Temperature and compositional dependence of the energy band gap of AlGaN alloys

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Deep-ultraviolet photoluminescence spectroscopy has been employed to study the temperature and compositional dependence of the band gap of $Al_xGa_{1-x}N$ alloys in the temperature range between 10 and 800 K. Band-edge emission peaks in $Al_xGa_{1-x}N$ alloys were fitted by the Varshni equation to obtain Varshni coefficients, which increase nonlinearly with x. The values of Varshni coefficients obtained for GaN and AlN binary compounds in the present study are in good agreement with the previously reported values. Based on the experimental data, the compositional and temperature dependence of the band gap of $Al_xGa_{1-x}N$ alloy has been empirically determined for the entire alloy range. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2142333]

AlGaN alloys are very attractive for the fabrication of ultraviolet (UV) and deep UV emitters, detectors, and other optoelectronic devices due to the capability of tuning the direct band gap in large energy range (3.4–6.1 eV). They have high mechanical hardness, high thermal conductivity, large dielectric constant, and high resistance to harsh environment. For device applications based on AlGaN alloys, improving the material quality and understanding of the fundamental properties are essential. Many properties of $Al_xGa_{1-x}N$ alloys are unknown due to the increased difficulties to grow high quality materials and decreased emission efficiency with increasing x.[1] Among the basic properties and parameters of $Al_xGa_{1-x}N$ alloys, the determination of the band gap and its variation with temperature and composition are fundamentally important to the design of practical devices based on these materials.

Compositional dependence of the Varshni coefficients α and β in ZnCdSe alloys between the temperature range 10 and 250 K has been investigated by Kuo *et al.*[2] Shih *et al.* studied the temperature dependence of the band gap in $Cd_xZn_{1-x}Te$ alloys ($x<0.58$).[3] They found a trend of compositional dependence of α and β. Temperature dependence of the band gap and Varshni coefficients have been previously measured for binary compounds, GaN and AlN.[4] Temperature dependence of the band gap of $Al_xGa_{1-x}N$ alloys has been previously measured in the composition range of $x<0.5$ and the temperature range between 10 and 300 K, but there was no report on Varshni coefficients (α and β).[5,6] Absorption spectra of molecular beam epitaxy (MBE) grown $Al_xGa_{1-x}N$ with $0\leqslant x\leqslant 1$ have been measured up to room temperature, from which a negligible composition dependence of α and β was observed.[7] Due to the large band gap and localization energy of excitons, a broader range and higher measurement temperatures are needed for the accurate determination of the temperature dependence of the band gap of AlGaN alloys. So far, the compositional and temperature dependence of the band gap of $Al_xGa_{1-x}N$ alloys in broad ranges has not yet been studied.

In this letter, we report the compositional and temperature dependence of the band gap of $Al_xGa_{1-x}N$ alloys covering the entire alloy range of x, $0\leqslant x\leqslant 1$. Compositional dependence of the Varshni coefficients, α and β, in AlGaN alloys has been empirically determined and a parabolic dependence was observed.

The 1-μm-thick $Al_xGa_{1-x}N$ alloys were grown by metalorganic chemical vapor deposition on sapphire (0001) substrates with AlN nucleation layers. Trimethylgallium and trimethylaluminium were used as Ga and Al sources, respectively. Electron dispersive x-ray and x-ray diffraction spectroscopies were employed to determine the Al contents. Atomic force microscope (AFM) and scanning electron microscope were used to characterize the surface morphology of these alloys. The root mean square of the surface morphology measured by AFM was about 1 nm. The samples were mounted stress free on a high temperature stage with a cold finger in a closed-cycle helium refrigerator and temperature was controlled between 10 and 800 K. Deep UV photoluminescence (PL) spectroscopy was employed to investigate the optical emission properties of these samples. The PL system consists of a frequency quadrupled 100 fs Ti:sapphire laser with an average power of 3 mW with excitation photon energy set at 6.28 eV (repetition rate of 76 MHz), and a monochromator (1.3 m).[8]

The temperature evolutions of the PL spectra of $Al_xGa_{1-x}N$ were measured from 10 to 800 K covering the entire range of alloys. Figures 1 and 2 show representative temperature evolutions of PL spectra of $Al_xGa_{1-x}N$ alloys for $x=0.38$ and 0.9. In general, PL emission intensity, I_{emi}, decreases with increasing temperature. We attribute the dominant band-edge emission lines at low temperatures to the localized exciton recombination.[6,9,10] The spectral peak positions were redshifted from 4.27 eV at 10 K to 3.92 eV at 800 K in $Al_{0.38}Ga_{0.62}N$ alloy. In $Al_{0.9}Ga_{0.1}N$, the dominant emission peak is redshifted from 5.77 eV at 10 K to 5.40 eV at 800 K. This redshift is due to the decreasing of the band gap with increasing temperature.

