Electrical and deep-level characterization of GaP$_{1-x}$N$_x$ grown by gas-source molecular beam epitaxy

M. Kaneko$^{a}$ and T. Hashizume$^{b}$

Research Center for Integrated Quantum Electronics, Hokkaido University, North 13, West 8, Kita-ku, Sapporo 060-8628 Japan

V. A. Odnoblyudov and C. W. Tu

Department of Electrical and Computer Engineering, University of California, San Diego La Jolla, California 92093-0407

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We have investigated electrical properties and deep levels of $n$-GaP$_{1-x}$N$_x$ grown on (100) $n$-GaP substrates by gas source molecular beam epitaxy. The x-ray photoelectron spectroscopy results showed no significant effects on the chemical bonding status of the host Ga-P matrix by the incorporation of small amounts of N atoms. In the Raman spectra, the zone-edge Ga-P-like vibration was observed at 387 cm$^{-1}$, originating from alloy disorder or local distortion of the GaP$_{1-x}$N$_x$ lattice. The electrical properties of the GaP$_{1-x}$N$_x$ surfaces were characterized using a Schottky contact structure. An ideality factor of 1.10–1.15 and a Schottky barrier height of 1.1 eV were obtained from the current-voltage characteristics of Ni/GaP$_{1-x}$N$_x$ diodes, indicating good interface quality. The thermal admittance spectroscopy clearly detected the Si donor level with an activation energy of 84±4 meV in GaP and GaP$_{1-x}$N$_x$. For the GaP$_{1-x}$N$_x$ samples, we observed deep levels probably associated with N-induced defects such as N-N pairs, N clusters, and an N-containing complex.


I. INTRODUCTION

The dilute nitride semiconductors, such as GaAsN, GaPN, and GaInPN, are promising materials for practical applications in optoelectronics,$^1$ such as visible-infrared LEDs,$^2$ the long-wavelength lasers,$^{1,3,4}$ emitting at 1.3 and 1.55 μm, and photovoltaic devices,$^5$ due to their unique properties induced by N incorporation into a host III–V matrix. In fact, Odnoblyudov and Tu very recently reported$^2$ that amber GaPN LEDs, successfully fabricated on a transparent GaP (100) substrate, showed excellent stability of the electroluminescence wavelength on the driving current, as compared with commercially available AlInGaP LEDs.

The isoelectronic traps formed by incorporation of N into a host semiconductor matrix, interact with the conduction band of host semiconductor. Thus, the conduction band of III–V–N semiconductors is modified drastically, thereby leading to the large bowing of the band gap in III–V–N alloys as described in the band-anticrossing model.$^6$–$^8$ In addition, the incorporation of N into conventional III–V compounds causes a large change in lattice constant, which is expected by Vegard’s law. In the case of GaP$_{1-x}$N$_x$, especially, it is theoretically predicted that only a 2% of N incorporation into the host GaP matrix makes its lattice constant to match that of Si.$^9,10$ Therefore, there is a possibility for integration of GaPN devices with Si devices utilizing the conventional Si technology.$^{11,12}$ For design and control of GaPN-based device structures, it is important to understand electrical properties of the GaPN surfaces, including junction characteristics, impurity and/or defect-induced electronic levels, and so on. Although structural and optical properties of GaP$_{1-x}$N$_x$ have extensively been studied,$^{7,13}$–$^{21}$ there are only a few literatures$^{22}$–$^{24}$ on their chemical and electrical properties.

In this paper, we characterize electrical properties and deep levels of $n$-type GaP$_{1-x}$N$_x$ alloy grown on (100) $n$-GaP substrates by gas-source molecular beam epitaxy (GSMBE), and compare them with those of a GaP layer.

II. EXPERIMENT

Figure 1 shows a schematic drawing of the GaP$_{1-x}$N$_x$ layer structure and the Schottky diode used in this study. The GaP$_{1-x}$N$_x$ wafers consisted of an $n$-GaP$_{1-x}$N$_x$ layer (0.5 μm) and an $n$-GaP buffer layer (0.3 μm) grown on $n$-GaP (100) substrates by GSMBE assisted by an rf-induced N plasma.$^{13}$

The substrate temperature was 510 °C for the growth of the GaP$_{1-x}$N$_x$ layers.$^{14}$ The Si doping concentration was designed to be 1×10$^{17}$ cm$^{-3}$ by controlling the temperature of the Si cell. The N concentration of the GaP$_{1-x}$N$_x$ layers was determined by x-ray diffraction. In this paper,
GaP$_{1-x}$N$_x$/GaP samples with $x=0$, 0.25, 0.42, and 0.62% were used. These wafers were prepared at UCSD.

