Photoluminescence related to Gd$^{3+}$:N-vacancy complex in GaN:Gd multi-quantum wells

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The photoluminescence of Gd-doped GaN multi-quantum wells (MQWs) is presented and discussed considering the formation of a Gd$^{3+}$:Nitrogen-vacancy (N-vacancy) complex. A lower energy photoluminescence peak was observed for the Gd-doped GaN MQW sample with respect to the main peak assigned to a neutral donor bound exciton (D$^0$X) of the undoped GaN MQW sample. The X-ray absorption near edge structure spectrum observed at Gd $L_{III}$-edge indicates a nitrogen vacancy adjacent to the Gd substituting the Ga ion in Gd-doped GaN MQW sample. Local stresses around the Gd dopants in Gd-doped GaN matrix generated due to the larger diameter of the Gd$^{3+}$ ion with respect to the Ga$^{3+}$ ion can be relieved by the creation of vacancies. The lower formation energy of N-vacancies in GaN matrix introduce them as a preferred candidate to relieve the generated stresses. A Gd$^{3+}$:N-vacancy complex consisting of a Gd$^{3+}$ ion and the created nitrogen vacancy adjacent to the Gd$^{3+}$ dopant is likely to form in GaN:Gd matrix. The lower photoluminescence peak energy observed in the Gd-doped GaN MQW sample is assigned to the recombination of an exciton captured at the Gd$^{3+}$:N-vacancy complex forming a small polaron-like state. A model is presented considering the small exciton-polaron population in defect sites captured around the Gd$^{3+}$ ions in the Gd-doped GaN.

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1. Introduction

Recently, the research on nitride semiconductors like AlN, GaN, InN and their alloys is rapidly increasing due to the prospects of new functional applications such as light emitting devices ranging from deep ultraviolet to infrared devices and single photon sources [1,2]. Modern diluted-doped semiconductors with rare-earth impurities open the field for new functional materials such as spintronic devices [3–5]. One of the rare earth diluted doped semiconductors, GaN doped with Gd$^{3+}$ ions, attracts the research interest due to its luminescence properties [6–8]. Native defects are always present in semiconductors and play a crucial role for semiconductor technology and device applications [9,10]. They are often formed during growth as compensation sources when dopants are introduced. Native defects such as nitrogen vacancies and their complexes are important participants in the defect kinetics in GaN [9,11]. The impurity – nitrogen vacancy complexes in doped GaN, drastically change their properties [12,13].

The photoluminescence spectra of a thick GaN layer show a near-band-edge emission at about 3.422 eV at room temperature and at about 3.483 eV at low temperature. The near-band-edge emission observed at low temperature is assigned to an exciton recombination bound at a neutral donor [14]. In addition, so-called, the blue luminescence around 2.7–3.0 eV and the yellow luminescence around 2.20–2.25 eV are often observed in an undoped GaN layer. The spectrum shape of the photoluminescence of these bands is always broad with a band shape close to Gaussian style, which is frequently observed for impurity centers [15,16]. These photoluminescence characteristics have been attributed to a gallium or nitrogen vacancy related transitions [14,17]. The vacancy may make a deep level in band gap or may act as a donor (acceptor). In GaN, the nitrogen vacancy supplies electrons to the conduction band. The recent theoretical work based on first principle calculations indicates that the nitrogen vacancy in GaN makes the energy level just below the conduction band and the gallium vacancy just above the valence band, concurrently addressing much higher formation energy of the gallium vacancy ($V_{Ga}$) than that of the nitrogen vacancy ($V_N$) [14,17,18]. Therefore, the
2. Experiments

2.1. Sample preparation

Two samples of Ga0.88Gd0.02N/Al0.12Ga0.88N and GaN/Al0.12Ga0.88N multi-quantum well (MQW) structures were grown on a sapphire substrate with a metalorganic vapor-phase epitaxy-grown n-type GaN (0001) template (around 2 μm thickness) by plasma-assisted molecular-beam epitaxy under nitrogen-rich conditions. Elemental Ga (purity: 7 N), Al (purity: 7 N), and RF plasma-assisted GaN layers were supplied as sources. The Ga and Al concentrations were fixed around 2% and 12%, respectively. The quantum well thickness is 1 nm while the barrier thickness is set to 9 and 18 nm alternatively. The temperature of the substrate was kept at 700 °C during the growth process of both samples. The quantum well structures were repeated 10 times, and the growth process was completed by a GaN (3 nm) cap layer. The Al composition (x = 0.12) of the barrier layers, AlxGa1-xN, is evaluated from the X-ray diffraction peak.

