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Bonding and diffusion of nitrogen in the InSbN alloys fabricated by two-step ion implantation

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We report bonding and diffusion behavior of nitrogen incorporated into InSb wafer by two-step implantation. Three nitrogen-containing regions, i.e., a surface accumulation region, a uniform region, and a tail region, were observed in the samples after post annealing. X-ray photoelectron spectroscopy measurements at different depths reveal that majority of the nitrogen forms In-N bonds in the uniform region but exists as interstitial defects in the tail region. The diffusion coefficients of nitrogen in InSb were obtained by fitting the modified Fick's law with experimental data and the activation energy of 0.55 ± 0.04 eV extracted confirms the interstitial dominating diffusion of nitrogen in the InSb wafer. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4734507>]

InSb_{1-x}N_x ternary compound semiconductors have been attracting more attention in recent years due to their importance in fundamental research and device applications as light sources and photodetectors in long wavelength infrared range.¹⁻³ Such alloys can be fabricated by molecular beam epitaxy, metalorganic chemical vapor deposition and low energy ion implantation and have been studied by several groups.¹⁻¹² As it has been reported, the replacement of a few percent of Sb element by small, highly electronegative and isoelectronic nitrogen atoms in the binary InSb could result in a dramatic reduction of the fundamental band gap of approximately 100 meV per atomic percent of nitrogen. And negative bandgap can be realized by incorporation of a few percent of nitrogen occupying the anion lattice sites.⁴ In addition, the Auger recombination rate is only about one third of that of the equivalent band gap mercury cadmium telluride (MCT) due to the high electron mass and conduction band nonparabolicity of the InSbN alloy, which makes it a promising material for long wavelength light sources and photodetectors.^{1,6} In this letter, we report the detailed nitrogen bonding profiles at different depths and nitrogen diffusion in InSb wafer, which have not been reported yet.

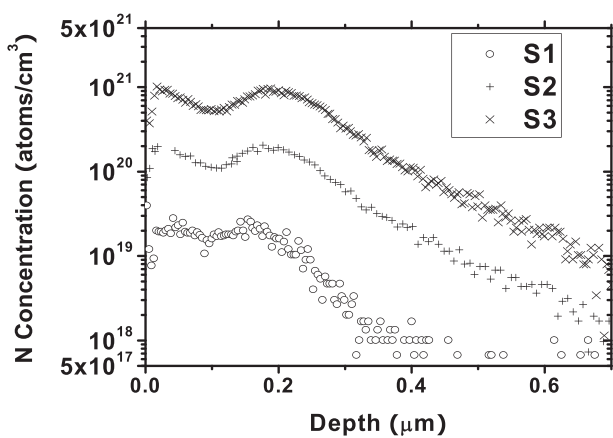
The InSbN alloys studied were fabricated by ion implantation of nitrogen into InSb (111) wafers. To form a relative thick and uniform layer of InSbN alloy in the InSb wafer, two-step implantation with energies of 33 keV and 150 keV was utilized. The corresponding doses associated with the two implantation energies are 2×10^{14} and 8×10^{14} ions/cm² for sample 1 (S1), 9.5×10^{14} and 4×10^{15} ions/cm² for sample 2 (S2), and 5.5×10^{15} and 2.4×10^{16} ions/cm² for sample 3 (S3), respectively. After completion of ion implantation, the samples were annealed at 550 K for 5 h in order to remove the implantation-induced defects and activate the

implanted nitrogen before tests. X-ray photoelectron spectroscopy (XPS) technique was employed to study the nitrogen bonding at different depths of the samples. To study the diffusion mechanism of nitrogen, annealing at a fixed temperature for different periods of time and at different annealing temperatures for a fixed period of time was conducted. During annealing, the samples were encapsulated between two silicon wafers to avoid contamination and release of nitrogen. For the annealing at a fixed three-hour period, the temperatures from 250–350 °C with an interval of 25 °C were selected. For the annealing at 277 °C, the periods of time were taken as 3, 5, and 10 h, respectively. The concentration profiles of N before and after annealing were measured by the secondary ion mass spectroscopy (SIMS).

