第 21 卷第 3 期 半 导 体 学 报 Vol. 21, No. 3
2000 年 3 月 CHINESE JOURNAL OF SEMICONDUCTORS Mar., 2000

Characterization of GaN_xAs_{1-x} Alloy Grown on GaAs by Molecular Beam Epitaxy*

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Abstract The GaN_xAs_{1-x} alloy has been investigated which is grown on GaAs (100) substrate by molecular beam epitaxy with a DC-plasma nitrogen source. The samples are characterized by high resolution X-ray diffraction (HRXRD) and low temperature photoluminescence (PL) measurements. Both HRXRD and PL measurements demonstrate that the crystalline and optical qualities of GaN_xAs_{1-x} alloy degrade rapidly with the increase of N composition. The nitrogen composition of 4.5% can be obtained in GaN_xAs_{1-x}/GaAs quantum well by optimizing growth conditions, through which a photoluminescence peak of 1201nm is observed at a low temperature (10 K). The dependence of GaN_xAs_{1-x} band gap energy on the nitrogen composition in this investigation corresponds very well with that of the theoretical one based on the dielectric model when considering the effect of the strain. At the same time, we also demonstrate that the bowing parameter of GaN_xAs_{1-x} alloy is composition dependent.

Key Words: Characterization, GaN_xAs_{1-x}, MBE
PACC: 8115G, 6110, 7865, 7125R
Article ID: 0253-4177(2000)03-0219-06

1 Introduction

GaN_xAs_{1-x}, the combination of small amount of nitrogen and GaAs, has been experimentally observed with the band gaps several hundreds meV lower than that of GaAs[1~4]. The alloy has attracted considerable attention in the applications of optoelectronic devices and fundamental research. However, because of much difference in

Project Supported by National Natural Science Foundation of China Under Grant No. 69896260, 69789802, 69776036 and 69988005, by National High Technology Research & Development (863) Program of China Under Grant No. 863-307-15-501, and project of the Chinese Academy of Sciences and the State Key Laboratory on Integrated Optoelectronics.

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Received 5 June 1999, revised manuscript received 3 November 1999

the atomic size and electronegativity between As and N, it is very difficult to incorporate large amounts of nitrogen into GaN_xAs_{1-x} as limits the development of those devices and fundamental research. To date, GaN_xAs_{1-x} alloy has been grown by gas source molecular beam epitaxy (GSMBE) or chemical beam epitaxy with organometallic chemical vapor deposition (MOCVD). The RF nitrogen radical and dimethylhydrazine are also employed during the growth. Although the non-equilibrium growth method[3] has been employed, there is still some nitrogen (x = 14.8%, on GaP substrate) being added to the GaAs. The band gap of GaN_xAs_{1-x} grown on GaAs (100) substrate has been reported to follow a linear dependence on nitrogen composition (it means the bowing parameter is constant), which is different from the results by Bi *et al.*, i.e., the bowing parameter of GaN_xAs_{1-x} band gap is composition dependent. However, since few data can be obtained for the GaN_xAs_{1-x} layer with higher nitrogen composition, the accuracy of the band gap energy dependence on N composition is doubtful.

In this paper, the GaN_xAs_{1-x} alloy grown on GaAs (100) substrate by molecular beam epitaxy with a DC-plasma nitrogen source has been investigated. The samples are characterized by high resolution X-ray diffraction and low temperature photoluminescence measurements. A nitrogen composition of 4.5% was obtained in GaN_xAs_{1-x}/GaAs quantum well by optimizing growth conditions, through which a photoluminescence peak of 1201nm was observed at a low temperature (10K). In the meantime, the dependence of GaN_xAs_{1-x} band gap energy on nitrogen composition was also studied.

