Incorporation behaviors of group V elements in GaAsSbN grown by gas-source molecular-beam epitaxy

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Abstract

We report the incorporation behaviors of As, Sb, and N atoms in GaAsSbN grown by gas-source molecular-beam epitaxy. We found that N atom is more reactive and competitive than Sb atom at the growth temperature ranging from 420 to 450 °C. The increment in Sb beam flux hardly changes the N composition. However, the increment in N flux retards the incorporation of Sb. In addition, the increment in As₂ flux makes the Sb and N compositions decrease at the same rate. Based on these results, we have successfully grown GaAsSbN epilayers lattice-matched to GaAs substrates. The energy gap at room temperature is as low as 0.803 eV. Negative deviation from Vegard's law in lattice constant is observed in these layers.

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1. Introduction

GaAsSbN is a promising dilute nitride with only one group-III element and has drawn a lot of attention recently because of the potential applications to GaAs-based long-wavelength detectors [1–4]. Since GaAsSbN has only one group-III element, the chemical change between the nitrogen and group-III atoms, observed in thermal-annealed InGaAsN [5], can be eliminated. Less blue shift in energy gap of thermal-annealed GaAsSbN has been reported [6], which is beneficial to long wavelength applications. However, the growth of this alloy is quite crucial because it contains three group-V elements. Understanding the incorporation behaviors of the three group-V elements is very essential for precise composition control, especially for the high-quality epilayers lattice-matched to GaAs. Previous studies on molecular-beam epitaxy (MBE) showed that adding Sb could enhance the incorporation of N [7–10]. In this paper, we report the behaviors of this

promising dilute nitride grown by gas-source molecular-beam epitaxy (GSMBE). We found that N incorporation is virtually invariant of Sb flux. Based on these simpler behaviors, GaAsSbN epilayers lattice-matched to GaAs have been successfully deposited.

2. Experimental procedures

A VG-V80H gas-source MBE system was used to grow all the GaAsSbN samples on (1 0 0) semi-insulating GaAs substrates. Pure arsine (AsH₃), precursor of As source, was leaked into the gas cell at 1000 °C to provide the As₂ beams for the epitaxy process. Sb source was supplied by an EPI cracking cell. The Sb₄ flux from the reservoir zone was cracked at 1050 °C to supply a mixed beam of Sb₂ dimer and Sb monomer. The Ga beam was supplied by EPI SUMO cell. Its flux was calibrated using an ion gauge to keep the growth rate at 1 μm/h. The N species was generated by an EPI uni-bulb RF plasma K-cell operating at a radio frequency of 13.56 MHz. A PBN shutter was placed in front of the K-cell to reduce the N flux and ionized species. All the bulk films are 1 μm in thickness.

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The composition of the GaAsSbN was quantified by JEOL JXA-8200 electron probe X-ray microanalyzer (EPMA). GaAs, GaN, and GaSb were used as standards for ZAF correction. To ensure that the probe region is indeed within the epitaxial layer, we intentionally grew a GaAsSbN layer on InP substrate and lowered the electron gun voltage until the In and P signals were undetectable. The lattice mismatch between epitaxial layer and substrate was confirmed by a Bede D1 high-resolution X-ray diffractometer. The absorption measurement was carried out using a tungsten–halogen lamp dispersed by a SPEX 500 M spectrometer as the light source. The transmitting light was detected by an InGaAs photodiode and the transmittance was retrieved by standard lock-in techniques.

3. Results and discussion

Fig. 1 shows the Sb and N compositions of GaAsSbN epilayers grown at 490 °C as functions of N flow rate. The AsH₃ flow rate and Sb to Ga beam equilibrium pressure (BEP) ratio for these samples were fixed at 2.79 SCCM and 0.4, respectively. When N flow rate is less than 0.2 SCCM, nitrogen is not detectable in GaAsSbN by EPMA. For larger flow rate, N composition increases at the expense of Sb incorporation. Since the reactive N species in the plasma is a complicated function of plasma power, gas pressure, and flow rate, such a threshold behavior is not uncommon. Next, we consider the effect of Sb flux on N incorporation. In the experiments, AsH₃ and N₂ flow rates were fixed at 2.79 and 0.76 SCCM, respectively. Three growth temperatures, 420, 450 and 490 °C, were chosen.

