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<th>Improvement of GaInNAs p-i-n photodetector responsivity by antimony incorporation</th>
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I. INTRODUCTION

The quaternary dilute nitride system, GaInNAs, has been receiving a lot of research attention ever since it was first reported by Kondow et al. GaInNAs offers high potential for realizing optoelectronic devices such as lasers and detectors on low cost GaAs-based platform operating in the range of 1.3–1.7 \( \mu m \). However, the incorporation of nitrogen into GaAs or GaInAs not only reduces its energy band gap, but also introduces crystal defects in the material that results in low photoluminescence (PL) efficiency and soft current-voltage (I-V) breakdown characteristic. While the exact origin of the defects is largely unknown, reports on high-resolution x-ray diffraction (HRXRD) and x-ray photoelectron spectroscopy (XPS) measurement on GaNAs grown by molecular beam epitaxy indicate that the defects are most probably in the form of interstitial N. Reports on GaNAs (Refs. 6 and 20) have shown that the possible candidates for interstitial N are the N–N split interstitials, N–As split interstitials, and (ASGa–NAs)\(_{\text{in}}\) complexes. So far, there is no direct evidence to link poor device performance to the presence of these interstitials, nor suggest a dominant effect from one of them. Reports of HRXRD, nuclear reaction analysis (NRA), and Rutherford backscatter spectroscopy (RBS) analyses on GaNAs and GaNAsN at compositions of 3.6\%–10.4\% have revealed no interstitial N.

Nevertheless, numerous reports on postgrowth heat treatment have shown that rapid thermal annealing under N\(_2\) ambient at high temperature (typically 750 °C for 1 min) can reduce the nitrogen-related defects in GaNAs and GaInNAs and improve the PL efficiency and decrease the carrier trap density. Recently, work on antimony (Sb) incorporation into dilute nitride materials has shown significant improvement in the GaInNAs (Ref. 12) crystal quality, especially in GaInNAsSb quantum well laser performance. In this paper, we report the improvement of GaInNAs/GaAs p-i-n photodetector responsivity following the incorporation of antimony into the quaternary material and presents measurements from deep level transient spectroscopy (DLTS) to support the effects leading to such improvement.

II. EXPERIMENTAL DETAILS

A. Device growth and fabrication

The GaInNAs/GaAs and GaInNAsSb/GaAs p-i-n photodetectors were grown on (100)-oriented \( n^+ \) GaAs substrates using molecular beam epitaxy (MBE) equipped with a radio-frequency (rf) nitrogen plasma source. Ultrahigh-purity nitrogen gas was supplied to the plasma source through a leak valve and mass flow controller, which precisely control the nitrogen flow rate. Gallium and indium fluxes are supplied by standard effusion cells. Arsenic and antimony fluxes are supplied by valved-cracker sources. The \( p \)-type dopant for GaInNAs/GaAs and GaInNAsSb/GaAs p-i-n photodetectors is beryllium and carbon, respectively. The \( n \)-type dopant for both devices is silicon. The growth temperature, layer thickness, and alloy composition of both devices are shown in Fig. 1. In both cases, the nominally undoped \( i \)-layer (Ga\(_{0.90}\)In\(_{0.10}\)N\(_{0.033}\)As\(_{0.967}\) and Ga\(_{0.96}\)In\(_{0.04}\)N\(_{0.028}\)As\(_{0.972}\)Sb\(_{0.005}\)) is grown closely lattice matched to GaAs with mismatch of about 0.02\%–0.04\%. The indium composition in the GaInNAsSb sample was reduced from 10\% to 4\% in order to maintain the lattice-matched condition to GaAs substrate.

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Based on a DLTS study of the InGaAs, Irvine and Palmer\textsuperscript{15} have reported that difference in indium composition from 4.5% to 18%\textsuperscript{16} did not have a significant effect on the deep-level trap concentration. Standard photolithography and wet etching process was used for creating the mesa structures. Metal contacts were formed on the $p$ and $n$ sides of the diode and thermally annealed for good Ohmic characteristic.

