Journal of Alloys and Compounds 506 (2010) 343–346

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

The growth of III–V nitrides heterostructure on Si substrate by plasma-assisted molecular beam epitaxy

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ARTICLE INFO

Article history:
Received 24 April 2010
Received in revised form 23 June 2010
Accepted 30 June 2010
Available online 13 July 2010

Keywords:
InGaN
SEM
PL
XRD
High work function metal contacts

ABSTRACT

This paper reports the growth of InGaN/GaN/AlN epitaxial layer on Si(1 1 1) substrate by utilizing plasma-assisted molecular beam epitaxy (PA-MBE) system. The as-grown film was characterized using high-resolution X-ray diffraction (HR-XRD) and photoluminescence (PL). High work function metals, iridium and gold were deposited on the film as metal contacts and their electrical characteristics at pre- and post-annealing were studied. The structural quality of this film is comparative to the values reported in the literature, and the indium molar fraction is 0.57 by employing Vegard's law. The relatively low yellow band emission signifies the grown film is of high quality. For metal contact studies it was found that the post-annealed sample for 5 min shows good conductivity as compared to the other samples.

1. Introduction

GaN-based materials receive great deal of attention because of the potential applications for optoelectronic devices operating in the whole visible spectral range and in electronic devices such as high temperature, high power, and high frequency transistor. The III-nitrides form a continuous alloy system with direct band gap ranging from 6.2 eV (AlN) to 0.7 eV (InN) with 3.4 eV for GaN. Consequently, the growth and physics of GaN-based materials have attracted tremendous scientific attention. Traditionally, the heterostructures of the conventional III–V compounds such as GaAs, GaP and InP are commonly grown by metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) techniques. However, the growth of GaN-based materials has been mainly performed using MOCVD, particularly, the GaN-based commercial optoelectronics devices, i.e. light emitting diodes and laser diodes. In contrast, MBE grown GaN-based optoelectronic devices are relatively lagged behind; this is attributed to the unavailability of suitable source of active nitrogen species. Nevertheless, with the development of efficient and reliable nitrogen plasma sources for MBE recently, the quality of the GaN-based epilayer has been improved tremendously. The use of MBE for the growth of GaN-based materials, in fact, has a number of advantages as compared to MOCVD. For instances, lower growth temperature, precise control of the alloy composition and thickness, abruptly layered structure, in situ monitoring of the surface structure on atomic scale, as well as less material sources consumption, and utilization of non-hazardous materials. Furthermore, growing p-type GaN-based materials are much easier than MOCVD as it requires no post-growth heat treatment for the activation of Mg dopant in the p-type GaN-based materials due to the hydrogen free environment. Conversely, growing p-type GaN-based materials using MOCVD requires post-treatment due to the generation of hydrogen species as by-products from the precursor [1–8].

Presently, substrates such as sapphire ($A1_2O_3$) or silicon carbide (SiC) are commonly used for the growth of high quality GaN films; however, there have been a great interest in growing GaN-based materials on Si substrates which offer not only low production cost but also attractive opportunity to incorporate GaN-based devices into Si-based technology. One of the major challenges in depositing GaN-based materials on Si is the large lattice mismatch between Si- and GaN-based materials, which inhibit the growth of high quality GaN-based materials. Therefore, a buffer layer such as AlN and SiC is used to minimize this problem. Intensive studies have been carried out to improve this problem. Recently, the enhancement of InGaN film quality has been reported by Kurouchi et al. with the insertion of thin InN layer. In another study, the film quality of InGaN was found to be improved when ZnO was used as a substrate instead of sapphire [9–12].

This article presents the growth of InGaN/GaN/AlN on Si(1 1 1) substrate by using plasma-assisted MBE (Veeco Gen II). The structural and optical properties of grown III-nitrides heterostructure were then analyzed by a variety of characterization tools. High-resolution X-ray diffractometer was used to assess and determine

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doi:10.1016/j.jallcom.2010.06.204

the crystalline quality and indium composition of InGaN. The optical quality of the film was investigated by photoluminescence (PL). In order to obtain the thickness of each epitaxy layer, field emission scanning electron microscopy (FE-SEM) image of the cross-section of the as-grown sample was done. Gold and iridium were deposited as metal contacts on the grown sample and their electrical characteristics under pre- and post-annealed condition were characterized.