Fig. 1. Sb and N mole fractions as functions of N flow rate in GaAsSbN epitaxial layers grown at 490 °C. The AsH₃ flow rate and Sb to Ga BEP ratio were 2.79 SCCM and 0.4, respectively.

420, 450 and 490 °C, were chosen. The power of the plasma cell was set at 200 W. As can be seen in Fig. 2, Sb composition increases linearly with the Sb flux. However, the N composition only slightly declines as the Sb flux increases. Recall the reduction in Sb composition resulting from the increase of N₂ flow rate; as evidenced in Fig. 1, we conclude that N atoms tend to supplant the Sb atoms in the incorporation process. This finding, however, is in conflict with the observation of previous reports that adding Sb will enhance the incorporation rate of N [7–10]. Harmand et al. attributed their Sb-dependent behavior to the dominance of metastable molecular N₂⁺ in their N source [7]. In our case, atomic N, another N species with high chemical potential, could dominate our nitrogen incorporation process. The high chemical potential makes the N adatoms more competitive in the incorporation process than Sb adatoms, and results in the aforementioned behavior.

The temperature-independent behavior of the nitrogen incorporation coincides with previous observations on InGaAsN and GaAsN [11]. A thermodynamic study for MBE grown GaAsN and InGaAsN showed that the unchanged nitrogen composition below 480 °C can be attributed to a near-unity sticking coefficient for nitrogen adatoms. In order to study the dominant species in the nitrogen plasma, we measured the dissociation fraction by using a quadrupole mass spectrometer to detect and compare the N₂⁺ signals with and without the plasma discharge [12]. The dissociation fraction is defined as the difference between the two signals divided by the signal with the discharge off. Fig. 3 shows the relationship

Fig. 2. Sb and N mole fractions as functions of Sb to Ga BEP ratio at three different growth temperatures, 420, 450 and 490 °C. AsH₃ and N₂ flow rates were 2.79 and 0.76 SCCM, respectively. The RF power of the N plasma cell is 200 W.

Fig. 3. Mole fraction of N in GaAsSbN as a function of activated N flow rate.

between the N mole fraction in GaAsSbN and the activated nitrogen flow rate, which is the product of nitrogen flow rate and the dissociation fraction. As can be seen, the N composition becomes linearly dependent on the atomic N flow rate as the flow rate is over its threshold value. Note that metastable N_2^+ is related to the N_2^+ signal with the plasma on. We found that the relationship between the N_2^+ signal and the nitrogen composition is not a monotonic increasing function. These findings allow us to infer that the dominant species in our source is atomic nitrogen.

As shown in Fig. 2, the Sb composition increases linearly with the Sb/Ga BEP ratio. However, lower growth temperature gives rise to higher Sb composition. This behavior has been observed in MBE-grown GaAsSb and was attributed to the differences in the sublimation energy and atomization energy of Sb and As [13]. The higher sublimation energy for Sb leads to the decrement of Sb incorporation at high temperature. Since the Sb composition in Fig. 2 is less than 0.2, saturation behavior in incorporation as reported in Ref. [13] is not observed.

Effect of AsH_3 flow rate on Sb and N compositions was also investigated. N_2 flow rate was fixed at 0.58 SCCM. Sb to Ga BEP ratio for these samples was 0.41. All the quaternary layers were grown at 490 °C. As can be seen in Fig. 4, the increment in AsH_3 flow rate leads to the slight decrement in Sb and N composition simultaneously. Due to the smallest sublimation energy, As cannot compete with Sb and N. Most of the As_2 impinged on the growth surface are desorbed. The slight decrements shown in Fig. 4 are simply due to the crowding effect of the enormous As adatoms. It is interesting that the Sb to N composition ratio approximately keeps a constant of ~ 6 through the

Fig. 4. Sb and N mole fractions as functions of AsH_3 flow rate. N_2 flow rate and Sb to Ga BEP ratio were 0.58 SCCM and 0.41, respectively. The growth temperature was 490 °C.

