Direct evidence of compositional pulling effect in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers

H.Y. Lin^a, Y.F. Chen^{a,*}, T.Y. Lin^b, C.F. Shih^c, K.S. Liu^b, N.C. Chen^d

^aDepartment of Physics, National Taiwan University, Taipei 106, Taiwan, Republic of China

^bInstitute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung, 202, Taiwan, Republic of China

^cDepartment of Materials Science and Engineering, National Tsing Hua University, Hsinchu 300, Taiwan, Republic of China

^dInstitute of Electro-Optical Engineering, Chang Gung University, Kwei-Shan, Tao-Yuan 333, Taiwan, Republic of China

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Abstract

We report the investigation on the compositional-pulling effect of crystalline $\text{Al}_x\text{Ga}_{1-x}\text{N}/(0001)$ sapphire epilayers by cross-sectional cathodoluminescence (CL) and energy-dispersive X-ray (EDX) analyses. Direct evidence for the compositional distribution was found in the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 < x < 0.3$) layers, which accompany the different optical phenomena arising from the change of the band gap. The band gap variation of the $1.7\text{ }\mu\text{m}$ $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers with the Al content rising from $x = 11\%$ to 30% was observed. It is consistent with the result of depth-resolved CL spectra acquired with increasing electron energies, which can also be used to reveal the spatial composition distribution along the growth direction. We emphasize here that the selective-wavelength CL image is a very powerful tool in exploring the correlation between the specific emission and the composition of inhomogeneous alloys.

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1. Introduction

Group-III nitride semiconductors (AlGaIn) can be developed for application in ultra-violet (UV) light emitters, UV photodetectors, white light emitters [1,2], and high-power electronics [3], because of its wide band gap distribution from 3.42 to 6.2 eV. The key issues for the growth of high-quality AlGaIn epitaxial layers are crack formation and poor crystallization [4]. Despite the large lattice mismatch (13–16%) between AlGaIn and sapphire, many studies have been focused upon the achievement of crack-free AlGaIn epilayers [5,6]. For example, a $1.5\text{ }\mu\text{m}$ -thick, crack-free AlGaIn with high AlN molar fraction was grown on sapphire, though the crystalline of AlGaIn degrades rapidly with increasing AlN molar fraction [4]. The pulling effect, one of interesting topics on the crystal growth [7], obviously arising from a lattice mismatch which

is needed to be studied. So far, the indirect evidence of the strain-induced composition pulling effects in AlGaIn films grown on low-temperature (LT) AlN-coated sapphire substrate has been demonstrated by X-ray diffraction, transmission electron microscopy (TEM), and optical absorption experiments [8]. Both the absorption measurements and cross-sectional TEM images illustrate the bilayer character for the AlGaIn films. However, no further conclusive evidence about the luminescent features and the aluminum (Al) distribution within the AlGaIn layers was reported. In contrast to AlGaIn films, the compositional pulling effect of InGaIn layer has been well investigated [9–11]. A linear decrease of the In mole fraction from 0.14 to 0.20 along the growth direction was found in a 75-nm thick InGaIn epilayers [11].

In this article, we report the investigation on the compositional distribution of crystalline AlGaIn epilayers by cross-sectional cathodoluminescence (CL) and energy-dispersive X-ray (EDX) analyses. The compositional pulling effect of the Al content was clearly observed by CL

*Corresponding author.

E-mail address: yfchen@phys.ntu.edu.tw (Y.F. Chen).

techniques. Especially, through selective-wavelength CL images, the correlation between the compositional distribution and optical property has been unambiguously established.

2. Experimental procedure

The $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers ($x < 0.3$) were grown by metal-organic chemical vapor deposition (MOCVD) directly on low-temperature (LT) GaN-coated sapphire (0001) substrates. Trimethylgallium (TMG), Trimethylaluminium (TMA), and ammonia (NH_3) were used as Ga, Al, and N sources. Before the growth of AlGaIn, the sapphire was firstly heated to 1100 °C. Afterwards the pressure of the reactor for the growth of AlGaIn was reduced to as low as 50 mbar to minimize parasitic reactions. Each growth of the AlGaIn layers was conducted under the same gas phase composition, TMA/(TMG + TMA). CL experiments were performed at room temperature with a JEOL-JSM 6500 scanning electron microscopy (SEM) using 1–30 kV electron beam. Excitation spectra were gathered by a PMT detector with a MonoCL3 CL system (Gatan Instruments). EDX analysis (Oxford Instrument) was used to determine the Al component. CL images were taken with a probe current of 8×10^{-9} A and an acceleration voltage of 5 keV.

3. Results and discussion

Fig. 1(a) is the cross-sectional SEM image of the 1.7 μm AlGaIn epilayer grown on sapphire. To specifically locate the exact origin of the radiation, CL spectrum was excited and collected from the cross-sectional region as shown in Fig. 1(a). Fig. 1(b) shows the cross-sectional CL spectrum of the sample excited by the electron beam with an acceleration voltage of 5 kV ($5 \mu\text{m} \times 5 \mu\text{m}$). In Fig. 1(b), it can be seen that the spectrum has a strong intensity at room temperature with a full-width at half-maximum (FWHM) of 26 nm. To explore the underlying origin of this broad spectrum, selective-wavelength CL images were taken. The selective-wavelength CL images taken at 324, 330, and 350 nm are shown in Figs. 1(c), (d), and (e), respectively. For the selective-wavelength CL image at 324 nm, the bright emission extends from the front surface and gradually diminishes near the buffer layer. As the monitored wavelength of the selected-wavelength CL image is red-shifted, for example, near 330 nm, the emission from the front surface becomes weaker, and the bright region is now located at the center region. However, for the selective-wavelength CL image monitored at 350 nm, the emission image turns into a column-like pattern near the AlGaIn/sapphire interface.

