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substrates

# Surface photovoltage spectroscopy characterization of InGaPN alloys grown on GaP substrates

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**Abstract**
$In_{0.176}Ga_{0.824}P_{1-y}N_y$ ($y = 1.5\%$–8.7%) alloys grown on GaP(001) substrates via metalorganic vapour phase epitaxy were characterized by surface photovoltage spectroscopy (SPS) in the temperature range between 125 and 400 K. The band gap energies are determined and their temperature dependences are analysed by Varshni and Bose–Einstein expressions. The parameters that describe the temperature variations of the band gap energies are evaluated and discussed. The surface photovoltage spectra also revealed that a transition from indirect to direct band gap is taking place for the N-incorporated samples and the quadratic correction for the band gap bowing is only applicable for low nitrogen containing samples.

## 1. Introduction

Due to the huge band gap bowing, common in the III–(III)–V–N-type alloys [1–4], $In_xGa_{1-x}P_{1-y}N_y$ is of great interest for well materials with a large barrier height for electron confinement in lattice-matched InGaPN/GaP quantum wells (QWs) [5]. The incorporation of N into the highly compressive-strained InGaP system results in a reduction of its lattice constant, thus reducing the strain in the InGaPN layer grown on the GaP substrate. The InGaPN alloy is an alternative to the GaPAsN alloy that yields high-optical-quality QWs with the lattice-matched GaPAsN/GaP heterostructure [6]. Despite its scientific interesting, to date, only a few relevant research reports have been published [7–9]. Additionally, most studies have

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employed photoluminescence (PL) spectra at low temperature; therefore, most of the electro-optical properties that have been examined have been limited to low temperatures. Detailed studies of the electro-optical characteristics at room temperature and higher temperatures are not only interesting but also necessary and important.

In this study, surface photovoltage spectroscopy (SPS) was used to characterize the $In_{0.176}Ga_{0.824}P_{1-y}N_y$ ($y = 1.5\%$–$8.7\%$) alloys grown on GaP(001) substrates by metalorganic vapour phase epitaxy (MOVPE). The photovoltage is mainly generated in the space-charge region at the surface. The SPS characterization was made in the temperature range from 125 to 400 K. The band gap energies are determined and their temperature dependences are analysed by the Varshni expression [10] and an expression containing the Bose–Einstein occupation factor for phonons [11, 12]. The parameters that describe the temperature variations of the band gap energies are evaluated and discussed.

## 2. Experimental details

Four $In_{0.176}Ga_{0.824}P_{1-y}N_y$ ($y = 1.5\%$–$8.7\%$) alloy films were grown on GaP(001) substrates by low-pressure (60 Torr) MOVPE. Trimethylgallium (TMG), trimethylindium (TMI), $PH_3$ and dimethylhydrazine (DMHy) were used as the source materials. After growth of a 0.3 $\mu$m-thick GaP buffer layer at 710 °C, a 0.3 $\mu$m-thick InGaPN epitaxial layer was deposited at 635 °C. The growth rate was around 1.0 $\mu$m h$^{-1}$. Films with various nitrogen concentrations were obtained by changing the molar flow ratio of DMHy to the total group V elements (DMHy + $PH_3$). The alloy compositions were determined from high-resolution x-ray diffraction and secondary ion mass spectroscopy data. For comparison purposes, an $In_{0.176}Ga_{0.824}P$/GaP sample without nitrogen was also grown and characterized.

In SPS measurement, the contact potential difference between the sample and a reference grid electrode is measured in a capacitive manner as a function of the photon energy of the probe beam by holding the grid fixed and chopping the probe beam at 200 Hz [13]. The light from a 150 W quartz–halogen lamp was passed through a PTI 0.25 m grating monochromator and focused onto the samples. It is known that, under low optical excitation, the photovoltage ($PV$) signal is proportional to the absorption coefficient $\alpha$ multiplied by the photon flux density $\Phi$ ($PV \propto \alpha\Phi$) [14, 15]. To verify that the measurements were performed under low optical excitation, the amplitude of the photovoltage near peak position was checked with various light intensities $I$ between $5 \times 10^{-6}$ and $5 \times 10^{-4}$ W cm$^{-2}$. The results indicate that, for $I \leqslant 3 \times 10^{-4}$ W cm$^{-2}$, $PV$ varies linearly with incident light intensity. Subsequently, incident light intensity maintained at a constant level of $\sim 10^{-4}$ W cm$^{-2}$ was used for the study. A beam splitter was placed in the path of the incident light. The intensity of this radiation was monitored by a power meter and was kept constant by a stepping motor connected to a variable neutral density filter placed in the path of the incident beam. The photovoltage spectrum on the metal grid was measured with a copper plate as the ground electrode, using a buffer circuit and a lock-in amplifier. A CTI model 22 closed-cycle cryogenic refrigeration system equipped with a model 32B digital temperature controller was used for low-temperature measurements. For the high-temperature experiments, each sample was mounted on one side of a copper finger of an electric heater, which enabled one to control and stabilize the sample temperature. The measurements were made with a temperature stability of 0.5 K or better.

