第 23 卷第 6 期 半 导 体 学 报 Vol. 23, No. 6
2002 年 6 月 CHINESE JOURNAL OF SEMICONDUCTORS June, 2002

Metalorganic Chemical Vapor Deposition of GaNAs Alloy Using Dimethylhydrazine as Nitrogen Precursor

Wei Xin, Ma Xiaoyu, Wang Guohong, Zhang Guangze, Zhu Xiaopeng and Chen Lianghui

(*National Engineering Research Center for Optoelectronic Devices, Institute of Semiconductors, The Chinese Academy of Sciences, Beijing* 100083, *China*)

Abstract: GaNAs alloy is grown by metalorganic chemical vapor deposition (MOCVD) using dimethylhydrazine (DMHy) as the nitrogen precursor. High-resolution X-ray diffraction (HRXRD) and secondary ion mass spectrometry (SIMS) are combined in determining the nitrogen contents in the samples. Room temperature photoluminescence (RTPL) measurement is also used in characterizing. The influence of different Ga precursors on GaNAs quality is investigated. Samples grown with triethylgallium (TEGa) have better qualities and less impurity contamination than those with trimethylgallium (TMGa). Nitrogen content of 5.688% is achieved with TEGa. The peak wavelength in RTPL measurement is measured to be 1278.5nm.

Key words: GaNAs; MOCVD; impurity; contamination; HRXRD; SIMS
EEACC: 0520F; 2530C; 4320J
CLC number: TN304.2+6 **Document code**: A **Article ID**: 0253-4177(2002)06-0565-06

1 Introduction

Recently, III-N-V semiconductor materials containing small amounts of nitrogen have attracted a great deal of attention[1~4]. Incorporating a small amount of nitrogen into traditional III-V alloys, such as Ga(In)As and Ga(In)P, not only reduces the lattice constant of the alloys, but also arises a large bowing of their bandgap energy[5]. Among them, Ga(In)NAs can be grown lattice-matched to GaAs, so it is expected to be a candidate for long wavelength lasers emitting at the fiber optical communication window (1.3 ~ 1.55μm) with high temperature performance[6,7], as well as for multi-junction solar cells[8].

Ga(In)NAs has been successfully grown by metalorganic chemical vapor deposition (MOCVD)[9], molecular beam epitaxy (MBE)[10,11], and chemical beam epitaxy (CBE)[12]. MOCVD is suitable for mass production and is one of the promising methods to grow the device materials; therefore, it has been widely used in the fabrication of the optoelectronic devices. In the MOCVD growth, DMHy has been widely used as the nitrogen source because DMHy dissociates more readily than NH_3 at low temperature (425℃) and has a high vapor pressure (2.07×10^4Pa at 25℃)[13].

In this paper, we report the MOCVD growth of GaNAs under different temperatures by using two different kinds of Ga precursors, i.e., TMGa and TEGa. The samples are characterized by HRXRD, RTPL and SIMS. Nitrogen content of

Wei Xin male, was born in 1974. Now he is working for his PhD degree and engaged in the research on MOCVD growth of optoelectronic materials and devices.

Received 30 November 2001, revised manuscript received 4 January 2002 ©2002 The Chinese Institute of Electronics

5.688% has been achieved. The influence of Ga precursors on GaNAs quality has been investigated.

2 Experimental procedure

Epitaxial growth was carried out in a AIX-200 water-cooled horizontal reactor under low pressure on (001) GaAs substrates. IR-bulbs were used to heat the susceptor. The carrier gas was palladium cell purified hydrogen. Two different kinds of Ga source materials were used in the growth, trimethylgallium (TMGa) and triethylgallium (TEGa). Dimethylhydrazine (DMHy) was used as the nitrogen source and arsine (AsH_3) as the As source. Metalorganic and hydride source materials were supplied by different gas line, and then joined into the reactor entrance. TMGa (or TEGa) and DMHy were joined in the metalorganic source line. The total pressure was typically 10^4Pa. The total gas flow rate was 6L/min and the growth rate was typically 1.8μm/h. Typical values of the [DMHy]/([DMHy] + [AsH_3]) were between 0.90 and 0.96. Those of [AsH_3]/Ⅲ were between 6 and 12. In-situ annealing was carried out at 700℃ for 10min.

