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Dilute Antimonide Nitride for Long Wavelength Infrared Photodetection

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Abstract. $\text{InSb}_{1-x}\text{N}_x$ materials were fabricated by direct nitrogen implantation into InSb wafer and they are characterized by X-ray diffraction, Hall measurement, X-ray photoelectron spectroscopy. In-N bonds are clearly demonstrated and other forms of nitrogen, such as antisites (N_{In}), interstitial N_2 , also exist in the grown films. The ratio to the total nitrogen bonds formed in the materials varies with preparation conditions. The optical bandgap data confirmed bandgap narrowing due to the incorporation of nitrogen. Photoconductive and photovoltaic photodetectors are fabricated and the cut-off frequencies of up to $11.5\text{ }\mu\text{m}$ are demonstrated.

Keywords: Indium antimonide, dilute nitride, ion implantation, infrared photodetector.

PACS: 71.55.Eq; 72.40.+w

INTRODUCTION

Photodetectors sensitive to infrared radiation in 8 to $12\text{ }\mu\text{m}$ wavelength region are of great importance as they have vast applications in thermal imaging and sensing environmentally important gases [1][2]. The currently used photodetectors are mainly made of the II-VI mercury cadmium telluride (MCT) and III-V semiconductors [3]-[12]. In recent years, dilute nitrides also become the favorite materials for photodetection[2], [13,14]. $\text{InSb}_{1-x}\text{N}_x$ alloy show dramatic band gap bowing with nitrogen composition due to band anticrossing between the localized resonant states of the nitrogen and the extended states of the conduction band [3][22][23]. Such alloys can be grown by molecular beam epitaxy (MBE) with electron cyclotron resonance (ECR) [3][16][17] and radio frequency (RF) plasma [18]-[20] as a nitrogen source, metalorganic vapor phase epitaxy [21] and low-energy ion implantation [22][23]. Murdin *et al* have reported that the Auger recombination rate in the InSbN alloy is only about one third of that of the equivalent band gap HgCdTe [19]. Veal *et al* have presented experimental evidence of a negative band gap in a thin layer of InSbN fabricated by low energy N implantation using high-resolution electron-energy-loss spectroscopy [25]. Merrick *et al* have observed $\sim 10\%$ red-shift in band gap of the InSbN alloy at room temperature using a Fourier transform infrared (FTIR) based photo-modulated transmission spectroscopic technique [22]. However, to the best of our knowledge, so far there is no report on the photodetection in the long wavelength range.

In this article, we report the realization of uniform InSbN alloys by multi-step ion implantation and successful fabrication of InSbN based photoconductive and photovoltaic photodetectors.

EXPERIMENT, RESULTS & DISCUSSION

Two groups of InSbN samples were fabricated by multi-step N ion implantation into the undoped (weak n-type) InSb(111) substrates. 3 samples in first group, labeled as S1, S2 and S3 were implanted N with dose of 2.0×10^{15} , 2.95×10^{15} and $4.95 \times 10^{15} \text{ cm}^2$ (for a target %N of 0.4%, 0.6% and 1%) with energies of 33keV and 150keV. 3 samples in second group, labeled as B1, B2 and B3 were implanted nitrogen with dose of 6.3×10^{16} , 7.56×10^{16} and $8.8 \times 10^{16} \text{ cm}^2$ (for a target N% of 5%, 6% and 7%) with energies of 90keV, 180keV and 530keV. And $2.0 \times 10^{15} \text{ cm}^2$ of magnesium was followed implanted into the second group samples with energy of 40keV to form the top p region. After implantation, a thermal annealing at 550K for 4 hours was carried out to all the samples before test. Secondary ion mass spectrometry (SIMS) measurements indicate that upon annealing, a nearly uniform N distribution with depth from about 25~400 nm can be obtained for the group 1 samples and the %N is basically the same as planned, whereas for the group 2 samples, the uniform N distribution part appears in the range of 0.1~0.7 μm from the surface, but the doped N% of sample B1, B2 and B3 are only 3.25%, 3.8% and 4.3%, less than the target ones. A surface accumulation of N is observed in all the samples due to out-diffusion of nitrogen.

Figure 1 shows the measured sheet carrier concentration of the 3 samples in group 1 as a function of temperature in the range of 90 to 300 K, measured by Hall-effect technique. The results of unimplanted InSb are also included. A few features can be observed. (1) The carrier concentrations in the three N-containing samples are higher than that in InSb. The increase in carrier concentration in the implanted samples is mainly due to the donor-type defects, such as antimony vacancies, created during the implantation process [17]. (2) With the increase of the implanted nitrogen, the carrier concentration decreases. This observation indicates the formation of $\text{InN}_x\text{Sb}_{1-x}$ alloys and can be explained by the acceptor nature of the highly electronegative nitrogen [17]. (3) The measured carrier concentrations are nearly unchanged at low temperature up to about 120 K, indicating the extrinsic nature of the carriers. The subsequent increase of the carrier concentration is due to thermal excitation.

