Resistive heated MOCVD deposition of InN films

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Abstract

Indium nitride (InN) film was successfully grown on sapphire (0001) substrate using a simple resistive heated metalorganic chemical vapor deposition (MOCVD) system by utilizing a pyrolytic boron nitride (PBN) heater with a precise temperature control within 1°C. Structural studies and optical property measurement by scanning electron microscope (SEM), X-ray diffraction (XRD), Raman spectroscopy and photoluminescence of the films were presented. An improved epitaxy was achieved in films grown at a high substrate temperature (540°C). The room temperature photoluminescence spectrum of the InN film showed a strong peak at 1.8 eV. Further high resolution transmission electron microscopy (HRTEM) investigation revealed some inclusion of nanocrystalline phase, which might be responsible for the strong photoluminescence signal. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Indium nitride (InN), with its wurtzite crystal structure and 1.9 eV direct band gap [1], is a promising III–V compound semiconductor for visible optoelectronics, high efficiency solar cells and high-speed electronics. The inclusion of nanocrystalline InN quantum dots is considered to be the origin of luminescence from InGaN light emitting diodes [2]. A tandem solar cell with an InN cell on the top and a Si cell at the bottom can theoretically achieve a maximum efficiency of 32.1% (AM1.5 global) [3,4], which is highly desirable for energy applications. Moreover, it is predicted that InN possesses a better transport property than GaAs in millimeter-wave electronics [5,6]. Therefore, more and more efforts are made in order to efficiently deposit InN films of better quality.

So far, most of the InN growth studies have been done on sapphire, GaN and GaAs [7–11], except for a few works done on the Si substrate [12–14]. Various methods have been used including metalorganic chemical vapor deposition (MOCVD) [7–11], magnetron sputtering [15], molecular beam epitaxy (MBE) [16], and halogen-transport vapor phase epitaxy (VPE) [17]. However, due to the lack of a

lattice-matched substrate and restricted growth conditions limited by the low dissociation temperature ($\sim 550^\circ\text{C}$) of InN itself [18], high quality InN films are not easily attainable. Several researchers have demonstrated improved epitaxy of InN on sapphire (0001) by nitridation of the substrate before growing films at a large V/III ratio [19,20] in a MOCVD system. The nitridation, which forms AlN buffer layer, helps lowering the mismatch between sapphire and InN down to 12%. The large V/III ratio during growth is useful to prevent indium droplet formation in the film.

Growth temperature plays an important role in the epitaxy even if large V/III ratio and nitridation were used. On one hand, the growth temperature should be kept relatively low ($< 550^\circ\text{C}$) to prevent the dissociation of InN. On the other hand, growing films at a lower temperature undermines the epitaxy of the film. To provide an alternative MOCVD design with better temperature control for InN deposition, we report here the growth of InN film using a simple MOCVD system, in which a resistive heater instead of an RF heated graphite susceptor was employed.

2. Experiments

A schematic diagram of the MOCVD apparatus for InN growth is shown in Fig. 1. The InN film was deposited on a sapphire (0001) substrate. Trimethylindium (TMIn:

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Fig. 1. Schematic diagram of the resistive heated MOCVD reactor for the growth of InN films.

(CH_3) $_3\text{In}$ kept at 12°C and high-purity NH_3 were used as the precursors. TMIn vapor was carried by 5–20 sccm purified N_2 gas and an additional 200 sccm N_2 gas was introduced downstream to increase the gas flow of the group-III line. NH_3 flow rate which varied from 1000 to 2500 sccm was mixed with TMIn before they were injected onto the substrate. A quartz shower was connected to improve the uniformity of the film.

The sapphire (0001) substrate, after degreasing, was placed on a molybdenum plate heated by a pyrolytic boron nitride (PBN) heater. Prior to growth, nitridation was carried out on the sapphire substrate at 900°C for half an hour. The InN film was grown at a substrate temperature ranging from 350 to 500°C for an hour. The growth temperature was stabilized during growth within 1°C . The thickness of the resultant film was about 300 nm , which corresponded to a growth rate of 300 nm h^{-1} in the present system. The InN films were characterized by XRD using a Rigaku D/MAX C diffractometer. The surface morphology and cross-section were studied using a Hitachi S800 scanning electron microscope (SEM). The structure and lattice image of the film were studied using a Philips CM200 high resolution transmission electron microscope (HRTEM). Micro-Raman and

Fig. 2. SEM micrographs of InN film grown at various substrate temperatures: (a) 360°C , (b) 480°C , (c) 510°C and (d) 540°C .

micro-photoluminescence spectra were obtained through a Renishaw system 2000 spectrometer with an Ar^+ laser as the light source.

3. Results and discussion

Fig. 2 shows the top view SEM images of InN films grown at various temperatures. It is clear that the epitaxy of InN film improved as the growth temperatures were raised from 360 to 540°C. At a temperature as low as 350°C, indium droplets formed and the InN grain size was small (Fig. 2(a)). At a higher temperature (480°C), the grain size increased and well-faceted InN crystallites were formed. As indicated in Fig. 2(b), some of the crystallites show preferred orientation, which is different from the (0001) direction of the substrate. The misorientated crystallites appeared to reduce as the temperature was raised to 540°C (Fig. 2(c) and (d)). The inset of Fig. 2(d) reveals some peeled-off portion of the film. The hexagonal InN mosaic pattern in the inset indicates that the InN film was epitaxially deposited.