In-situ monitoring of the growing surfaces was recorded during growth by reflection high-energy electron diffraction. No formation of metal droplets on the surfaces during the growth is detected. The 0°-2θ X-ray diffraction rocking curves for the grown samples showed the diffraction peaks of GaN (0002). No other X-ray diffraction peaks were detected, indicating that the grown samples have no other orientation except the c-axis orientation. The detailed structural characterizations are reported in Refs. [8,20].

2.2. Optical measurements

The optical spectra were observed using continuous wave of a 325.0 nm wavelength of a He-Cd laser (KIMMON IR series) with a fixed power of 18 mW as an excitation light source. The emitted light from the samples was dispersed in a 1 m grating monochromator (JASCO CT-100, blazed at 300 nm). Both the entrance and exit slits of the monochromator were set to 1 mm. The spectrum intensities were recorded out through a lock-in technique. An ACTI Cryogenics closed-cycle helium cryostat was used to cool the samples from room temperature down to 8 K. A low energy pass filter was incorporated in the monochromator to cut off the direct laser light scattered by the sample. No correction for the spectrum response of the monochromator and the photomultiplier (650U type) is made.

2.3. X-ray absorption measurements

To identify the nitrogen vacancy in the GaGdN layers, we examined the spectra of the XANES around the Gd LIII-edge, using a synchrotron radiation. The measurements were performed at a beamline BL5A in PF, KEK. The storage-ring ran at an electron energy of 2.5 GeV and in an electron current of 450 mA under top-up operation. The monochromatization of the X-rays from the synchrotron radiation was made through a Si (1 1 1) double- crystal monochromator and the monochromatized X-rays were focused on the sample with a pseudo-conical shape mirror in a 1 mm × 1 mm beam size. The XANES spectra around the Gd LIII-edge were recorded by monitoring the X-ray fluorescence intensity of the Gd LIII line, using a solid-state detector (SSD, Ge:Li) with 19 elements. A high purity (99.95%) aluminium pipe was set just before the sample to block the detector reception of elastic and inelastic scattering by air in the X-ray path to the sample. The sample was mounted on a stand prepared in particular with about 7° to the incident X-ray beam to expose the samples with X-rays. The polarization direction of the incident X-ray beam is set parallel to the surface of the sample. The typical sample size is 5 mm in width and 10 mm in length. The spectra were taken with 0.8 eV step in energy and 3 s per each point in accumulation time. Measurements were performed at room temperature.

2.4. Theory of multiple scattering for analysis of XANES spectra

The XANES theory used to investigate vacancies is based upon the short-range-order full Multiple Scattering theory developed by Fujikawa et al. [21,22]. Here we briefly introduce the concept of the theory used in the analysis of the observed XANES spectra. Using Green’s function method, the X-ray absorption intensity I(ω) is given by Eq. (1) for photon energy ω:

\[ I(\omega) \cong \frac{1}{\pi} \text{Im}(\langle \Delta \gamma(\omega) | \Delta \gamma(\omega) \rangle) \]

(1)

where |\( \Delta \gamma(\omega) \rangle\) is the initial core-electron state, and \( \Delta \) is the electron–photon interaction operator. Photoelectron propagator \( g(\omega) \) gives information about scattering of a photoelectron by surrounding atoms in solids. Furthermore, \( g(\omega) \) includes many-body effects which describe decay process of photoelectron with energy \( e \) in inelastic scattering. From Eq. (1), X-ray absorption is interpreted as propagation of the photoelectron from an absorbing site to the same site in solids.

