Interband transitions in GaN$_{0.02}$As$_{0.98-x}$Sb$_x$/GaAs single quantum wells studied by contactless electroreflectance spectroscopy

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Interband transitions in GaN$_{0.02}$As$_{0.98-x}$Sb$_x$/GaAs single quantum wells (SQWs) with $0 < x \leq 0.11$ have been investigated by contactless electroreflectance (CER). CER features related to the ground and excited state transitions have been observed and compared with those obtained from theoretical calculations, which were performed in the framework of the effective mass formalism model. It has been concluded that these SQWs are type I and the conduction band offset for this material system decreases from 80% to 50% when the Sb composition is increased from 0% to 11%. It shows that the band gap discontinuity for GaNAsSb/GaAs material system can be simply tuned by a change in Sb concentration.

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I. INTRODUCTION

Dilute-nitride III-V compound semiconductors are of considerable research interest from both the fundamental and technological points of view. In addition to GaInNAs, GaNAsSb appears to be a promising alloy for GaAs-based lasers operated at long wavelengths, i.e., at 1.3 and 1.55 μm. However, very few studies of GaNAsSb have been reported since the initial proposal in 1999 (Ref. 3) and many fundamental optical properties of GaNAsSb are still unknown. One of the remaining unresolved issues with respect to electronic properties of GaNAsSb/GaAs quantum well (QW) structures involves the band gap discontinuity and its change with an increase in Sb composition. In the case of Sb-free QWs, i.e., GaNAs/GaAs QWs, many different results on the conduction band offset have been published to date.14–24 Most researchers are in agreement that GaNAs/GaAs QW structures are type I and the conduction band offset for GaN$_{0.02}$As$_{0.98}$/GaAs QWs is close to 80%.23,24 It is expected that the incorporation of Sb atoms into a GaN$_{0.02}$As$_{0.98}$/GaAs QW significantly influences the conduction and valence band offsets because GaAs/GaAs QWs are type II for electrons25,26 or are type I with a very small conduction band offset.27 Recently, we have shown that the conduction band offset equals 50% for GaN$_{0.02}$As$_{0.87}$Sb$_{0.11}$/GaAs SQWs.13 However, further investigation of GaNAsSb/GaAs QWs is still required. The aim of this paper is to study the optical transitions for a set of GaN$_{0.02}$As$_{0.98-x}$Sb$_x$/GaAs SQWs with $0 < x \leq 0.11$. In order to investigate the quantum well transitions we have applied contactless electroreflectance (CER) spectroscopy. This technique, similar to photoreflectance (PR) spectroscopy, is an excellent tool to investigate both the fundamental and higher order QW transitions. Moreover, CER has a number of advantages over PR for the study of QW structures. CER does not require a laser as the pump beam and avoids the photoluminescence background due to this pump beam. Also, CER spectra are free of below band gap oscillation features, which are often observed in PR spectra, especially for GaAs-based structures grown on n-type GaAs substrates.32 The analysis of CER data together with theoretical calculations makes it possible to determine material parameters such as the band gap discontinuity. Such procedures have been often applied in studies for different semiconductor structures.30,31,33

The focus of this paper is the application of CER spectroscopy to GaN$_{0.02}$As$_{0.98-x}$Sb$_x$/GaAs single QWs (SQWs) with $0 < x \leq 0.11$ in order to determine the energies of the interband transitions and to extract the conduction band offset for this system by matching experimental data with theoretical calculations performed within the effective mass approximation.

II. SAMPLES AND EXPERIMENT

The GaNAsSb/GaAs SQW samples prepared for this study were grown on semi-insulating (100) GaAs substrates by solid-source molecular beam epitaxy (MBE) in a Varian Mod Gen-II system. Details of the growth process are described elsewhere.10,11 The SQW structure is composed of a 250 nm thick GaAs buffer layer, 50 nm thick GaAs:N layer with the nitrogen concentration of ~0.1%, 60 Å thick GaN$_{0.02}$As$_{0.98-x}$Sb$_x$ QW, and 50 nm thick GaAs cap layer. The GaAs:N layer is not an intentional part of the structure, but a result of the growth method used. The concentration of Sb atoms into GaN$_{0.02}$As$_{0.98-x}$Sb$_x$ layer for the three samples is 3%, 6%, and 11%, respectively. All samples were not annealed. The content of GaNAsSb layer and the width of QW were determined by secondary ion mass spectroscopy and high resolution x-ray diffraction (HRXRD) measurements as being close to the nominal values.

