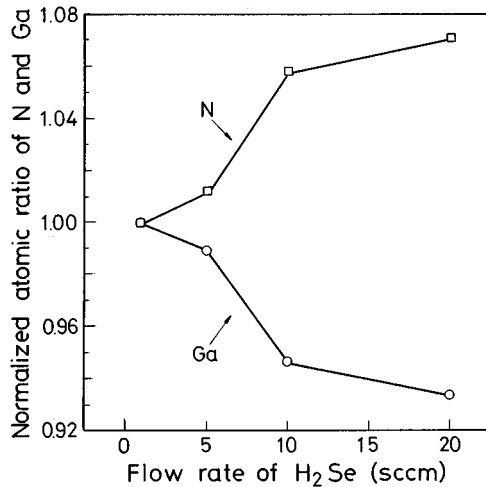


FIG. 6. Normalized atomic ratio of N and Ga as a function of the flow rate of H₂Se measured by x-ray wavelength dispersion spectrometry.

metastability. However, the microscopic origin of the localized state is still unknown. Let us now look at several recent results, which are very useful in resolving this problem. It is found that the yellow emission can be reduced in the doped films when Ge and Mg are used as the dopants.^{7,22} In this instance, the reduction of the yellow emission in Ge-doped or Mg-doped GaN is consistent with the nitrogen antisite (N_{Ga}) hypothesis proposed by Suski *et al.*²³ because Ge or Mg atoms could fill the Ga vacancies and reduce the formation of N_{Ga}. If the N_{Ga} hypothesis for the yellow emission is correct, we shall expect that the yellow emission should be enhanced for the GaN films with the dopants that substitute nitrogen sites. This is a result of the enhancement in the number of N_{Ga}, due to the filling of the dopants in the nitrogen lattice. To confirm this prediction, we perform the experiments on Se-doped samples, in which the Se atom can replace the N site and serves as a donor. In Fig. 6 we show the dependence of the atomic percentages of N and Ga on the flow rate of H₂Se as measured by x-ray wavelength dispersion spectrometry.^{10,11} The atomic percentages of N and Ga are normalized by that of the undoped GaN specimen. The atomic percentage of N increases with increasing H₂Se flow rate, while that of Ga decreases. This situation provides an excellent opportunity for the formation of N_{Ga}. Thus we shall expect that the number of N_{Ga} should increase with the H₂Se flow rate. The dependence of the yellow emission on the H₂Se flow rate is shown in Fig. 7, in which the band-edge emission is also included. We can clearly see that the relative intensity between the yellow emission and the band-edge emission increases with the H₂Se flow rate. Previously, a similar behavior was also observed in Se-doped GaN thin films.⁸ This result is in good agreement with the prediction that the increase of the H₂Se flow rate increases the number of N_{Ga} and hence enhances the yellow emission. Thus the

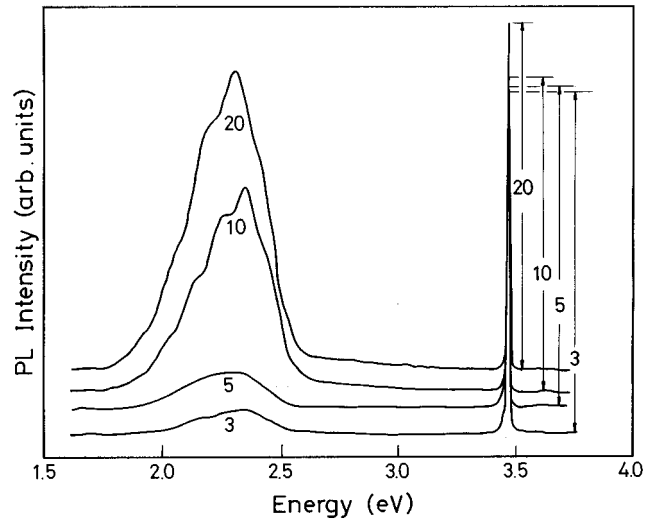


FIG. 7. Photoluminescence spectra of Se-doped *n*-type GaN films with the flow rate of H₂Se indicated as 3, 5, 10, and 20 SCCM. The spectra were taken at 10 K using a He-Cd laser excitation source at 325 nm.

hypothesis that the microscopic origin of the yellow emission can be attributed to the existence of N_{Ga} is consistent with our current experimental results.

It is interesting to note that an extensive theoretical study of the N_{Ga} in GaN has been reported recently.²⁴ It was found that the N_{Ga} undergoes, in a different charge state, a large spontaneous displacement from the ideal geometry and the connection between the N_{Ga} and the yellow luminescence has been suggested. This theoretical work thus provides further background to support our interpretation of the yellow emission in GaN epitaxial films.

IV. CONCLUSION

In conclusion, we have performed resonant Raman scattering, photoconductivity, and photoluminescence to study the nature of the yellow emission in GaN films. Our results establish that the transition of the yellow emission is from the conduction-band edge to a localized state and the localized state has a metastable property. Similar to many deep defects in other III-V and II-VI compounds,^{25,26} the metastability of the localized state can produce the PPC effect. According to the previous reports on the GaN films with the dopants that substitute Ga sites and our results on Se-doped GaN in which the Se atom replaces the N site, we suggest that the deep defect involving in the yellow emission may be attributed to the nitrogen antisite.

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