2. Experimental details

2.1. Growth of InGaN

InGaN(~360 nm)/GaN(~50 nm)/AlN(~210 nm) epitaxy layers were grown on Si(1 1 1) substrate using plasma-assisted molecular beam epitaxy (PA-MBE) system (Veeco Gen II). High purity sources such as gallium (7N), aluminium (6N5) and indium (7N) were installed in the Knudsen cells. Reactive nitrogen species were generated by channeling high purity nitrogen to radio frequency (RF) source. The resultant nitrogen plasma was at nitrogen pressure of 1.5×10^{-5} Torr under 300 W rated discharge power. Before loading the substrate to the PA-MBE system, the Si(1 1 1) wafer (3-inch) was cleaned using Radio Corporation of America (RCA) method. After loading the substrate into the PA-MBE system, the substrate was outgassed in the load-lock and buffer chamber; next it was transferred to the growth chamber. Surface treatment was done to the substrate to ensure the absence of SiO_2, leaving only clean Si substrate. This was done by depositing a few monolayer of Ga on the substrate at 750 °C, which resulted in the formation of Ga_2O_3. The clean Si surface was further confirmed by the presence of prominent Kikuchi lines shown by reflection high-energy diffraction (RHEED). Prior to the growth of nitride layers, a few monolayer of Al were deposited on the Si surface to inhibit the formation of Si_xN_y, which is detrimental to the growth of the subsequent epitaxy layers. The formation of such amorphous layer has been observed by many groups [13,14]. Calleja et al. [14] reported that the growth of GaN epilayer on Si_xN_y will lead to polycrystal with full width at half maximum (FWHM) values from XRD measurements between 70 and 100 arcmin. It is well known that the lattice matching between GaN and Si(1 1 1) was very large, i.e. 17%, which will result in poor crystalline quality [13–16]. Therefore, a buffer layer is highly desired.

Prior to the growth of the buffer layer, the substrate temperature was set to 808 °C. The buffer layer was grown by setting the Al and N shutters to open simultaneously for 15 min. Next, the GaN layer was deposited on the buffer layer for 33 min under substrate temperature of 800 °C. Prior to the growth of InGaN epitaxy layer, the substrate temperature was reduced to 700 °C, subsequently the In and Ga effusion cells were heated up to 925 and 930 °C respectively to initiate the growth of InGaN. The final growth process lasted about 30 min.

2.2. Deposition of metallic contacts

The as-grown InGaN on Si(1 1 1) substrate was cleaved into a few pieces. Gold (Au) contacts (~500 nm) were deposited on it by employing thermal evaporation (Edwards, Auto 306) of gold. The Au-coated samples subsequently were transferred to the DC sputtering system (Edwards, Auto 306) in order to coat iridium (Ir) contacts (~100 nm) on them. Some of the samples were annealed under nitrogen ambient with flow rate of 4 L/min, 450 °C, for 5 and 10 min.

2.3. Characterization

The as-grown sample was characterized accordingly. Structural phase analysis was done by employing high-resolution X-ray diffraction (HR-XRD, PANalytical X'pert Pro MRD) method with Cu $K_{\alpha 1}$ radiating wavelength at 0.15406 nm. Such method can be used to determine the molar fraction of indium in the sample. The optical properties of the film were characterized by photoluminescence (PL) measurement (Jobin Yvon HR800UV) with He–Cd laser operates at 325 nm as an excitation source. The cross-section electron micrograph of the as-grown sample was obtained using FE-SEM (Zeiss, Leo Supra 50VP). The electrical behaviour of the metal contacts on the film was determined by current–voltage measurement system (Keithley Model 82).

3. Results and discussion

Fig. 1 shows the 2θ scan of the XRD spectrum of the sample grown by MBE. The XRD measurement confirmed that the heterostructure of III-nitrides was epitaxially grown on Si(1 1 1). These can be seen from the presence of the peaks at 34.59°, 36.09°, 72.96° and 76.50°, which correspond to GaN(0 0 0 2), AlN (0 0 0 2), GaN(0 0 0 4) and AlN(0 0 0 4), respectively. In addition, a weak peak appears at 32.99°, which can be attributed to InGaN(0 0 0 2). The

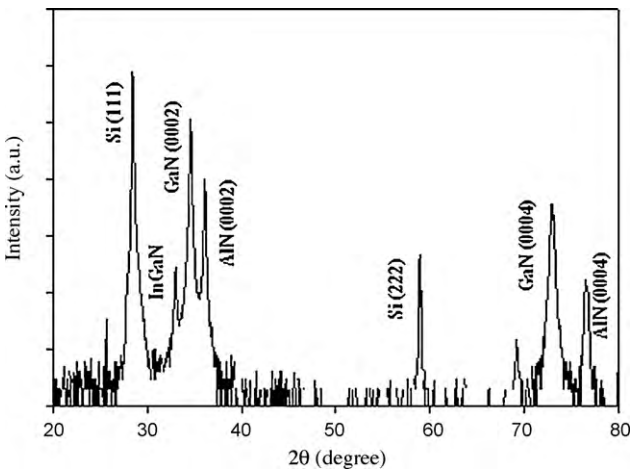

Fig. 1. XRD spectrum of the InGaN/GaN/AlN/Si sample.