**B. Photocurrent and DLTS measurement**

Photocurrent measurement on the $p$-$i$-$n$ devices were carried out using a 100 W quartz tungsten halogen lamp and monochromator in conjunction with a lock-in amplifier. The photocurrent setup was calibrated using an InGaAs photodiode and optical power meter.

Trap activation energies, carrier capture cross sections, and trap densities were obtained from deep-level transient spectroscopy (DLTS) measurements. The DLTS spectra were analyzed using standard techniques.\textsuperscript{16} Since the $i$ layer in the $p$-$i$-$n$ photodetector structure is the nominally undoped GaInNAs (or GaInNAsSb), the DLTS spectra mainly arise from deep-level defects present in this layer.

**III. RESULTS AND DISCUSSION**

**A. Photoresponsivity**

Figure 2(a) shows the nonilluminated current-voltage ($I$-$V$) characteristics of the 400 $\mu$m diameter GaInNAs/GaAs and GaInNAsSb/GaAs $p$-$i$-$n$ photodetector. It clearly indicates that the GaInNAsSb/GaAs $p$-$i$-$n$ photodetector has lower reverse biased dark current compared to GaInNAs/GaAs. It also shows that the GaInNAs/GaAs $p$-$i$-$n$ photodetector exhibits more prominent soft-breakdown behavior compared to GaInNAsSb/GaAs. Such soft-breakdown behavior may be associated with midenergy gap defect states that have caused high generation-recombination current and tunneling current. Figure 2(b) shows the photoresponsivity of the 400 $\mu$m diameter GaInNAs/GaAs and GaInNAsSb/GaAs $p$-$i$-$n$ photodetector under reverse bias of $-2.0$ V. The photoresponsivity value of the GaInNAs/GaAs and GaInNAsSb/GaAs photodetectors at $\lambda = 1.35 \mu$m is 0.016 and 0.097 A/W, respectively. At $\lambda = 1.0 \mu$m, the responsivity is 0.032 A/W (GaInNAs/GaAs) and 0.29 A/W (GaInNAsSb/GaAs), respectively. These measurements clearly provide evidence that the introduction of Sb into GaInNAs resulted in approximately tenfold improvement in the photoresponsivity. The photoresponsivity of both samples cut off at $\lambda = 1.35 \mu$m, suggesting that the energy band gap of both $i$ layers is $\sim 0.92$ eV.

**B. DLTS-majority-carrier (hole) trap**

The results of DLTS measurement on both samples are shown in Fig. 3. For comparison, the same reverse bias and filling pulse ($V_p$) was used on both samples. For $V_p < 0$ V, only majority carriers (holes) are significant in the $p$-type GaInNAs layer; thus the DLTS peaks observed were from hole traps. For the GaInNAs/GaAs sample, two hole traps, labeled H-1 and H-2, were observed and their Arrhenius plots are shown in the inset of Fig. 3. The H-1 peak was scaled up $5\times$ for better comparison. For the GaInNAsSb/GaAs sample, only H-3 peak was observed. The activation energies and hole capture cross sections obtained from the Arrhenius plot and trap concentrations are shown in Table I. For calculations of the hole capture cross...
section, the hole effective mass is assumed to be the same as that of GaAs, $m_p^* = 0.5 m_o$, since the valence-band structure of GaInAsN is reported to be similar to that of GaAs.\(^{17}\)