## 3. Results and discussion

Figure 1 shows the room-temperature surface photovoltage (SPV) spectra for five $In_{0.176}Ga_{0.824}P_{1-y}N_y$ samples with various nitrogen compositions of $y = 0$, 1.5%, 2.3%, 7.4%,

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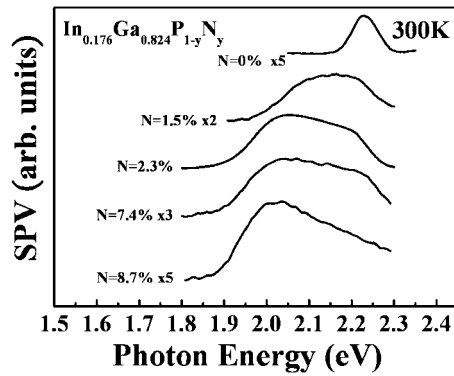
**Figure 1.** Surface photovoltage spectra for five $In_{0.176}Ga_{0.824}P_{1-y}N_y$ samples with various nitrogen compositions $y = 0\%$, 1.5%, 2.3%, 7.4%, and 8.7%, measured at room temperature.

and 8.7%. As described earlier in the experimental section, under low optical excitation the photovoltage signal $PV$ is proportional to the absorption coefficient $\alpha$ multiplied by the photon flux density $\Phi$ ($PV \propto \alpha\Phi$) [14, 15]. The latter is equal to the light intensity $I$ divided by the photon energy $E$: $\Phi = I/E$. Thus, by keeping $I$ constant, one has $PVE \propto \alpha$. It has been reported that the band structure of $In_xGa_{1-x}P$ with indium composition $x < 0.27$ is indirect [16] and we therefore analysed the SPS spectrum for the $y = 0$ sample using the relation $(PVE)^{1/2}$ versus $E$. The band gap energy can be obtained by extrapolating the linear part of the plot $(PVE)^{1/2}$ versus $E$ to zero. As shown in figure 2(a), the fit using $(PVE)^{1/2}$ versus $E$ yields a satisfactory result which agrees well with the indirect band gap character of $In_xGa_{1-x}P$ with indium composition $x < 0.27$. The indirect band gap is determined to be $2.147 \pm 0.03$ eV. On the other hand, the N-containing samples exhibited direct band gap character and the SPV spectra are depicted in figure 2(b). The SPV spectra that were obtained were fitted well using the relation $(PVE)^2$ versus $E$, which is the characteristic of a direct band structure. The obtained band gap energy values of $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloys at room temperature are $2.002 \pm 0.025$, $1.935 \pm 0.025$, $1.922 \pm 0.025$, and $1.900 \pm 0.025$ eV for samples with nitrogen content of $y = 1.5\%$, 2.3%, 7.4%, and 8.7%, respectively. The use of SPS for the extraction of $E_g$ is, at heart, nothing more than an emulation of an absorption spectrum. However, as opposed to transmission spectroscopy, for example, SPS does not require light collection and therefore can be performed on arbitrarily thick samples and does not require the sample to be removed from the substrate. One must bear in mind that the obtained value of $E_g$ is only approximate.

The results indicate that incorporation of small amounts of N into $In_{0.176}Ga_{0.824}P$ changes the nature of the fundamental optical transition from an indirect-gap transition in $In_{0.176}Ga_{0.824}P$ to a direct-gap transition in $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloys. This finding is quite similar to the previous report on GaPN alloys [17] where N-induced transformation from indirect to direct gap has been explained in terms of the band anticrossing model.

