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Effects of structural defects on the activation of sulfur donors in GaN_xAs_{1-x} formed by N implantation

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The effects of structural defects on the electrical activity of S doped GaN_xAs_{1-x} layers formed by S and N coimplantation in GaAs are reported. S and N ions were implanted to the depth of about 0.4 μm. Electrochemical capacitance voltage measurements on samples annealed at 945°C for 10s show that in a thin (<0.1 μm) surface layer the concentration of active shallow donors is almost an order of magnitude larger in S and N co-implanted samples than in samples implanted with S alone. The activation efficiency of S donors also shows a broad minimum at a depth of about 0.2 μm below the surface. The results of these electrical measurements are correlated with the distribution of structural defects revealed by transmission electron microscopy (TEM). The TEM micrographs show that in addition to a band of dislocation loops commonly found in ion implanted GaAs, an additional band of small voids is observed in samples co-implanted with S and N. The location of this band correlates well with the region of reduced electrical activation of S donors, suggesting that formation of the voids through N accumulation results in a lower concentration of "active", substitutional N atoms.

Keywords: GaN_xAs_{1-x}, TEM, microstructure, implantation

Incorporation of a small amount of N (up to ~5%) into III-V semiconductors leads to a dramatic reduction of the energy gap of the resulting group III-N_x-V_{1-x} alloys. The effect has been observed experimentally in a large variety if III-N-V alloys including, GaNAs [1-4], GaInNAs [3,5], GaNP [6,7], InNP [8,9], and AlGaNAs [10] The issue of the N-induced band gap reduction has been addressed by a number of recent theoretical studies [3,5-8]. It has been shown, based on the band anticrossing model [11,12] that the N-induced downward shift of the conduction band edge and a large increase of the electron effective mass lead to great improvements of the electrical activation of group VI donors [13]. The enhanced electrical activation was observed in as grown selenium doped GaInNAs [14] as well as in sulfur implanted GaN_xAs_{1-x} [15]. A large increase in the electrical activation of sulfur (S) co-implanted with nitrogen in GaAs has also been observed [16]. In the case of N and S co-implanted GaAs, however, the increase in the electrical activation of sulfur donors was measured only in the near-surface region. In order to understand the mechanism leading to such behavior we performed detailed structural studies using transmission electron microscopy (TEM) to make it possible correlate the structural defect distribution with depth profiles of electrical measurements.

In this study we used two GaAs wafers. The first one was implanted only with S and the second co-implanted with S and N. Multiple energy ion implantation was used in both cases, resulting in ~ 0.4 µm thick layers with ~$3.3x10^{20}/cm^3$ of N and ~0.2µm thick layers with ~$6x10^{19}/cm^3$ of S. After implantation wafers were covered by other GaAs wafers (in order to prevent As outdiffusion) and annealed at

945°C for 10 s by rapid thermal annealing (RTA) in a flowing N_2 ambient. Cross-sectional TEM specimens were prepared by the standard method of mechanical thinning followed by ion milling. TEM studies were carried out using a TOPCON 002B microscope operated at 200 kV.

TEM studies performed on these wafers showed the presence of subsurface layers of post-implant damage. The distribution of structural defect present in these layers was studied using bright field TEM images of both materials are shown in Fig.1. In the sample implanted with S only [see Fig. 1(a)] a highly defective layer containing stacking faults, a dislocation network and small angle grain boundaries was observed below the surface. The thickness of this layer varied within the range: ~0.05 – 0.10 μm. Below this layer to a depth of ~ 0.2 μm a high quality crystal layer was observed. However in the middle of this layer at a depth of about 0.13 μm below the surface a narrow band of tiny defects was present. High resolution electron microscopy studies suggested that they were stacking fault tetrahedra. Such defects have been previously reported in implanted GaAs [17,18]. The main structural feature visible in this sample was a band of defects present in a layer at a depths from ~0.2 μm to ~0.3 μm below the surface. These defects were dislocation loops with an average size of ~ 10 nm, located on {111} planes surrounding extrinsic stacking faults. Such a band of dislocation loops is a typical feature in implanted and then annealed GaAs.

TEM studies of the S and N co-implanted sample [see Fig. 1(b)] showed different structural features compared to those observed in the sample implanted with S only. The only similarity was the presence of the band of dislocations loops at the depth of ~0.2 μm to ~0.3 μm below the surface. This band was slightly narrower and the loops were larger (with an average size of ~15 nm) than in the sample implanted only with S. There were pits observed at the surface of the sample co-implanted with N and S, probably originating from too high an annealing temperature or stacking fault formation. In this sample a broad layer containing a high density of small voids (of an average size of about 4-5 nm) was observed. They were located mostly in a layer extending from ~ 0.1 μm to ~ 0.3 μm below the surface. Their concentration rapidly decreased outside this area.

