Unintentionally doped InN grown onto an atomically flat AlN intermediate layer using plasma-assisted molecular beam epitaxy


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Unintentionally doped InN has been grown onto an atomically flat AlN intermediate layer on top of the Si(111) substrate using plasma-assisted molecular beam epitaxy (PA-MBE). Though there are lots of micrometer-size indium droplets randomly distributed on the top of the surface, the highest electron mobility of this InN thin film measured at room temperature by van der Pauw method is still higher than 1000 cm²/V s with a carrier concentration of 5–8.9 × 10¹⁸ cm⁻³. A symmetrical X-ray rocking curve is measured and the full-width-at-half-maximum (FWHM) of this sample is 1089 arcsec. In the meantime, the threading dislocation (TD) density of this material is estimated to around 9.8 × 10⁸ cm⁻² – 7.5 × 10⁹ cm⁻² depending on the probing regions that are studied by the etching technique and field-emission scanning electron microscopy (FE-SEM). (2 × 1) in situ reflection high-energy electron diffraction (RHEED) patterns show that this sample is grown under In-rich environment with possible In-terminated surface. From the FE-SEM pictures which were taken from the samples after 10 minutes etching in hydrochloride, the surface morphology shows In-polarity-like patterns that coincide with those procured in RHEED. To select and grow a high-quality laminated AlN as intermediate layer is believed to be the major step in obtaining this high electron mobility InN thin film on Si substrate.

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1 Introduction

Wurtzite InN has attracted great attention recently due to that the real bandgap of this material may be much smaller than the values of 1.89–2.1 eV which have long been accepted [1–3]. The group led by Davydov in Russia and Matsuoka in Japan separately reported that the true gap of InN might be located at 0.7–1.0 eV [4–7]. Meanwhile, the electron transport property of InN would be the best among III-nitride semiconductors (such as GaN, and AlN) when the effective mass of 0.11m₀ (m₀: the mass of the electron) was taken at the Γ point based on theoretical calculations [8]. According to the new findings that are described above, obviously, InN is extremely important both in optoelectronic and electronic devices. This novel material cannot only enlarge the emission/detection range of the nitride-based semi-
conductors from ultraviolet to infrared, but also possibly boost the operating speed of modern electronics. However, most of the samples used in the above research are grown on sapphire substrates which have poor thermal conductivity, electrically insulated and very hard to process. These disadvantages highly limited the development and production of III-nitride semiconductors. Recently, it has been proposed to use stacked buffer layers (i.e. AlN/β-Si3N4/Si) for the formation of the coincident lattices that can be used to overcome the heteroepitaxial growth with large lattice mismatch and it might be a suitable technique to grow InN on Si using MBE [9]. Also, this structure (AlN/β-Si3N4/Si) will be useful for separating the contribution between InN and Si while performing Hall measurements due to the large bandgap of single crystalline AlN. This study aims at growing high quality single crystalline InN on Si substrate using simpler techniques and wish to extend the research in fabricating high electron mobility transistors (HEMT) in the near future.

2 Experimental

The PA-MBE system described in this study is originally installed for the growth of III-nitrides. This MBE system consists of two chambers which are buffer (loading/unloading) and growth chambers. The vacuum level of the buffer chamber and the growth chamber are always maintained at less than $1 \times 10^{-8}$ Torr and $1 \times 10^{-10}$ Torr by using a Varian V-250 turbo pump and a CTI-CT8 cryogenic pump, respectively. There are five conventional Knudsen cells equipped with this system. Three cells are for the aluminium, gallium, indium, and the other two are for magnetism, and silicon dopants. For the growth of InN, 7N5 indium metal is selected to be the group III source and the nitrogen source (group V) is provided by the radio frequency plasma (RF-plasma) generator feeding with 6N9 high purity nitrogen gas. The N2 gas purifier is used to ensure the high purity of the nitrogen gas. The sample did not undergo any process except the standard chemical cleaning before it is put into the growth chamber. The standard chemical cleaning process using acetone, isopropanol, HF:H2O (1:10) and then dipping into HF buffer solution before DI water rinse was applied to clean the surface contamination and the native oxide prior to load the Si substrate into the growth chamber. To keep a consistent process, the total exposure time of the substrate in the air after the chemical cleaning process and prior to loading into the buffer chamber is kept less than 10 min. Because of the variance of the pyrometer reading which maybe originating from the influence of the coating that contaminated the quartz window, the temperature disclosure in this study is all based on the reading of the thermal couple ($T_c$) which is located behind the substrate holder. The thermal cleaning process was carried out at $830 \, ^\circ C$ under the operating pressure of around $10^{-7}$ Torr for 40 min until the sharp and clear ($7 \times 7$) RHEED pattern is shown. This step is very important and quite critical to the material quality and the surface roughness in the following growth of the AlN thin film. The high-temperature AlN layer was directly grown on top of the Si substrate without using any buffer layer under the pressure of $1.2 \times 10^{-6}$ Torr. The beam equivalent pressure (BEP) of Al and the V/III ratio during the growth are stabilized at $1.5 \times 10^{-7}$ Torr ($\text{Al}_{\text{BEP}} = 1.5 \times 10^{-7}$ Torr) and 20, respectively. A 0.8 µm thick InN layer is grown on the 0.073 µm thick AlN at $T_c = 380 \, ^\circ C$. $\text{In}_{\text{BEP}}$ of $2.5 \times 10^{-7}$ Torr with N/III = 20 are the growth parameters used for this growth. The sample is rotated at 3 rpm (round per minute) till the end of the growth.