A plot of energy band gap versus N concentration, obtained from room-temperature SPS measurements, for the $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloys system is displayed in figure 3. For comparison purposes, the low-temperature (10 K) PL peak energy positions [7] are also depicted in figure 3. As shown in figure 3, by increasing the N concentration from $y = 0$ to 2.3% the energy gap red-shifts by 208 meV, corresponding to a 340 meV red-shift of the PL peak. With a further increase in the N concentration, the red-shift of the band gap slows down dramatically. It is well known that the incorporation of a small amount of nitrogen in
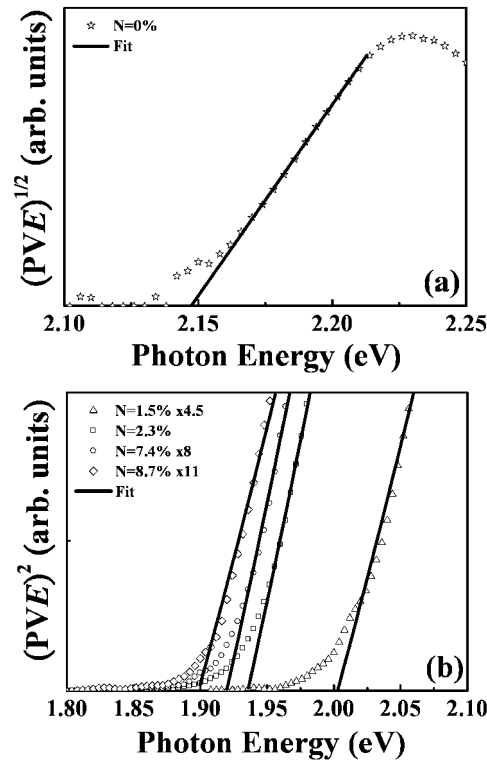
**Figure 2.** Spectral dependence of $PV$ for the $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloys with (a) $y = 0\%$ displayed in coordinates $(PVE)^{1/2}$ versus $E$, (b) $y = 1.5\%$, 2.3%, 7.4%, and 8.7% plotted in coordinates $(PVE)^2$ versus $E$.
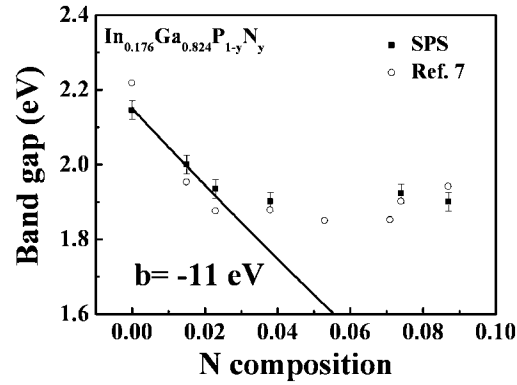


**Figure 3.** Band gap energy of $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloys as a function of nitrogen composition $y$. The solid line is the result fitted by the quadratic correction $\Delta E_g(x) = bx(x - 1)$ in the range 0–2.3%. For comparison purposes, the low-temperature (10 K) PL peak energy positions taken from [7] are also shown.

III–V semiconductors such as InP [18], GaAs [19] and GaP [20] results in a strong reduction of the band gap in those materials. This behaviour is usually described well by the quadratic correction $\Delta E_g(x) = bx(x - 1)$, with $b$ being the bowing coefficient. The obtained bowing
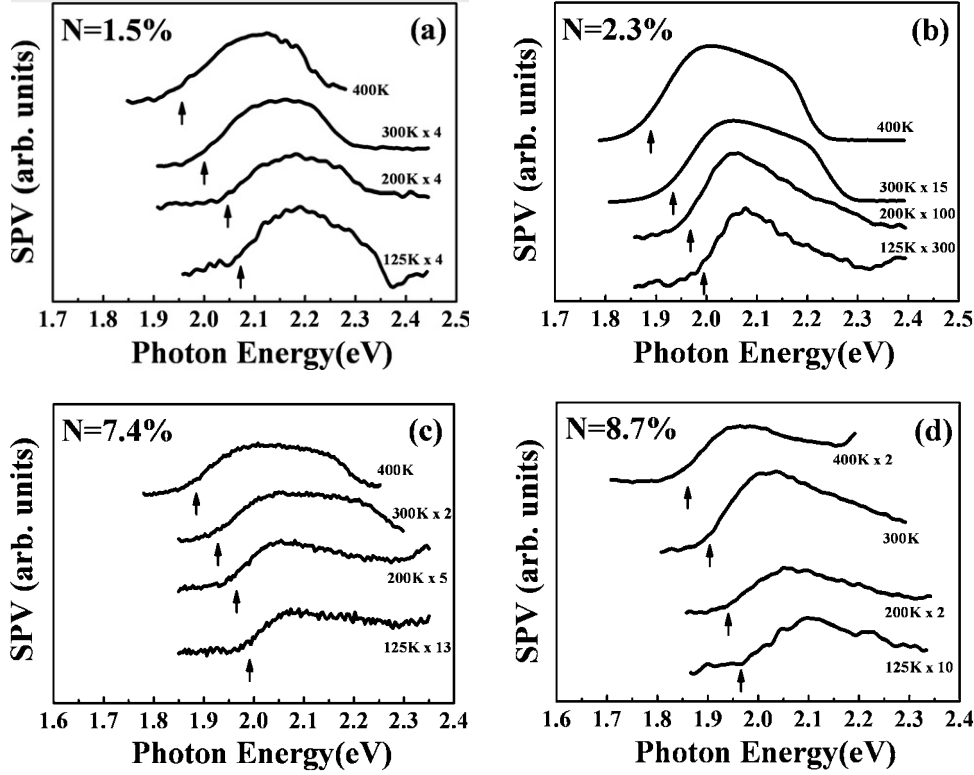
**Figure 4.** SPV spectra for four investigated $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloys: (a) 1.5%, (b) 2.3%, (c) 7.4%, and (d) 8.7%, at 125, 200, 300, and 400 K, respectively. The fitted band gap energy positions are indicated by arrows.