The nitrogen content of the samples was mainly determined by high-resolution X-ray diffraction (HRXRD) using a long fine focused X-ray generator and a copper target ($\lambda_{CuK\alpha 1}$ = 0.154056nm). The photoluminescence (PL) measurement was carried out at room temperature. The luminescence was excited by a 532nm wavelength doubled-YAG laser, and detected with a InGaAs detector. Different nitrogen, carbon and oxygen content and their distributions of the samples were measured by secondary ion mass spectrometry (SIMS).

In the experiments, four samples were grown and characterized. All of the samples consist of a GaAs buffer layer, a strained GaNAs layer, and a GaAs cap layer. Detailed structures and growth conditions are shown in Table 1.

Table 1 Structures and growth conditions for four samples

Sample name	A	B	C	D
GaNAs layer thickness/nm	350	270	130	96
Cap layer thickness/nm	115	180	230	65
Growth temperature/℃	570	570	570	510
[DMHy]/([DMHy] + [AsH_3])	0.93	0.96	0.96	0.96
Ga precursor	TMGa	TMGa	TEGa	TEGa

3 Results and discussion

Two main kinds of measurement that are often used to determine the nitrogen content in GaNAs are SIMS, and HRXRD. In SIMS measurement, the contents of the elements can be directly obtained. The only shortage of SIMS is that standard samples are required to do the calibration of the sensitivity factors in the measurement. The accuracy of standard determines the accuracy of the attained value. Normal standard samples used are N-implanted GaAs[3]. In HRXRD measurement, the layer mismatch is measured and then the nitrogen content can be deduced from the mismatch value by using Vegard's law. There are two factors that can arise error in determining the nitrogen content in GaNAs layer in HRXRD measurement. One is the strain relaxation of the epitaxial GaNAs layer. In the calculations of the nitrogen content, the GaNAs layer is regarded as fully strained. But according to Matthews and Blakeslee's model[14], the epilayer is fully strained until the thickness of the strained layer exceeds certain value, named "critical thickness". Then strain relaxation should occur and the epilayers should become partially relaxed. The critical thickness value decreases with increasing nitrogen content. The influence of strain relaxation on HRXRD results includes the broadening of the epilayer peak, the disappearance of the pendellosung fringes, and the change of the position of the epilayer peak. In the case of GaNAs, the distance between the GaNAs and the substrate peak should be reduced, the calculated mismatch should also be smaller than the actual value. This leads to smaller nitrogen content calculated. Another factor is the

influence of the impurities on the mismatch, especially carbon, which is often contained in the epilayer grown under low temperature. Low temperature is necessary to get high nitrogen content by MOCVD. Carbon also leads to the GaAs lattice reduction, as nitrogen does. It is impossible to get rid of the effect of carbon in the calculation of nitrogen content by HRXRD measurement unless the exact carbon content is attained. This leads to the calculated value larger than the actual one. In this paper, we combined HRXRD with SIMS measurement to determine the nitrogen content in the samples.

Figure 1 shows the measured and simulated (004) HRXRD results of the four samples. The strained mismatch of each sample is − 4511, − 5166, − 5036, − 11639ppm, respectively. The corresponding nitrogen content calculated from the results by using Vegard's law is 2.211%, 2.532%, 2.468% and 5.704%, respectively. The simulations were done with these parameters and assumed that no any strain relaxation occurred in the samples.