A conventional experimental set-up with a tungsten halogen lamp (150 W) as a probe light source, a 0.55 m monochromator and InGaAs pin photodiode was applied for obtaining CER spectra. Samples were mounted in a capacitor. The top electrode of the capacitor is a copper-wire mesh...
which is semitransparent for light. This electrode was kept at a distance of 0.1–0.3 mm from the sample surface while the sample itself was fixed on the bottom copper electrode. A maximum peak-to-peak alternating voltage of ~0.9 kV was applied. The frequency of the ac voltage was 285 Hz. Phase sensitive detection of CER signal was made using a lock-in amplifier. Other relevant details of CER set-up are described in Refs. 28, 29, and 33.

III. THEORETICAL APPROACH

The calculations of QW energy levels have been performed within the framework of the effective mass approximation. The influence of strain on the band structure is taken into account, but excitonic effects are neglected. The biaxial strain was calculated based on the Pikus-Bir Hamiltonian\(^34\) as is shown below.

For the \(E_0\) critical point in GaNAsSb the hydrostatic component of the strain, \(\delta\varepsilon_{HH}\), shifts the valence and conduction bands. This total shift corresponds to the change in the band gap energy due to a hydrostatic deformation, which is proportional to the deformation potential \(a\), that is measured. The total shift should be divided between the valence and conduction bands proportionally to the potential constants \(a_V\) and \(a_C\), where \(a=a_V+a_C\). The shear component, \(\delta\varepsilon_S\), removes the valence band degeneracy, giving a separate \(E_{HH}\) (related to heavy holes) and \(E_{LH}\) (related to light holes). If the effect of the strain-induced coupling with the spin-orbit split band is negligible, the energy of conduction and valence bands can be expressed in terms of the unstrained value as

\[
E_C = E_0 + \delta\varepsilon_C^C, \quad E_{HH} = E_0 + \delta\varepsilon_H^V + \delta\varepsilon_S, \quad E_{LH} = E_0 + \delta\varepsilon_H^V - \delta\varepsilon_S + \cdots.
\]

The values of the \(\delta\varepsilon_C^C\), \(\delta\varepsilon_H^V\), and \(\delta\varepsilon_S\) are given by following formulas:

\[
\delta\varepsilon_C^C = 2a_C \cdot \left(1 - \frac{C_{12}}{C_{11}}\right)\varepsilon, \quad \delta\varepsilon_H^V = 2a_V \cdot \left(1 - \frac{C_{12}}{C_{11}}\right)\varepsilon, \quad \delta\varepsilon_S = b \cdot \left(1 - 2\frac{C_{12}}{C_{11}}\right)\varepsilon
\]

where \(\varepsilon\) is the strain in the plane of the interfaces, \(C_{11}\) and \(C_{12}\) are elastic stiffness constants, and \(b\) is the shear deformation potential, respectively. All the parameters have been obtained by linear interpolation between the parameters of a relevant binary semiconductor\(^35\) according to Eq. (3),

\[
Q(x,y) = y \cdot Q_{GaN} + (1-x-y) \cdot Q_{GaAs} + x \cdot Q_{GaSb},
\]

where \(Q_i=b_i\) or \(C_{12}^i\) (\(i=GaN, GaAs,\) and GaSb). The parameters of binary compounds used in our calculations are listed in Table I.

