

The origin of 2.78 eV emission and yellow coloration in bulk AlN substrates

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(Received 13 October 2009; accepted 2 December 2009; published online 29 December 2009)

The yellow color of bulk AlN crystals was found to be caused by the optical absorption of light with wavelengths shorter than that of yellow. This yellow impurity limits UV transparency and hence restricts the applications of AlN substrates for deep UV optoelectronic devices. Here, the optical properties of AlN epilayers, polycrystalline AlN, and bulk AlN single crystals have been investigated using photoluminescence (PL) spectroscopy to address the origin of this yellow appearance. An emission band with a linewidth of ~ 0.3 eV (at 10 K) was observed at ~ 2.78 eV. We propose that the origin of the yellow color in bulk AlN is due to a band-to-impurity absorption involving the excitation of electrons from the valence band to the doubly negative charged state, (V_{Al}^{2-}) , of isolated aluminum vacancies, $(V_{Al})^{3-/2-}$ described by $V_{Al}^{2-} + h\nu = V_{Al}^{3-} + h^+$. In such a context, the reverse process is responsible for the 2.78 eV PL emission. © 2009 American Institute of Physics. [doi:10.1063/1.3276567]

Free-standing, native nitride substrates with low dislocation densities and high crystalline quality are highly desirable for the epitaxial growth of next generation III-nitride devices such as short-wavelength light emitting diodes, laser diodes, solar blind ultraviolet (UV) detectors, surface acoustic wave devices, and high frequency microwave devices. In particular, the availability of bulk AlN crystals as a native substrate for III-nitride epitaxial growth will help to achieve practical deep UV (DUV) optoelectronic device structures by reducing dislocation density. Currently, several groups are developing various techniques for the growth of bulk AlN crystals.¹⁻⁸ Recent reports of homoepitaxial layer growth and device fabrication using bulk AlN substrates have already demonstrated potential applications.⁶⁻⁸

Despite recent progress made in nitride epilayers and devices on AlN substrates, critical issues remain. For DUV applications, bulk AlN substrates should be transparent from the visible to DUV region. However, all sizeable bulk AlN substrates exhibit a yellow or dark amber color. A correlation between the yellow coloration of bulk AlN and a broad absorption band centered around 2.86 eV was previously reported.⁹ Samples with relatively low oxygen contamination have an absorption band starting around 2.0 eV with a maximum at around 2.86 eV. However, the yellow coloration completely disappears in transparent AlN containing high levels of oxygen contamination ($\sim 10^{19}$ – 10^{20} cm⁻³). The disappearance of the yellow coloration was accompanied by a reduced absorption band centered at 2.86 eV. More recently, a similar broad absorption centered around 2.8 eV was reported in bulk AlN crystals with oxygen levels $\sim 1 \times 10^{19}$ cm⁻³, again with the absorption being more prominent in samples containing fewer oxygen impurities.¹⁰ Thus, the yellow appearance of bulk AlN is widely believed to be related to a broad absorption band centered around 2.86 eV. However, the physical origin of this absorption band has not been understood.

In this letter, we studied the origin of the yellow appearance in AlN. Samples studied included c-AlN epilayers grown on sapphire by metal organic chemical vapor deposi-

tion, polycrystalline c-textured AlN grown by physical vapor transport, and bulk m-AlN single crystals produced by sublimation crystal growth using polycrystalline AlN wafers as seeds.⁸ The epilayer, polycrystalline, and bulk AlN samples appear in transparent, light yellow, and amber colors under room light. These samples were determined to contain about 1.5×10^{17} , 1.0×10^{18} , and 2×10^{18} cm⁻³ of oxygen impurities, respectively, via SIMS measurements. Photoluminescence (PL) properties were investigated by employing our specially designed DUV laser spectroscopy system, which consists of a frequency quadrupled Ti-sapphire laser with a 76 MHz repetition rate. The excitation wavelength was set at 197 nm (6.31 eV).¹¹

