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Bandgap Engineering of InSb by N incorporation by Metal-Organic Chemical Vapor Deposition

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Abstract

Bandgap engineering is necessary for the application of InSb in long wavelength infrared photodetection. InSbN alloys hetero-epitaxially were therefore deposited on GaAs substrate by metal-organic chemical vapor deposition (MOCVD), expecting a large band gap reduction by N incorporation for long wavelength infrared photodetection. The effects of post annealing treatment on the structural and optical properties of the grown InSbN alloy have been well studied. Photoluminescence measurement (PL) indicated that the longest PL wavelength obtained at 10 K is $\sim 7.2 \mu\text{m}$ for the InSbN alloys, which manifests an extension of PL wavelength as large as $\sim 1.8 \mu\text{m}$ in comparison to the undoped InSb epilayers, suggesting a successful band gap reduction by the N incorporation. X-ray photoelectron spectroscopy (XPS) measurements show that three kinds of nitrogen bonds co-exist in the alloys and their percentages vary with annealing conditions. This observation can explain the peak shifts of X-ray diffraction (XRD) and PL spectra. The comparison to our previous works reveals that the InSbN alloys grown on GaAs substrate can achieve more nitrogen incorporation and band gap reduction than the alloys grown on InSb and GaSb substrates.

1. Introduction

III–V semiconductors are an important family of materials which are widely used for infrared photodetection applications [1-4]. Among them, InSb specifically attracted more attentions since it combines a direct narrow band gap and high electron mobility simultaneously [5]. Accordingly, it has been used in the high-speed, low-noise infrared detector which covers the so-called atmospheric window between 3 and 5 μm . To expand the detection window of InSb based IR detector into longer wavelength region, the energy band engineering of InSb is required. The incorporation of nitrogen (N) into the lattice of InSb is believed to be an effective way to tailor its band structure, due to the N induced band gap bowing effect. According to the band anti-crossing model, the N incorporation density required for 0.1 eV band gap shift in InSbN alloy is only about one percent [6]. Therefore, InSbN alloy has high potential to cover the long infrared wavelength, and thus is considered as a promising alternative for HgCdTe in far infrared detection [7-8]. Previous work indicates that high quality InSbN alloy could be obtained by homo-epitaxy on InSb substrate or ion implantation. However, the incorporation of N is limited to only a few percent due to the nature of the fabrication methods. As a consequence, the band gap reduction is not able to reach the 8 - 12 μm atmosphere transmission window [9-13].

GaAs has been used as the substrate for the growth of InSb epilayers for many years and the growth of this material on GaAs substrate have already been explored by various growth techniques, such as Liquid phase epitaxy (LPE), atomic layer epitaxy (ALE), molecular beam epitaxy (MBE), magnetron sputtering, plasma assisted epitaxy (PAE) and metal-organic chemical vapor deposition (MOCVD) [14-20]. Despite the large lattice mismatch between InSb and GaAs, very high mobility InSb alloys have been obtained epitaxially on GaAs substrate by several groups [21-23]. The use of GaAs substrate is specifically interested because its wide band gap and semi-insulating nature facilitate electrical isolation and decrease parasitic capacitances. It is also convenient for the signal processing circuits and integration of infrared detection like silicon charge-couple devices (CCD).

Hence, the growth of InSbN on GaAs substrate is very useful for infrared photodetecting devices. To date, limited work has been done on the hetero-epitaxial growth of InSbN by using MOCVD [24]. In this paper, we report the InSbN alloys grown on GaAs (100) substrate by MOCVD. The N incorporation effect, annealing impact on energy band gap were carefully studied.

2. Experiment

InSbN alloys were grown on the semi-insulating GaAs (100) substrate by using MOCVD. The precursors used for the growth were trimethylgallium (TMSb), trimethylindium (TMIn) and dimethylhydrazine (DMHy). The input TMSb/TMIn (Sb/In) and DMHy/(TMSb+DMHy) (N/(Sb+N)) source flux ratios were kept at 4.2 and 0.9, respectively. The growth temperature was set at 410 °C. The reactor pressure was kept at 100 mbar and the growth time was 30 mins. Hydrogen was used as carrier gas and the growth rate was $\sim 0.6 \mu\text{mh}^{-1}$. The alloy structures and N composition were analyzed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Optical properties of the samples were characterized by photoluminescence (PL). Besides, post-annealing treatments at different temperatures and durations were performed to study the effects on the structure and N bonds of the InSbN alloys.