The STAIB RH15 RHEED system is utilized for in situ monitoring where the filament current set at 1.4 A and the electron beam energy is 15 kV. Hall measurement by the van der Pauw method is performed at room temperature with 7N5 indium metal used to make the ohmic contact for electrical connecting. Post analysis including the hydrochloride etching, FE-SEM, energy dispersive X-ray detection (EDX), atomic force microscopy (AFM), high resolution X-ray diffraction (HRXRD), and transmission electron microscopy (TEM), are applied to characterize the InN thin film properties and to study the microstructures of the InN/AlN heterostructure.

3 Results and discussion

The structure of the sample used in this study is InN/AlN/Si(111). The carrier concentration and electron mobility of this material are measured at room temperature by the van der Pauw method. The highest
In situ RHEED patterns during the growth: (a) and (b) show the \((1 \times 1)\) streaky patterns after 20 min of the AlN growth at \(T_c = 780 \, ^\circ\text{C}\). The thickness of the AlN layer is 73 nm. (c) This streaky mixed with spotty pattern was taken after 2.5 min growth of InN. The \((2 \times 1)\) pattern gradually appeared and then turned to a \((1 \times 1)\) pattern which shows that the sample was grown under In-rich environment. The spotty fixture only shows up in certain crystal orientation as in (d) (3.5 min growth of InN). After 60 min of the growth, (e) and (f), the streaky RHEED patterns appear and imply the flat surface of the InN thin film growth using PA-MBE. The STAIB RH15 RHEED system is utilized for in situ monitoring where the filament current is set at 1.4 A and the electron beam voltage is 15 kV (the electron wavelength is around 0.10 Å).

The electron mobility measured is 1172 cm\(^2/V\)s with the unintentional doping concentration of \(8.9 \times 10^{18} \, \text{cm}^{-3}\).

The sample is measured many times within six months for the confirmation of the Hall data. Through the long term data collecting process, the electron mobility of this InN sample is always higher than 1000 cm\(^2/V\)s and the lowest electron concentration measured in this system is \(5 \times 10^{18} \, \text{cm}^{-3}\). To ensure that the measured value is indeed the real value of the InN, AlN material with very large bandgap (i.e. \(~6.2 \, \text{eV}\) is used as the intermediated layer in order to provide good isolation between InN and the Si substrate. This structure is good both for the high quality film growth on Si substrate and for accurate Hall measurement. To be surprised, though the lattice mismatch between the AlN and InN is very large (~16%); the lattice constants of wurtzite InN and AlN are \(a_{\text{AlN}} = 3.104 \, \text{Å}, \ c_{\text{AlN}} = 4.966 \, \text{Å}\) and \(a_{\text{InN}} = 3.548 \, \text{Å}, \ c_{\text{InN}} = 5.760 \, \text{Å}\), respectively) [10, 11], the electron mobility of this MBE grown InN is still as high as 1172 cm\(^2/V\)s with the unintentional doping concentration of \(8.9 \times 10^{18} \, \text{cm}^{-3}\) measured at room temperature with improved surface morphologies.