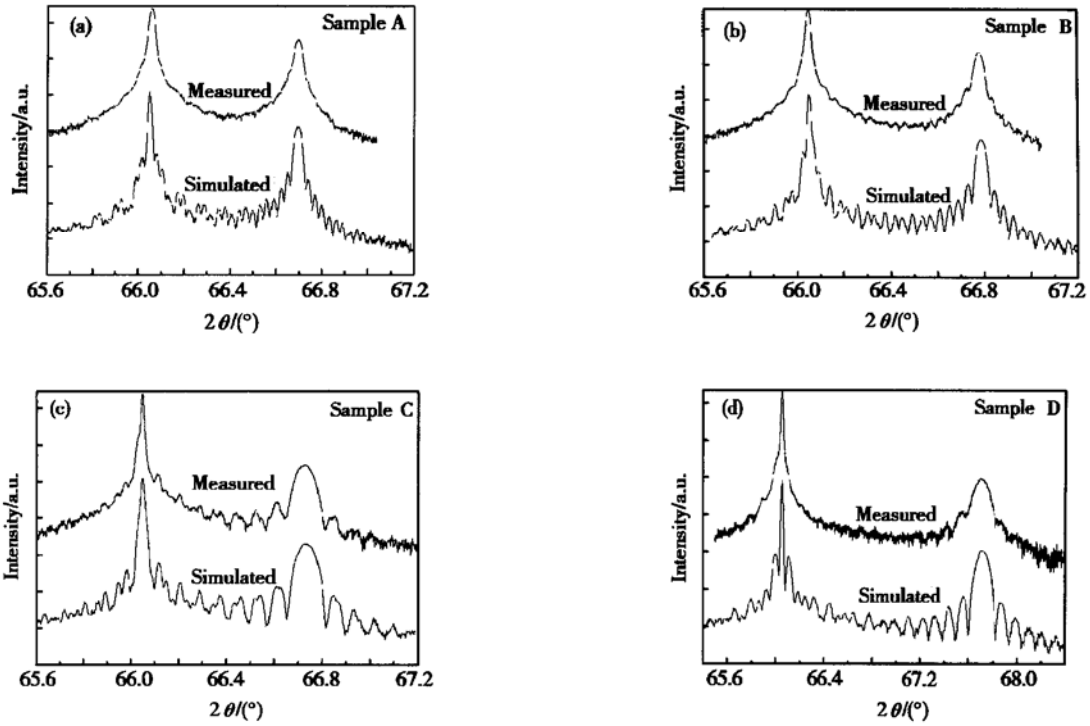

Fig. 1 Measured and simulated HRXRD results of GaNAs/GaAs samples

Figure 2 shows the RTPL results of the four samples. The peak wavelengths of sample A, B, C and D are 1092.60, 1104.10, 1100.50 and 1278.5nm, respectively.

The distributions of different elements in the samples are shown in Fig. 3. The elements include nitrogen, carbon and oxygen. The latter two are the main impurities in MOCVD grown samples, which should affect the performance of optoelectronic devices greatly. It should be noticed that only relative values are shown in the figures for lack of standard samples.