The real-space multiple scattering theories are useful for the calculation of XANES spectra in distorted system because this method does not need the periodic structure. In this scheme, the X-ray absorption intensity \( \sigma \) from the core orbital with angular momentum \( \ell \) at site \( A \) (X-ray absorbing atom) is given by Eq. (2) for photoelectron kinetic energy:

\[ \sigma = \frac{8}{3} \text{Im} \left\{ \sum_{n=1}^{N} \exp(i(q_{n}-q_{0})) \rho_{\ell}(1/G_{LL}^{(1\ell)}(1/L^{2}\ell))\left[ s_{\ell}(1-x^{-1})^{\ell} \right] \right\} \]

(2)

Here \( G_{LL}^{(1\ell)} \) includes the selection rule of photo-absorption by linearly polarized X-rays, and \( \rho_{\ell}(1) \) describes the overlap between the initial core-electron state and the \( l \)-th partial wave of a photoelectron. The phase shift of the \( l \)-th partial wave at site \( A \) is represented by \( q_{0} \). It arises when a photoelectron goes out from \( A \) and returns from the other sites. We introduce the matrix element \( X_{\ell}^{A} \) of the atomic site index \( x \) and \( \beta \), and angular momentum \( \ell \) and \( \ell \). The explicit form of the matrix element is given by Eq. (3),

\[ \Delta X_{\ell}^{A} = t_{\ell}^{A}G_{LL}(R_{A} - R_{B})(1 - \delta_{\ell 0}) \]

(3)

where \( t_{\ell}^{A} \) represents the scattering of a photoelectron inside the \( x \) site, and Green function \( G_{LL}(R_{A} - R_{B}) \) in an angular momentum representation describes propagation of a photoelectron from site \( B \) to site \( A \). Thus \( X_{\ell}^{A} \) represents that a photoelectron goes out from site \( B \) and is scattered at site \( A \). The inverse matrix \( (1 - X)^{-1} = 1 + X + X^{2} + \cdots \) describes the infinite order of the multiple scattering inside the cluster, which we are considering.

3. Results

3.1. XANES analysis

The analyses of the XANES spectra around the Gd LIII-edge in GaGdN have been reported recently [19]. Some model calculations assumed the formation of nitrogen vacancy locating at N2. The calculation model up to the first nearest neighbors around the Gd ion. A vacancy exists at N2, one of the equivalent three legs of the triangle in wurtzite structure. The shift of the Gd ion to the vacancy position is 0.5 Å.
non-apex of a triangular pyramid built up by GdN\textsubscript{4} as shown in Fig. 1. However, the calculations have not included the randomness of a vacancy site because N\textsuperscript{3+} has three equivalent sites. The vacancy position and the polarization direction of incident X-rays contribute to the structures of X-ray absorption spectra in a single crystal. In this context, we perform multiple scattering calculations for the Gd-doped GaN in the case of the single nitrogen vacancy including the N\textsuperscript{3+} randomness. Here, it is worth noticing that the nitrogen vacancy in Gd-doped GaN sample, which adjoins the doped Gd\textsuperscript{3+} ion, is not generated under the stoichiometric or gallium-rich-growth condition but only under the nitrogen-rich-growth condition [19].

All calculations are done by using a cluster with 7 Å including 125 atoms. This cluster size is within usual cases since the inelastic mean free path restricts the size of the cluster in real space. The cluster has only a centered Gd ion as an absorbing atom. Fig. 1 shows the structure of model up to the first nearest neighbor atoms around the Gd ion with a nitrogen vacancy. In the calculation model the Gd ion is substituted at a Ga site of GaN. The c-axis of wurtzite structure is the anisotropic direction. The polarization direction of the incident X-ray beam is perpendicular to the c-axis in the calculations. The nitrogen vacancy adjacent to the Gd ion is located at one of equivalent three legs of the triangle in wurtzite structure for one vacancy model. In addition, the Gd ion in the model is shifted up to 0.5 Å to the nitrogen vacancy position. The calculated result is obtained by taking the average for three different N\textsuperscript{3+} vacancy spectra with the fixed X-ray polarization. We also calculate for the model, with no vacancies and Gd shift, but the Gd–N bond lengths are expanded; 2.23 Å (c-direction) and 2.26 Å (the other direction). These Gd–N distances are referred to X-ray absorption fine structure analysis in another crystal growth condition [23]. The model’s structure beyond the first nearest neighbor atoms is the same as wurtzite GaN.