The detailed in situ RHEED patterns during the growth of the AlN and InN are shown in Fig. 1. Figures 1(a, b), (c, d) and (e, f) are the RHEED patterns of the AlN, early-stage InN, and InN growth after 20 min, 2.5 min [in Fig. 1(d) 3.5 min], and 60 min that are taken at 780 °C, 380 °C and 380 °C, respectively. The clear \((1 \times 1)\) streaky pattern, shown in Fig. 1(a, b), reflects that the flat AlN is successfully grown onto the Si(111) substrate without forming other undesired layers [12, 13]. The HRXRD and TEM microstructure analyses have confirmed this which will be shown later.

The symmetrical rocking curve and two-theta scan is obtained through a Bede-D1 high-resolution X-ray diffractometry (HRXRD) and the result is shown in Fig. 2. Figure 2(a) shows typical 2theta-omega scan which confirms that wurtzite single crystal quality AlN and InN epitaxial thin films have been successfully grown onto the Si(111) substrate. The interface of the AlN/InN heterostructure is very sharp, there is not any other peak (for example, the AlInN) in the \(2\theta–\omega\) scan. The peaks that are located at 28.46°, 31.39°, 32.94°, and 36.10°, respectively, are identified to be Si(111), InN(002), In(101) and...
Fig. 2 (online colour at: www.pss-b.com) HRXRD results: (a) 2θ–ω scan and (b) (002) symmetrical rocking curve. The In(101) peak shows the randomly distributed In droplets which is also confirmed by FESEM. Part (b) shows that the material quality of the MBE growth of InN can be improved even though the lattice mismatch between the AlN and InN is very large.

AlN(002). Figure 2(b) is the (002) symmetrical rocking curve of the AlN and InN thin films and the FWHM of the AlN and InN is 1386 and 1089 arcsec. Based on the rocking curve result, the material quality of the 0.8 µm InN is better than that of the 73 nm thick AlN which clearly shows that the material quality of the MBE grown InN can be improved even though the lattice mismatch between AlN and InN is very large. To combine the information provided by HRXRD and RHEED, the epitaxial relations between the InN thin film and Si(111) substrate can be deduced as [(0001)\text{InN}] || [111]\text{Si} and [(2\overline{2}0)]\text{AlN/InN} || [-\overline{1}10]\text{Si} \[9, 14\].

Fig. 3 (online colour at: www.pss-b.com) Post analysis of the surface morphology of the InN/AlN heterostructure is also evaluated. The surface roughnesses of the 0.8 µm thick InN thin film grown on top of the 0.073 µm thick AlN layer, measured by AFM with analyzing area of 500 nm × 500 nm, are 1.73 nm (InN) and 2.27 nm (RMS), respectively.
Laminated and sharp heterostructure of the InN/AlN/Si has been obtained using PA-MBE. The cross-sectional EDX data show that the atomic concentration of the In and N of this InN is very close to 1:1. Meanwhile, there is no oxygen signal that has been found in this sample within the detecting level using EDX.

There are a lot of papers which have reported that InN could only grow within a very narrow processing window [13–18] to obtain a smooth InN film with sharp hetero-interface. We have overcome the difficulties by inserting an atomically flat AlN layer between InN and Si. The sharp interface with an atomic concentration of In and N of this InN of approximately 1:1 has been measured by cross-sectional FE-SEM and EDX which are shown in Fig. 4. Meanwhile, there is no oxygen signal that has been found in this sample within the detecting level using EDX. Post analysis of the surface morphology of the InN/AlN heterostructure is also evaluated. The surface roughnesses of the 0.8 µm-thick InN thin film grown on top of the 0.073 µm thick AlN layer, measured by AFM with analyzing area of 500 nm × 500 nm, are 1.73 nm (InN) and 2.27 nm (RMS), respectively (Fig. 3). The latter AlN data was obtained from a separate run with AlN layer only under the same growth conditions.

To estimate the TDs of the InN thin film grown onto Si(111) substrate, TEM analysis is used. Figure 5(a) is the result of the cross-sectional analysis using conventional TEM. It is very clear that there is not any unwanted layer existing in the InN/AlN/Si structure and confirms the sharp interface observed by FE-SEM (see also Fig. 4(a)). The density of TDs calculated using this TEM picture is around 5 × 10^7 cm^-2 that is a number very close to the best data of GaN directly grown on sapphire substrate [19].