In Fig. 1(a), we compare the 300 K PL spectra of c-AlN epilayers, polycrystalline c-AlN, and bulk m-AlN with an above band-gap excitation. The AlN epilayer and polycrystalline AlN exhibit dominant free exciton (FX) emission peaks at 5.98 and 5.96 eV, respectively.^{8,12,13} However, the FX transition at 5.95 eV and broad emission lines at 4.0 and 2.76 eV have comparable emission intensities in bulk m-AlN. The impurity band around 4.0 eV was previously identified as a donor-acceptor-pair type transition involving a shallow donor and an aluminum vacancy (V_{Al}) complex with 2/1 negative charges, either $(V_{Al}-O_N)^{2-/1-}$ or

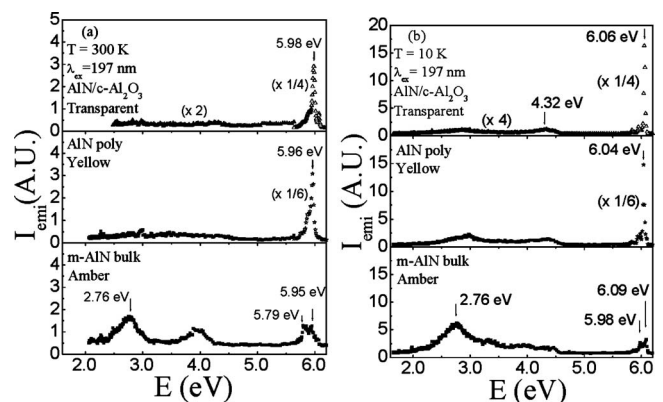


FIG. 1. (a) Room temperature (300 K) and (b) low temperature (10 K) PL spectra of AlN hetero-epilayer, polycrystalline AlN, and bulk AlN single crystal under above band-gap excitation scheme with 197 nm laser.

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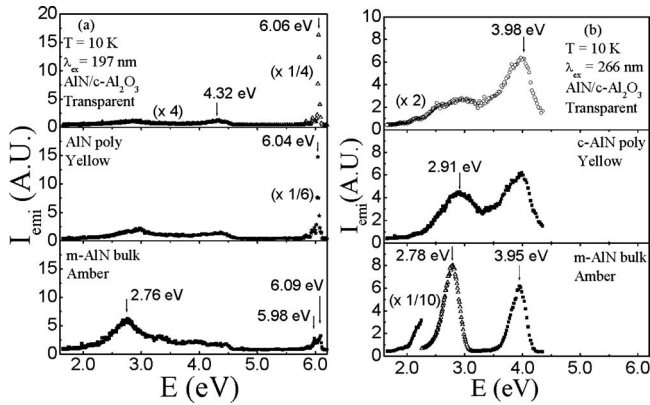


FIG. 2. Low temperature (10 K) PL spectra of AlN hetero-epilayer, polycrystalline AlN, and bulk AlN single crystal under: (a) above (197 nm) and (b) below (262 nm) band gap excitation.

$(V_{\text{Al}}-\text{Si}_{\text{Al}})^{2-/-}$.¹⁴ Figure 1(b) compares the 10 K PL spectra of the same set of samples, which shows an obvious blue shift of the FX line to 6.06 (6.04) eV in the AlN epilayer sample (polycrystalline AlN). The 10 K spectra of all three samples display visible features at about 4.32 eV. The impurity transition at 2.76 eV is more prominent in bulk AlN at 10 K. Here, we will concentrate our efforts to exploring the mechanism of the 2.76 eV emission line in AlN and understanding why bulk AlN substrates come with an undesirable yellow color.