<table>
<thead>
<tr>
<th>Parameter (unit)</th>
<th>GaN</th>
<th>GaAs</th>
<th>GaSb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy-hole mass (m_{hh}/m_0)</td>
<td>0.847</td>
<td>0.35</td>
<td>0.25</td>
</tr>
<tr>
<td>Light-hole mass (m_{lh}/m_0)</td>
<td>0.237</td>
<td>0.09</td>
<td>0.044</td>
</tr>
<tr>
<td>CB hydrostatic deformation potential (a_C^C (eV))</td>
<td>-6.71</td>
<td>-7.17</td>
<td>-7.5</td>
</tr>
<tr>
<td>VB hydrostatic deformation potential (a_V^V (eV))</td>
<td>-0.69</td>
<td>-1.16</td>
<td>-0.8</td>
</tr>
<tr>
<td>Shear deformation potential (b (eV))</td>
<td>-2.0</td>
<td>-2.0</td>
<td>-2.0</td>
</tr>
<tr>
<td>Elastic constant (C_{11} (GPa))</td>
<td>293</td>
<td>1221</td>
<td>884.2</td>
</tr>
<tr>
<td>Elastic constant (C_{12} (GPa))</td>
<td>159</td>
<td>566</td>
<td>402.6</td>
</tr>
</tbody>
</table>

The strain present in our samples has been determined directly by HRXRD measurements to be, respectively, \(\varepsilon=-0.5\%\) for GaN\(_{0.02}\)As\(_{0.87}\)Sb\(_{0.11}\)/GaAs QWs, \(\varepsilon=-0.06\%\) for GaN\(_{0.02}\)As\(_{0.91}\)Sb\(_{0.08}\)/GaAs QWs, and \(\varepsilon=0.2\%\) for GaN\(_{0.02}\)As\(_{0.95}\)Sb\(_{0.03}\)/GaAs QWs. According to the band anticrossing model (BAC) model\(^1,2,36\), the influence of nitrogen localized states on the valence band structure is neglected. Hence, it can be assumed that the effective mass of light and heavy hole does not change significantly after adding of nitrogen atoms. Therefore the light and heavy hole masses are calculated according to Eq. (3) with effective masses of relevant binary semiconductors taken after Ref. 35. The electron effective mass has been assumed to be 0.09 \(m_0\) after Ref. 8. This assumption indicates an increase in the electron effective mass in comparison to the N free sample. Note that such an electron effective mass is in accordance with the BAC model prediction.\(^1,2,36\) We calculated that the electron effective for GaN\(_{0.02}\)As\(_{0.98}\) is 0.1 \(m_0\) with the BAC model. Other analyses also show that the electron effective mass for GaN\(_{0.02}\)As\(_{0.98}\) is \(\sim 0.1 m_0\). Unfortunately, BAC parameters for GaNAsSb are unknown and \(m_0\) cannot be extracted from the BAC model. It is expected that incorporation of Sb atoms decreases the electron effective mass because it also decreases the band gap energy. The value of 0.09 \(m_0\) in Ref. 8 has been determined for GaNAsSb/GaAs QW with 30% Sb and 1.5% N. Thus, we can expect that in our samples, the electron effective mass is between 0.09 \(m_0\) and 0.01 \(m_0\). In general, the electron effective mass in our samples can vary with the Sb content (decreases with the larger Sb content), but the change should be small since the total variation of Sb content is only 8%. Finally, we conclude that for these samples, the best approach is to calculate the energy levels with the same value of the electron effective mass, i.e., \(m_e=0.09 m_0\). It has been found that the BAC model with GaNAsSb parameters is insufficient to describe the GaNAsSb band gap. Therefore the band gap energy of the GaNAsSb layer has been adjusted to the experimental value of the QW ground state transition. The conduction- and valence-band offset, \(Q_C\) and \(Q_V\), are defined as \(Q_C=\frac{\Delta E_C}{(\Delta E_C + \Delta E_V)}\) and \(Q_V=1-Q_C\), where \(\Delta E_C\) and \(\Delta E_V\) are the conduction- and valence-band discontinuities at the heterojunction. Note that in our calculations, we assume \(Q_C\) before taking into account the strain effects as it is shown in Fig. 1. In our calculations, the \(Q_C\) is treated as a free parameter.
amplitude and phase of the line shape, and respectively. The term energy and the broadening parameter of the transitions, re-