At the same time, in order to have more accurate estimation and to doubly confirm the TDs calculated from the TEM, FE-SEM is taken to monitor the change of the morphology before and after hydrochloride (HCl) etching. As known, the etching technique is a simple and reliable technique that can be used to check the polarity of the nitride-based material and also good to further confirm the finding of the TDs through the TEM analysis. The changes of the surface morphology after 10 min HCl etching is obviously due to the much faster etching rate of the indium droplets compared with the InN thin film and the micrometer-size randomly distributed indium droplets no longer existed on top of the as-grown InN surface.

From the images that are shown in Fig. 5, it can be seen that the InN surface after HCl etching remains smooth which implies that this sample is highly probably In-polarity InN and this result coincides with those procured in RHEED [20]. In addition, this 0.8 µm thick InN layer after 10 min etching using HCl reveals lots of hexagonal etching pits. However, the shape of the pits that are observed here (which have been shown in Fig. 5(c)) is quite different compared with the previous report [20]. These pits have
Micro-analysis using TEM and FE-SEM. (a) Conventional TEM (300 KV) used to estimate the TDs of this InN thin film grown onto Si(111) substrate. The density of TDs calculated using this TEM picture is around $5 \times 10^7 \text{cm}^{-2}$. Meanwhile, it is very clear that there is not any unwanted layer existing in this InN/AlN/Si structure. (b) The surface morphology of the InN after 10 min HCl etching is observed using FE-SEM. (c) From the picture, it can be seen that the InN surface after HCl etching remains smooth which implies that this sample is highly possibly In-polarity InN. The hexagonal pits are direct evidence of the TDs and the pit number can be used to estimate the density of the dislocations. The shape of the pits observed here is quite different compared with the previous report [20].

Also revealed the direct evidence of TDs and the number of pits can be used to estimate the density of the dislocations. The density of TDs is estimated using these pictures which have an area around 1.0 µm$^2$ for each photo. The dislocation density in this study is around $9.8 \times 10^8 \text{cm}^{-2} - 7.5 \times 10^9 \text{cm}^{-2}$ based on the etching technique and FE-SEM analysis depending on the probing regions.

There is another point that we would like to point out here. The conventional TEM and FE-SEM micro-analyses have shown uniform InN in a certain scale (~300 nm). The atomic concentration of this InN thin film does not show any fluctuation within the detection limit of EDX. HRXRD has also proved that single crystal quality InN has been successfully achieved on Si substrate. However, the surface morphology of this InN after 10 min HCl etching (Fig. 5) shows a texture-like pattern that implies non-uniformity of this InN. In order to make a real device, large area uniformity is necessary and this will be one of the major challenges for crystal growth in the future.

4 Conclusion

The InN/AlN heterostructure is selected to grow on Si(111) using PA-MBE under well-controlled growth conditions. To be surprised, though the lattice mismatch between the InN and AlN is large, the InN grown onto the AlN can still yield a very high electron mobility at high unintentional doping concentration level with improved surface morphology. According to the hydrochloride etching technique and FE-SEM observation, this InN thin film shows the In-polarity-like pattern that coincides with those procured in RHEED. The threading dislocation density of this material is estimated to around $9.8 \times 10^8 \text{cm}^{-2} - 7.5 \times 10^9 \text{cm}^{-2}$ depending on the probing regions that are studied by the etching technique and FE-SEM. The surface roughness of this InN thin film measured by AFM is 2.27 nm (RMS) with the analyzing area of 500 nm × 500 nm. The FWHM of the symmetrical HRXRD of the InN is...
1,094 arcsec. The cross-sectional EDX data show that the atomic concentration of In and N of this InN is very close to 1:1. At the same time, there is no oxygen signal that has been found in this sample within the detecting level using EDX. The highest electron mobility of the 0.8 µm thick InN measured by the van der Pauw method is as high as 1172 cm²/V s with the unintentional doping concentration of $8.9 \times 10^{18}$ cm⁻³ at room temperature. Meanwhile, this is one of the highest value that has ever been reported in the literature based on InN grown on Si(111) using MBE so far. To choose and grow high-quality laminated AlN as intermediate layer is believed to be the major step in obtaining this high electron mobility InN thin film on Si substrate. However, in order to achieve device quality material, how to achieve the large area uniformity of InN growth and to lower the unintentional doping level are still two of the major concerns in crystal growth.

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