The observed distribution of structural defects correlated well with electrical measurements performed on these samples. Depth profiles of free electron concentration obtained for these materials by electrochemical capacitance voltage (ECV) are shown in Fig.2. The calculated distributions of implanted species are also shown in this figure. One can see from these results that the electron concentration profile measured for the sample implanted only with S differs drastically from that obtained for the one co-implanted with S and N. For both samples these line profiles have qualitatively similar shape. In the near-surface region for a thickness of about 0.1 μm there is a maximum of electron concentration. Then as distance from the surface increases this concentration rapidly decreases, resulting in a characteristic dip visible on these profiles. Despite these qualitative similarities there is a significant difference between the two profiles. In the co-implanted sample the density of free electrons in the near-surface region is almost an order of magnitude higher that in the sample implanted with S only. On the other hand, the depth of the dip measured for the co-implanted sample is much larger than in the sample with S only. In addition, this dip is much broader (0.2 μm comparing to 0.1 μm) in the co-implanted sample.

Comparison of the measured free electron concentration profiles with structural defect distributions shows a correlation between these results. In the sample implanted only with S the dip in the electrical profile correlates well with the location of the band of dislocation loops. It is likely that a significant fraction of the S implanted into this region becomes inactive by accumulating around the dislocation cores. This mechanism is probably also partially responsible for the reduced electrical activation of S in the co-implanted sample. However, it seems that in this case the presence of voids is an even more important mechanism for reducing the electrical activity of S. These voids were most likely formed as agglomerates of vacancies filled with N and act as defect centers compensating electrical activity of S donors. This argument is supported by the observed very large activation efficiency of S donors in the void-free region within the ~0.1μm layer near the surface, where N is incorporated in the As sublattice forming a layer of GaN_xAs_{1-x} alloy.

In summary, structural defect distributions, observed by TEM in GaAs implanted with S and co-implanted with S and N, were correlated with electrical measurements performed on the same samples. It was found that in the co-implanted sample that besides the typical implantation induced structural defects voids are formed in the material. We believe that that these voids were filled with N and were responsible for the reduced activation of S donors. On the other hand experimental results indicate that large N-induced enhancement of the donor activation efficiency can only be realized in the void-free region where GaN_xAs_{1-x} alloy was formed.

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Figure captions

Fig. 1. TEM micrographs of GaAs samples implanted with S (a), and co-implanted with S and N (b).

Fig. 2. ECV measured net donor concentration profiles for the GaAs samples implanted with S alone and S+N after RTA at 945 °C for 10s. The calculated atomic depth profiles for both S and N are also shown.