IV. RESULTS AND DISCUSSION

Figure 2 shows the CER spectra obtained from the GaN$_{0.02}$As$_{0.98-x}$Sb$_x$/GaAs SQWs with different Sb concentra-
tions. All CER spectra are dominated by a GaAs band gap bulklike signal at the energy of $\sim$1.42 eV. This signal could be a superposition of CER resonances related to absorption in the GaAs cap and buffer layers. The contribution from the two signals can change from sample to sample due to different band bending at the surface and at the buffer/substrate interface. Therefore, the shape of GaAs signal is not exactly the same for the three samples.

In the case of GaN$_{0.02}$As$_{0.87}$Sb$_{0.11}$/GaAs SQW, a CER feature related to the GaAs:N layer is observed at the energy of $\sim$1.37 eV. This feature confirms the presence of an intermediate GaAs:N layer due to plasma ignition and stabiliza-
tion prior to the QW. Such a feature has been observed in our previous PR study performed for similar QW structures.$^{13,32,33}$ Note that the GaAs:N related transition is not observed for the two remaining SQWs. We believe that this phenomenon is associated with the lower amount of N in the intermediate layer.

Below the GaAs signal (in the case of the GaN$_{0.02}$As$_{0.87}$Sb$_{0.11}$/GaAs SQW, below the GaAs:N related transition) CER features associated with the optical transitions in GaNAsSb/GaAs SQWs are clearly observed. These features are analyzed using the low-field electromodulation Lorentzian line shape functional form$^{28,37}$

$$\frac{\Delta R}{R}(E) = \text{Re} \left[ \sum_{j=1}^{n} C_j \cdot e^{i \theta_j} (E - E_j + i \cdot \Gamma_j)^{-m_j} \right],$$

(4)

where $n$ is the number of the optical transitions and spectral functions used in the fitting procedure, $C_j$ and $\theta_j$ are the amplitude and phase of the line shape, and $E_j$ and $\Gamma_j$ are the energy and the broadening parameter of the transitions, re-

with parameters taken from the fit.

The identification of CER resonances was possible due to a series of calculations. The notation $nmHL$ denotes the transition between $n$th heavy hole (light hole) valence sub-

band and $m$th conduction subband. The resonance at the lowest energy originates from the $11H$ transition, which is a fundamental transition for all SQW samples. In addition to the $11H$ transition, the CER spectra show an $11L$ transition (i.e., the lowest energy transition for light holes) and transitions between excited QW states. The $11L$ transition is typi-
cally not resolved for GaNAs/GaAs QWs (Refs. 23 and 24) primarily due to its lower intensity in comparison to the $11H$ transition and convolution with the $11H$ transition. However, the $11L$ transition has been observed many times for other QW systems,$^{38-40}$ especially compressively strained QWs. Thus, the $11L$ transition should be considered for GaNAsSb/GaAs QWs.