2 Experimental Procedures

The samples were grown in a VG80H MKII MBE system on GaAs (100) substrates. A DC active nitrogen plasma was used as the nitrogen source. The sample consisted of a 500nm GaAs buffer layer, a strained GaN_xAs_{1-x} layer and a 100nm GaAs cap layer. The nitrogen composition and the layer thickness were determined through the simulation of the experimental diffraction patterns on the basis of the X-ray dynamical diffraction theory. The growth temperature was in the range of 450℃~ 580℃. The growth rate of GaAs was 1.5μm/h. During the growth, the background pressure was $1\sim 5\times10^{-5}$ Pa. The optimized growth could be found elsewhere[5].

HRXRD measurements were performed with a JPN Rigaku SLX-1A double-crystal X-ray diffractometer, a conventional 12kW X-ray generator and a copper target ($\lambda CuK\alpha_1$ = 0.154056nm) as the radiation source. PL measurements were carried out at 10K with a He-Ne laser exciting. A liquid nitrogen cooling Ge detector was used to detect the signal at the exit of a 50cm monochromator through a phase lock-in amplifier.

3 Results and Discussions

Researching into two samples, we obtain the high-resolution X-ray diffraction (HRXRD) (004) rocking curves and its dynamic simulation in Fig. 1. Comparing the

experimental curves with the simulated ones for the two samples, the lattice mismatch in the growth direction are − 0.142% and − 0.631% while the nitrogen compositions 0.7% and 3.1%, respectively. Both thickness of GaN_xAs_{1-x} layer in the two samples are 200nm. The Pendellösung fringes of the sample with a $GaN_{0.007}As_{0.993}$ layer in Fig. 1 *a* is clear and the full-width at half-maximum (FWHM) of the $GaN_{0.007}As_{0.993}$ peak is narrow, all of which indicate that the interface between GaAs and $GaN_{0.007}As_{0.993}$ is abrupt while the quality of $GaN_{0.007}As_{0.993}$ layer is good. However, for the sample with $GaN_{0.031}As_{0.969}$ layer in Fig. 1 *b*, the Pendellösung fringes disappears and the FWHM of the $GaN_{0.031}As_{0.969}$ peak broadens. The disappearance of Pendell? sung fringe and the broaden of FWHM possibly result from the strain relaxation because the thickness of $GaN_{0.031}As_{0.969}$ layer exceeds its critical value.

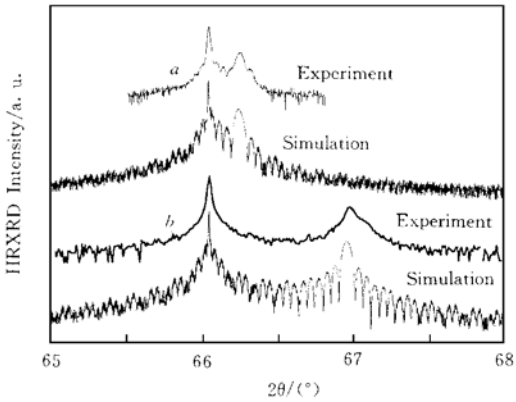

FIG. 1　Experimental and Simulated X-ray Diffraction Curves of Two GaNAs/GaAs Samples

The thickness of GaNAs layer is estimated to be 200nm. The nitrogen composition of *a* and *b* are 0.7% and 3.1%, respectively.

To avoid the influence of strain relaxation, the thickness of GaN_xAs_{1-x} layer should be selected carefully for all the samples used in PL measurements. According to Methew´s model, 5nm thickness GaN_xAs_{1-x} layer is far less than its critical value till the nitrogen composition is over 14%. To observe the strong luminescence, the 5nm thickness GaN_xAs_{1-x} is sandwiched by GaAs to form a GaN_xAs_{1-x}/GaAs strained layer quantum well structure. The low temperature photoluminescence spectra of three samples with different nitrogen compositions are shown in Fig. 2. The nitrogen compositions are 1.5%, 2.45% and 4.48%, respectively. Only one PL peak was observed in our PL measurements, as is different from Weyers´s reports[1, 2]. According to their reports, two PL peaks were observed and the lower energy peak was considered to be associated with As vacancies. A higher As pressure in our MBE growth could reduce the As vacancies, which might result in only one GaN_xAs_{1-x} PL peak observed in our