According to the above result, the selective-wavelength CL images reveal very important information that the region responsible for the emission of a particular wavelength locates at different depth of the thin film. It is well known that the shorter emission wavelength corresponds to the higher Al composition in the $\text{Al}_x\text{Ga}_{1-x}\text{N}$

Fig. 1. (a) Cross-sectional scanning electron microscopy profile of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayer on sapphire, (b) Cross sectional cathodoluminescence spectrum of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ on sapphire substrate ($E = 5$ keV, field of view = $5 \mu\text{m}$), (c) CL image taken at 5 kV for λ at 324 nm, (d) CL image taken at 330 nm, and (e) CL image taken at 350 nm.

layer. We therefore conclude that the Al content has a gradual evolution and increases along the growth direction of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer. This result provides the first direct evidence that the compositional pulling effect does exist in

$\text{Al}_x\text{Ga}_{1-x}\text{N}$ films grown on LT GaN-coated (0001) sapphire substrates. The compositional pulling effect has been reported and studied previously in other material systems [9,11]. It has been attributed to the compressive biaxial strain caused by the lattice mismatch between the epilayer and buffer layer. It is believed that some particular atoms will be expelled from the epilayer during the initial stage of the growth to reduce the strain energy from the thermodynamics aspect. In the case of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ film grown on LT GaN-coated sapphire system, the large mismatch between the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ film and sapphire substrate can result in an extensive biaxial strain in the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ film depending primarily upon the Al composition and film thickness. In the initial stage of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ film growth, most Al atoms are pulled out of the film. This results in a deposition of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ film with lower Al content. Therefore, a gradual strain reduction in the grown $\text{Al}_x\text{Ga}_{1-x}\text{N}$ film forms as the growth continues, which leads to the subsequent deposition of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer with higher Al content by the same gas-phase composition, TMA/(TMG+TMA).

In order to gain a deeper insight into Al compositional distribution induced by the pulling effect, we have performed EDX measurements along the cross-sectional profile. Here, care has been taken to avoid the signal arising from the Al atoms of the sapphire substrate. For the spatial EDX measurements, the distance between the measured spot and the substrate was kept at least $0.5\text{ }\mu\text{m}$ apart. The electron penetration depth R_e of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin film can be estimated as follows [12,13]:

$$R_e = \frac{0.0276A}{\rho Z^{0.889}} E_b^{1.67} (\mu\text{m}). \quad (1)$$

For the electron acceleration voltage of 5 keV and assuming the Al content of 30%, the electron penetration depth is estimated to be around $0.5\text{ }\mu\text{m}$. With the increase of Al from 5% to 30%, R_e only increases slightly. The in-depth

distribution of Al content along the growth direction determined by the EDX measurement with the electron beam size of $0.45\text{ }\mu\text{m}$ in diameter is shown in Fig. 2. It is found that the Al contents in the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers increase gradually from 11% ($0.5\text{ }\mu\text{m}$ away from the substrate) to 30% (near the surface). To further confirm our results, several samples with the same growth condition have been examined as shown in Fig. 2 with different symbols.

The influence of the in-depth distribution of Al content along the growth direction can be also observed by using the conventional CL measurement, i.e., an electron beam of variable energy is incident upon the front surface and the luminescence is detected from the front surface as well. Fig. 3(a) shows the CL spectra of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers with electron beam energies ranging from 1 to 15 keV (scan

Fig. 2. Al concentrations (■, ▲, ●, denote the Al concentrations of three lines along the growth direction) versus the distance from the sapphire.

Fig. 3. (a) Cathodoluminescence spectra acquired at different electron beam energy (1–15 keV, scan region: $22\text{ }\mu\text{m} \times 22\text{ }\mu\text{m}$) from the front side of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ on sapphire, (b) Al concentration versus the distance from the sapphire substrate converted from Fig. 3(a).

region: $22\mu\text{m} \times 22\mu\text{m}$), in which the CL peak shifts to lower energies with increasing electron beam energy. Because the higher acceleration voltage implies the deeper electron penetration depth, the red shift indicates that the deeper region has a lower Al concentration. According to Eq. (1), we are able to estimate the electron penetration depth. Since the compositional dependence of the band gap of AlGaIn alloys has been reported previously [14], we can convert the results of the CL peaks at different electron beam energies into the evolution of Al composition along the growth direction as shown in Fig. 3(b). The obtained results are in good agreement with the measurement by EDX as shown in Fig. 2.

Finally, let us examine the selective-wavelength CL image monitored at 350 nm as shown in Fig. 1(e). Based on the column-like pattern revealed in this image, we may attribute the origin of the significant shoulder at 350 nm shown in Fig. 1(b) to the emission arising from dislocations due to its column-like image. The study along the line shown here should be able to obtain valuable information for the correlation between the defect distribution and its optical properties.

4. Conclusion

We have investigated the pulling effect of AlGaIn epilayers grown on LT GaN-coated sapphire substrate by cross-sectional cathodoluminescence and energy-dispersive X-ray (EDX) analyses. A good correlation between optical and structural properties has been observed, which provides direct evidence for the existence of compositional pulling effect in AlGaIn films. It is worth emphasizing here that the measurement of selective-wavelength CL image can provide a unique feature for examining the correlation between structural and optical properties. We believe that it is a very useful technique to explore the compositional

and defect distribution in solids, especially for inhomogeneous materials.

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