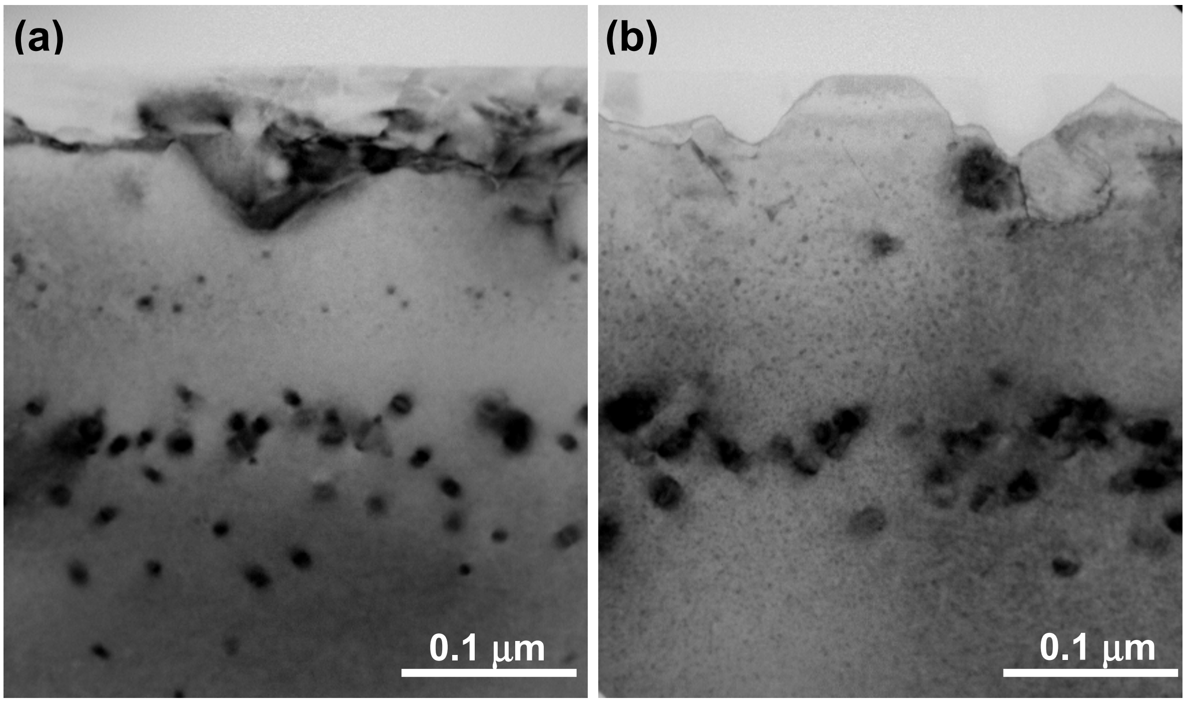
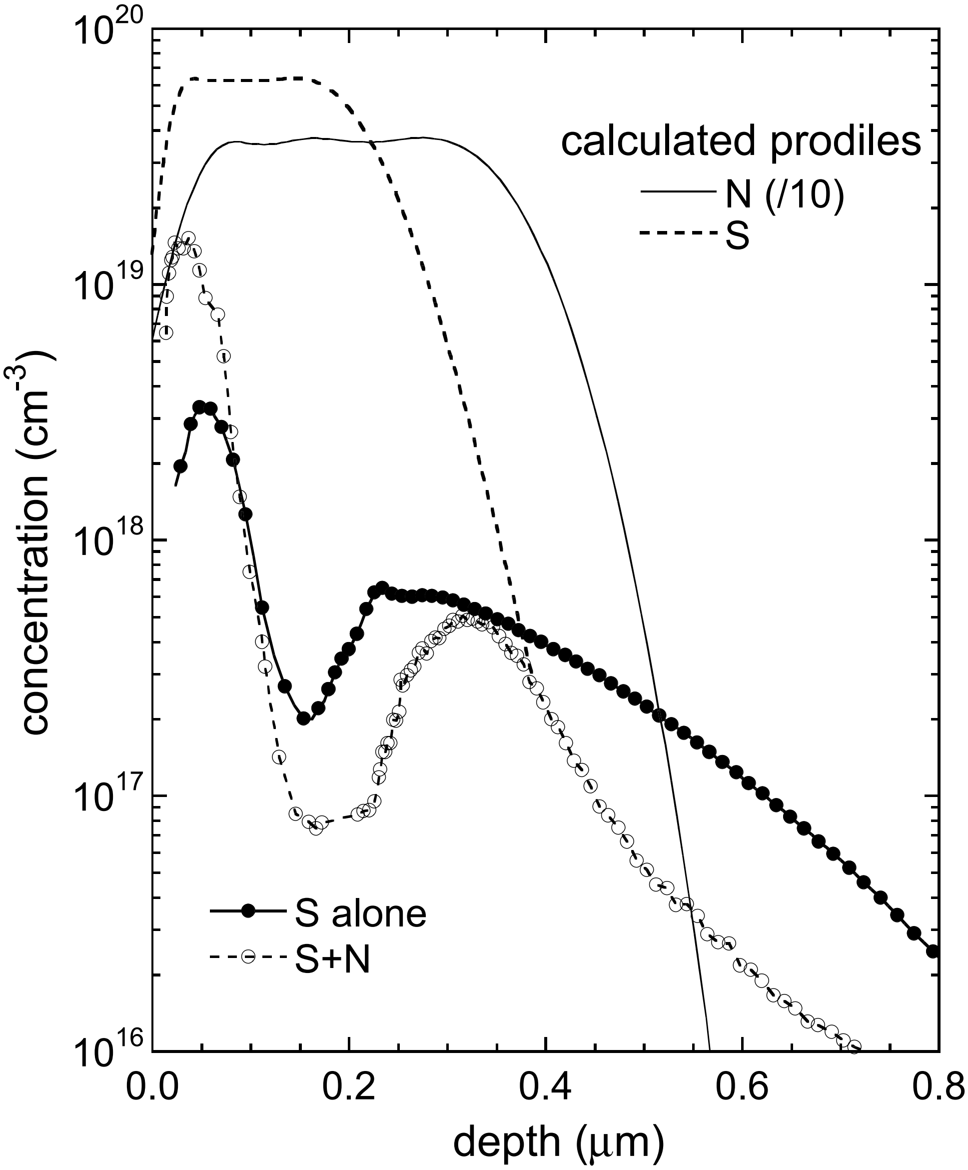


Fig. 1



calculated prodiles
N (/10)
S
S alone
S+N
concentration (cm^{-3})
depth (μm)
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
0.0
0.2
0.4
0.6
0.8

Fig. 2