

Deep impurity transitions involving cation vacancies and complexes in AlGa_xN alloys

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Deep ultraviolet (UV) photoluminescence (PL) spectroscopy has been employed to study deep impurity transitions in Al_xGa_{1-x}N (0 ≤ x ≤ 1) epilayers. Two groups of deep impurity transitions were observed, which are assigned to the recombination between shallow donors and two different deep level acceptors involving cation vacancies (V_{cation}) and V_{cation} complexes in Al_xGa_{1-x}N alloys. These acceptor levels are pinned to two different energy levels common to Al_xGa_{1-x}N alloys (0 ≤ x ≤ 1). The deep impurity transitions related with V_{cation} complexes were observed in Al_xGa_{1-x}N alloys between x=0 and 1, while those related with V_{cation} were only observed in Al_xGa_{1-x}N alloys between x=0.58 and 1. This points out to the fact that the formation of V_{cation} is more favorable in Al-rich AlGa_xN alloys, while V_{cation} complexes can be formed in the whole range of x between 0 and 1. The implications of our findings to the UV optoelectronic devices using AlGa_xN alloys are also discussed. © 2005 American Institute of Physics. [DOI: 10.1063/1.1943489]

With the tremendous progress of III-nitrides R & D in terms of both fundamental understanding as well as devices applications, AlN becomes more critical for the further understanding of AlGa_xN alloys and for III-nitride device development.¹ Recently, AlGa_xN alloys, particularly Al rich AlGa_xN alloys have attracted much interest due to their applications in solid-state UV light sources for bioagent detection as well as general lighting.^{2,3} The yellow line (YL) with emission energy at around 2.15 eV is the dominant impurity transition in GaN in many cases. The material quality of GaN is strongly correlated with the YL intensity. The YL in GaN is commonly attributed to a donor-to-acceptor pair (DAP) transition between a shallow donor and a deep acceptor whose origin is related with Ga vacancy (V_{Ga}) or V_{Ga} complexes in GaN.⁴⁻⁶ For AlN, a broad violet line (VL) around 3.40 eV is often observed and believed to be related with Al vacancy (V_{Al}) or V_{Al} complexes, analogous to the YL in GaN.⁶ Understanding impurity transitions in AlGa_xN alloys is very important for improving the fundamental understanding of material as well as device performance, since the presence of strong impurity transitions is detrimental to optoelectronic devices using AlGa_xN epilayers.

In this letter, we report the results of impurity transitions involving V_{Al} and V_{Al} complexes in Al_xGa_{1-x}N epilayers grown on sapphire substrates by metalorganic chemical vapor deposition (MOCVD). In many cases, two groups of deep impurity transitions were observed in both undoped and Si-doped Al_xGa_{1-x}N epilayers. These emission lines are assigned to the recombination between a shallow donor and two different deep acceptors, based on the results of spectral peak positions, temperature dependence, and decay lifetime measurements. The deep acceptors involved here have been identified as isolated cation vacancies that are three-negatively charged states (V_{cation}^{3-}) and V_{cation} complexes that are two-negatively charged states ($V_{\text{cation}}\text{-complex}^{2-}$) in Al_xGa_{1-x}N alloys. The YL in GaN has been observed and discussed as a special case of a group of impurity transition in AlGa_xN alloys. This observation is important in two aspects. First, we can better understand the origin of the YL

with additional information from AlGa_xN alloys. Second and more importantly, it also helps us to better understand impurity properties in AlGa_xN alloys. By understanding impurity transitions in AlGa_xN alloys, we could also identify exclusively the origin of the VL in AlN.

The 1 μm thick undoped and Si-doped Al_xGa_{1-x}N epilayers were grown by MOCVD on sapphire (0001) substrates. Trimethylgallium (TMG), trimethylaluminum (TMA), and NH₃ were used as Ga, Al, and N sources, respectively. The Al contents of Al_xGa_{1-x}N (0 ≤ x ≤ 1) alloys were determined by energy dispersive x-ray (EDX) measurements and x-ray diffraction (XRD) as well as the flow rates of TMG and TMA. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were employed to examine the surface morphology of these AlGa_xN epilayers. AFM measurements show the root-mean-squares (rms) of AlGa_xN epilayers studied here are comparable to that of GaN (about 1 nm in a 2 μm × 2 μm scan). The secondary ion mass spectroscopy (SIMS) measurements were performed (by Charles Evans & Associates) for AlGa_xN epilayers to measure the Si-dopant and oxygen concentrations. The deep UV picosecond time-resolved laser spectroscopy system used here consists of a frequency quadrupled 100 fs Ti:sapphire laser with excitation photon energy set around 6.28 eV (with a 76 MHz repetition rate and a 3 mW average power) and a monochromator (1.3 m). A microchannel-plate photomultiplier tube (MCP-PMT) together with a single photon counting system was used to collect time-resolved PL data and the time resolution of the detection system is about 20 ps.⁷