Table 1
The 2θ XRD peak positions of different crystal planes and their relative intensity.

2θ peak position (°)	Crystal plane	Rel. intensity (%)
28.475	Si(1 1 1)	100
32.986	InGaN	0.06
34.593	GaN(0 0 0 2)	22.26
36.092	AlN(0 0 0 2)	1.74
58.914	Si(2 2 2)	0.02
69.208	In	Too low
72.964	GaN(0 0 0 4)	0.59
76.5	AlN(0 0 0 4)	0.03

positions of the peaks and the corresponding crystal planes as well as the relative intensity are compiled in Table 1.

XRD rocking curve measurement (not shown) was done to determine the crystalline quality of the epilayers. From the measurements, the full width at half maximum (FWHM) of the (0 0 0 2) plane for AlN, GaN and InGaN epilayers are 24.2, 24.8 and 6.8 arcmin, respectively. From the literature, the use of Si(1 1 1) substrate to grow III-nitrides, particularly GaN, always produces relatively low crystal quality, i.e. from 20 to 70 arcmin were typically reported [13,14,17,18]. The high value of FWHM suggests that it is difficult to grow high quality GaN-based materials on Si(1 1 1) substrate. The growth of poor crystal quality of the GaN-based epilayers is mainly attributed to the large difference in lattice constant, crystal structure and thermal expansion coefficient between the Si- and GaN-based materials [19]. From Fig. 1 and Table 1, the intensity of InGaN is found to be relatively low, i.e. it is approximately three orders of magnitude smaller than GaN, and this indicates that the thickness of InGaN epilayer was very thin. The modeling of the $\omega/2\theta$ XRD spectra showed that the thicknesses of the GaN and InGaN were 200 and 8 nm, respectively. The indium molar fraction, x, based on the chemical formula $In_xGa_{1-x}N$, can be determined from Vegard's law (as-shown in Eq. (1)) based on XRD results [20]:

$$x = \frac{c_{InGaN} - c_{GaN}}{c_{InN} - c_{GaN}}, \quad (0 < x < 1) \tag{1}$$

where c_{InGaN}, c_{GaN}, and c_{InN} is the actual c-plane lattice constant of InGaN, GaN, InN epilayer respectively.

It was found that the indium molar fraction of the InGaN epilayer was 0.57. It is well known that InGaN materials are difficult to be grown, particularly InGaN with high indium molar fraction. The difficulties in growing high quality InGaN materials can be due to several problems, such as the large difference in interatomic spacing between InN and GaN, which resulted in a solid phase miscibility gap [21]. In addition, the relatively high vapor pressure of InN as compared to the vapor pressure of GaN [22], as well as the dif-

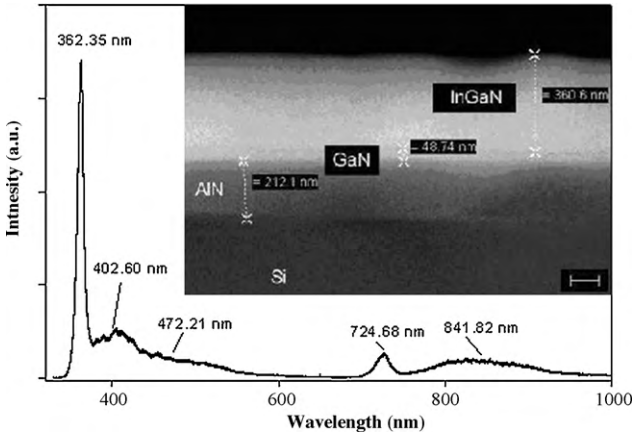

Fig. 2. PL spectrum of the InGaN/GaN/AlN/Si sample. Inset is the cross-section of the sample, with scale bar rated at 100 nm.

ference of formation enthalpies of InN and GaN will cause a strong indium surface segregation on the growth front [23,24]. Apart from that, InGaN deposition is complicated by thermodynamic instability of InN. At higher growth temperature, InN will tend to dissociate faster than being adsorbed [25]. Therefore, it is not surprising to obtain a thin InGaN epilayer for 30 min growth at temperature of 700 °C.