To verify the bonding configuration of the incorporated N, the In 3d, Sb 3d, and N 1s core level spectra of the InSbN samples were measured by X-ray photoelectron spectroscopy (XPS). To prevent the oxidation effect at the sample surface, N 1s spectra at a depth of 80nm from the surface were measured for the group 1 samples. And for second group of samples, spectra at about 200nm from the surface were measured since the SIMS results shows that the junction depth at that position. There are mainly 4 components in the N 1s spectrum: N bonded to the In at the binding energy of 396.9meV, N bonded to both In and Sb at 397.9meV [20], N bonded to the Sb at 399.0meV [25][26] and the interstitial N state at 403.8meV [20]. By taking account of the different atomic sensitivity factors [23], the %Nsb for all samples are calculated from the area covered by each composition, which are 75%, 74% and 67% for group 1 samples, and 11.1%, 10.5% and 9.9% for group 2 samples, respectively. Based on the simulated bandgap modol of InSbN as a function of %N at temperature of 30K [24][13][29,30], the energy band gaps of the two groups of samples at 30 K are extracted from XPS and SIMS results are 204.6meV, 191.5meV and 171meV for S1, S2 and S3, and 198meV, 194meV and 192meV for B1, B2 and B3, respectively.

FIGURE 1. Measured sheet carrier concentrations of the sample S1, S2 and S3 by Hall Effect technique. The data of the InSb wafer is also included for comparison.

FIGURE 2. Schematic of an $\text{InSb}_{1-x}\text{N}_x$ photodiode fabricated using photolithographic technique in clean room environment

The experimental determination of the energy band gap of such alloys is not easy as the band gaps become narrower due to the incorporation of N substituting Sb site. We achieved the band gap information by directly measuring the photocurrent with a house-made system. The infrared source used is an Oriel 6575 ceramic element mounted in a lamp house, with similar irradiation the blackbody at 1450 K. And a $5\mu\text{m}$ low-pass filter was used to prevent the higher-order light components from contributing to the absorption in the concerned wavelength range.

To measure the photocurrent, we fabricate the group 1 samples into photoconductive detectors by cutting them into rectangular slabs, and solder the indium contacts on two ends of the slabs to form ohmic contacts. And gold wires were then bonded as the terminal leads. Whereas the second group samples are fabricated to photovoltaic detectors by creating the mesa-like structures by using standard photolithographic techniques in the clean room environment. The devices have a diameter of $250\mu\text{m}$, as illustrated in Fig. 2.

The I-V results of group 2 samples show the rectifying, indicating the p-n diodes formed. Fig. 3 shows the I-V curve of sample B2 measured at 30 K in the range of -2 to 1.5 V. Considering the parasitic series and parallel resistances in the device, we used a clever algorithm to extract the diode parameters [31]. The theoretical fitting in figure 3 presents the simulated parameters for our diode are: $I_s = 0.258\text{nA}$, $n = 1.9$ and $R_s = 0.9\Omega$, $R_{sh} = 26\Omega$. These parameters showed that the fabrication condition of these diodes was not ideally, the process needed to be improved.

The photocurrent spectra of sample S2 and B3 measured at 30 K are shown in Fig. 4 as examples. It is seen that the highest photocurrent peak in all the samples appear at about $5.3\mu\text{m}$ which originates from the binary InSb (234meV at 30K). With the incorporation of nitrogen, the photo-spectra extend to longer wavelengths. Another peak appears in the long wavelength side corresponding to the InSbN contribution. The deconvolution of the photocurrent spectra reveals that the absorption peaks at long wavelength side are at about $6.1\mu\text{m}$, $6.5\mu\text{m}$ and $7.3\mu\text{m}$ for samples S1, S2 and S3, and $6.30\mu\text{m}$, $6.33\mu\text{m}$ and $6.47\mu\text{m}$ for samples B1, B2 and B3, respectively. These correspond to the energy band gaps of about 203meV , 190.8meV and 169.9meV , for group 1 samples and 196.7meV , 195.5meV and 191.7meV for group 2 samples, respectively. They are in excellent agreement with the theoretical values calculated by the band anticrossing model from XPS results.

In addition, the cut-off wavelengths of all samples also shift towards long wavelength. They are about $7.2\mu\text{m}$, $10.3\mu\text{m}$ and $11.5\mu\text{m}$ for S1, S2 and S3, and $7.6\mu\text{m}$, $7.9\mu\text{m}$ and $9.4\mu\text{m}$, respectively. By comparing the performance of photoconductive detectors and photovoltaic detectors, we found that although the implanted nitrogen concentrations of second group samples are higher than the first one, the detected wavelengthes of photovoltaic devices are all shorter than that of the photoconductive devices. That is because the junctions of the diodes are about $0.2\mu\text{m}$, and the photo-response is mainly from the depletion region where the N% is much lower than that near surface. We believe that devices with shallow junctions can better control the detected wavelength and improve the performance of photovoltaic photodetectors.

CONCLUSION

In conclusion, we have demonstrated photoconductive and photovoltaic detectors based on $\text{In}_x\text{Sb}_{1-x}$ alloys by multi-step nitrogen ion implantations into InSb wafers. As high as 75% (S1 & S2) of the implanted nitrogen is found to substitute Sb sites to form In-N bonds and the percentage of the In-N bonds decreases with the increase of the implanted nitrogen. Such devices can effectively detect long-wavelength infrared radiations and the detected peak wavelength can be controlled by monitoring the implanted nitrogen dose. They can also be potential candidate for terahertz photodetection.

FIGURE 3. Measured and theoretical simulated current-voltage characteristics of the sample B2 at 30 K.

FIGURE 4. Measured photocurrent spectra of S2 and B3 at 30 K. The two solid curves are for peak fitting.

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