3. Results and discussion

Rapid annealing treatments of the as-grown InSbN alloys were carried out in nitrogen ambience at 440 °C, 450 °C and 460 °C, respectively. The annealing is under atmospheric pressure and the duration is kept at 3 mins. Figure 1 shows the XRD spectra of samples before and after annealing at different temperatures. A prominent peak located around 62° was observed in all the four samples. Obvious peaks referring to $\text{InSb}_{1-x}\text{N}_x$ epilayer were observed, indicating that nitrogen has been incorporated into InSb. The XRD peak intensity of the InSbN layer becomes stronger after annealing, indicating that the film crystallinity is improved by the annealing treatment. The

separation between the epilayer and substrate peak in two-theta indicates the lattice mismatch. In addition, the InSbN peak is observed to be shifting towards the main GaAs peak as the annealing temperature increases. This peak shift should be caused by the change of N bonds in the alloy, which will be discussed later.

To study the optical property and the N incorporation effect on the band-gap, PL measurements at 10 K were performed for the alloys annealed at different temperatures, and the spectra are shown in Figure 2. Without annealing, the PL emission seems too low to be detected. After the thermal treatment, a PL peak at $\sim 7.2 \mu\text{m}$ starts to appear. As the annealing temperature creeps up to 450 °C, the PL peak intensity increases significantly, indicating an improvement on the alloy crystal quality [25]. We didn't perform the treatment under temperatures above 460 °C because the luminescence intensity of the alloy began to decline at 460 °C. The large broadness of the PL emission should be due to the existing defects and compositional nonuniformity of the InSbN alloy. The defects may lead to band-tailing effect due to the impurity band broadening from heavy doping, and thus widen the PL peak [26]. Besides, due to the big lattice mismatch substrate used and high N incorporation, compositional nonuniformity or even phase separation may happen to the InSbN alloys, which could be revealed from the wide XRD diffraction peaks of InSbN layers as shown in Fig. 1. This compositional nonuniformity will make the band gap of the alloy fluctuate in a wide range and thus significantly broaden the PL peak [27]. Figure 3 shows the PL spectra of the sample annealed at 450 °C for 3 and 10 mins, respectively. It is seen that the PL peak moves to longer wavelength with increasing annealing time and the emission peak reaches $\sim 8 \mu\text{m}$ for the annealing duration of 10 mins, which suggests that the part of the substitutional N could be enhanced by longer duration of treatment [13]. We didn't prolong the annealing time further since the emission intensity becomes degraded.

To see the dependence of the band gap energy on temperature, PL spectra were measured at different temperatures and the results of the alloy annealed at 450 °C for 3 mins is shown in Figure 4. With increasing measuring temperature, the PL peak shifts toward longer wavelength. Table 1 gives the values of the PL wavelength under different measuring temperatures. The PL peak moves from 7.2 μm at 10 K to $\sim 7.8 \mu\text{m}$ at 100 K. Since the peak intensity drops down dramatically, the PL spectra above 100 K are not recorded.

XPS was used to investigate the annealing induced shifts in XRD and PL. Figure 5(a) and 5(b) show the XPS spectra of the samples in N1s region before and after annealing at 450 °C, respectively. Three types of nitrogen bonds can be extracted from the XPS curves. They are substitutional In-N at a binding energy of $(396.3 \pm 0.2 \text{ eV})$, interstitial N (In-N-Sb) at $397.9 \pm 0.2 \text{ eV}$ and antisite Sb-N at $399 \pm 0.2 \text{ eV}$ [28]. Without annealing, the XPS spectra indicate that the In-N bonds take up only about 22.8% of the total N in the layer, while the interstitial In-N-Sb and antisite Sb-N bonds are 18.8% and 58.4%, respectively.

After annealing at 450 °C, the In-bonds increased from 22.8% to 25.1%. The interstitial In-N-Sb bonds decreases significantly from 18.8% to 15.2% and the Sb-N bonds increase from 58.4% to 58.7%. It is well known that substitutional In-N bonds contribute to the band gap narrowing of the alloy. According to the model suggested by Chen et al [29], interstitial N leads to lattice expansion while substitutional and antisite N results in lattice contraction. Accordingly, the changes of the nitrogen bonds can explain the increased PL peak wavelength and the shift of X-ray diffraction peaks. According to the band gap reduction measured by PL, the percentage of substitutional In-N is estimated to $\sim 0.85\%$. With combining the PL and XRD results, the total N atoms incorporated into the grown alloy is about 3.4%.