In Fig. 2, we compare low temperature (10 K) PL spectra of all three samples with (a) above band gap excitation with a 197 nm (6.30 eV) laser line and (b) below band gap excitation with a 262 nm (4.739 eV) laser line. For below band gap excitation, the emission line at 4.32 eV is completely disappeared with the concomitant appearance of narrower and stronger emission lines related to $(V_{\text{Al}}-\text{O}_{\text{N}})^{2-/-}$ or $(V_{\text{Al}}-\text{Si}_{\text{Al}})^{2-/-}$ at 3.95 eV in all three samples. The emission line at 2.76 eV in the bulk m-plane sample is blue shifted to 2.78 eV with enhanced intensity and narrowed spectral linewidth. Interestingly, the transparent AlN epilayer shows the lowest (sometimes negligible) emission at 2.78 eV, while the amber colored m-plane bulk AlN shows a remarkably strong emission at this energy. This indicates a stronger PL emission at 2.78 eV from more yellowish samples, which contain higher concentrations of oxygen impurities.

The temperature dependence of the below band gap excitation PL spectra in the bulk m-AlN (measured around 2.78 eV) is shown in Fig. 3(a). The emission line is quite broad and peak position does not change with temperature. The Arrhenius plot for the PL intensity of the 2.78 eV emission line from 10 to 400 K is shown in Fig. 3(b). The solid line is the least-squares fit of the experimental data with the following equation:¹⁵

$$I(T) = I(0)[1 + ae^{-E_0/KT}]^{-1}, \quad (1)$$

where $I(T)$ and $I(0)$ are the PL intensities at temperature T and 0 K, a is a constant, and E_0 is the activation energy of PL intensity. We obtained a thermal activation energy (E_0) of about 78 meV from the fitting. The physical meaning of this activation energy is not clear at this point.

In order to understand the mechanism of the 2.78 eV emission line in AlN, we have measured the excitation intensity (I_{exc}) dependence of this emission line, which is shown

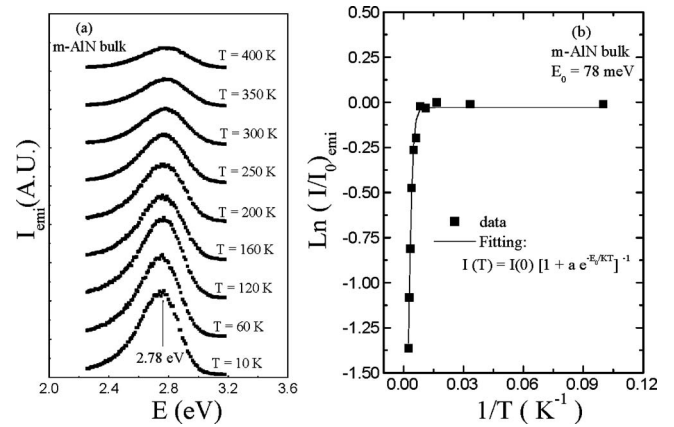


FIG. 3. (a) Temperature dependent PL spectra of bulk m-AlN around 2.78 eV with 262 nm excitation from 10 to 400 K. (b) The Arrhenius plot of the PL intensity of 2.78 eV emission line in m-AlN bulk.

in Fig. 4(a). Blueshifting of the peak position with an increase in I_{exc} , which is typical of donor-acceptor-pair (DAP) type transition, was not observed here, suggesting that the 2.78 eV emission line is not a DAP type transition. Based on the energy positions we already know for V_{N} , V_{Al} , and V_{Al} -related complexes,^{14,16} the involvement of a conduction band or shallow donor is unlikely. The most plausible explanation that supports the PL spectral peak position data and the I_{exc} -dependence of PL intensity is a transition from the isolated aluminum vacancy $(V_{\text{Al}})^{3-/-}$ to the valence band. $(V_{\text{Al}})^{3-/-}$ is a deep center with two different charge states, triply negative charged V_{Al}^{3-} , and doubly negative charged V_{Al}^{2-} . This deep center changes its charge state from one to another by absorption (V_{Al}^{2-} to V_{Al}^{3-}) or emission (V_{Al}^{3-} to V_{Al}^{2-}) and readjusts its energy with an inward or outward relaxation of the neighboring atoms.¹⁷

