High growth rate deposition of oriented hexagonal InN films

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Abstract

Highly oriented nanocrystalline indium nitride (InN) films were successfully grown on Si(111) substrate. The growth rate of InN film can be enhanced fourfold by a double-zone metal organic chemical vapor deposition system consisting of a high temperature NH₃ pre-cracking zone and a low temperature deposition zone. A maximum growth rate of 6 μm/h was achieved due to the high cracking efficiency of NH₃. Meanwhile, the growth temperature of the substrate can be varied from 350 to 600 °C, which provides more flexibility for the film structure. While X-ray diffraction revealed the (0001) texture of the film, the high-resolution transmission electron microscopy study concluded the growth of highly oriented nanocrystalline hexagonal InN, which may lead to potential solar cell and optoelectronic applications. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Indium nitride (InN), a III–V compound semiconductor with a stable wurtzite crystal structure and a direct band gap of 1.9 eV [1], is promising for visible optoelectronics and high efficiency solar cells. It is predicted that a tandem solar cell with a Si cell at the bottom and a higher bandgap cell of 1.85 eV on the top can achieve a maximum efficiency of 32.1% (AM1.5 global) [2], which is highly desirable for energy applications. Therefore, the 1.9 eV bandgap InN has the potential to be used for non-toxic, high efficiency solar cells when integrated with Si. So far, most of the InN growth studies have been done on sapphire, GaN and GaAs [3–8], except for a few works done on the Si substrate [9,10]. Various methods have been used including metal organic chemical vapor deposition (MOCVD) [3–8], magnetron sputtering [11], molecular beam epitaxy (MBE) [12], halogen-transport vapor phase epitaxy (VPE) [13], and laser-assisted CVD using HN₃ as a

nitrogen source [14]. However, high quality InN has not been achieved mainly due to the lack of a lattice-matched substrate and restricted growth conditions owing to low dissociation temperature of InN itself [15]. Normally the growth temperature should be kept relatively low (~500 °C) to prevent the dissociation of InN. However, the limited cracking efficiency of N₂ or NH₃ at such temperatures results in a relatively low growth rate. In this paper, we report the growth of nanocrystalline InN on Si(111) with a growth rate of 6 μm/h using a double zone MOCVD system.

2. Experimental

A schematic diagram of the MOCVD apparatus for the InN growth is shown in Fig. 1. Trimethylindium [TMIn: (CH₃)₃In] kept at 10 °C and high-purity NH₃ were used as the precursors. TMIn vapor was carried by 40–80 sccm high-purity N₂ gas and another 200 sccm N₂ gas was added down stream to increase the gas flow of the group-III line. The NH₃ flow rate was varied from 800 to 1600 sccm, which corresponds to a V/III ratio of several hundreds. To prevent pre-reaction

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Fig. 1. Configuration and temperature distribution of the double zone MOCVD reactor for InN growth.

between TMIn and NH_3 , the two gases were fed into the chamber through separate quartz tubes. The tube delivering NH_3 passed over a high temperature graphite zone of 600–900 °C to enhance NH_3 cracking. The preheated NH_3 gas was mixed with TMIn right above the substrate and injected vertically onto the substrate. Prior to placing the Si(111) substrates into the reactor, the substrates were first cleaned in an acetone and then methanol ultrasound bath for 3 min each, followed by subsequent cleaning in 8% HF solution and deionized water, and finally dried in nitrogen gas. The substrate temperature during growth can be varied from 400 to 600 °C. Typical temperature profile of the chamber was shown in the lower part of Fig. 1. TMIn was introduced to the chamber before NH_3 to prevent amorphous SiN_x formation, which was reported to severely degrade the film quality [8]. The films thus deposited were characterized by XRD using a Rigaku D/MAX C diffractometer. The morphology and the thickness, typically 0.2–6 μm , of the films were studied using a Hitachi S800 scanning electron microscope (SEM). The structure and lattice image of the film were studied using a Philips CM200 transmission electron microscope (TEM). Raman spectra were obtained through a Renishaw system 2000 micro-Raman spectrometer with an Ar^+ laser as the light source.

3. Results and discussion

Fig. 2 displays a typical θ – 2θ XRD scan showing strong InN(0002), InN(0004) and Si(111) peaks at 31.3°, 65.3° and 28.4°, respectively, indicating that hexagonal InN (h-InN) is grown with strong (0001) texture on the Si(111) substrate. The lattice constant obtained from the XRD data is 5.73 Å. Besides the InN(0002) peak, additional small peaks corresponding to InN (10–11), (10–12), (10–13) indicate the polycrystalline nature of the film. Typical SEM images (not

Fig. 2. XRD θ – 2θ scan of the InN/Si(111) film and its peak assignment.

shown here) of the film indicate columnar structure, which is typical for CVD growth of lattice-mismatched materials. The top view reveals fine grain structures with hexagonal pyramids, which is common for film growth with a lattice mismatch larger than 4% (8% in our case). The large mismatch in our system even resulted in cracking of the films when the thickness exceeded 1 μm . Therefore, the thickness of the sample was kept below 0.6 μm to avoid cracking of the films.