whole AsH_3 flow rate range. The nearly constant ratio indicates that the lattice mismatch to GaAs of the layers is almost unchanged. Therefore, the V to III ratio of the epitaxial layers can be varied without significantly affecting the lattice mismatch of the layers. Furthermore, this finding also implies that the strain and surface free energy may play a role in the incorporations of Sb and N in these nearly lattice-matched GaAsSbN layers. Recall Fig. 1, the increase of N incorporation leads to the decrease of Sb. Since the sum of N and Sb compositions is approximately a constant, the N incorporation does not affect As composition. In other words, the highly reactive N atom replaces Sb atom in the incorporation process. This is the most efficient way to reduce the strain energy and is certainly supported by thermodynamics. This finding, again, indicates the important role of strain-related surface free energy in the growth.

Three nearly lattice-matched samples with high nitrogen composition were grown on GaAs substrates at three different temperatures, 420, 450, and 490 °C, with the same nitrogen conditions, 300 W in RF power and 0.76 SCCM in nitrogen flow rate. The growth parameters and the properties are summarized in Table 1. As can be seen, the nitrogen compositions of these three samples are within 3.0–3.3%, which is consistent with the finding that the incorporation of nitrogen is nearly independent of temperature and Sb flux. The lattice mismatches, determined from the high-resolution XRD spectra shown in Fig. 5, are all within 10^{-3} . The bumps on the low angle shoulder of the epilayer peaks, as evidenced in the spectra, indicate the existence of compositional fluctuation in the alloys. It is worth to note that the measured compositions of these

Table 1

Growth conditions, compositions determined from EPMA, lattice mismatch determined from XRD, deviation from Vegard's law, and absorption edge data of three GaAsSbN samples

Sample ID	Growth temperature (°C)	N Rf plasma condition		EPMA data		Sb/N ratio	(004)XRD mismatch	Deviation from Vegard's law	Absorption edge (eV)
		Power (W)	N ₂ flow rate (SCCM)	Sb (%)	N (%)				
C2106	490	300	0.76	9.8±0.1	3.0±0.1	3.27	4.8 × 10 ⁻⁴	-2.7 × 10 ⁻³	0.847
C2107	450	300	0.76	11.0±0.1	3.3±0.3	3.33	7.9 × 10 ⁻⁴	-3.0 × 10 ⁻³	0.816
C2221	420	300	0.76	11.7±0.1	3.1±0.3	3.77	5.7 × 10 ⁻⁴	-5.7 × 10 ⁻³	0.803

Fig. 5. High-resolution XRD spectra of three GaAsSbN samples grown at 420, 450 and 490 °C, respectively. The N compositions of these samples are within 3.0–3.3%. The mismatches are all within 10⁻³.

samples deviate from the lattice-match compositions predicted by Vegard's law. If the lattice constant obeys Vegard's law, GaAs_{1-x-y}Sb_yN_x alloy requires an Sb/N ratio (y/x) of 2.56 to achieve the lattice match to GaAs. The binary lattice constants of GaAs, GaSb and GaN taken for this calculation are 5.6532, 6.0959 and 4.52 Å, respectively. As can be seen in Table 1, the Sb/N ratio is within 3.2–3.8, indicating a negative deviation from Vegard's law in these GaAsSbN samples. Negative deviation from Vegard's law has been observed in GaAsN epilayers grown by GSMBE [14] and MOCVD [15] and has been attributed to high substitutional nitrogen density and to vacancy-containing defect complexes stabilized by hydrogen by a recent study based on a plane-wave pseudopotential density function theory [16]. Fig. 6 shows the absorption spectra of the as-grown GaAsSbN samples at room temperature. The energy gaps are extracted from the absorption coefficient formula for direct semiconductors, $\alpha h\nu \propto (h\nu - E_g)^{1/2}$, where α is the absorption coefficient,

Fig. 6. Absorption spectra of three GaAsSbN samples. Solid curves are the experimental results, while the dotted curves represent the fitting curves based on the formula for direct semiconductor, $\alpha h\nu \propto (h\nu - E_g)^{1/2}$ where α is the absorption coefficient, $h\nu$ the photon energy, and E_g the energy gap.