The proposed energy level diagram is shown in Fig. 5, which involves the levels introduced by both the charge states of $V_{\text{Al}}^{3-/-}$; namely, a broad absorption band from 2.1 to 2.9 eV, and emission lines at ~ 2.78 and 3.2 eV. Upward and downward arrows indicate the corresponding absorption and emission lines, respectively. The PL emission at 3.2 eV is a DAP type transition involving a shallow donor and a $V_{\text{Al}}^{3-/-}$ deep acceptor, which is observed as a 3.4 eV line in actual measurement due to some coulomb energy on the order of ~ 0.2 eV.^{14,16} Note that the V_{Al}^{3-} state is unable to capture any more electrons and is only able to participate in the

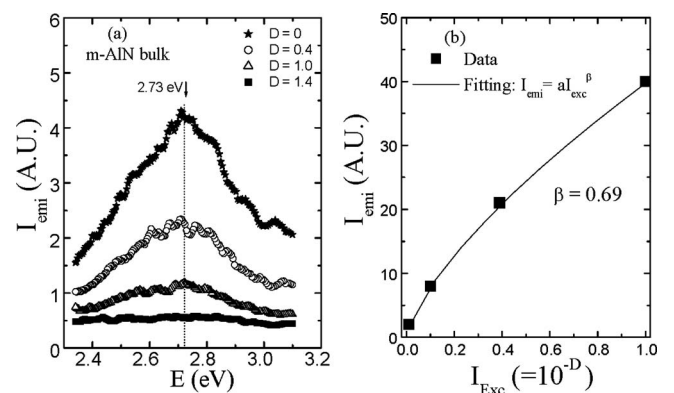


FIG. 4. (a) Excitation intensity dependent PL spectra measured on bulk m-AlN single crystal around 2.73 eV emission line with 197 nm excitation. (b) Peak emission intensity at 2.73 eV as a function of excitation intensity.

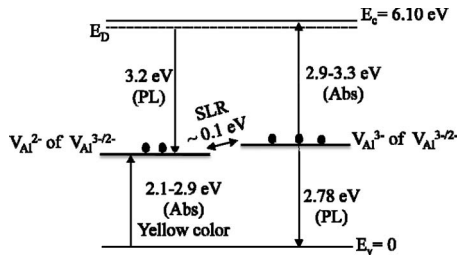


FIG. 5. Energy level diagram of isolated aluminum vacancies (V_{Al}) in AlN including the two charge states, V_{Al}^{3-} and V_{Al}^{2-} , of $V_{\text{Al}}^{3-/2-}$ level with a small lattice relaxation (SLR) between these two states.

absorption process in which one of its electrons is excited to the conduction band or to the shallow donor to become V_{Al}^{2-} . For the absorption around 2.8 eV to happen, V_{Al} must be available in the V_{Al}^{2-} state. This absorption results in the excitation of electrons from the valence band to the V_{Al}^{2-} state and its transformation into a V_{Al}^{3-} state as illustrated in Fig. 5. All possible absorption and emission mechanisms involving the $V_{\text{Al}}^{3-/2-}$ deep center in AlN can be summarized in the following set of equations:

$$V_{\text{Al}}^{2-} + h\nu = V_{\text{Al}}^{3-} + h^+ (2.1 - 2.9 \text{ eV absorption responsible for yellow color}), \quad (2)$$

$$V_{\text{Al}}^{3-} + h\nu = e^- + V_{\text{Al}}^{2-} (2.9 - 3.3 \text{ eV absorption from } V_{\text{Al}}^{3-} \text{ to the conduction band}), \quad (3)$$

$$D^0 + V_{\text{Al}}^{2-} = V_{\text{Al}}^{3-} + D^+ + h\nu (\text{responsible for } 3.4 \text{ eV PL emission}), \quad (4)$$

$$V_{\text{Al}}^{3-} + h^+ = V_{\text{Al}}^{2-} + h\nu (\text{responsible for } 2.78 \text{ eV PL emission}), \quad (5)$$

where D^0 represents a shallow donor level.