The Raman spectrum of a typical InN/Si(111) film is shown in Fig. 3. The h-InN related peak at 487 cm^{-1} (E_2 mode) could be clearly identified. The $\text{A}_1(\text{LO})$ modes shifted toward lower wavenumber at 583 cm^{-1} . Both peaks were broadened with respect to those reported in the literature [16,17]. This broadening may be attributed to strain and defects in our film.

The temperature dependence of the InN growth rate is shown in Fig. 4. In Fig. 4a, the growth rate as a function of substrate temperature without NH_3 preheating is shown. As expected, the growth rate increases with substrate temperature. However, it starts to decrease when the substrate temperature is above 500 °C, presumably due to the dissociation of InN. A maximum growth

Fig. 3. Raman spectrum of the InN/Si(111) film.

rate of 1.5 $\mu\text{m/h}$ at 500 $^{\circ}\text{C}$ is obtained, which is relatively high compared to published works [4]. When additional graphite was inserted for preheating NH_3 to form the double zone system, a strong temperature dependence of the growth rate was observed. As shown in Fig. 4b at a fixed substrate temperature of 500 $^{\circ}\text{C}$, a maximum growth rate of 6 $\mu\text{m/h}$ is achieved at a NH_3 preheating temperature of 750 $^{\circ}\text{C}$. The high growth rate is attributed to the highly efficient NH_3 cracking at elevated preheating temperature. However, too high a temperature would cause heating of the adjacent substrate surface and resulted in the dissociation of the InN. Although the V/III ratio of our growth condition is much lower than those reported in the literature [3,4], no indium droplets were observed on the surface, indicating sufficient supply of active nitrogen due to the efficient NH_3 cracking in the double zone system.

To study the detailed structure of the InN film thus grown, HRTEM is applied to investigate the structure and the lattice image. As shown in the cross-sectional image of the film in Fig. 5, nanocrystallites of approximately 10 nm diameter are observed throughout the film. It should be pointed out that the long wavelength fringes (as circled) in the figure is attributed to the interference of waves from neighboring grains misoriented with a small azimuthal angle to each other. This implies that these nanocrystallites are highly oriented to each other. The TEM diffraction (TED) of the sample is depicted in the inset of the figure, showing a discrete diffraction spot with twofold symmetry, indicating highly oriented crystals despite the polycrystalline nature of the film. The orientation of the crystallites is also reflected in the XRD pattern in Fig. 2, wherein the (0002) peak dominates the entire spectrum. A detailed calculation using the 0.3 $^{\circ}$ FWHM of the (0002) peak and 0.1 $^{\circ}$ instrumental resolution, we obtained an average grain size of 30 nm from the Scherrer equation [18]. This is comparable to the 10-nm grain size measured directly from the TEM image.

After calibrating the camera constant of the TED photograph using a single crystal Si sample, the d-

Fig. 5. High resolution cross-sectional TEM image of InN grown on Si(111) substrate with the TED at the inset.

spacings of the InN can be obtained from the radius of the spots measured from the center of the diffraction pattern. A computer program was utilized to draw circles (not shown in Fig. 5) from the center of the diffraction pattern to match the diffraction spots and resulted in 14 of them. A comparison of the 14 lattice spacings measured by TED and its corresponding values reported in the literature were listed in Table 1. Small deviation between the lattice spacing values and its corresponding literature values in the table confirms the growth of hexagonal InN films. The lattice constants of $a=3.56$ $\text{\AA}$ and $c=5.67$ $\text{\AA}$ were thus determined. To confirm this observation, a direct measurement of the lattice spacing from the lattice image in Fig. 5 yields 3.00, 2.82 and 2.10 $\text{\AA}$, which agree well with the lattice spacing of (10–10), (0002) and (10–12) planes, respectively.

Fig. 4. (a) The growth rate of InN as a function of substrate temperature without NH_3 preheating. (b) The growth rate as a function of preheating graphite temperature at a substrate temperature of 500 $^{\circ}\text{C}$. The arrow in the figure indicates the reported growth rate in the literature.