In previous works, we have reported the growth and properties of InSbN alloys on InSb and GaSb substrates, respectively [13, 30]. Certain amount of N incorporation and band gap reduction have also been achieved for the InSbN alloys on these substrates. In order to figure out the effects of the substrate on InSbN alloys, we have summarized the values of N incorporation, distribution of N bonds and band gap wavelength obtained for the InSbN alloys on InSb, GaSb and GaAs substrates, respectively. The detailed information is indicated in Table. 2. It is shown that the largest N incorporations achieved are 0.26%, 1.9% and 3.4% for the InSbN alloys on InSb, GaSb and GaAs substrates, which indicates that the N incorporation to InSb is promoted on substrate with higher lattice mismatch to InSb. The reason for this observation is probably due to the lattice pulling effect from the lattice-parameter mismatch [31-32], which suggests that the alloying material composition is pulled from the chemical-equilibrium one toward the composition that minimizes mismatch and therefore the excess energy.

The effect of different N bonds on the lattice of InSbN alloy has already been studied in our earlier report [13]. It was demonstrated that only interstitial In-N-Sb will lead to lattice dilation, while lattice contraction will be resulted from left N bonds such as substitutional In-N, antisite Sb-N and interstitial N-N. The distributions of N bonds in InSbN alloys indicated in Table 2 show that the substitutional In-N and antisite Sb-N take most part of the N incorporation while interstitial In-N-Sb only accounts for a small portion, consequently leading to a total effect of lattice contraction on the InSbN alloys. The lattice mismatches of InSb, GaSb and GaAs to the InSb substrate are 0%, 6.4 and 12.6%, respectively. Due to the lattice pulling effect, the InSbN alloy deposited on substrate with a larger lattice mismatch is consequently capable of allowing more N incorporation.

Although the distributions of substitutional In-N indicate no big difference, the contents of substitutional In-N are 0.07%, 0.5% and 0.85% for the InSbN alloys on InSb, GaSb and GaAs substrates, respectively, due to the distinction among the total N incorporations. As a result, the band gap wavelengths of the three types of InSbN alloys measured at 10 K are 5.6 μm , 6.3 μm and

7.2 μm , indicating an apparent proportional relationship to the lattice mismatch for substrate adopted. Fig. 6 summarized the dependencies of band gap energy on temperature for InSbN alloys on InSb, GaSb and GaAs substrates. Due to the absence of measurement results at high temperature, the variation tendency of band gap energy beyond 100 K has been fitted based on experimental data below 100 K by Varshni equation for InSbN alloys on GaSb and GaAs substrates. According to the fitted curves, the band gap energies for InSbN alloys on GaSb and GaAs substrates estimated at room temperature are 0.116 eV (10.6 μm) and 0.092 eV (13.5 μm). This indicates that the band gap wavelengths of InSbN alloys obtained on GaSb, GaAs substrates have already been included in the long wavelength atmospheric transmission window.

From all the results indicated above, it could be concluded that the substrate with a larger lattice mismatch is beneficial to the N incorporation and thus the extension of the band gap wavelength of InSbN alloy. However, it should be admitted that the InSbN alloy quality will degrade seriously when growing on a large lattice mismatch substrate. Therefore, further endeavor has to be paid on the balance between the N incorporation and crystal quality of InSbN alloy.

4. Summary

InSb_{1-x}N_x alloys were hetero-epitaxially grown on GaAs substrate by MOCVD and the effects of annealing treatment with various temperatures and durations on the properties of the InSb_{1-x}N_x alloys were studied. The incorporated nitrogen atoms co-exist in the alloy in the forms of In-N, In-N-Sb and Sb-N bonds. The In-N bonds increase while the In-N-Sb bonds decrease after annealing. The comparison made among the properties of InSbN alloys on InSb, GaSb and GaAs substrates indicates that the InSbN alloys grown on a substrate with larger lattice mismatch to InSb can allow more nitrogen incorporation and thus achieve larger band gap reduction.

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Figure captions:

Fig. 1. XRD spectra obtained from (004) diffraction of the as-grown and annealed $\text{InSb}_{1-x}\text{N}_x$ samples.

Fig. 2. PL spectra of the InSbN alloys with and without annealing treatment, measured at 10 K.

Fig. 3. PL spectra of the alloys annealed at 450 °C for 3 and 10 mins, measured at 10 K.

Fig. 4. Temperature dependence of PL spectra of the alloy annealed at 450 °C for 3 mins.

Fig. 5. XPS spectra in N1s of InSbN alloy. (a) As grown, (b) after annealing at 450 °C for 3 mins.
and (c) Distributions of N bonds of the alloys before and after annealing treatment.

Fig. 6 Dependencies of band gap energy on temperature for InSbN alloys on InSb, GaSb and GaAs substrates.