The presence of oxygen impurities tends to create more V_{Al} as the formation energy (E_{form}) is reduced.^{17,18} As more V_{Al}^{2-} states of $V_{\text{Al}}^{3-/2-}$ become available, optical absorption is more probable, as explained by Eq. (2) for $2.1 \text{ eV} \leq h\nu \leq 2.9 \text{ eV}$ absorption and thus samples tend to appear more yellowish. After V_{Al}^{2-} state captures one more electron, it becomes V_{Al}^{3-} and the nearest neighbor lattice sites undergo a small inward relaxation compared to the V_{Al}^{2-} state, and gains some energy.¹⁷ Based on the observed PL emission involving the $V_{\text{Al}}^{3-/2-}$ level and the band-gap of AlN, we believe that the energy gained by this lattice relaxation is on the order of $\sim 0.1 \text{ eV}$. As illustrated by Eqs. (2)–(5), electrons in the $V_{\text{Al}}^{3-/2-}$ levels can participate in either absorption or emission. When the electron in the V_{Al}^{3-} state recombines with a hole in the valence band, it becomes a V_{Al}^{2-} state by emitting a 2.78 eV photon, which is represented by Eq. (5). Again, the more oxygen is incorporated into the sample, the more V_{Al} form during the growth and hence the stronger the 2.78 eV emission. This was observed in the three samples studied here and is also in agreement with the previous observation of enhanced 2.71 and 2.88 eV peaks as oxygen concentration increases.¹⁹

However, the situation will be different for AlN with higher concentrations of O impurities ($\sim 10^{19} - 10^{20} \text{ cm}^{-3}$) (Refs. 8 and 9) than those of the samples we studied here

($\sim 10^{17} - 10^{18} \text{ cm}^{-3}$). In the case of $[V_{\text{Al}}] \ll [O]$, no more isolated vacancies $V_{\text{Al}}^{3-/2-}$ will be available for the absorption process of Eq. (2) to occur. Instead, the oxygen atoms, which replace the N sites, form complexes with Al vacancies like $(V_{\text{Al}}-O_{\text{N}})^{2-/1-}$ or $(V_{\text{Al}}-2O_{\text{N}})^{1-/0}$. Thus, AlN materials with high O impurity concentrations in fact appear less yellow. This explanation is consistent with the previously reported results of transparent AlN, in which a $(V_{\text{Al}}-2O_{\text{N}})^{1-}$ related absorption band around 4.7 eV emerged, while the 2.8 eV band completely disappeared in samples containing the highest oxygen concentrations ($1.2 \times 10^{21} \text{ cm}^{-3}$).^{8,9}

In summary, we have carried out optical studies on different AlN samples by PL measurement to address the question of why bulk AlN crystals appear yellow in color. We propose that the absorption band centered around 2.8 eV, which corresponds to the excitation of electrons from the valence band to the V_{Al}^{2-} state of $(V_{\text{Al}})^{3-/2-}$, is responsible for the yellowish color of bulk AlN substrates. We observed a PL peak with a line width of $\sim 0.3 \text{ eV}$ at 2.78 (2.76) eV under below (above) band gap excitation, which we believe is caused by the recombination between electrons in the V_{Al}^{3-} state of the $(V_{\text{Al}})^{3-/2-}$ level and holes in the valence band. Understanding the origin of yellow coloration in bulk AlN will be crucial toward achieving high quality transparent bulk AlN substrate for III-nitride based optoelectronic devices.

This work is supported by DOE under Grant no. FG02-09ER46552. H.X.J. and J.Y.L. would like to acknowledge the support of Edward Whitacre and Linda Whitacre endowed chairs through the AT&T foundation.

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