The procedure for correlating measured data with theory is described here. The QW transition energies were calculated as a function of $Q_C$ using the approach described in the Sec. III. These energies were then compared with those found from CER spectra using a plot shown in Fig. 3. Here, the experimental transition energies are shown as horizontal dashed lines while those calculated are shown as solid
curves. Using this method, the optimal match between theory and experiment can be determined by comparing the data with calculated energies. Note that the accuracy of $Q_C$ determination by this method is improved if additional QW transitions were observed, i.e., transitions related to excited states such as $22H$, $32H$, etc. Finally, we assumed that the $Q_C$ changes linearly with the rise in Sb composition, as it is shown in Fig. 4. It has been determined that $Q_C$ is 72% and 64% for GaN$_{0.02}$As$_{0.95}$Sb$_{0.03}$/GaAs and GaN$_{0.02}$As$_{0.92}$Sb$_{0.06}$/GaAs SQWs, respectively. Please note that in our calculations, we assume that the electron effective mass does not change with an increase in Sb concentration. This assumption can affect the conclusions relating to the $Q_C$ value. If an electron effective mass which is too small is assumed, the determined conduction band offset is also too small. It is suspected that this effect is important for SQW samples with 3% of Sb. The assumed electron effective mass ($0.09 m_0$) could be too low since the electron effective mass for the Sb-free SQW is higher than $0.09 m_0$ (see the discussion in Sec. III) and Refs. 23, 24, and 41 and the incorporation of only 3% of Sb has negligible influence on the electron effective mass. Thus for this SQW, we have performed calculations with larger electron effective mass in order to estimate the error associated with different electron effective masses. Note that the change in the electron effective mass among the samples cannot be too large because the total variation in Sb content is only 8%. In order to find a reasonable limit for the increase in the electron effective mass, we examined the GaAs$_{1-x}$Sb$_x$ alloy. The effective mass for this alloy has been calculated after Eq. (3) and has been found to increase from 0.062 $m_0$ to 0.066 $m_0$ (less than 7%) with Sb content from 11% to 3%. We then assumed the limit electron effective mass increase in the GaN$_{0.02}$As$_{0.98}$-Sb$_{0.02}$ alloy is similar (e.g., <10%). Figure 5 shows calculations performed for the SQW with 3% Sb for three different electron effective masses and various $Q_C$ together with experimental data (horizontal dashed line). The energy difference between the $22H$ and $11H$ transitions is shown because the curves relating to different electron effective masses are more visible on such a figure. The electron effective masses are larger by 6% ($0.005 m_0$) and 11% ($0.01 m_0$) than the previously assumed value. It is clearly visible that the conduction band offset rises with the increase in the electron effective mass. For electron effective masses which are larger by 6%, the conduction band offset is close to 70%. This value agrees very well with the trend in $Q_C$ shown in Fig. 4 by the thick line. It confirms the conclusion that the conduction band offset in GaNaSb/GaAs SQW decreases with an increase in Sb concentration.

The depth of the electron ($\Delta E^e_C$), light hole ($\Delta E^{LH}_V$), and heavy hole ($\Delta E^{HH}_V$) QWs obtained after the linear interpolation between $Q_C$ for Sb free and 11% Sb SQWs are shown in Fig. 6. For an increase in Sb composition from 0% to 11%, the depth of the hole QW increases by factor of ~5 (~200 meV) while the depth of the electron QW varies by less than 20% (~50 meV). In addition, the strain in the QW changes from tensile to compressive with an increase in Sb composition. The three samples shown in Fig. 2 correspond to tensile strained (3% Sb), nearly unstrained (6% Sb), and compressively strained (11% Sb) GaNaSb/GaAs SQWs.
INTERBAND TRANSITIONS IN

FIG. 6. Calculated variation of the electron $\Delta E_{c}^*$ light-hole $\Delta E_{LH}^*$, and heavy-hole $\Delta E_{v}^{HH}$ discontinuities for GaN$_{0.02}$As$_{0.98-x}$Sb$_x$/GaAs SQWs as a function of Sb composition.

However, for the three SQWs, the transition with the lowest energy is related to heavy hole due to the significant difference between heavy and light hole masses ($\sim 0.36 m_0$ vs $\sim 0.09 m_0$). For GaNAs/GaAs QWs, the transition related to the light hole is often not resolved in PR or CER spectra because its intensity is typically weaker than the intensity of the transition related to the heavy hole. However, as it has been shown for tensily strained GaNAs (Ref. 2) and GaNAsSb (Ref. 10) layers, the fundamental band gap is between the light hole and conduction bands. PR resonances related to the light hole are clearly observed despite the fact that its intensity is weaker than the intensity of the transition related to the heavy hole. Therefore, we conclude that the transition related to the light hole must be considered in our CER spectra. However, for the GaN$_{0.02}$As$_{0.98-x}$Sb$_x$/GaAs SQW with 3% Sb, a clear observation of two separate resonances related to 11$H$ and 11$L$ is impossible due to the convolution of the 11$H$ and 11$L$ transitions ($\sim 9$ meV) caused by broadening ($\sim 40–50$ meV) of the CER resonance. The 11$H$-11$L$ splitting increases with larger Sb content and a CER feature related to the 11$L$ transition is clearly resolved for GaN$_{0.02}$As$_{0.98-x}$Sb$_x$/GaAs SQWs with 6% and 11% of Sb atoms, as shown in Fig. 2.

