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This paper reports the atmospheric-pressure MOVPE growth of In-rich InAlN. All InAlN films prepared here (Al content:0~ 0.43) do not show phase separation. The incorporation of Al in InAlN is decreased with increasing growth temperature. A decrease in Al content is also observed for films grown at a position farther from the up-stream end of the susceptor. The marked decrease in the Al content along the gas flow direction seems to be caused by the shortage of TMA supply at the downstream by the parasitic reaction of TMA. A single-crystalline InAlN film with an Al content of 0-0.43 is successfully grown by adjusting growth temperature and TMA/(TMI+TMA) molar ratio. FWHM of X-ray rocking curve for InAlN is increased with increasing Al content. The carrier concentrations in InAlN films are comparable to that in InN (1-5 x 10^{19} cm^{-3}). All the single-crystalline InAlN films with an Al content of 0-0.3 show a photoluminescence at room temperature.

1 Introduction

High quality single-crystalline film of InN has been obtained by the advancement of the growth technology in recent years. As a result of that, the band-gap energy of InN has revised from about 1.9eV to about 0.7eV [1]. This means that InAlN should have a band-gap energy in the range of 0.7eV-6.2eV. Therefore, InAlN is one of the promising materials for high efficiency multijunction tandem solar cell, which is composed of subcells with a band-gap energy in the range of 0.7eV - 2.5eV.

The growth of high-quality InAlN seems to be difficult because the optimum growth temperatures for InN and AlN are largely different. The growth of the InAlN film in all composition regions has been realized with the MBE growth method [2], while it was reported that In-rich InAlN with an In content >32% grown by MOVPE showed the phase separation [3]. Thus, the growth behaviour of InAlN has not yet been fully understood.

In this paper, we report the MOVPE growth of In-rich InAlN. Since the quality of MOVPE InN was markedly improved by using atmospheric-pressure growth [4], the atmospheric-pressure growth has been employed in the present study. In this paper we reported that a single-crystalline InAlN film with an Al content 0- 0.43 is successfully grown by adjusting growth temperature and TMA/(TMI+TMA) molar ratio.

2 Experimental

Using an atmospheric-pressure MOVPE system with a horizontal reactor, InAlN with a thickness 0.5-0.8 μm is grown on a nitrided (0001) sapphire substrates at 600-700°C in the pressure of 730 Torr. A 20 nm thick GaN layer grown at 550°C is used as a buffer. Ammonia (NH_3), trimethylindium (TMI), trimethylaluminum (TMA), triethylgalliu (TEG) is used as sources. TMA/(TMI+TMA) molar ratio is varied from 0.5 to 0.9. Sapphire substrates are placed at a distance of 45, 90 and 135 mm from the up-stream end of the 180 mm-long carbon susceptor.

The composition of grown films is determined by using X-ray diffraction (ω/2θ) and the optical absorption methods. X-ray diffraction for InAlN is measured with a double-crystal X-ray diffraction system (Rigaku, ATX-E). Full width at half maximum (FWHM) of X-ray rocking curve is also measured. In order to check the crystalline quality, reflection high energy electron diffraction (RHEED) pattern is observed. Optical absorption is measured at room temperature with a double monochrometer optical system (Perkin Elmer, Lambda 19). Photoluminescence (PL) spectrum is measured at room temperature by using a He-Cd laser (442nm, 300mW) as an excitation source and a LN-cooled InGaAs pin photodiode (Hamamatu Photonics, G7754-01) as a detector. Carrier concentration and mobility in InAlN are measured with the van der Pauw method.

3 Results and discussion

First, the effects of growth temperature, growth position and TMA/(TMA+TMI) molar ratio on the composition and crystallinity of grown InAlN are studied. Figure 1 shows the XRD patterns around (0002)-plane of InAlN. The samples are grown at a different TMA/(TMA+TMI) molar ratio at the substrate position 45mm. It is noted that all films prepared here do not show phase separation, although FWHM of XRD for InAlN is increased with increasing Al content. Additionally, it is confirmed that these samples show the spot RHEED patterns, indicating that single-crystalline InAlN films are obtained.