The temperature dependence of band gap of different semiconductors has been described by different equations.[4–6,11–14] Among them, Varshni equation is being used most often to describe nonlinear temperature dependence of the band gap. Figure 3 shows the temperature dependence of the band-edge emission peak between 250 and 800 K for different compositions ($0\leqslant x\leqslant 1$). The solid

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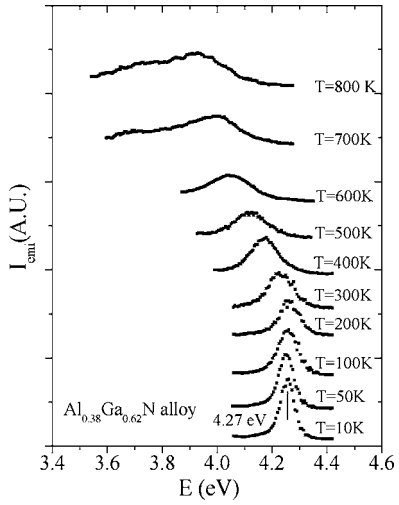

FIG. 1. PL spectra of $Al_{0.38}Ga_{0.62}N$ alloy measured from 10 to 800 K.

curves are the least squares fit of experimental data with the Varshni equation[15]

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T}, \tag{1}$$

where $E_g(0)$ is the band gap of $Al_xGa_{1-x}N$ alloy at $T=0$ K; α is an empirical constant; and β is associated with the Debye temperature. Above the Debye temperature, the band gap changes almost linearly with temperature due to linear changes of lattice parameters and electron-phonon interaction. Because of the large localization energies of excitons in AlGaN alloys, experimental values of the band-edge emission peaks deviate from Varshni equation in the low temperature region (<200 K)[6] and higher measurement temperatures are necessary for an accurate determination of α and β. We apply Eq. (1) to fit with experimental data obtained in the high temperature range 200–800 K, where the effect of exciton localization is negligible. This allows us to determine α and β with unprecedented accuracy. From Fig. 3, the fitted values of $E_g(0)$ are 3.495 eV for $x=0$, 4.311 eV for $x=0.38$, 4.961 eV for $x=0.6$, 5.649 eV for $x=0.8$, and 6.064 eV for $x=1$. Whereas, α and β increase from 0.94 meV/K and 791 K for $x=0$ to 2.63 meV/K and 2082 K for $x=1$. To further validate the present method for obtaining the values of α and

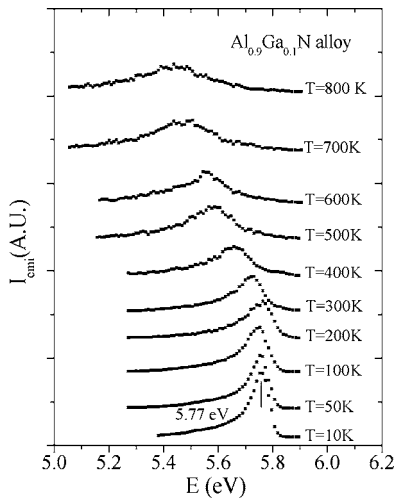

FIG. 2. PL spectra of $Al_{0.9}Ga_{0.1}N$ alloy measured from 10 to 800 K.

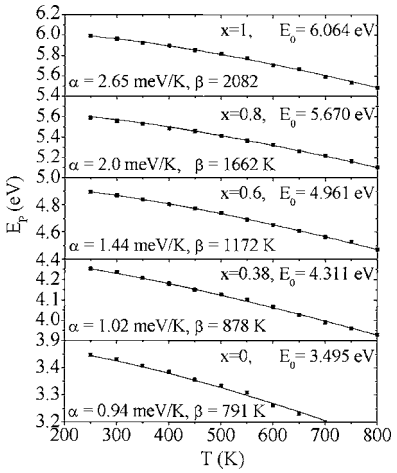

FIG. 3. Temperature dependence of the band-edge emission peak between 250 and 800 K for $Al_xGa_{1-x}N$ alloys with different $x(0 \leqslant x \leqslant 1)$. The solid curves are the least squares fit of the data with Eq. (1). The fitted values of □ and □ are also indicated.