Fig. 2 shows three curves; for the calculated Gd L\textsubscript{III}-edge XANES spectra together with the observed one. The experimental spectrum of the present Gd-doped GaN MQWs shows a peak at 7245 eV without a shoulder structure. The calculated spectrum for the model of the Gd-doped GaN structure with no vacancy shows a shoulder peak at 7252 eV and a small hump at 7268 eV. The result for the model with no nitrogen vacancy is inconsistent with the observed spectrum as given in Fig. 2. However, the characteristics of the calculated spectrum with no nitrogen vacancy are consistent with the observed spectrum of other Gd-doped GaN samples grown under the stoichiometric or slightly Ga-rich growth conditions [23]. On the other hand, the calculated spectrum for the one vacancy model shows a weak shoulder and no hump structure at 7268 eV. These spectral features are roughly consistent with the observed spectrum as shown in Fig. 2. Therefore, these calculations indicate that at least one nitrogen vacancy exists adjacent to the Gd ion in Gd-doped GaN MQWs grown under the current crystal growth conditions. As a full-potential scheme (model) is not employed in this simulation, the strong edge structure, so-called white line, is hardly reproduced well in the present theoretical stage. However, our result properly catches the characteristics of the spectrum. As evidence, it is noticeable that the gallium vacancy on the second neighbors almost does not affect to the XANES spectra.

### 3.2. Photoluminescence spectra

The photoluminescence spectrum from bulk GaN crystals usually shows a near-band-edge emission around 3.422 eV at room temperature and around 3.483 eV at low temperature. Two additional broad bands referred as a blue emission and a yellow luminescence are frequently observed in the visible region. The photoluminescence spectra of GaN(1 nm)/Al\textsubscript{0.12}Ga\textsubscript{0.88}N and Ga\textsubscript{0.98}Gd\textsubscript{0.02}N(1 nm)/Al\textsubscript{0.12}Ga\textsubscript{0.88}N MQWs prepared under the same growth conditions are shown in Fig. 3. The undoped GaN MQW sample shows a photoluminescence peak of the excitonic transition at 3.664 eV. The main photoluminescence peak for the Gd doped GaN MQW sample is observed at 3.598 eV. A weak hump is recognized at 3.483 eV for both samples, this hump is attributed to the luminescence from the GaN template, which is grown on the sapphire substrate. The large blue shift of the excitonic transition peak relative to the GaN template infers the quantum confinement effect in the thin quantum well layers of 1 nm. The red energy shift of the main photoluminescence peak of Gd-doped with respect to the undoped GaN MQW sample having the same thickness and grown under the same conditions is 66 meV [8]. The observed photoluminescence peak energy in the undoped GaN MQW sample agrees well with the thickness dependence of quantum confinement transition energies reported for the GaN wells with a similar barrier composition [24]. The large energy shift observed in Gd-doped GaN MQW sample is associated with the Gd dopant in GaN matrix, this red energy shift can be attributed to a complex formed by the Gd ion dopant and a nitrogen vacancy created in the region deformed by the Gd dopant. Fig. 4 presents the photoluminescence spectra of the same sample, Ga\textsubscript{0.98}Gd\textsubscript{0.02}N(1 nm)/Al\textsubscript{0.12}Ga\textsubscript{0.88}N MQW, observed at various temperatures. The higher energy side of the photoluminescence spectra is slightly deformed by a low energy pass filter incorporated in the monochromator. The variation of the photoluminescence peak energy for the

![Fig. 2. Calculated Gd L\textsubscript{III}-edge XANES spectra for the Gd-doped GaN together with the experimental data. The calculation for the one vacancy model shows negligibly small shoulder and no hump structures, which are consistent with the observed result.](image)

![Fig. 3. Photoluminescence spectra from the GaN(1 nm)/AlGaN MQW, dotted line, and GaGdN(1 nm)/AlGaN MQW, solid line, samples measured at 10 K.](image)
undoped and Gd-doped GaN MQW samples as a function of temperature is shown in Fig. 5. The photoluminescence peak shows a blue shift with increasing temperature at the low temperature region (10–50 K), and subsequently displays the standard red-shift behavior.

The small blue shift between 10 and 50 K (≈3 meV) is attributed to the lattice contraction with increasing temperature, so-called negative thermal expansion (NTE), which is frequently found in crystals with non-centrosymmetry at low temperatures [25,26]. As lattice constants influence the potential for an electron in the valence and conduction bands of crystals, the band gap can be controlled by the lattice parameters. Such behavior is realized under pressure. The band gap of semiconductors increases by the lattice contraction if the contraction is small. Consequently, the NTE of GaN contributes to the small blue shift of the band gap at low temperatures.

