MOVPE Growth and Characterization of Dilute In_xGa_{1-x}As_{1-y}N_y on GaAs for 1 eV Band-gap Solar Cells

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Abstract: $In_xGa_{1-x}As_{1-y}N_y$ (x = 11.6 and 30%, 0 < y \leq 3.1%) alloy films were grown on GaAs (001) substrates by lowpressure (60 Torr) metalorganic vapor phase epitaxy (MOVPE). Structural and optical properties of the InGaAsN films were investigated. With incorporation of N, a reduction of compressive strain and a strong red shift in the alloy band-gap were clearly observed. The InGaAsN alloy films with emittion

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at room temperature in the energy range of 0.98-1.26 eV were grown. For the 11.6%In films, the N concentrations as high as 3.1% were measured, with corresponding band-gaps of 0.98 eV at 300 K. On the other hand, for the ~30%In film ($0 < y \le$ 1.5%), the energy dispersive X-ray (EDX) spectroscopy measurements show significant In fluctuations and, consistent with this observation, the luminescence spectra which is attributed to the strong localization emission. In addition, the experimental results indicate that the increase of In concentration strongly effects the crystalline quality of the InGaAsN.

Keywords: InGaAsN, MOVPE, EDX/TEM, compositional inhomogeneities, PL, PR.

Introduction

The dilute quaternary group-III arsenide nitride semiconductor InxGa1-xAs1-yNy has attracted rapidly growing interest because the addition of a few percent of nitrogen decreases the bad-gap energy significantly and also compensates for the compressive strain introduced by the incorporation of In [1]. This makes InxGa1-xAs1-yNy alloy system interesting for a 1.0 eV GaAs-lattice-matched solar cell. Kurtz et al [2] have demonstrated that the addition of 1.0 eV InGaAsN layers to the InGaP/GaAs tandem structure can improve the internal quantum efficiency by more than 70%, due to the collection of InGaAsN

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layers of longer wavelength infrared light, which are not absorbed through both InGaP and GaAs layers. To realize 1.0 eV band-gap solar cells, an increase in the N concentration in InGaAsN is necessary. However, the increase in the N incorporation remarkably degrades the alloy quality, due to the limit of extreme immiscibility that is a characteristic of the III-(III)-V-N alloys, resulting in the formation of highly inhomogeneous material. In this work, we carried out the growth of InGaAsN alloy films and investigated their structural and optical properties.

Experimental Procedure

InxGa1-xAs1-yNy (x = 11.6% and ~ 30%, y \leq 3.1%) alloy films were grown on GaAs (001) substrates by lowpressure (60 Torr) MOVPE. Trimethylgallium (TMG), trimethylindium (TMI), AsH3 and dimethylhydrazine (DMHy) were used as the source materials. After the growth of a 0.3 µmthick GaAs buffer layer at 700°C, an InGaAsN layer with the thickness of 300-500 nm was deposited at 530 and 600°C. The films with various N concentrations were obtained by changing the molar flow ratio of DMHy to the total group V elements.

In order to examine the lattice constants of the InGaAs(N) films perpendicular (a^{\perp}) and parallel (a//) to the GaAs (001) surface, both symmetric and asymmetric reflections were measured by the (004) 20/ ω scan and the (115) $\Delta\omega$ -scan and $\Delta(\omega/2\theta)$ -scan mapping [3]. For the controlled InGaAs films,

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the composition of the film can be easily estimated from the relaxed lattice-constant (ao) using Vegrad's law, i.e., ao depends linearly on the In concentration (x). In the present case, the quaternary InxGa1-xAs1-yNy alloys consisted of four binary compounds: GaAs, cubic-GaN, InAs and cubic-InN. The N concentration (y) in the InxGa1-xAs1-yNy films with a nominal In content (x) determined from the controlled InGaAs films, can be calculated from ao expressed by

$$ao = (2C12 a// + C11 a^{\perp}) / (2C12 + C11)$$
(1)

ao = (1-x) [(1-y) aGaAs + y aGaN] + x [(1-y) aInAs + y aInN] (2)

C11,12 ao = xy aInN C11,12InN + x(1-y) aInAs C11,12InAs + (1-x)y aGaN C11,12GaN + (1-x) (1-y) aGaAs C11,12GaAs (3)

where C11 and C12 are the elastic constants for InxGa1-xP1yNy, and aGaAs, aGaN, aInAs and aInN are the equilibrium lattice constants of GaAs, cubic-GaN, InAs and cubic-InN, respectively [4, 5]. Since the elastic constants of InxGa1-xAs1yNy are not available, they can, thus, be derived from the elastic constants of the four binary compounds by using the interpolation scheme. Secondary ion mass spectroscopy (SIMS) confirmed the presence of nitrogen.

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Micro-structure of the epitaxially grown InGaAsN alloy layers was investigated by transmission electron microscopy (TEM). Energy dispersive X-ray (EDX) analysis in the TEM was used to examine the compositional inhomogeneities. The optical properties of the epitaxially grown InGaAsN alloy layers were characterized by photoluminescence (PL) and photoreflectance (PR) using a standard lock-in technique and liquid-nitrogen-cooled Ge photodetector (North-Coast EL-817L).