An ohmic contact consisting of a Ge/Au/Ni/Au layered structure was formed on the back side of a sample by electron beam deposition, followed by annealing at 380 °C for 5 min in an N$_2$ ambient. The GaP$_{1-x}$N$_x$ surface was cleaned with acetone and ethanol using an ultrasonic cleaner. Then the sample was rinsed with de-ionized water, and dried with nitrogen. In order to remove the native oxide from the sample was formed using an x-ray photoelectron spectroscopy (XPS) analyzer and a monochromated Al K$_\alpha$ radiation source ($h\nu$ = 1486.6 eV). The energy scale was calibrated with the Au 4f spectrum ($h\nu$=84.0 eV), and the static electrification was compensated using the energy position of the C 1s core level in the C-H bond ($h\nu$=285.0 eV). The structural properties of GaP$_{1-x}$N$_x$ alloys were characterized by a Raman scattering spectroscopy system (Horiba Jobin Yvon T64000) using the 514.5 nm line of an Ar$^+$ laser. The 180° backscattering geometry was used throughout the experiments. The spectra of the (100) surfaces were taken in polarization configuration $x(y',y')$, where $x$ denotes the [100] axis and $y'$ denotes the [011] axis. The spectral resolution of the system was about 0.6 cm$^{-1}$. Electrical properties of fabricated Ni/GaP$_{1-x}$N$_x$ Schottky structures were examined by conventional current-voltage ($I-V$), capacitance-voltage ($C-V$), and thermal admittance spectroscopy measurements, using an HP4156A parameter analyzer and an HP4192A impedance analyzer. The sample temperature was swept from 30 to 300 K in a cryostat.

III. RESULTS AND DISCUSSION

A. XPS and Raman characterization

To investigate chemical and structural properties of the GaP$_{1-x}$N$_x$ alloys basically, we carried out XPS and Raman measurements. Figure 2(a) shows the XPS P 2p core-level spectra obtained from the GaP$_{1-x}$N$_x$ ($x=0$, 0.25, and 0.62%) surfaces at an electron escape angle of 45°. Three peaks at 129.8, 130.5, and 135 eV, originating from the P 2p$_{1/2}$, P 2p$_{3/2}$, and P-oxide bond, respectively, were observed. The shapes and the energy positions of P 2p peaks remained unchanged with a slight variation in the N composition. A similar result was obtained for the Ga 3d spectra. Therefore, it is found that the slight incorporation of N less than 1% had no significant impact on the chemical bonding status of the host GaP matrix. The valence band (VB) spectra were shown in Fig. 2(b). The onset of the VB spectrum was the same for the three samples, indicating the same energy position of the VB maximum. On the other hand, a slight change was observed in the spectrum shapes by the addition of N into the host GaP matrix. The intensity of the broad peak at around 4 eV decreased with increasing the N composition. It may reflect modification of the density of states in VB, although the reason for this is not clear at present. A numerical calculation predicted a variation of the total valence charge densities for GaP$_{1-x}$N$_x$ with different N compositions.

Figure 3(a) shows typical resonant Raman scattering spectra of the GaP$_{1-x}$N$_x$ alloys. There were three vibration components relating to a strong longitudinal-optic (LO) phonon mode at 405 cm$^{-1}$, a weak transverse-optic (TO) phonon mode at 366 cm$^{-1}$, and an additional mode (labeled as X) at 387 cm$^{-1}$, respectively. The spectra obtained were normalized by the intensity of the LO line for comparison. On the basis of the present symmetry configuration, the TO phonon vibration should be prohibited even for the GaP sample. However, we observed the TO peak even in the (100) GaP substrate. Thus, the incompleteness of scattering geometry and/or the imperfection of crystalline quality is probably responsible for a slight peak of the TO phonon. For GaP$_{1-x}$N$_x$, the X mode was observed at 387 cm$^{-1}$, and its intensity increased with the N composition. A similar scattering mode has already been reported in the GaAsP$_{1-x}$N$_x$ alloys and GaP$_{1-x}$N$_x$ alloys. Even though the origin of this mode is not known clearly, it has been expected that the compositional disorder (alloy disorder) or the N-induced lattice strain of GaP$_{1-x}$N$_x$ alloys can affect the host GaP LO phonon vi-
bration, leading to the activity of the X mode. To investigate the influence of the annealing process for metallization of ohmic contact on the structural properties of GaP$_{1-x}$N$_x$ alloys, the Raman spectra were compared before and after the annealing process as shown in Fig. 3. After annealing at 380 °C for 2 min, the TO phonon peak and the X peak slightly decreased. In addition, we observed the narrowing of the full-width at half maximum (FWHM) at the LO phonon scattering line. The result indicates an improvement of the crystalline quality, probably due to the uniformity improvement of the N composition during the anneal.