4. Discussion

4.1. Temperature dependence of photoluminescence energy

The observed red shift of the exciton peak energy between 50 K and 300 K for the undoped GaN MQW sample in the present study amounts to 42 meV. For GaN thin film, the reported red shift of the energy band gap by increasing temperature to room temperature reaches about 61 meV [27]. The observed value of the red shift with increasing temperature in the present GaN MQW sample is smaller than that of pure GaN thin film by 19 meV. This reduction in the red energy shift could be attributed to interfacial stresses results from the lattice mismatch between the GaN quantum wells and the AlGaN barrier layers. The in-plane lattice constant of AlGaN barrier layers is smaller than that of GaN quantum well layers. This lattice mismatch between GaN quantum wells and AlGaN barrier layers will result in compressive stresses in the GaN well layers [28,29]. These interfacial compressive stresses imposed on the GaN quantum well layers are expected to result in a blue shift of the photoluminescence owing to an expansion of GaN band gap [30–33]. The generated compressive stresses become stronger at higher temperatures because the thermal expansion coefficient of GaN wells is larger than that of AlGaN barrier layers. On the other side, the energy band gap will show a red shift with increasing temperature. The smaller red energy shift can be explained by considering two contributions working in opposite directions with increasing temperature. The blue energy shift will decrease the net red energy shift of the band gap with increasing temperature in GaN MQWs compared with GaN thin films. In the Gd-doped GaN MQWs sample, the red shift is 46 meV (see Fig. 5), which is a bit larger than the pure GaN MQWs. The contribution of the N-vacancy to the observed larger red shift in the Gd-doped GaN compared with the nondoped GaN MQWs can be elucidated by a partial relief of the compressive stresses due to the created N-vacancies in the Gd-doped sample [19]. Being mobile, N-vacancies can contribute more as stresses compensating candidates by site redistribution with increasing temperature. In this case, the band expansion with temperature due to the created stresses will be smaller and consequently the temperature dependent red shift of the band gap will be a dominant.

4.2. N-vacancy formation

Due to the large ionic radius of a Gd$^{3+}$ ion compared with a Ga$^{3+}$ ion, the Gd$^{3+}$ doping in GaN is expected to introduce vacancies as a mechanism to release the created strain and to compensate the tight circumstance around the Gd$^{3+}$ ions in GaN matrix. As described in the previous sections, the model simulations using the full multiple scattering theory indicate that nitrogen vacancy, which adjoins the doped Gd$^{3+}$ ion and locates at non-apical position of the triangular pyramid formed by GdN$_4$, is created under the current growth conditions. The observed X-ray diffraction profile for the present Gd-doped MQWs sample shows only one peak associated with GaN (0002) while no peak originated from GaGdN was observed, which is expected to be observed at a lower
It is worth noting that the X-ray diffraction profile for other Gd-doped MQW sample, which does not show the existence of N-vacancy in XANES profile, shows a peak related to GaGdN at a lower diffraction angle. This observation indicates that in the present sample, GaN:Gd crystal has the same lattice constant on the long range order as GaN matrix. In other words, there is no expansion of the lattice in spite of a ratio of Ga is substituted by Gd ions with the larger ionic diameter. Therefore, it is plausible to consider that the GaGdN crystal relaxes to that of the GaN lattice due to the nitrogen vacancies created as a mechanism to relieve the strain in GaGdN layers. Recent first-principle calculation qualitatively identifies, and strongly supports this interpretation [18]. These calculations give a potential dip at the N-vacancy site adjoining the Gd ion of about 0.4–0.5 eV. The existence of N-vacancies and their pairing with impurities in doped GaN have been reported experimentally, for example, the formation of Mg$_{Ga}$V$_{N}$ complex in Mg-doped GaN and Be$_{Ga}$V$_{N}$ complex in Be-doped GaN have been reported by positron annihilation experiments [34,35].