Fig. 2 shows the PL spectrum of the sample. The PL spectrum is dominated by an intense and sharp peak at 362 nm, which is attributed to the band edge emission of GaN. Peaks at 403, 472 and 725 nm are probably due to impurities or native defects (such as Mg, C or N vacancy, Ga vacancy) related recombination [26,27]. Relatively low yellow band emission is observed; this indicates that the thin film is of good optical quality. Apart from this, there is a broad peak centred at 842 nm (1.47 eV). The presence of this broad peak could be attributed to the emission of InGaN.

Fig. 3 shows the current–voltage relationship of the Au/Ir contacts on the InGaN sample. The gradual increase of electrical resistance could be observed, i.e. 5 min annealed, 10 min annealed and as-deposited shows the lowest, intermediate and highest resistance respectively. This can be determined by measuring the current drawn for each sample at a forward bias of 3 V. At bias of 3 V, the as-deposited, 5 min annealed, 10 min annealed sample having a forward current of 4.4 mA, 26 mA, 17.6 mA respectively.

One plausible reason for such characteristics was that the 5 min annealing resulted in a better interfacial between the InGaN and Au/Ir layers, hence a better conductivity was obtained. When the sample is annealed for 10 min, alloy formation could have occurred between the Au and InGaN layer, hence there was a change in resistance. The role of the Ir layer may have acted as a protective layer for Au. Alloy formation between Ir and Au layer was not expected as recent reports showed that the alloy of Ir and Au was absent when annealing was done at 500 °C [28]. On the other hand, the high current magnitude could be due to the presence of indium residues in the sample, which was not fully participated in the formation of InN.

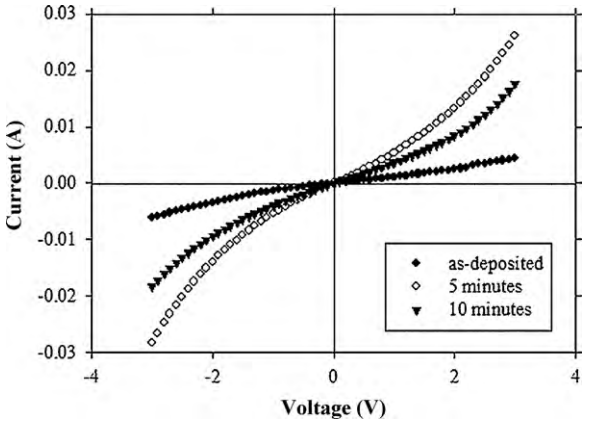

Fig. 3. Current–voltage relation for the Au/Ir contacts on InGaN sample.

4. Conclusions

In summary, the growth of InGaN/GaN/AlN on Si(1 1 1) substrate has been performed using plasma-assisted molecular beam epitaxy. The structural, optical and electrical properties of the thin film have been analyzed by HR-XRD, PL and current–voltage measurements. The structural quality of the thin film is comparative to the reported values in the literature. Sharp and intense band edge emission of GaN was observed in the PL measurement with the relatively low yellow band emission, indicative of good optical quality of the thin film. The sample that undergone 5 min of annealing resulted in better conductivity as compared to other samples.

Acknowledgements

The authors would like to thank Universiti Sains Malaysia for its financial support under the RU grant 1001/PFIZIK/811155 and incentive grant 1001/PFIZIK/821066.