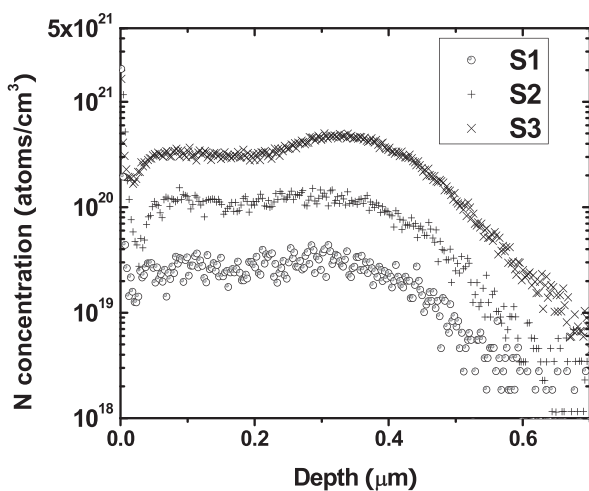
Figure 1(a) shows the depth profiles of the as-implanted three wafers. The total implanted doses are about 1×10^{15} , 4.95×10^{15} , and 2.95×10^{16} ions/cm², respectively, which are obtained by integrating the area of the implantation profile and consistent with the designed values. The two peaks originated from the two implantations are obviously observable in each of the profiles. Fig. 1(b) shows the nitrogen distributions in the three samples after being annealed at 550 K for 5 h. It is observed that thermal annealing makes the two nitrogen peaks in each sample flattened and a nearly nitrogen-uniform region of about 400 nm thick is formed. In addition, there are also an accumulation region of nitrogen at the surface of the samples and a tail region inside the wafer.

To study the bonding behavior of nitrogen and verify the uniformity of In-N bonds in the nitrogen uniform region, XPS measurements were performed at the surface and at different depths of the samples with the help of Ar⁺ etching after the samples were annealed at 550 K for 5 h. The spectra of N1s core level recorded from S3 are shown in Figure 2. Surprisingly, no In-N bond is observed at the surface of the sample. Instead, there is a big broad peak at about 401.5 eV which is a combination of three peaks located at 399 eV,

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(a)



(b)

FIG. 1. Nitrogen distribution in (a) the as-implanted three samples which were implanted twice with energy of 33 keV 0 and 150 keV and with the total doses of about 1×10^{15} (S1), 5×10^{15} (S2), and 3×10^{16} (S3) ions/cm², respectively, and (b) the samples after annealing at 550 K for 5 h, measured by SIMS.

400.7 eV, and 401.8 eV, respectively. The main peak at 400.7 eV is believed to be due to the N-O bonds¹³ while the peaks at 399 eV and 401.8 eV can be attributed to N-Sb bonds⁹ and nitrogen radicals,¹⁴ respectively. On the high energy side, there is also a small peak at 403.8 eV which is attributed to interstitial molecules nitrogen.^{9,10} After etching off about 20 nm from the surface with argon ions, the main nitrogen peak shifts to the lower binding energy side. The dominant peak is at 397.5 eV which is the mixed In-N-Sb compound.¹² There is also a peak at 396.5 eV which is attributed to the In-N bonding resulting from the substitutional occupation of N to the Sb sites which is the main source for energy band reduction of the alloy material.^{2,10,12} There are also four other peaks on the high binding energy side. They are located at about 399 eV, 400.7 eV, 402 eV, and 403.8 eV and correspond to Sb-N, N-O, nitrogen radicals and interstitial N₂, respectively.

In order to get bonding information in the uniform region, the sample was etched to about 200 nm and 300 nm