Figure 1 shows the room temperature (300 K) PL spectra of a set of undoped Al_xGa_{1-x}N epilayers with x between 0 and 1 with relatively low impurity concentrations (<10¹⁸ cm⁻³). The peak positions related with the band-edge transitions exhibit a blueshift with increasing x, shifting from 3.42 eV for GaN to 5.96 eV for AlN.⁸ The deep impurity peak positions also show a blueshift with increasing x, shifting from 2.15 eV for GaN to 3.90 eV for AlN. The yellow line (YL) around 2.15 eV has been extensively studied in GaN, which most likely involves V_{Ga} or V_{Ga} complexes such as $V_{\text{Ga}}\text{-O}_N$ or $V_{\text{Ga}}\text{-Si}_{\text{Ga}}$.^{5,6} However, the exact mechanism of the YL in GaN is still under debate. The 3.9 eV emission line

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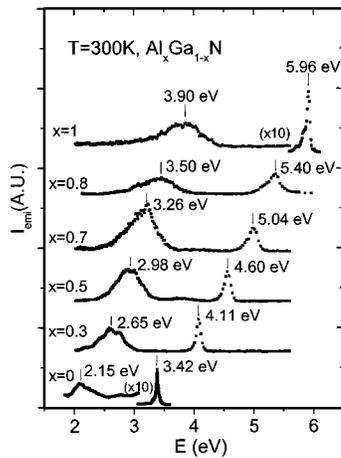


FIG. 1. Room temperature PL spectra of a set of undoped $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers ($0 \leq x \leq 1$) with relatively low impurity concentrations ($< 10^{18} \text{ cm}^{-3}$), including both the band edge and deep impurity transitions associated with YL in GaN.

in AlN has not been previously reported and could be observed only in undoped AlN with relatively low impurity concentrations ($< 10^{18} \text{ cm}^{-3}$). The relative intensity between band edge and deep impurity transitions depends strongly on the growth condition, similar to the YL in GaN.

Another group of deep impurity transitions, which is distinctly different from the YL in GaN, were also observed in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers with higher impurity concentrations. Figure 2 shows the 300 K PL spectra of another set of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers with x between 0.58 and 1 grown under different conditions with higher impurity concentrations (either due to doping with Si or unintentional doping with O). The deep impurity transitions in this set of samples also exhibit a blueshift from 2.56 eV for $\text{Al}_{0.58}\text{Ga}_{0.42}\text{N}$ to 3.40 eV for AlN. The observed band-edge transition in AlN was at 5.95 eV, which is slightly different from that of undoped AlN shown in Fig. 1 (5.96 eV), probably due to the different magnitudes of strain involved. Comparing the results shown in Figs. 1 and 2, one can conclude that the presence of high impurity concentration favors the VL at 3.40 eV over the 3.90 eV line in AlN. Our preliminary studies show that the VL in AlN is a DAP transition involving a shallow donor and a deep acceptor. The intensities of these deep impurity transitions are on the same order as those of the band-edge trans-

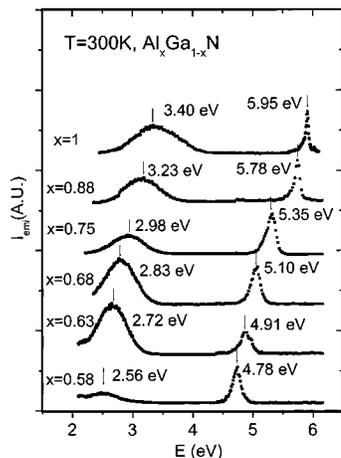


FIG. 2. Room temperature PL spectra of a set $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers ($0.58 \leq x \leq 1$) with higher impurity concentrations, including both the band edge and deep impurity transitions associated with VL in AlN.