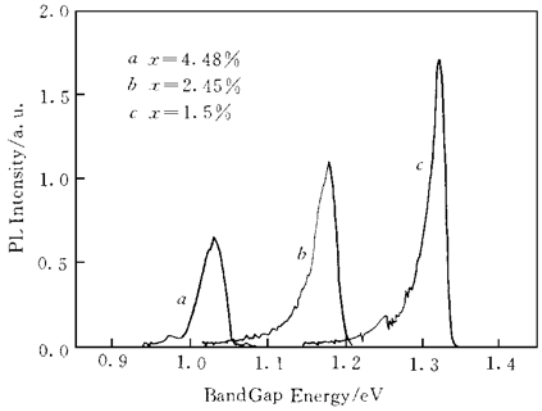

FIG. 2　Low Temperature Photoluminescence Spectra for Three GaNAs/GaAs Samples.

The nitrogen compositions of the three samples are 1.5%, 2.45% and 4.48%, respectively.

experiment. The dependence of PL peak shift on nitrogen composition is in agreement with Weyers's reports. It was also seen that the PL intensity decreased rapidly and the FWHM was broadened with the increase of nitrogen composition. The 33.8meV FWHM of the sample with 4.48% nitrogen composition is larger than the 22.2meV one with 1.5% nitrogen composition. Since the effect of the strain relaxation has been excluded, the quality degradation of the GaN_xAs_{1-x}/GaAs mainly results from the increase of the nitrogen composition.

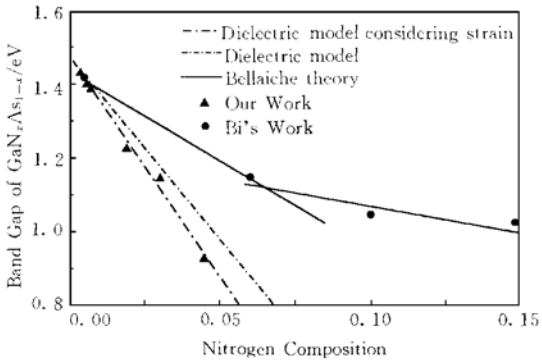

FIG. 3 The Dependence of GaNAs Band Gap Energy on Nitrogen Composition

The dependence of GaN_xAs_{1-x} band gap on the nitrogen composition is shown in Fig. 3. The theoretical band gaps, based on the dielectric model[1] and on the first principle supercell model[6] are also shown. And the low temperature PL measurements have been extrapolated to room temperature. It can be seen that the GaN_xAs_{1-x} band gap decreases rapidly with the nitrogen composition increasing. Our results have a small deviation from the earlier reports by Kondow[7] and Ougazzaden[8] *et al*. The band gap measured in the sample with $GaN_{0.045}As_{0.955}$ layer is 1.03eV at 10K, which corresponds to the wavelength of 1201nm. The measured band gap energies correspond very well with the theoretical ones based on the dielectric model, considering the effect of the strain. However, compared with the results reported by Bi *et al*.[6], a large deviation is seen. Bi's results are consistent with the theoretical predictions by Bellaiche[6]. However, their thickness of GaN_xAs_{1-x} layers grown on GaP substrate have been over their critical values though the nitrogen composition is as small as 0.5%. We have proved that the critical thickness is such a key factor[9] that determines the quality of GaN_xAs_{1-x} layer. Once the thickness of GaN_xAs_{1-x} layer is over the critical value, it will not be less accurate to determine the nitrogen composition by HRXRD. His believed that the discrepancy of band gap of GaN_xAs_{1-x} grown on GaAs and GaP results from the difference of substrates and the less accuracy in determining nitrogen composition.