β for AlGaN ternary alloys by fitting Eq. (1) with high temperature ($T>200$ K) data, we note that the present values of α and β obtained for binary compounds GaN and AlN using data in the high temperature range of 200–800 K are very close to the previously measured values using experimental data ranging from low to high temperatures (10–700 K).[4] The direct comparison can be made for GaN and AlN binary compounds because the exciton/carrier localization effect due to compositional fluctuation in GaN and AlN is absent. The measured compositional dependence of α and β in $Al_xGa_{1-x}N$ alloys for $0 \leqslant x \leqslant 1$ is shown in Fig. 4, which clearly exhibits a trend of parabolic increase of α and β with x. Based on experimental data, we obtain the following empirical equations to describe α and β:

$$\alpha(x) = (1-x)\alpha(\mathrm{GaN}) + x\alpha(\mathrm{AlN}) - cx(1-x), \tag{2}$$

$$\beta(x) = (1-x)\beta(\mathrm{GaN}) + x\beta(\mathrm{AlN}) - dx(1-x), \tag{3}$$

where c and d are related to quadratic terms of $\alpha(x)$ and $\beta(x)$, and α(GaN), α(AlN), β(GaN), and β(AlN) are the Varshni coefficients for the binary compounds of GaN and AlN. Solid curves shown in Fig. 4 are the least squares fit of the experimental data of $\alpha(x)$ and $\beta(x)$ with Eqs. (2) and (3).

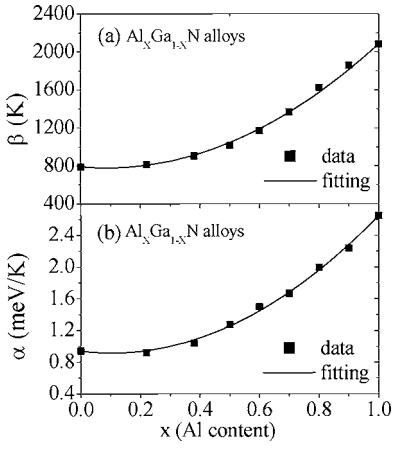

FIG. 4. Compositional dependence of the Varshni coefficients (a) □x and (b) □x in $Al_xGa_{1-x}N$ for $0 \leqslant x \leqslant 1$. Solid curves are the least square fit of the data with Eqs. (2) and (3) for □(x) and □(x), respectively.

Fitted values of c for $\alpha(x)$ are 2.15 meV/K and d for $\beta(x)$ is 1561 K. By knowing $\alpha(x)$, $\beta(x)$, c, and d together with Eq. (1), compositional and temperature dependence of the energy gap, $E_g(x,T)$ of $Al_xGa_{1-x}N$ alloys for the entire alloy range $0 \leqslant x \leqslant 1$ can be obtained and described by

$$E_g(x,T) = E_g(x,0) - \frac{\alpha(x)T^2}{\beta(x)+T}, \tag{4}$$

where $E_g(x,0)$ can be written in terms of the low temperature band gaps of GaN and AlN—the commonly known compositional dependence of the band gap of $Al_xGa_{1-x}N$:

$$E_g(x) = (1-x)E_g(\mathrm{GaN}) + xE_g(\mathrm{AlN}) - bx(1-x), \tag{5}$$

where $b(\approx 1$ eV) is the bowing parameter, E_g(GaN) the low temperature band gap value of GaN (≈ 3.5 eV), and E_g(AlN) the low temperature band gap value of AlN (≈ 6.1 eV). It is important to note that, compared to the previous published work, the present study employed a broader measurement temperature range covering much higher temperatures, which we believe is necessary for obtaining accurate measurements of compositional and temperature dependence of the energy band gap of AlGaN alloy.

In summary, we have measured compositional and temperature dependence of the band gap of $Al_xGa_{1-x}N$ alloys covering the entire alloy range, $0 \leqslant x \leqslant 1$, by employing deep UV PL spectroscopy measurements up to 800 K. Band-edge emission peaks were fitted with the Varshni equation to obtain Varshni coefficients α and β. A parabolic dependence of α and β with x in $Al_xGa_{1-x}N$ was observed, from which we have obtained an empirical equation that describes the compositional and temperature variations of the energy band gap of AlGaN alloys.

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