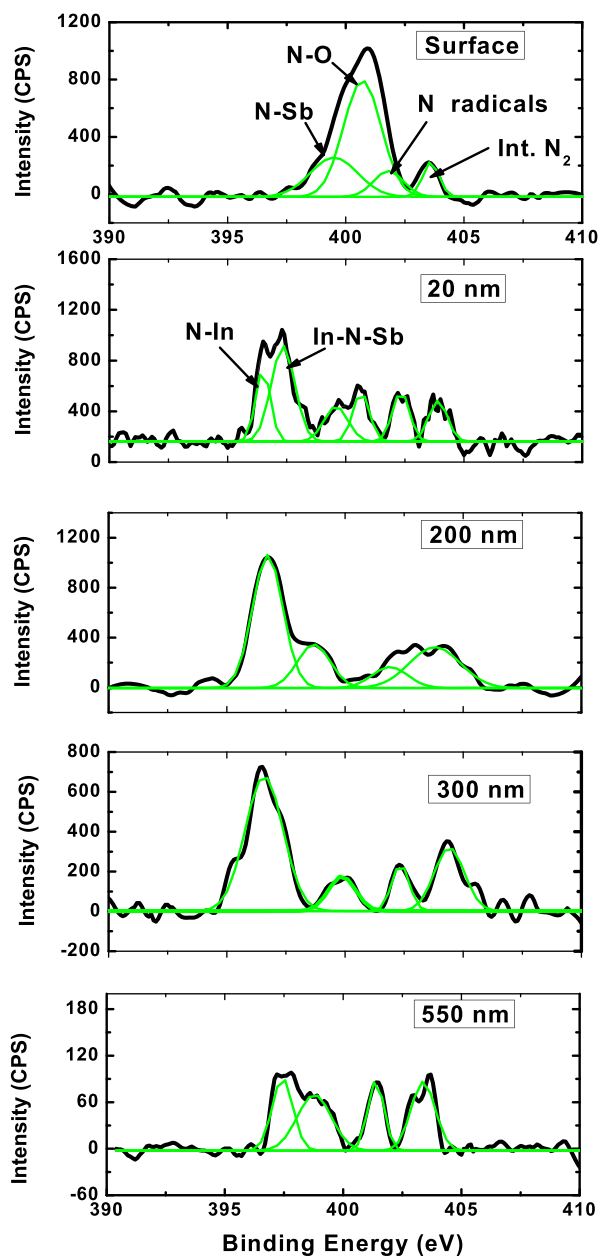


FIG. 2. Nitrogen bonding at different depths measured by x-ray photoelectron spectroscopy.

from surface, respectively. The XPS results reveal that In-N bonds dominate and the numbers of the In-N bonds are similar at the two depths, although there are also small peaks for Sb-N bonds, N-O bonds and interstitial nitrogen. This observation confirms the formation of a uniform InSbN alloy by the two-step ion implantation. However, the Sb-N signal at 300 nm is weaker than at 200 nm. The smaller number of Sb-N bonds at the depth of 300 nm may be related to the implantation caused defects which are less than at 200 nm.

When the sample was etched to about 550 nm, however, the XPS signal becomes very weak. This is because this depth is at the tail region where the nitrogen concentration becomes much less. It is interesting to note that there is no In-N bonding observed in the tail region but the interstitial nitrogen and In-N-Sb bonds become significant. It is well known that post annealing to the implanted sample will not only recover the implantation induced damage and activate

implanted dopants but also cause diffusion. The XPS results in the tail region may imply that interstitial nitrogen dominates the diffusion during the annealing process.

To verify the diffusion behavior of nitrogen, the samples were annealed at different temperatures for a fixed period of time and at a fixed temperature for different periods of time. Fig. 3 shows the nitrogen profiles of the sample with a dose of 2.95×10^{16} ions/cm² after being annealed for 3, 5 and 10 h at 550 K, respectively. As the annealing time increases, more and more nitrogen diffuses into the InSb substrate. At the same time, more nitrogen also diffuses and accumulates at the surface region. The SIMS results for the same sample but annealed at different temperatures for 3 h, illustrated in Fig. 4, also show the same behavior. And both the amount of the accumulated nitrogen at the surface and the depth of the diffusion in the InSb wafer increase with increasing annealing temperature and the period of time.

According to Fick's law, the depth and time dependent concentration $N(x, t)$ can be expressed as,¹⁵

$$N(x, t) = \frac{Q}{\sqrt{2\pi(\Delta R_p^2 + 2Dt)}} \exp\left(-\frac{(x - R_p)^2}{2\Delta R_p^2 + 4Dt}\right), \quad (1)$$

where Q is the dose, R_p is the projected range, ΔR_p is the standard deviation, D is the diffusion coefficient, and t is the annealing time. In our case, since each sample is implanted twice with different energies, we propose the following equation to describe the profile,

$$N(x, t) = \frac{Q_1}{\sqrt{2\pi(\Delta R_{p1}^2 + 2Dt)}} \exp\left(-\frac{(x - R_{p1})^2}{2\Delta R_{p1}^2 + 4Dt}\right) + \frac{Q_2}{\sqrt{2\pi(\Delta R_{p2}^2 + 2Dt)}} \exp\left(-\frac{(x - R_{p2})^2}{2\Delta R_{p2}^2 + 4Dt}\right), \quad (2)$$

where the first and second terms of the equation correspond to the nitrogen concentrations implanted in the two implantations, respectively. Q_1 and Q_2 are the doses of the two implantations, respectively. By fitting Eq. (2) with the measured nitrogen profiles shown in Figs. 3 and 4, parameters like the diffusion coefficient, projected range and standard deviation can be extracted. The derived diffusion coefficients

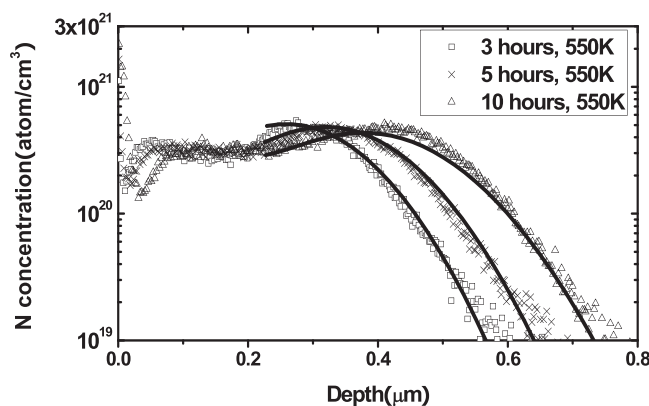


FIG. 3. Nitrogen distributions after annealing for various periods of time at 550 K. The solid lines are the fittings using Eq. (2).