As shown in Table I, for the GaInNAs/GaAs $p-i-n$ sample, the activation energy ($E_a$) of the H-1 and H-2 traps is 0.15 eV (0.17$E_g$) and 0.40 eV (0.43$E_g$), respectively. According to reports on DLTS results of dilute nitride materials,\(^{18,19}\) defect-related hole trap level ranging from 10 to 0.21 eV (or $0.09E_g$–$0.21E_g$) above the valence band (for energy band gap of 1–1.15 eV and nitrogen composition of 1%–2.9%) are associated with nitrogen-related defect trap levels. Their activation energy values may vary slightly due to differences in energy band gap of the material, but they are from the same defect type. Atomic and electronic structure calculations on N interstitials in GaAs alloys using first-principles method performed by Arola et al.\(^{20}\) have shown that the N–N and N–As interstitial defects are among the most probable ones to be formed in GaNAs. Further first-principles calculation of nitrogen solubility and its defect formation energy in GaAs performed by Zhang and Wei\(^{6}\) have shown that under arsenic-rich and gallium-rich conditions, the defect formation energy of N–N interstitials is always lower than that of N–As interstitials. This suggests that under most GaNAs growth conditions, the N–N interstitial defects are more dominant than N–As interstitials. The reported calculations have also shown that the arsenic antisite defects (As atoms in Ga sites), As$_{Ga}$, will become more dominant than N–N interstitials at some point under As-rich conditions. Since most dilute nitride materials grown under As-rich conditions by MBE are carried out at relatively low growth temperature, it is highly probable that As$_{Ga}$ will be the dominant defect type. Similar growth condition was also used for growing our GaInNAs/GaAs and GaInNAsSb/GaAs $p-i-n$ photodetector samples. First-principles calculation of electronic structure and defect formation energy in GaInNAs (or GaInNAsSb) are not yet available for reference. Therefore, in the absence of such information, and assuming the type of interstitial defects in GaNAs is the same as those in GaInNAs, we believe that the observed H-1 trap in the GaInNAs/GaAs $p-i-n$ sample, which has activation energy of 0.15 eV, is related to N–N interstitial defects, and the H-2 trap, which has activation energy of 0.40 eV (0.43$E_g$), is related to As antisite defects (As$_{Ga}$). This is because, for As antisite defects in GaAs, the activation energy is 0.614 eV,\(^{21}\) which is also 0.43$E_g$. This type of defect is commonly known as EL2 defect (midgap defect) in GaAs, which is an efficient carrier recombination center, that would cause detrimental effect on device performance in GaAs.

Interestingly, as shown in Fig. 3, the DLTS spectra of the GaInNAsSb/GaAs $p-i-n$ photodetector exhibits only one DLTS peak at 260 K, labeled as H-3. The H-1 trap, which is related to N–N interstitial defects, was not observed in the GaInNAsSb/GaAs $p-i-n$ photodetector. Thus, we believe that incorporation of Sb into GaInNAs has suppressed the formation of N–N interstitial defects. The observed H-3 trap, which has activation energy of 0.39 eV (0.42$E_g$), is believed to be related to the same type of defect trap as that of H-2 in GaInNAs. By comparing the intensity of the H-3 peak with that of H-2, we observed a great reduction in the DLTS signal intensity. This indicates a significant reduction in As antisite defects arising from the incorporation of Sb into the GaNAs material. Further analysis of the H-2 peak in the GaInNAs/GaAs sample and H-3 peak in the GaInNAsSb/GaAs sample also revealed about one order reduction in trap concentration in the Sb-containing sample. More importantly, the reduction of the H-3 DLTS peak, suppression of the H-1 peak, and reduction in H-3 trap concentration are all closely correlated with reduction in the nonilluminated reverse biased dark current and tenfold increase in photoresponsivity of the GaInNAsSb/GaAs device as shown in Figs. 2(a) and 2(b).

![FIG. 3. Majority-carrier DLTS spectra of GaInNAs/GaAs $p-i-n$ (solid lines) and GaInNAsSb/GaAs $p-i-n$ (dashed line) structures. The spectra for H-1, H-2, and H-3 were obtained using pulse width of 20 ms, reverse bias of $-2.0$ V, and filling pulse voltage of $-0.2$ V. The inset graphs show the Arrhenius plots from which the activation energies and hole-capture cross section from H-1, H-2, and H-3 were determined.](image)
From the above observations, we believe that the lower performance in the GaInNAs/GaAs p-i-n photodetector is mainly due to the presence of high concentration of $A_SGa$ defects arising from the low temperature used for growing the GaInNAs layer, which in effect promotes an As-rich surface. The nitrogen-related defects as observed in the $H-1$ DLTS peak is believed to have less significant impact on the photoresponsivity. This is because its activation energy level is not as near to the midgap energy level as compared to the $H-2$ defect, which is an efficient electron-hole recombination center. The results clearly show that incorporation of Sb into GaInNAs not only significantly suppressed the nitrogen-related defects, but also reduced the $A_SGa$ defects in the material.