Results and Discussion

InxGa1-xAs1-yNy alloy films with different compositions corresponding to the room-temperature (RT) PR signal (Eo transition) wavelength range of 0.98-1.26 eV were grown. Highresolution X-ray diffraction (HRXRD) studies demonstrate that the epitaxial layer-GaAs substrate mismatch, $\Delta ao/a$, is in the range of +0.2 - +1.94% and decreases with the N incorporation. The In content in the controlled InGaAs layers were 11.6% (530°C) and 27.5% (600°C). The N contents in the InxGa1xAs1-yNy alloy layers with x = 11.6% were calculated to be 0-3.1%. Adding N into InGaAs was assumed not to affect the In incorporation, which was confirmed by our results obtained from SIMS measurements. On the other hand, with further increase in the In content up to ~30%, the In incorporation for such a high concentration was remarkably influenced by the presence of N as analyzed via combined results from HRXRD

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and SIMS. The results show that the In content increased from x = 27.5 (InGaAs) to x = 31.1% (InGaAsN) when the N content increased from y = 0 to y = 1.5%. The reason for this anomalous behaviour is not clear at this time.



Figure 1. PL spectra for $In_xGa_{1-x}As_{1-y}N_y$ with different In and N contents at 12 K and room-temperature, showing redshift of peak energy with increasing N concentration. (a) For 11.6% In samples, N content ranges from y = 0% to y = 2.9%. (b) For In contents of $x \sim 30\%$, the N content ranges from y = 0 to y =1.5%. The vertical solid-arrows (a) and dashedarrows (b) indicate the positions of E_o obtained from PR at room temperature and 10 K [7], respectively.

Figure 1(a) illustrates the low-temperature (LT, 12 K) and RT-PL spectra of the InxGa1-xAs1-yNy alloy layers with low In content (x = 11.6%) and varied N contents (0% \leq y \leq 3.1%). Note that all PL spectra were obtained from as-grown samples without post-growth thermal annealing. The RT-PL

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properties are excellent for all samples with a single near bandedge emission, which is in good agreement with the PR signal of the Eo transition as indicated by vertical arrows, without defectrelated deep-level luminescence. The peak energy of both LTand RT-PL was red-shifted by increasing the composition of N up to y = 3.1%. Since the incorporation of N leads to a clear reduction of the compressive in-plane strain from $\Delta a/l/a =$ 0.43% to $\Delta a///a = 1.5 \times 10{-}3\%$, thus, both the reduction in compressive in-plane strain and the direct effect of N on the band-gap energy contribute to the observed energy shift. In addition, experimental results on the close lattice-matched In0.116Ga0.884As0.969N0.031 layer on GaAs showed RT-PL at about 1.0 eV. In Fig. 1(b), the 12 K-PL spectra of the ~30%In-containing layers showed a very broad peak with the full width at half maximum (FWHM) of 120-145 meV, centered at an energy 0.87 - 0.97 eV for various compositions (x, y). The former emission demonstrates a strong redshift with increasing N content, as expected for a decrease in the band-gap. It is found that the PL peak maximum is much lower than the energy position of 10 K-Eo transition, as indicated by the dashedarrows. Such long wavelength PL emission is considered as a result from the quantum-dot-like composition fluctuation of both In and N [6].

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Figure 2. The cross sectional TEM images of InGaAsN alloy films with In and N contents of (a) x = 11.6% and y = 3.1% and (b) x = 31.1% and y = 1.5%, respectively. The arrows represent the position of InGaAsN/GaAs interfaces.

Figures 2(a) and 2(b) show the cross sectional TEM micrographs of the In0.116Ga0.884As0.969N0.031 (low Incontent) and In0.311Ga0.689As0.985N0.015 (high In-content) layers, respectively. For the low In-content layer there are no misfit dislocations. It is known that the InGaAsN layer is grown coherently due to the small lattice mismatch with the GaAs substrate (Δa ///a ~ +1.5x10-3%). Meanwhile, for the high Incontent layer shown in Fig. 2(b), there are not only many misfit dislocations near the interface due to large lattice mismatch (Δa ///a ~ +1.94%), but also many defects in the InGaAsN layer.

Compositional analysis was performed by EDX/TEM spot analysis. Figure 3(b) illustrates the results of EDX spot analysis for the same specimen shown in Figs. 2(b) and 3(a). It is noted that point B shown in high-resolution TEM image (Fig. 3(a)) indicates the region near the InGaAsN/GaAs interface, showing

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high density of dislocations. On the other hand, point A indicates the region above point B which exhibits nearly defect free InGaAsN. It is clearly seen that signal intensity of In is higher for region B (In-rich region) compared to region A (In-poor region). These results can be interpreted assuming the existence of InGaAsN quantum dot-like regions having various In concentrations due to compositional inhomogeneity whose lateral dimension are smaller than 10 nm. This value is a spatial resolution of the system.



Figure 3. (a) Cross-sectional high-resolution TEM image of the same InGaAsN layer, which was shown in Fig. 2(b).(b) Results of the EDX/TEM spot analysis for the sample shown in (a) (as indicated by dashed circles).

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Combined with these results, thus, the LT-PL spectra shown in Fig. 1(b) may be described by the following model; the compositional fluctuation results in the formation of quantum dot-like regions (~10 nm) in the microscopic scale and the emissions from the localized states are dominant in the LT-PL spectra. On the other hand, for the defect free layer, as shown in Fig. 1(a), the RT-PL spectra of the InxGa1-xAs1-yNy films (x = 11.6%, y = 3.1%) can be attributed to the near bandedge emission in agreement with the PR signal of the Eo transition. This is an expected result due to the typical behavior of the near-band-edge emissions.

Conclusions

By adjusting the In and N contents, the band-gaps as low as 0.98 eV were obtained in the close lattice-matched In0.116Ga0.884As0.969N0.031 alloy layers. It was found that the structural properties of the InGaAsN alloy films are related to the carrier localization. Based on these results, the effects of compositional fluctuation of In and N on the carrier localization at low temperature, which corresponds to the extended defects, were discussed. Our results can be very useful for fuller understanding of the structural and optical properties of the InGaAsN-based 1.0 eV band-gap solar cells.

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