References

[1] J. Senawiratne, A. Chatterjee, T. DetchProhm, W. Zhao, Y. Li, M. Zhu, Y. Xia, X. Li, J. Plawsky, C. Wetzel, Thin Solid Film 518 (2010) 1732–1736.
[2] H. Sakai, T. Koide, H. Suzuki, M. Yamaguchi, S. Yamasaki, M. Koike, H. Amano, I. Akasaki, Jpn. J. Appl. Phys. 34 (1995) 1429–1431.
[3] P. Laukkanen, S. Lehkonen, P. Usimaa, M. Pessa, A. Sepala, T. Ahlgren, E. Rauhala, J. Cryst. Growth 230 (2001) 503–506.
[4] S. Dalmasso, B. Damilano, N. Grandjean, J. Massies, M. Leroux, J.-L. Reverchon, J.-Y. Duboz, Mater. Sci. Eng. B82 (2001) 256–258.
[5] S. Gradečak, F. Qian, Y. Li, H.-G. Park, C.M. Lieber, Appl. Phys. Lett. 87 (2005) 173111.
[6] C. Xiong, F. Jiang, W. Fang, L. Wang, C. Mo, H. Liu, J. Lumin. 122–123 (2007) 185–187.
[7] J. Liu, W.S. Tam, H. Wong, V. Filip, Microelectron. Reliab. 49 (2009) 38–41.
[8] Y. Kamii, I. Waki, H. Fujioka, M. Oshimaa, H. Miki, M. Okuyama, Appl. Surf. Sci. 190 (2002) 348–351.
[9] M. Kurouchi, T. Yamaguchi, H. Naoi, A. Suzuki, T. Araki, Y. Nanishi, J. Cryst. Growth 275 (2005) e1053–e1058.
[10] N. Li, S.-J. Wang, E.-H. Park, Z.C. Feng, H.-L. Tsai, J.-R. Yang, I. Ferguson, J. Cryst. Growth 311 (2009) 4628–4631.
[11] Hironori Komaki, Teruyuki Nakamura, Ryuji Katayama, Kentaro Onabe, Masashi Ozeki, Tetsuo Ikari, J. Cryst. Growth 301–302 (2007) 473–477.
[12] Y.E. Romanyuk, D. Kreier, Y. Cui, K.M. Yu, J.W. Ager III, S.R. Leone, Thin Solid Films 517 (2009) 6512–6515.
[13] A. Ohtani, K.S. Stevens, R. Beresford, Appl. Phys. Lett. 65 (1994) 61–63.
[14] E. Calleja, M.A. Sanchez-Garcia, F.J. Sanchez, F. Calle, F.B. Naranjo, E. Munoz, S.I. Molina, A.M. Sanchez, F.J. Pacheco, R. Garcia, J. Cryst. Growth 201/202 (1999) 296–317.
[15] T.L. Tansley, E.M. Goldys, M. Godlewski, B. Zhou, H.Y. Zuo, The contribution of defects to the electrical and optical properties of GaN, in: S.J. Pearton (Ed.), GaN and Related Materials I, Gordon and Breach Science Publishers, 1997.
[16] J.W. Yang, C.J. Sun, Q. Chen, M.Z. Anwar, M. Asif Khan, S.A. Nikishin, G.A. Seryogin, A.V. Osinsky, L. Chernyak, H. Temkin, Chimin Hu, S. Mahajan, Appl. Phys. Lett. 69 (1996) 3566–3568.
[17] J. Ristic, M.A. Sanchez-Garcia, E. Calleja, A. Perez-Rodriguez, C. Serre, A. Romano-Rodriguez, J.R. Morante, V.R. Koegler, W. Skorupa, Mater. Sci. Eng. B93 (2002) 172–176.
[18] W. Ju, D.A. Gulino, R. Higgins, J. Cryst. Growth 263 (2004) 30–34.
[19] T. Lei, M. Fanciulli, R.J. Molna, T.D. Moustakas, R.J. Graham, J. Scanlon, Appl. Phys. Lett. 59 (1991) 944–946.
[20] F.K. Yam, Z. Hassan, Superlattices Microstruct. 43 (2008) 1–23.
[21] I. Ho, G.B. Stringfellow, Appl. Phys. Lett. 69 (1996) 2701–2703.
[22] T. Nagatomo, T. Kuboyama, H. Minamino, O. Omoto, Jpn. J. Appl. Phys. 28 (1989) 1334–1336.
[23] Yoshihiro Kangawa, Tomonori Ito, Yoshinao Kumagai, Akinori Koukitu, Appl. Surf. Sci. 216 (2003) 453–457.
[24] G.B. Stringfellow, J. Cryst. Growth 312 (2010) 735–749.

[25] M.A.L. Johnson, W.C. Hughes, W.H. Rowland Jr., J.W. Cook Jr., J.F. Schetzina, M. Leonard, H.S. Kong, J.A. Edmond, J. Zavada, J. Cryst. Growth 175/176 (1997) 72–78.
[26] G. Popovici, H. Morkoc, Growth and doping of defects in III-nitrides, in: S.J. Pearton (Ed.), GaN and Related Materials II, Gordon and Breach Science Publisher, 2000, Chapter 3.
[27] V. Bougrov, M. Levinshtein, S. Rumyantsev, A. Zubrilov, Gallium nitride (GaN), in: M.E. Levinshtein, S.L. Rumyantsev, M.S. Shur (Eds.), Properties of Advanced Semiconductor Materials, GaN, AlN, InN, BN, SiC, SiGe, John Wiley & Sons, Inc., 2001, Chapter 1.
[28] L.F. Voss, L. Stanfford, B.P. Gila, S.J. Pearton, F. Ren, Appl. Surf. Sci. 254 (2008) 4134–4138.