As shown in Fig. 3, typical θ - 2θ XRD scan of the InN films grown at 540°C revealed only the InN (0002), InN (0004) and sapphire (0006) at 31.3, 65.4 and 41.7°, respectively, indicating that the (0001) hexagonal InN was grown epitaxially on the sapphire (0001) substrate. The lattice constant obtained from the XRD data is 5.70 Å, which is quite close to the reported value [21]. Note that the θ - 2θ XRD scans for those films grown at 480°C contained mainly two extra peaks, InN (100) and InN (101) at 29.3 and 32.9°, respectively. These two peaks can be clearly seen only when the XRD data was plotted in log-scale as in the

Fig. 4. Typical Raman spectrum of the InN/sapphire film.

inset of Fig. 3. The existence of less than 1% extra peaks is attributed to different directional growth, which undermines the quality of the film.

Fig. 4 shows the Raman spectrum of a typical InN film. The h -InN related peak at 443, 488 and 588 cm^{-1} are attributed to the $A_1(\text{TO})$ mode, E_2 mode and $A_1(\text{LO})$ mode, respectively. The Raman spectrum in Fig. 4 is agreeable with other reports in the literature for thin films [22–24] as well as for single crystals [25]. The FWHM of the peaks reaches the instrumentation limit of the spectrometer indicating a good quality of the film.

Fig. 5 shows a typical photoluminescence spectrum of the InN samples measured at room temperature. The spectrum clearly shows a broad peak at 1.8 eV, which is close to the

Fig. 3. XRD θ - 2θ scan of the InN/sapphire film and its peak assignment. The inset shows a log-scale of the spectrum revealing the otherwise invisible peaks.

Fig. 5. Room temperature photoluminescence spectrum of the InN film.

Fig. 6. HRTEM image of the InN film with the TED in the inset.

Table 1

Comparison of the lattice measured using TED and the corresponding date ($a = 3.3566 \text{ \AA}$, $c = 5.7009 \text{ \AA}$) reported in the literature [21]

D (TED) ($\text{\AA}$)	hkl	D (XRD) ($\text{\AA}$)	Deviation (%)
4.1064895			
3.0422748	100	3.07998	1.2
2.9056187	002	2.85001	−1.95
2.5962445	101	2.69986	3.84
2.1259104	102	2.08991	−1.72
1.7892228	110	1.76998	−1.09
1.6080278	103	1.61339	0.33
1.5340098	200	1.53097	−0.20
1.5124983	112	1.50397	−0.57
1.4830075	201	1.47797	−0.34
1.3894175	004	1.42598	2.56
1.2914233	104	1.29096	−0.04
1.209434	203	1.19266	−1.40

1.86 eV measured by Tansley and Foley [26] using optical absorption technique. Multiple components of the photoluminescence are readily identified in the spectrum. To resolve each component of the PL spectrum, low temperature measurement is currently underway. A temperature dependence of the band edge transition will provide much insight into the material properties of InN, which has never been reported.

To study further the detailed structure of the InN film thus grown, HRTEM was applied. As shown in Fig. 6, nanocrystallites of 5–10 nm diameter were observed throughout the film. It should be pointed out that the long wavelength fringes in the figure are due to the interference of two neighboring grains misaligned with small azimuthal angle to each other. The TEM diffraction (TED) pattern of the sample is depicted in the inset of the figure. A comparison of lattice spacing measured by TED and XRD is listed in Table 1. Good agreement within 4% deviation was achieved between the TED and XRD measurements. The most prominent lattice spacing measured directly from the lattice image is $2.57 \text{ \AA}$, which corresponds to the (101) plane in Table 1. The nanocrystalline feature observed in the HRTEM image is distinctive to such compound. It has also been reported in the literature that nanocrystalline InN inclusion tend to be formed in $\text{In}_x\text{Ga}_{1-x}\text{N}$ system [2,27,28]. Interestingly, these nanocrystallites have been identified to play a key role in the high efficiency emission of the III-nitride system. A similar effect in the red emission of the InN may also exist. The 5–10 nm InN quantum dot, in particular, is highly desirable for optoelectronic applications such as high efficiency, low threshold, high thermal stability lasers. More detailed study is underway to probe these possibilities.

4. Conclusions

Growth of InN films using a simple resistive heated MOCVD was reported in this paper. By utilizing a PBN heater, good quality InN films were deposited on sapphire (001) substrates. XRD measurement indicated highly

oriented (001) directional growth of the films with small fraction of (101) component. Raman spectra of the films mainly composed of E_2 , $A_1(\text{TO})$ and $A_1(\text{LO})$ modes of InN, is agreeable with the literature values. HRTEM revealed that the films exhibited pseudo-epitaxy in that they consisted of 5–10 nm InN nanocrystallites with small azimuthal misalignment. Furthermore, strong photoluminescence spectra of the films were observed at room temperature, which opened up potentials for high efficiency, low cost, environmentally benign optoelectronic devices.

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