coefficient $b = -11 \pm 1$ eV for $y = 0$–2.3% is found to be smaller than the corresponding values associated with the incorporation of nitrogen in InP ($b = -16$ eV) [18] or GaP ($b = -14$ eV) [20]. For higher nitrogen content, it is noted that the quadratic correction by $\Delta E_g(x) = bx(x - 1)$ is rather poor for our present experimental study. The poor agreement is not too surprising, as the quadratic model predicts a continuing increase in the red-shift, whereas the experimental evidence points to a saturation of the band gap bowing. It seems that for high nitrogen content, correction with a quadratic relationship, with the bowing parameter $b$ being a constant, is over-simplified. The present study seems to indicate a nitrogen-concentration-dependent bowing effect [21]. Further study has been underway to include a more complete collection of N-containing InGaP materials to investigate the effect.

Displayed in figures 4(a)–(d) are the experimental SPV spectra of samples with nitrogen content $y = 1.5\%$, 2.3%, 7.4%, and 8.7% at several temperatures between 125 and 400 K. The fitted band gap energy values are indicated by the arrows. As is the case for general semiconductor properties, the band gap energies of $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloys show a red-shift with an increase in temperature. Figure 5 shows the temperature dependence of band gap energies $E_g(T)$ determined from SPS measurements for samples with nitrogen contents $y = 1.5\%$, 2.3%, 7.4%, and 8.7%. The solid lines are the least-squares fits to the Varshni semi-emprical relationship [10]:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T}, \tag{1}$$
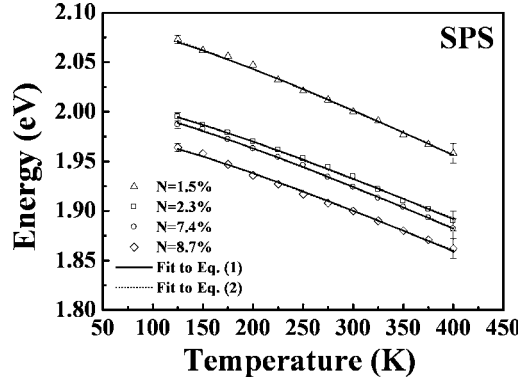
**Figure 5.** The temperature variations of the band gap energies for (a) 1.5%, (b) 2.3%, (c) 7.4%, and (d) 8.7%, with representative error bars. The solid curves are least-squares fits to the Varshni semi-empirical relationship and dotted curves are fitted to the Bose–Einstein-type expression.

**Table 1.** Values of the Varshni- and Bose–Einstein-type fitting parameters, which describe the temperature dependence of the band gap of $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloys grown on GaP, InGaPN films grown on GaAs, GaAs, GaAsN, GaP and GaPN films grown on GaP.