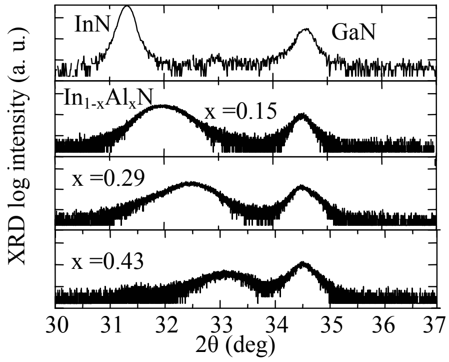

Figure 1 XRD ω/2θ patterns of around (0002)-plane of InAlN grown at a different TMA/(TMA+TMI) molar ratio at the substrate position 45 mm.

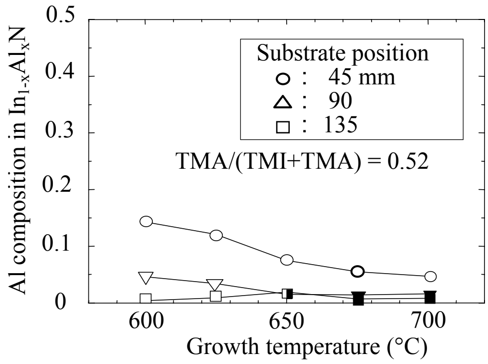

Figure 2 Growth temperature dependence of Al composition in InAlN for films grown at a different position. Open and closed symbols show single crystalline and polycrystalline, respectively.

Figure 2 shows growth temperature dependence of Al composition in InAlN films grown at a different substrate position. It is found that the incorporation of Al in InAlN is decreased with increasing growth temperature. A marked reduction of Al content is also observed for films grown at a position farther from the upstream end of the susceptor. This shows that each sample has an Al composition gradient along the gas flow direction, because the substrate rotation during the growth is not employed in this study. Actually, the gradient of Al composition is 3-4%/cm. Such a large gradient of the composition is a cause for the broad XRD patterns shown in Fig. 1. The marked decrease in the Al content along the gas flow direction seems to be caused by the shortage of TMA supply at the downstream by the parasitic reaction of TMA [5]. As can be seen Fig. 2, the InAlN films become polycrystalline when they are grown at the position 90 and 135 mm and at a temperature above 650°C . Since those samples have very small amount of Al, the thermal decomposition of InN component at the high temperature seems to be the cause for the polycrystalline growth.

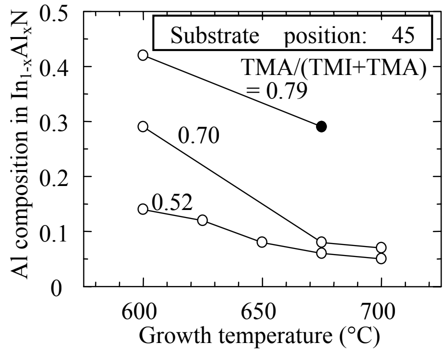

Figure 3 Growth temperature dependence of Al composition in InAlN for films grown with a different TMA/(TMI+TMA) ratio. Open and closed symbols show single crystal and poly-crystal, respectively.

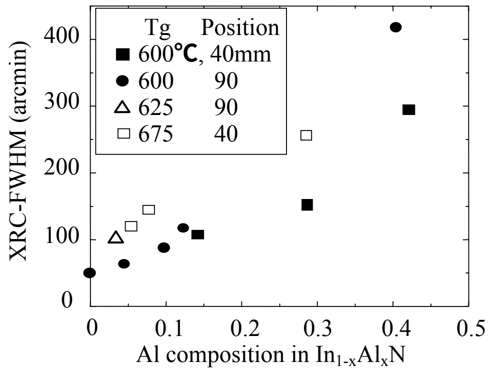

Figure 4 FWHM of XRC for InAlN films as a function of Al composition. Samples are grown at a different temperature and at a different position on the susceptor.

