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 ~7.2 μm for the InSbN alloys, which manifests an extension of PL wavelength as large as ~ 1.8 μm 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.

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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 atm 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 min. Hydrogen was used as carrier gas and the growth rate was ~0.6 μmh^{-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 min. Fig. 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 InSb$_{1-x}$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 Fig. 2. Without annealing, the PL emission seems too low to be detected. After the thermal treatment, a PL peak at ~7.2 μm 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]. Fig. 3 shows the PL spectra of the sample annealed at 450 °C for 3 and 10 min, respectively. It is seen that the PL peak moves to longer wavelength with increasing annealing time and the emission peak reaches ~8 μm for the annealing duration of 10 min, 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 min is shown in Fig. 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 ~7.8 μm 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. Fig. 5(a) and (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 ± 0.2 eV), interstitial N (In-N-Sb) at 397.9 ± 0.2 eV and antisite Sb-N at 399 ± 0.2 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
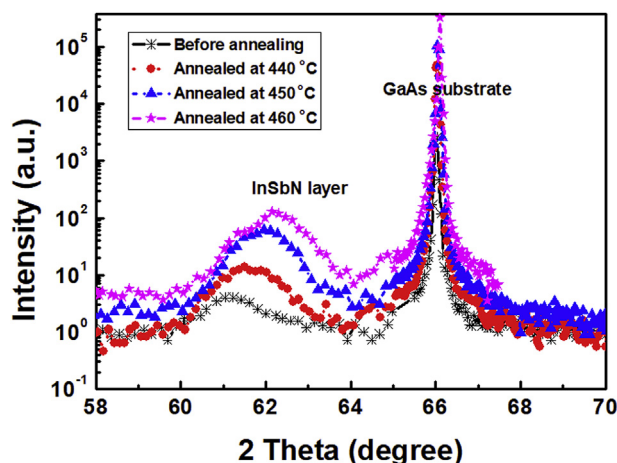

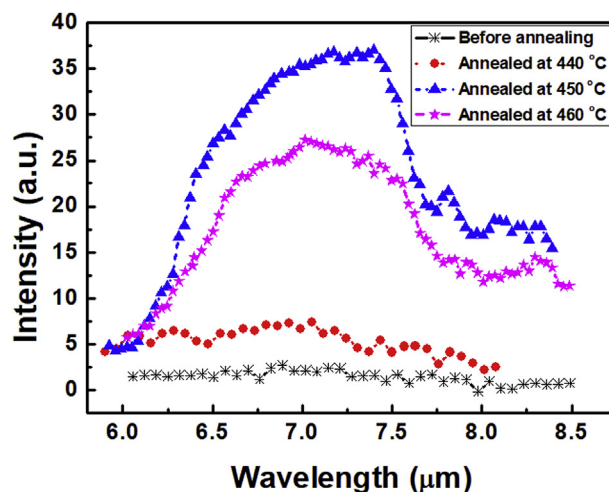**Fig. 1.** XRD spectra obtained from (004) diffraction of the as-grown and annealed InSb$_{1-x}$N$_x$ samples.

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