B. I-V and C-V behavior of Ni/GaPN Schottky junctions

Figure 4 shows typical I-V characteristics of the Ni/GaP$_{1-x}$N$_x$ Schottky diodes measured at room temperature (RT). We observed good linearity in the ln($J$)-$V$ curves for 6–10 orders of magnitude in current, indicating that the simple thermionic-emission transport was dominant at the Schottky interfaces. The difference in saturation current at the higher bias is attributed to the difference in carrier concentration of the GaP$_{1-x}$N$_x$ layers. By applying the standard thermionic emission analysis to the experimental I-V curves, the ideality factors, $n$, are estimated to be 1.10–1.15 for all the GaP$_{1-x}$N$_x$ samples. We also found that the values of the Schottky barrier height (SBH) derived from the I-V plots was 1.1 eV, without depending on the N composition. These results indicated that relatively good Schottky contacts were fabricated on the GaP$_{1-x}$N$_x$ surfaces.

Figure 5 shows the C$^2$V plots for the GaP and GaP$_{1-x}$N$_x$ samples. From the plots at $f=1$ MHz, we estimated the densities of the shallow donors, $N_D$, in the GaP and GaP$_{1-x}$N$_x$ layers. Table I summarizes the evaluated values of the ideality factor, SBH, and shallow donor density of GaP and GaP$_{1-x}$N$_x$ with different N composition. In spite of the fact that we used the same Si doping condition during the epitaxial growth, the shallow donor density decreased with

<table>
<thead>
<tr>
<th>$x$ in GaP$_{1-x}$N$_x$ (%)</th>
<th>$n$ value$^a$</th>
<th>SBH$^b$ (eV)</th>
<th>$N_D$ $^b$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.11</td>
<td>1.10</td>
<td>1.9×10$^{17}$</td>
</tr>
<tr>
<td>0.45</td>
<td>1.12</td>
<td>1.09</td>
<td>9.0×10$^{16}$</td>
</tr>
<tr>
<td>0.62</td>
<td>1.15</td>
<td>1.08</td>
<td>6.0×10$^{16}$</td>
</tr>
</tbody>
</table>

$^a$Derived from I-V.

$^b$Derived from C-V.
increasing the N composition in the GaP$_{1-x}$N$_x$ layers. A similar reduction of electron concentration was reported by Furukawa et al.\textsuperscript{24} in the S and Te-doped GaP$_{1-x}$N$_x$ layers grown by rf-MBE. They suggest that such reduction of the carrier concentration could arise from the N-impinging desorption of the dopants from the surface during growth, or the electron capture by N-related deep levels. The frequency dispersion of capacitance obviously appeared in the C-V characteristics for the GaP$_{1-x}$N$_x$ samples, indicating the existence of deep levels in the GaP$_{1-x}$N$_x$ alloys.

C. TAS study

To investigate shallow and deep levels in the GaP$_{1-x}$N$_x$ layers, we employed TAS measurements in the GaPN samples. Figure 6(a) shows admittance (capacitance and conductance corrected by the angular frequency) spectra from a Ni/GaP diode at a temperature ranging from 30 to 300 K. The measurements were performed at a modulation frequency from 100 kHz to 1 MHz. The bias voltage was 0 V. For the GaP sample, the capacitance curves showed nearly plateau behavior for each frequency at temperatures ranging from 100 to 300 K. Then, the capacitance suddenly decreased at the temperature around 60 K. At the same temperature, the conductance curves showed the maximum values. Figure 6(b) shows admittance spectra taken from a Ni/GaP$_{1-x}$N$_x$ (x=0.62%) Schottky diode. In contrast to the capacitance curves of the Ni/GaP diode in Fig. 6(a), there were two inflection points for the Ni/GaP$_{1-x}$N$_x$ diode, as indicated by the arrows in Fig. 6(b). The corresponding two peaks were observed in the conductance curves. This result exhibits that the GaP$_{1-x}$N$_x$ alloy has at least two trap levels.