Figure 3 shows the growth temperature dependence of Al composition in InAlN films grown at the position 45 mm with a different TMA/(TMI+TMA) molar ratio. As can be seen in Fig. 3, the InAlN film of the Al composition about 0.43 is successfully obtained by increasing TMA/(TMI+TMA) molar ratio up to 0.79 and lowering the growth temperature to around 600°C. The grown film becomes polycrystalline under the conditions of a high TMA/(TMA+TMI) molar ratio (~0.8) and a high growth temperature (~675°C). This would be attributed to the effects of immiscibility of the ternary alloys.

Figure 4 shows the FWHM of X-ray rocking curve (XRC) for InAlN films as a function of Al composition. All samples shown here are single-crystalline. The FWHM of XRC increases remarkably with increasing Al composition. One can see that the samples grown at a higher temperature show a larger FWHM.

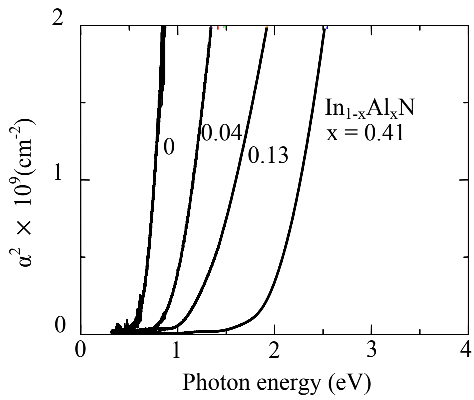

Figure 5 Optical absorption of InAlN films with a different Al composition.

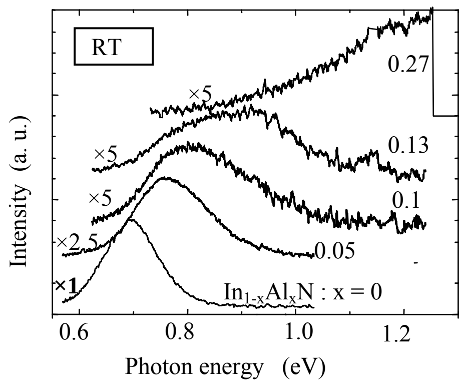

Figure 6 Photoluminescence spectra at room temperature for InAlN films with a different Al composition.

Figure 5 shows the result of the optical absorption measurements of typical InAlN films. As can be seen in this figure, a film with a band gap of about 2eV is successfully obtained. The change in band gap energy with Al content for sample obtained in this study is in agreement with that obtained using the bowing parameter reported by Terashima et al. [2]

Figure 6 shows the PL spectra measured for InAlN films. The InAlN films with an Al content of 0-0.3 show a PL spectrum even at room temperature. Although the PL intensity is decreased with increasing Al content, the intensity difference between InN and InAlN is less than one order of magnitude even for the film with Al content 0.3. The FWHM of PL spectrum is increased with increasing Al content. This reason is not clear at this moment, but would be probably attributed to the effects of the composition gradient in the InAlN films.

The carrier concentration of InAlN films grown at 600°C is in the range of 2-5 x 10^{19} cm^{-3} and does not show a marked dependency on Al composition. On the other hand, the mobility decreases from 200 for InN to 10 cm^2/Vs for x = 0.43 with increasing Al composition. Usually, a carrier concentration less than 10^{19} cm^{-3} and a mobility higher than 1000 cm^2/Vs can be obtained for MOVPE InN by optimizing the growth conditions [6]. Since the optimization of the growth conditions of the InN films have not made sufficiently in this study, the carrier concentration of InN is considerably high (>10^{19} cm^{-3}). It is believed that carrier concentration of InAlN will be reduced by optimizing the growth conditions such as V/III ratio.

4 Conclusion

The growth of In-rich InAlN film by atmospheric-pressure MOVPE has been studied. Single-crystalline InAlN films with an Al composition of 0-0.43 are successfully obtained by adjusting growth temperature, TMA/(TMA+TMI) molar ratio, and substrate position on the susceptor. Although FWHM of XRD is increased with increasing Al content, phase separation is not observed for the films obtaining in this study. Photoluminescence is observed for the films even at the room temperature and the intensity difference between InN and InAlN are less than one order of magnitude even for the film with Al content 0.3. Detailed optimization of the growth conditions and further characterization for InAlN films will be needed as the next steps.

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