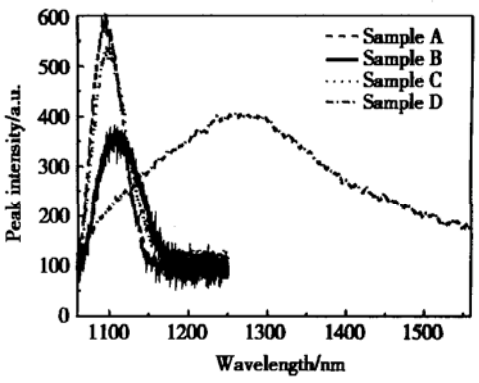

Fig. 2 RTPL results of the samples

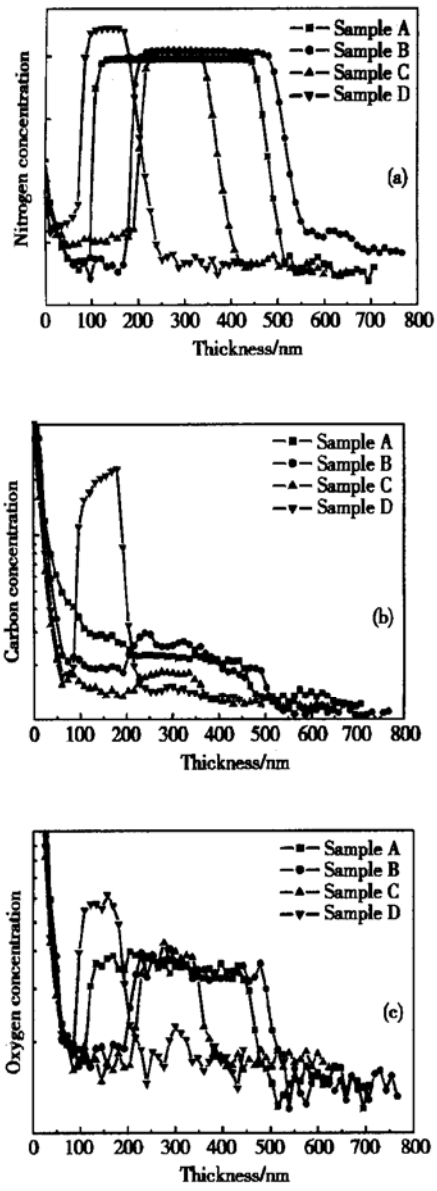

Fig. 3 N, C, O distributions measured by SIMS

It is shown from the HRXRD results of sample C that the measured curve fits for the simulated one very well. The pendellosung fringes are very clear. It is shown that the crystal quality is very well and no any strain relaxation occurs in this sample. It can be seen in the SIMS results that only slight increase of carbon content was found. This means that carbon has only negligible effect on the lattice constant of GaNAs. So the nitrogen content in sample C can be calculated by the HRXRD results and it can be used as the "standard sample". The absolute values of nitrogen content in other samples can be achieved from the SIMS results. By using this method, the nitrogen content obtained in sample D is 5.688%, slightly smaller than the HRXRD result, 5.704%. The difference between them is attributed to the influence in the HRXRD result of observed high carbon content and small strain relaxation in the sample.

We can see from the PL results of the samples that with the increasing of the nitrogen content, the peak wavelength shifts to long wavelength side, the full width at half maximum (FWHM) of the PL spectrum also increases. This means that the optical quality of the GaNAs layer becomes bad. It is mainly due to the large size and electro negativity difference between As and N.

Comparing the results of sample A and B, we can see that by increasing the [DMHy]/([DMHy] + [AsH_3]) ratio, the nitrogen in the sample can also be increased.

In the growth of sample B and C, we only change the Ga precursor from TMGa to TEGa at the same molar flow rate and keep other growth parameters unchanged. The nitrogen content achieved by using the two precursors at the same molar flow rate is nearly the same. The growth rate decreases from 27nm/min to 13nm/min. This means that TMGa is a more efficient Ga precursor than TEGa. But comparing the results of sample B and C, we can conclude that samples grown with TEGa have better quality than those with TMGa. From the HRXRD results, we can see that although the nitrogen content is nearly the same, the pendellosung fringes of sample C are more clear than those of sample B. This means that the crystal quality of samples grown with TEGa is better than that of samples with TMGa. In the RTPL measurement, the FWHM of sample C is narrower and the PL intensity is higher than those of sample B. It also shows that the samples grown by TEGa have much better optical quality. In Fig. 3 (b), the effect of different precursors can be directly seen from the difference of carbon content. By changing the Ga precursor from TMGa to TEGa, the carbon

content is reduced to about one half. This is mainly due to the different behavior of carbon atoms in the ethyl and methyl radicals. It is known that, in the MOCVD growth, TEGa is pyrolyzed unimolecularly by β-hydride elimination with the formation of ethylene[15],

$$Ga(C_2H_5)_3 = C_2H_4 + GaH(C_2H_5)_2$$

without the production of reactive carbon-containing species. On the other hand, TMGa is pyrolyzed by producing highly reactive CH_3 radicals, which leads to much higher carbon contamination. Along with the breaking of CH_3 radicals, which leaves large amount of carbon contamination in the material, hydrogen atom incorporation in the epitaxial films from TMGa may also be higher than that from TEGa. Hydrogen can affect the crystal quality because hydrogen can terminate the crystal bond. The elimination of carbon and hydrogen can explain the better quality achieved by TEGa. So TEGa is more suitable for growing GaNAs than TMGa.