In addition to normally allowed transitions, such as 11$H$, 11$L$, and 22$H$, nominally forbidden transitions could be important for our samples due to factors including (i) imperfections in the squarelike profile of the QW, (ii) a surface electric field or (iii) a mixing of hole wave functions leading to a nonzero overlap of electron and hole wave functions for such transitions as 21$H$. However, the overlap is rather small and the oscillator strength for the nominally forbidden transitions is much smaller than that of ones allowed. Therefore these transitions are neglected in our fit (except the 32$H$ transition for GaN$_{0.02}$As$_{0.98-x}$Sb$_{11}$/GaAs SQW). However, it should be stated that CER features associated with these transitions can interfere with CER resonances related to allowed transitions (21$H$ with 11$H$ and 12$H$ with 22$H$) because the energy separation between the first and the second heavy-hole levels is comparable to the broadening of the PR resonance ($\sim 45$ meV vs $\sim 40–80$ meV). The presence of weak CER features related to 21$H$, 31$H$, or 21$L$ could be a reason for the broadening of CER resonances related to the 11$H$ and 22$H$ transitions is quite large. If we neglected the 32$H$ transition and we fitted the spectrum from the 11% Sb QW with three resonances (similar to that of the QW with 6% Sb) we obtain the same energies for 11$H$ and 11$L$ transitions and different energy for the 22$H$ transition. In this case, we fitted the CER spectrum of the 11% Sb QW sample with four resonances. The introduction of the fourth resonance is fully justified because the rise of Sb content causes the band gap energy of GaNAsSb to decrease ($\sim 17$ meV per 1% of Sb). This leads to a redshift of the 11$H$ and 22$H$ transitions, as is seen in Fig. 2. In addition a third energy level appears for heavy holes and hence the 32$H$ transition appears between resonances related to 22$H$ and GaAs-related transitions.

CER measurements at low temperatures did not help to separate CER resonances in a significant manner. As it has been shown in Ref. 42, the broadening of QW transitions for a GaInNAs/GaAs SQW is very similar at 10 K and room temperature. Similar behavior has been observed for samples investigated in this article. This phenomenon is typical of III-V-N compounds and is associated with large alloy inhomogeneities for this material system. Finally, the low temperature CER (or PR) spectra of GaNAsSb/GaAs SQWs are comparable to CER (PR) spectra measured at room temperature. Therefore only room temperature CER spectra are analyzed in this article.

The observation of interband transitions related to excited states, such as 22$H$ or 32$H$, confirms that GaN$_{0.02}$As$_{0.98-x}$Sb$_x$/GaAs QWs with 0$<x$<0.11 are type I. An interesting observation in this material system is the large sensitivity of $Q_c$ to the Sb concentration. For SQWs shown in this article, we were able to tune the $Q_c$ from 80% to 50% with only an increase in Sb composition from 0% to 11%.

V. CONCLUSIONS

Interband transitions in GaN$_{0.02}$As$_{0.98-x}$Sb$_x$/GaAs SQWs with 0$<x$<0.11 have been investigated by CER spectroscopy. The ground 11$H$ and 11$L$ transitions and the excited state transitions such as 22$H$ and 32$H$ were observed in the CER spectra. The experimental QW transition energies were compared with theoretical predictions based on an effective mass formalism model. The $Q_c$ was varied to obtain a match between theory and measured data. It has been concluded that the $Q_c$ decreases from 80% to 50% with an increase in Sb content from 0% to 11%. It corresponds to an increase of the depth of the hole QW by factor of 5 ($\sim 200$ meV) and a variation of the depth of the electron QW is less than 20% ($\sim 50$ meV). These results demonstrate that the band gap discontinuity in the GaNAsSb/GaAs material system is very sensitive to Sb composition and can be simply tuned by a change in this composition.

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