Table 1

Comparison of the lattice spacing measured using TED and the corresponding data ($a=3.5366$ Å, $c=5.7009$ Å) reported in the literature [21]

D (Å) (TED)	hkl	D (Å)	Deviation (%)
3.04	100	3.069	−0.7
2.90	002	2.850	1.8
2.73	101	2.700	1.1
2.13	102	2.090	1.9
1.79	110	1.770	1.1
1.61	103	1.613	−0.6
1.53	200	1.531	0.0
1.51	112	1.504	0.7
1.48	201	1.478	0.0
1.40	004	1.430	−2.1
1.33	202	1.352	−1.5
1.29	104	1.291	0.0
1.21	203	1.193	1.7

However, the nanocrystalline feature of the HRTEM image is unique to such compounds. The nanocrystalline nature of the InN films thus grown has also been reported in other systems such as nanocrystal InN inclusion in $\text{In}_x\text{Ga}_{1-x}\text{N}$ growth [19,20]. The fact that the nanocrystalline nature of InN may play an important role in the high efficiency emission of the III-nitride system could lead to a similar effect in the red emission of the InN. 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 verify such possibilities.

4. Conclusion

High growth rate deposition of oriented nanocrystalline InN films using the double zone MOCVD method is reported in this paper. By utilizing an NH_3 preheating design, nanocrystalline InN films were deposited on Si(111) at a growth rate of 6 $\mu\text{m}/\text{h}$, which is fourfold higher than the growth rate reported in the literature. Detailed characterization of the films has been performed using SEM, Raman, XRD and HRTEM. The nanocrystalline nature of the films and high growth rate of the process open up potential for high efficiency, low

threshold, low cost and environmentally benign optoelectronic materials including high efficiency solar cells.

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References

- [1] T.L. Transley, C.P. Foley, J. Appl. Phys. 59 (1986) 3241.
- [2] E.N. Matthias, B.M. Allen, IEEE Trans. Electron Devices, ED-34 (1987) 257.
- [3] A. Wakahara, T. Tsuchiya, A. Yoshida, J. Cryst. Growth 99 (1990) 385.
- [4] M. Sato, Jpn. J. Appl. Phys. 36 (1997) 595.
- [5] Q. Guo, M. Nishio, H. Ogawa, A. Yoshida, Jpn. J. Appl. Phys. 38 (1999) L490.
- [6] A. Yamamoto, Y. Yamauchi, M. Ohkubo, A. Hashimoto, J. Cryst. Growth 174 (1997) 641.
- [7] S. Yamaguchi, M. Kariya, S. Nitta, T. Takeuchi, C. Wetzel, H. Amano, I. Akasaki, J. Appl. Phys. 85 (1999) 7682.
- [8] Y.C. Pan, W.H. Lee, C.K. Shu, H.C. Lin, C.I. Chiang, H. Chang, S.D. Lin, M.C. Lee, W.K. Chen, J. Appl. Phys. 38 (1999) 645.
- [9] A. Yamamoto, M. Tsujino, M. Ohkubo, A. Hashimoto, J. Cryst. Growth 137 (1994) 415.
- [10] S.E. Aleksandrov, V.A. Zykov, T.A. Gavrikova, D.M. Krasovitskii, Semiconductors 32 (1998) 412.
- [11] T.J. Kistenmacher, S.A. Ecellberger, W.A. Bryden, J. Appl. Phys. 74 (1993) 1684.
- [12] C.R. Abernathy, S.J. Pearton, F. Ren, P.W. Wisk, J. Vac. Sci. Technol. B11 (1993) 179.
- [13] O. Igarashi, Jpn. J. Appl. Phys. 31 (1992) 2665.
- [14] Y. Bu, L. Ma, M.C. Lin, J. Vac. Sci. Technol. A11 (6) (1993) 2931.
- [15] O. Ambacher, M.S. Brandt, R. Dimitrov, T. Metzger, M. Stutzmann, R.A. Fischer, A. Miehr, A. Bergmaier, G. Dollinger, J. Vac. Sci. Technol. B14 (6) (1996) 3532.
- [16] M.C. Lee, H.C. Lin, Y.C. Pan, C.K. Shu, J. Ou, W.H. Chen, W.K. Chen, Appl. Phys. Lett. 73 (1998) 2606.
- [17] H.J. Kwon, Y.H. Lee, Appl. Phys. Lett. 69 (1996) 937.
- [18] B.D. Cullity, Element of X-Ray Diffraction, 2nd ed., Addison Wesley, Reading, MA, 1978, pp. 284–285.
- [19] C.C. Liao, S.W. Feng, C.C. Yang, Y.S. Lin, K.J. Ma, C.C. Chuo, C.M. Lee, J.I. Chyi, Appl. Phys. Lett. 76 (2000) 318.
- [20] H.C. Yang, P.F. Kuo, T.Y. Lin, Y.F. Chen, K.H. Chen, L.C. Chen, J.I. Chyi, Appl. Phys. Lett. 76 (2000) 3712.
- [21] W. Paszkowicz, Powder Diffr. 14 (4) (1999) 258.