Moreover, another advantage of TEGa for low temperature growth is that TEGa has much lower pyrolysis temperature than TMGa. So, TEGa but not TMGa was used in the growth of sample D at 510℃. Nitrogen content of 5.688% was achieved. The RTPL peak wavelength was 1278.5nm. The pendlosung fringes can also be seen from the HRXRD results. This indicated relatively high crystal quality of the epitaxial GaNAs layer could be attained even at such high nitrogen content. But for the RTPL result, the FWHM of the curve is very wide, which shows that the GaNAs grown under such a low temperature has poor optical quality. The broadening of the RTPL peak is attributed to three reasons. The first is the low growth temperature, the second is the nitrogen content increasing, and the last is the impurity contamination. The relative values of carbon and oxygen contents are shown in Fig. 3 (b) and (c). These two kinds of impurities are the main ones that can affect the quality of the epitaxial films greatly in MOCVD growth. Compared to those of sample C, the oxygen content was increased by two folds, and the carbon content was increased by nearly one order. The high oxygen should partly attribute to the relatively high water content in DMHy, and it also due to the small As/Ⅲ ratio (about 5) used in the experiment to attain high [DMHy]/([DMHy] + [AsH_3]) ratio. It has been reported that in the growth of GaAs with AsH_3, a drastic increase of oxygen content occurs in low temperature growth[16] with the reduction in Ⅴ/Ⅲ ratio. But for the samples grown with tertiarybutylarsine (TBAs), only small variations in oxygen content was found and it is almost independent of the applied Ⅴ/Ⅲ ration. So, in order to improve the crystal quality further, the impurity should be eliminated. The possible solutions include increasing of the As/Ⅲ ratio or changing the As precursor from AsH_3 to TBAs.

4 Conclusion

In this paper, GaNAs grown by MOCVD is investigated. TEGa and TMGa were used as the Ga precursor in the growth of GaNAs respectively. TEGa compared to TMGa shows many advantages in the growth of GaNAs.

SIMS and HRXRD measurement were combined in determining the nitrogen content in the samples. Nitrogen content of 5.688% has been obtained in the growth with TEGa. The RTPL peak wavelength was 1278.5nm. The FWHM was very wide partly because carbon and oxygen contamination occurrs under low temperature. For further improving the quality, the impurity must be eliminated.

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采用二甲基肼为氮源进行 GaNAs 的金属有机化学气相沉积生长

韦 欣 马骁宇 王国宏 张广泽 朱晓鹏 陈良惠

(中国科学院半导体研究所 光电子器件国家研究中心, 北京 100083)

摘要: 采用 MOCVD 方法, 利用二甲基肼为氮源, 进行了 GaNAs 材料的生长. 利用高分辨 X 射线衍射与二次离子质谱测试方法确定了材料中氮的组分. 采用室温光致发光谱测量了样品的光学性质. 讨论了不同的镓源对 GaNAs 材料质量和其中的杂质含量的影响, 结果证明三乙基镓在 GaNAs 的低温生长中比三甲基镓具有更大的优势. 采用三乙基镓生长的 GaNAs 中氮的含量达到 5.688%. 光致发光谱的峰值波长为 1278.5nm.

关键词: GaNAs; 金属有机化学气相沉积; 杂质; 沾污; 高分辨 X 射线双晶衍射; 二次离子质谱

EEACC: 0520F; 2530C; 4320J

中图分类号: TN304.2+6 **文献标识码**: A **文章编号**: 0253-4177(2002)06-0565-06

韦 欣 男, 1974 年出生, 博士研究生, 目前的主要研究方向为半导体光电子器件研制和Ⅲ-Ⅴ族化合物半导体材料的 MOCVD 生长.

2001-11-30 收到, 2002-01-04 定稿

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