$h\nu$ the photon energy, and E_g the energy gap. As shown in the figure, the fitting on the GaAsSbN sample grown at 420 °C gives the lowest energy gap of only 0.803 eV. The high N incorporation enhances the negative deviation in lattice constant, which requires more Sb to meet the lattice match condition and thus results in lower energy gap. However, the absorption spectra in Fig. 6 also show a strong below-band-edge absorption. Since the XRD spectra of these samples indicate the existence of the composition fluctuation, we ascribe the below-band-edge absorption to the band tail states resulting from the fluctuation.

4. Conclusion

We have studied the incorporation behaviors of the three group V elements, As, Sb and N of GaAsSbN alloys grown by GSMBE. In response to the increment in N₂ flow rate, N composition increases at the expense of Sb composition. On

the contrary, as the Sb flux increases, the N composition hardly changes in the temperature range from 420 to 490 °C. In addition, when AsH₃ flow rate increases, Sb and N decrease at similar rates, which is beneficial for keeping the lattice constant unchanged. Based on these findings, we successfully grew GaAsSbN on GaAs with mismatch less than 10^{−3}. The lowest energy gap of these GaAsSbN alloys is 0.803 eV at room temperature. The lattice constants are smaller than those predicted by Vegard's law, i.e., negatively deviates from Vegard's law.

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References

- [1] G. Ungaro, G. Le Roux, R. Teissier, J.C. Harmand, *Electron. Lett.* 35 (1999) 1246.
- [2] W. Ha, V. Gambin, M. Wistey, S. Bank, S. Kim, J.S. Harris, *Proc. SPIE* 4651 (2002) 42.
- [3] S. Wicaksono, S.F. Yoon, W.K. Loke, K.H. tan, B.K. Ng, *J. Appl. Phys.* 99 (2006) 104502.
- [4] H. Luo, J.A. Gupta, H. C. Liu, *Appl. Phys. Lett.* 86 (2005) 211121.
- [5] S. Kurtz, J. Webb, L. Gedvilas, D. Friedman, J. Geisz, J. Olson, R. King, D. Joslin, N. Karam, *Appl. Phys. Lett.* 78 (2001) 748.
- [6] L.F. Bian, D.S. Jiang, P.H. Tan, S.L. Lu, B.Q. Sun, L.H. Li, J.C. Harmand, *Solid State Comm.* 132 (2004) 707.
- [7] J.C. Harmand, G. Ungaro, L. Largeau, G. Le Roux, *Appl. Phys. Lett.* 77 (2000) 2482.
- [8] K. Volz, V. Gambin, W. Ha, M.A. Wistey, H. Yuen, S. Bank, J.S. Harris, *J. of Crystal Growth* 251 (2003) 360.
- [9] H.B. Yuen, S.R. Bank, M.A. Wistey, J.S. Harris, *J. Appl. Phys.* 96 (2004) 6375.
- [10] S. Wicaksono, S.F. Yoon, K.H. Tan, W.K. Cheah, *J. of Crystal Growth* 274 (2005) 355.
- [11] V.A. Odnoblyudov, A. Yu. Egorov, A.R. Kovsh, A.E. Zhukov, N.A. Maleev, E.S. Seminova, V.M. Ustinov, *Semicond. Sci. Technol.* 16 (2001) 831.
- [12] R.W. McCullough, J. Geddes, J.A. Croucher, J.M. Woolsey, D.P. Higgins, M. Schlapp, *Schlapp, J. Vac. Sci. Technol. A* 14 (1996) 152.
- [13] C.A. Chang, R. Ludeke, L.L. Chang, L. Esaki, *Appl. Phys. Lett.* 31 (1977) 759.
- [14] W. Li, M. Pessa, J. Likonon, *Appl. Phys. Lett.* 78 (2001) 2864.
- [15] J.N. Beaudry, R.A. Masut, P. Desjardins, P. Wei, M. Chicoine, G. Bentoumi, R. Leonelli, F. Schiettekatte, S. Guillon, *J. Vac. Sci. Technol. A* 22 (2004) 771.
- [16] N. Shtinkov, P. Desjardins, R.A. Masut, *Phys. Rev. B* 74 (2006) 035211.