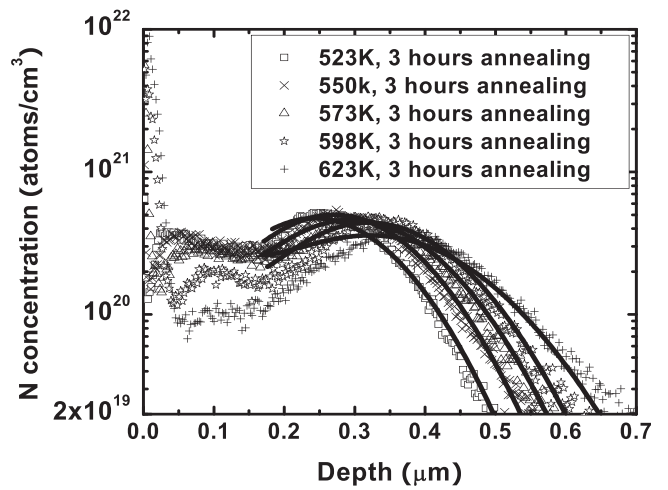


FIG. 4. Nitrogen distributions after annealing at various temperatures for 3 h. The solid lines are the fitting results using Eq. (2).

were plotted in Fig. 5 and they follow the Arrhenius relationship well,

$$D = D_0 \exp\left(\frac{-E_a}{k_b T}\right), \quad (3)$$

where E_a is the activation energy with a value of 0.55 ± 0.03 eV, k_b is the Boltzmann constant, and D_0 is the pre-exponential factor with a value of $1.09 \pm 0.6 \times 10^{-10}$ cm²/s. The same fitting to the other samples annealed at different conditions were also done and the diffusion coefficients extracted are similar.

Basic diffusion mechanisms in crystals include defect independent processes and defect dependent processes.¹⁶ Generally, the latter processes are easier to take place because of lower activation energy. The activation energy values are between 0.5 and 1.5 eV for the interstitial diffusion, and between 3 and 5 eV for the vacancy diffusion in both silicon and gallium arsenide. The activation energy of 0.55 ± 0.04 eV, derived from Fig. 5, indicates an interstitial nitrogen dominant diffusion mechanism which is consistent with the XPS data.

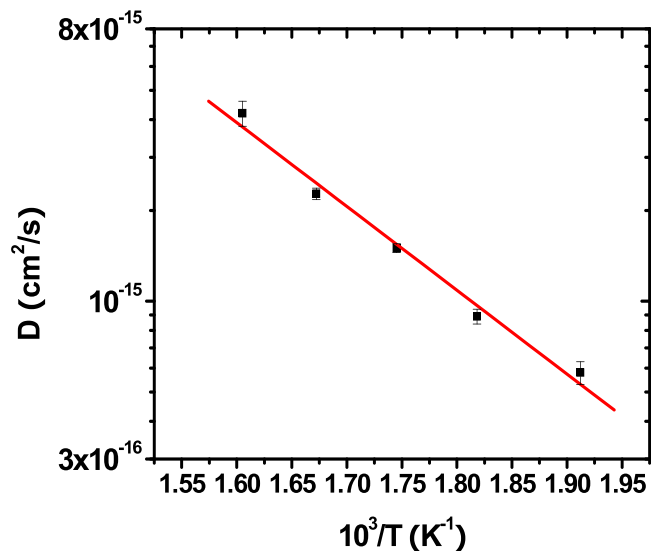


FIG. 5. Extracted diffusion coefficients plotted against temperature.

Boske *et al.* studied nitrogen diffusion in GaAs from a GaAs/GaAsN/GaAs structure by annealing it in an arsenic rich environment.¹⁷ They reported activation energy of 2.27 eV and proposed a kick-out model for the diffusion mechanism, which involves the virtually immobile nitrogen on the arsenic sublattice, interstitial nitrogen and interstitial arsenic elements. In the InSbN samples fabricated by two-step implantation, about 62% of the incorporated nitrogen ions form In-N bonds and most of the rest exist as interstitial species. The latter is believed to be the main source for the interstitial diffusion of nitrogen in the tail region.

In conclusion, the bonding and diffusion behavior of the implanted nitrogen ions in the InSb wafer is investigated. A nearly uniform InSbN region can be formed by two-step implantation after post annealing and the majority of the implanted nitrogen ions in the region form In-N bonds. Upon annealing, the implanted nitrogen will diffuse towards both surface and inside the InSb wafer. The out-diffused nitrogen accumulates at the surface while the nitrogen diffusion inside the InSbN wafer shows an interstitial dominant mechanism.

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