Further analyses on the carrier capture kinetics of the GaInNAs/GaAs and GaInNAsSb/GaAs p-i-n samples were carried out by varying the filling pulse time at a fixed DLTS defect peak temperature. The results of DLTS signal versus filling pulse time (or pulse period) of both samples are shown in Figs. 4(a), 4(b), and 5 for $H-1$, $H-2$, and $H-3$ peaks, respectively. The inset graphs are their respective ln$[1 − ΔC_o/ΔC_o^p]$ versus filling pulse time plots. By using the following equation,

$$σ_p = σ_o \exp[−ΔE_o/k_BT] ,$$

where $k_B$ is the Boltzmann constant, their respective carrier cross-section activation energies were determined. $ΔE_o$ is the cross-section activation energy and $σ_p$ is the carrier capture cross section. The true activation energy (or energy level position within the band gap) is equal to the difference between the apparent activation energy and the cross-section activation energy. The DLTS signal is the amplitude of the capacitance transient. For an ideal point defect, the capacitance transient has an exponential characteristic and its amplitude $ΔC_o$ is related to the filling pulse time $t_p$ by

$$ΔC_o = ΔC_o^p [1 − \exp (−c_p t_p)] ,$$

where $ΔC_o^p$ is the saturated amplitude of the capacitance transient and $c_p$ is the hole capture rate. The energy levels and cross-section activation energy of the $H-1$, $H-2$, and $H-3$ defect peaks are listed in Table I. It is noted that all the respective ln$[1 − ΔC_o/ΔC_o^p]$ versus filling pulse time plots do not form a straight line. Therefore, we believe that the $H-1$, $H-2$, and $H-3$ defect peaks do not behave as an ideal point defect with distinct energy level; but rather having an extended defect behavior. This seems to indicate that the defects are in the form of structural dislocations due to lattice relaxation. However, we rule out such a possibility because the GaInNAs and GaInNAsSb layers were grown closely lattice matched to GaAs with mismatch of only $0.02\%–0.048\%$. Hence, no lattice relaxation could have occurred in our samples. We believe that the observed nonexponential dependence of the capacitance transient is most probably caused by alloy compositional fluctuation, which has created a series of closely spaced discrete energy levels.

**IV. CONCLUSION**

In this paper, we have shown that the incorporation of Sb into GaInNAs has significantly improved the p-i-n photodetector performance with $\sim 10\times$ increase in the photoresponsivity. DLTS measurement of the GaInNAs/GaAs sample revealed two hole-trap levels; one at 0.152 eV, which is related to nitrogen-related defects, and another at 0.400 eV.
which is related to As\textsubscript{Ga} antisite defects. The low temperature for growing dilute nitride materials using MBE is most probably one of the contributing factors to the formation of such defects. Under such growth conditions, the formation of N–N interstitials is believed to be more favorable compared to N–As interstitials. Following the incorporation of Sb into GaInNAs, the nitrogen-related defects were suppressed and the As\textsubscript{Ga} antisite defects were significantly reduced. These effects were evident from the absence of the nitrogen-related defect peak in the DLTS spectra, and reduction in the As\textsubscript{Ga} antisite related defect signal in the GaInNAsSb/GaAs p-i-n sample.

The nonexponential dependence of capacitance transient suggests that the defects do not behave as ideal point defects with distinct energy level; but rather having an extended defect behavior. This could possibly be due to alloy compositional fluctuation. Further optimization of GaInNAsSb growth conditions are necessary to minimize the formation of As\textsubscript{Ga} antisite defects and improve the photoresponsivity of the detector.