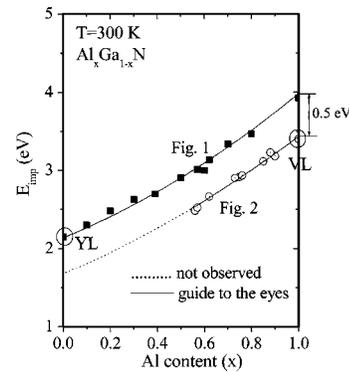


FIG. 3. PL peak positions (E_{imp}) of deep impurity transitions obtained from Fig. 1 (closed squares) and 2 (open circles) as functions of x . The peak positions of the YL in GaN and VL in AlN are also indicated. The solid lines are guide to the eyes.

sitions. Interestingly, this group of deep impurity transitions was not observable in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers with $x < 0.58$.

In Fig. 3, we plot the PL spectral peak positions (E_{imp}) of the observed two groups of deep impurity transitions as functions of Al content (x) obtained from Figs. 1 (closed squares) and 2 (open circles). The peak positions of both deep impurity transitions show continuous increase with x and the two plots are almost parallel with each other with a separation of about 0.5 eV, indicating that the impurity transitions are of the similar nature. However, it is also clear that the transitions shown in Figs. 1 and 2 involve two different impurity levels. In Fig. 3, the solid lines are a guide to the eyes, while the dotted line indicated that the transitions were not observable in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers. The spectral peak positions of the YL in GaN and VL in AlN are also indicated. The results shown in Fig. 3 clearly demonstrate that the origin of the YL in GaN is different from that of the VL in AlN because they belong to two different groups of impurity transitions.

To identify the origins of these deep impurity transitions, we plot the deep acceptor energy levels (E_A) with E_v and E_c as functions of x in Fig. 4. The YL in GaN and VL in AlN are also indicated. The band gap (E_g) of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ can be described by $E_g(x) = (1-x)E_g(\text{GaN}) + xE_g(\text{AlN}) - bx(1-x)$ with the bowing parameter being $b = 1 \text{ eV}$.⁸ The energy band gaps of GaN and AlN are taken as 3.44 and 6.05 eV at room temperature, respectively.⁹ The conduction (E_c) and valence (E_v) band offset parameters are assumed to be 70% and 30% for the GaN/ $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) heterostructure, respec-

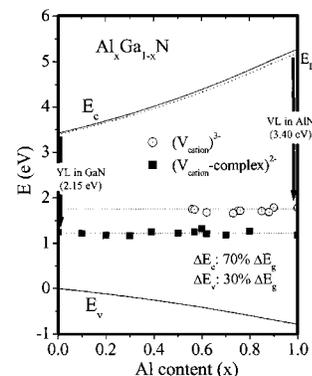


FIG. 4. Acceptor levels (E_A) obtained from Fig. 1 (closed squares) and 2 (open circles) as functions of x . E_c and E_v are also included with E_D^0 being the shallow donor level. The valence band maximum of GaN is chosen as $E = 0$. The YL in GaN and VL in AlN are also indicated.

tively. The valence band maximum of GaN is chosen as $E = 0$. Our preliminary studies suggest that the deep impurity transitions involved in Figs. 1 and 2 are a DAP type involving two different deep acceptors and the shallow donors. The observed very long decay lifetimes of longer than 1 μs support this assignment. The chemical origin of the shallow donors involved here is believed to be either Si or O in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers. The ionization energies (E_D^0) of the shallow donors are assumed to increase linearly from 25 to 86 meV with varying x from 0 to 1 in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers.^{10,11} The deep acceptor levels determined below will not change significantly even if a different range of shallow donor level is used between 60 and 200 meV. The acceptor levels (E_A) involved in the transitions shown in Figs. 1 and 2 can be deduced by $E_A(x) = E_g(x) - E_{\text{imp}} - E_D + E_v$ with $E_v = -0.3\Delta E_g(x)$ and $E_c = E_g(\text{GaN}) + 0.7\Delta E_g(x)$ with neglecting the Coulomb interaction between the ionized donors and acceptors. It is interesting and important to note that the deduced acceptor levels as functions of x are **horizontal lines** in the whole range of x , as demonstrated in Fig. 4. This clearly indicates that these levels are pinned to the energy levels common to $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys with an energy separation of 0.5 eV. This is very common for deep acceptors in other semiconductors as well as III-nitrides¹¹⁻¹³ as a consequence of the large binding energies and very strong localization of deep acceptors.