4.3. Local potential model around Gd$^{3+}$:N-vacancy complex

Here, we introduce a potential model around the Gd$^{3+}$ ion to elucidate the red shift of the photoluminescence observed in the Gd-doped GaN MQW sample. A lower potential is created in the deformed regions around the Gd$^{3+}$:N-vacancy sites and may strongly work to capture excitons. Consequently, a small exciton polaron-like state is formed (Fig. 6). Different parameters can contribute to produce the lower potential in the deformed regions around Gd$^{3+}$:N-vacancy sites. As well known, an exciton often travels dressed with a phonon in crystals and consequently, a deformed local potential is associating the exciton, generally named “an exciton-polaron state”. The formation of an exciton-polaron was already reported for the diluted magnetic semiconductors CdMnTe, CdMnSe and also in the ionic crystal AgBr [36–38]. We will call the captured exciton in the present case a small-exciton-polaron-like state.

Fig. 7 shows a schematic representation of the semi-quantitatively potential levels for both Gd-doped and the non-doped GaN MQWs samples. An exciton is captured at the defect site around Gd$^{3+}$:N-vacancy complex in Gd-doped GaN and a small exciton-polaron-like state is formed. First, we construct the energy levels of the quantum confined exciton in the band gap of the non-doped GaN MQW. The nitrogen vacancy that naturally arises during GaN crystal growth forms a shallow donor state with an energy level located around 7 meV below the bottom of the conduction band [17]. In the present case, the GaN well thickness, 1 nm, is considerably small compared with the free exciton Bohr radius. Thus, the exciton will be confined in the quantum well, contracted in size and consequently has a larger binding energy. The reported value of the binding energy of bulk GaN is about 28 meV and the Bohr radius is 3 nm [39]. A binding energy of 33 meV of the exciton confined in a GaN quantum well of 1 nm can be adopted from Ref. [40]. Therefore, an energy level of 40 meV is expected to lie below the bottom of the conduction band in the case of an exciton coupled to a N-vacancy, Fig. 7a. The emitted exciton resulting from the recombination from this energy level to the valence band can be ascribed to the photoluminescence peak of 3.664 eV observed at 10 K for the nondoped GaN MQWs sample, Fig. 3. In Gd doped GaN MQWs sample, the red shift of the photoluminescence energy relative to the nondoped GaN with the same layer thickness is 66 meV. This red energy shift of the peak is associated with the localized Gd$^{3+}$:N-vacancy complex and can be attributed to the small exciton-polaron like state formed in the deformed region around the Gd$^{3+}$:N-vacancy complex. For the Gd-doped MQW samples, the potential dip at the N-vacancy position adjacent to the Gd$^{3+}$ ion is estimated to be 0.4–0.5 eV by first principle method [18]. The exciton in the GaN:Gd MQW is likely to bound to this potential dip and forms a small exciton-polaron like state. The wave function of the small exciton-polaron-like state spreads to the potential dip and the small-exciton-polaron-like state will be contracted in size with a larger binding energy. We assume that the Bohr diameter of the exciton in the small-exciton-polaron like state is 1 nm, which is the GaN well layer thickness. Thus the small exciton-polaron like state has a binding energy, inversely proportional to its radius, around 84 meV. An energy level lies at 3.598 eV above the valence band represents the bound state of the small-exciton-polaron-like state in the GaGdN quantum well and will ascribe the observed photoluminescence peak observed in our Gd doped GaN MQWs sample, as shown in Fig. 7b. Thus the energy level of the bound state of the exciton refers to 22 meV.

5. Conclusions

The existence of a nitrogen vacancy adjoining the Gd$^{3+}$ ion dopant in Gd-doped GaN multiquantum well structure has been confirmed by the analysis the XANES spectra around the Gd L$_{3\alpha}$ edge, applying the full multiple-scattering theory. N-vacancy...
formation can be generated only under the nitrogen rich growth condition. The N-vacancy does not locate at the apex of the triangle in wurtzite structure but at one site of the three equivalent legs. The observed photoluminescence shows lower exciton peak energy of the bound exciton in Gd-doped with respect to the nondoped GaN MQW sample. A model considering the creation of the nitrogen vacancy associating with the Gd doping and the formation of Gd$^{3+}$:N-vacancy complex is presented. The lower photoluminescence peak energy of the Gd-doped GaN quantum wells is assigned to the captured excitons at the distorted regions around Gd$^{3+}$:N-vacancy complex. For the small exciton-polaron-like state, like a Bohr exciton, the wave function spreads to the potential dip created by Gd$^{3+}$:N-vacancy complex and will have a larger binding energy.

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