At the temperature in which a conductance maxima appears at each frequency, a thermal emission rate of the trap level, $e^a_n$, is expressed by the following equations:\textsuperscript{25}

$$e^a_n(T_m) = \omega = \sigma_b N_C \nu_th \exp\left(-\frac{E_a}{kT_m}\right)$$

$$= \sigma_b N_C \nu_thT_m^2 \exp\left(-\frac{E_a}{kT_m}\right),$$

where $\omega$ is the angular frequency, $T_m$ is the temperature at which the maximum of conductance appears, $\sigma_b$ and $E_a$ are thermal cross section and activation energy of a trap level, $N_C$ is the effective density of states at the conduction band minimum, $\nu_th$ is the thermal velocity, and $k$ is the Boltzmann constant. From Arrhenius plots of the temperature-corrected angular frequency, we can estimate activation energies of trap levels.

Figures 7(a) and 7(b) show the Arrhenius plots of the temperature-corrected emission rates of the trap levels and the energy level diagrams for the GaP$_{1-x}$N$_x$ alloy systems, respectively. For Fig. 7(b), we assumed a constant energy level for the valence band maximum in the GaP$_{1-x}$N$_x$ alloy system, according to the BAC model. Then the energy of the conduction band minimum is simply determined by the band gap energy of GaP$_{1-x}$N$_x$ in the literatures.\textsuperscript{7,13} As shown in Fig. 7(a), the trap level with a thermal activation energy of

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Level & Energy (eV) \\
\hline
Valence band maximum & 2.34 \\
Conduction band minimum & 0.34 \\
\hline
\end{tabular}
\caption{Energy levels of GaP$_{1-x}$N$_x$ alloy.}
\end{table}
about 84±4 meV exists in all the samples. This value is very close to the ionization energy of a Si donor occupying the Ga site in the GaP lattice.\(^\text{[29-31]}\) No pronounced change in the activation energy of the Si donor was observed in the GaP\(_{1-x}\)N\(_x\) alloys. Furukawa et al.\(^\text{[24]}\) also reported almost the same activation energy for the S dopant in GaP\(_{1-x}\)N\(_x\) (\(x = 0\% - 1.9\%\)).

In addition to the Si donor level, we detected deeper trap levels for the GaP\(_{1-x}\)N\(_x\) alloys, labeled by \(E_{D1}\) and \(E_{D2}\) in Fig. 7(b). These levels have a tendency to become deeper in energy with an increasing N composition. Again, these levels were not detected in GaP but in GaP\(_{1-x}\)N\(_x\), indicating that the origin of the levels is related to defects induced by the incorporation of N atoms. From the detailed PL analysis, Buyanova et al.\(^\text{[13]}\) suggested the existence of deep levels related to N-N pairs and/or N clusters in the GaP\(_{1-x}\)N\(_x\) alloy. Furukawa et al.\(^\text{[24]}\) pointed out the possibility for complex defects consisting of shallow impurities and N atoms. From deep level transient spectroscopy measurements in the GaAsN alloy, in addition, Johnston and Kurtz\(^\text{[32]}\) very recently detected the deep trap whose density correlated with both the N composition and the electron concentration. Since we observed the reduction of the Si donor density (Table I) and the peak intensity of conductance for the Si donor in the GaP\(_{1-x}\)N\(_x\) samples, we observed deep levels probably associated with N-induced defects such as N-N pairs, N clusters, and N-containing complexes.

IV. CONCLUSION

Electrical properties and deep levels of GaP\(_{1-x}\)N\(_x\) (\(x = 0\% - 0.62\%)\) grown by gas-source molecular beam epitaxy were investigated using the Ni Schottky contact structures. The XPS analysis showed that no significant effects on the chemical bonding status of the host Ga-P matrix by the incorporation of small amounts of N atoms. We observed similar Raman spectra of the GaP\(_{1-x}\)N\(_x\) layers to those reported in the literatures. The Schottky \(I-V\) characteristics provided the ideality factors of 1.10–1.15 and a barrier height of 1.1 eV, indicating good interface quality between the metal and GaP\(_{1-x}\)N\(_x\). From the capacitance-voltage measurement, we found the reduction of the shallow donor density with the N composition in the GaP\(_{1-x}\)N\(_x\) layers. The thermal admittance spectroscopy clearly detected the Si donor level with an activation energy of 84 meV in GaP and GaP\(_{1-x}\)N\(_x\). For the GaP\(_{1-x}\)N\(_x\) samples, we observed deep levels probably associated with N-induced defects such as N-N pairs, N clusters, and N-containing complexes.