The formation energies (E_{form}) of V_{cation} and $V_{\text{cation-complex}}^{2-}$ as well as other impurities as functions of Fermi level, E_F , have been calculated in GaN and AlN.^{6,14,15} Since $(V_{\text{Ga-complex}})^{2-}$ has the lowest E_{form} regardless of E_F in GaN, the origin of the YL in GaN is attributed to $(V_{\text{Ga-complex}})^{2-}$ such as $V_{\text{Ga-O}_N}$ or $V_{\text{Ga-Si}_{\text{Ga}}}$ rather than $(V_{\text{Ga}})^{2-}$ or $(V_{\text{Ga}})^{3-}$.⁶ However, the E_{form} of $(V_{\text{cation}})^{3-}$ decreases with increasing x in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys and becomes the lowest and negative with increasing E_F ($E_F > 5.8$ eV) in AlN, indicating that $(V_{\text{cation}})^{3-}$ can be formed spontaneously during the growth of AlN.^{6,14} Thus, $(V_{\text{cation}})^{3-}$ is the most favorable native defect and accountable for the VL (3.40 eV) in AlN with high impurity concentrations, in which E_F is relatively high. The presence of impurities such as Si or oxygen can enhance the formation of V_{cation} and the intensity of VL in AlN, since E_F increases with an increase of the impurity concentration.

It is commonly believed that the origin of VL in AlN is the same as that of YL in GaN.⁶ However, based on results shown here, we believe that the VL in AlN is a DAP transition involving a shallow donor and a $(V_{\text{Al}})^{3-}$ deep acceptor. On the other hand, the optical transition line at 3.90 eV in AlN shown in Fig. 1 has the same origin as the YL in GaN, which is attributed to a DAP transition involving a shallow donor and a $(V_{\text{Al-complex}})^{2-}$ deep acceptor. The possibility of $(V_{\text{Al}})^{2-}$ as the origin of a deep acceptor in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys can be excluded due to its higher formation energy than $(V_{\text{Al-complex}})^{2-}$. The binding energies of $(V_{\text{Al}})^{3-}$ and $(V_{\text{Al-complex}})^{2-}$ in AlN can be obtained from Fig. 4 to be about 2.60 and 2.10 eV (with a difference of 0.50 eV), respectively. The calculated binding energy of $(V_{\text{Al}})^{3-}$ varies from 2.10 to 2.60 eV, while that of $(V_{\text{Al-complex}})^{2-}$ is about 1.60–1.90 eV.^{6,15} The calculated difference in binding energies between $(V_{\text{Al}})^{3-}$ and $(V_{\text{Al-complex}})^{2-}$ is about 0.5 eV,⁶ which agrees very well with our experimental value. These facts again support our assignment that acceptors involved in

the DAP transitions shown in Fig. 1 are $(V_{\text{cation-complex}})^{2-}$ and in Fig. 2 are $(V_{\text{cation}})^{3-}$. The absence of deep impurity transitions related with $(V_{\text{cation}})^{3-}$ for materials with $x < 0.58$ is consistent with the fact that $(V_{\text{cation-complex}})^{2-}$ are more favorable in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys with low x ($x < 0.58$).^{6,14,15}

The existence of strong deep impurity transitions related with $(V_{\text{cation}})^{3-}$ also correlates with reduced electrical conductivities in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys with $x > 0.58$. Our experimental results support the claim that $(V_{\text{cation}})^{3-}$ is very stable, giving the strong deep impurity transitions in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys with $x > 0.58$, which may be a cause of the reduced n -type conductivity in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys with high x , particularly in AlN, due to its ability to capture three electrons.

In summary, we have investigated the impurity transitions in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers between $x=0$ and 1 grown on sapphire by MOCVD. Two groups of deep impurity transitions were observed in both undoped and Si-doped $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers. The origins of two different acceptors involved in the deep impurity transitions have been identified as $(V_{\text{cation-complex}})^{2-}$ in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys between $x=0$ and 1 and $(V_{\text{cation}})^{3-}$ in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys between $x=0.58$ and 1. The YL and VL in GaN and AlN have been identified as special cases of these impurity transitions in AlGaN alloys. Our experimental results indicate that the formation of $(V_{\text{cation}})^{3-}$ is more favorable in Al-rich AlGaN alloys, while $(V_{\text{cation-complex}})^{2-}$ are more favorable in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys with lower x . The two acceptor levels related with $(V_{\text{cation}})^{3-}$ and $(V_{\text{cation-complex}})^{2-}$ are pinned to the energy levels common to $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys with an energy separation of 0.5 eV. The presence of $(V_{\text{cation}})^{3-}$ and $(V_{\text{cation-complex}})^{2-}$ in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys with $x > 0.58$ lead to the reduced conductivities and are detrimental to the optoelectronic devices using $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers with high x .

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