The rapid variations of GaN_xAs_{1-x} band gap with the increase of nitrogen compositions indicate that the bowing parameter $b(x)$ of this alloy is very large. It can be determined by the following equation:

$$b(x) = \frac{xE_g(\mathrm{GaN}) + (1-x)E_g(\mathrm{GaAs}) - E_g(\mathrm{GaN}_x\mathrm{As}_{1-x})}{x(1-x)}$$

where $E_g(\mathrm{GaAs})$ and $E_g(\mathrm{GaN})$ are temperature dependent variables and can be obtained

by semi-experience Varshni equation, $E_g(GaN_xAs_{1-x})$ is the experimentally determined band gap energy of GaN_xAs_{1-x}. As shown in Fig. 4, we can see that the bowing parameter of GaN_xAs_{1-x} is not only very large but also strongly composition dependent, which is different from the conventional semiconductor alloys whose bowing parameters are usually composition independent and small (less than 1eV). As discussed by Wei[10] *et al.*, the greater bowing parameter mainly resulted from the spatial separation and the sharply localized band edge in the alloy due to the great differences in sizes of the As and N atoms and their atomic orbital energies. Theoretical calculations by Sakai *et al.*, based on the Van Vechtan model, predict a negative band gap for GaN_xAs_{1-x} with nitrogen composition in the range of 9.5% ~ 86.7%. According to their conclusions, semi-metal properties of the GaN_xAs_{1-x} can be expected. At the same time, the bowing parameter is also reported to be constant. However, our data show that the bowing parameter of GaN_xAs_{1-x} decreases from initial 36eV (x = 0.45%) to 16eV (x = 4.5%). Supposing the bowing parameter continuously decreases with the nitrogen composition increasing, it would be reasonable to expect the semiconductor properties of the GaN_xAs_{1-x} alloy in the whole nitrogen composition range. Furthermore, the variation of the bowing parameter with the nitrogen composition also reflects the ordering of GaN_xAs_{1-x} alloy. Bellaiche *et al.*[11, 12] have studied the effects of short-range and long-range orderings on the GaN_xAs_{1-x} alloy. They pointed out that the bowing parameters of random alloys and ordering alloys are different. The higher the orderings is, the larger the bowing parameter will be. Our results indicate that the ordering of GaN_xAs_{1-x} lowers with the increase of nitrogen composition.

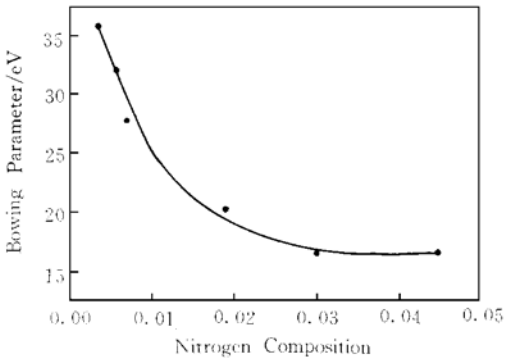

FIG. 4 Dependence of Bowing Parameter of GaNAs on Nitrogen Composition

4 Conclusions

The GaN_xAs_{1-x} alloy grown on GaAs (100) substrate by molecular beam epitaxy with a DC-plasma nitrogen source was investigated. The samples are characterized by high resolution X-ray diffraction and low temperature photoluminescence measurements. It has been proved that the quality of GaN_xAs_{1-x} alloy degrades with the increase of nitrogen compositions. A nitrogen composition of 4.5% is obtained in GaN_xAs_{1-x}/GaAs quantum well by optimizing the growth conditions, through which a photoluminescence peak of 1201nm is observed at a low temperature (10K). The dependence of GaN_xAs_{1-x} band gap energy on nitrogen compositions is also studied and it is found that it corresponds very well

with the theoretical band gap energy based on the dielectric model when considering the effect of the strain. At the same time, we also demonstrate the bowing parameter of GaN_xAs_{1-x} alloy is composition dependent.

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