| Samples | $E_g(0)$ (eV) | $\alpha$ (meV K$^{-1}$) | $\beta$ (K) | $a_B$ (meV) | $\Theta_B$ (K) | $dE_g/dT$ (meV K$^{-1}$) |
|---|---|---|---|---|---|---|
| $In_{0.176}Ga_{0.824}P_{0.985}N_{0.015}/GaP$[a] | $2.092 \pm 0.005$ | $0.51 \pm 0.05$ | $200 \pm 50$ | $56 \pm 10$ | $250 \pm 50$ | $-0.44$ |
| $In_{0.176}Ga_{0.824}P_{0.977}N_{0.023}/GaP$[a] | $2.014 \pm 0.005$ | $0.48 \pm 0.05$ | $200 \pm 50$ | $53 \pm 10$ | $250 \pm 50$ | $-0.40$ |
| $In_{0.176}Ga_{0.824}P_{0.926}N_{0.074}/GaP$[a] | $2.008 \pm 0.005$ | $0.47 \pm 0.05$ | $200 \pm 50$ | $52 \pm 10$ | $250 \pm 50$ | $-0.40$ |
| $In_{0.176}Ga_{0.824}P_{0.913}N_{0.087}/GaP$[a] | $1.982 \pm 0.005$ | $0.46 \pm 0.05$ | $200 \pm 50$ | $51 \pm 10$ | $250 \pm 50$ | $-0.37$ |
| $In_{0.46}Ga_{0.54}P_{0.995}N_{0.005}/GaAs$[b] | $1.862$ | $0.51$ | $255$ | $53$ | $250$ | $-0.38$ |
| $In_{0.46}Ga_{0.54}P_{0.99}N_{0.01}/GaAs$[b] | $1.825$ | $0.49$ | $255$ | $53$ | $250$ | $-0.37$ |
| GaAs[c] | $1.522$ | $0.58$ | $300$ | | | $-0.50$ |
| $GaAs_{0.9703}N_{0.0297}$[d] | $1.154$ | $0.61$ | $560$ | | | $-0.31$ |
| GaP[c] | $2.338$ | $0.62$ | $460$ | | | $-0.53$ |
| $GaP_{0.919}N_{0.081}$[e] | $2.870$ | $0.54$ | $460$ | | | |

[a] This work.
[b] Reference [22].
[c] Reference [23].
[d] Reference [24].
[e] Reference [25].

where $E_g(0)$ is the band gap energy at 0 K. The constant $\alpha$ is related to the electron (exciton)–average phonon interaction strength and $\beta$ is closely related to the Debye temperature. The obtained values of $E_g(0)$, $\alpha$ and $\beta$ for samples with nitrogen content of $y = 1.5\%$, 2.3%, 7.4%, and 8.7% are listed in table 1. We have also fitted the experimental data to a Bose–Einstein expression [11, 12]:

$$E_g(T) = E_g(0) - \frac{2a_B}{[\exp(\Theta_B/T) - 1]}, \tag{2}$$

where $E_g(0)$ is the band gap energy at 0 K, $a_B$ represents the strength of the electron (exciton)–average phonon interaction, and $\Theta_B$ corresponds to the average phonon temperature. Shown by the dotted lines in figure 5 are least-squares fits to equation (2). The obtained values for the various parameters are also given in table 1. For comparison purposes, the parameters for the band gap energies of InGaPN films grown on GaAs substrates [22], GaAs [23], GaAsN [24], GaP [23], and GaPN [25] films are also listed in table 1.

The parameter $\alpha$ of equation (1) can be related to $a_B$ and $\Theta_B$ in equation (2) by taking the high-temperature limit of both expressions. This yields $\alpha = 2a_B/\Theta_B$. Comparison of the numbers presented in table 1 shows that this relation is indeed satisfied. From equation (2), it is straightforward to show that the high-temperature limit of the slope of the $E_g(T)$ versus $T$ curve approaches a value of $-2a_B/\Theta_B$. The calculated value of $-2a_B/\Theta_B$ for band gap energy equals $-0.45$, $-0.42$, $-0.42$, and $-0.41$ meV K$^{-1}$ for samples with nitrogen content of $y = 1.5\%$, 2.3%, 7.4%, and 8.7% respectively, which agrees well with the values of $[\mathrm{d}E_g/\mathrm{d}T] = -0.44$, $-0.40$, $-0.40$ and $-0.37$ meV K$^{-1}$, as obtained from the linear extrapolation of the high-temperature (200–400 K) SPS experimental data.

As shown in table 1, the parameters that describe the temperature variations of the band gap energies of $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloys are quite similar to those of InGaPN films grown on GaAs substrates. The values of $\alpha$ and $\mathrm{d}E_g/\mathrm{d}T$ for $In_{0.176}Ga_{0.824}P_{1-y}N_y$ are smaller than that of GaP films. The results are similar to the GaAsN and GaAs compound systems, where the temperature-induced shift of the band gap energy in GaAsN is also substantially reduced by the presence of N in GaAs [24].

## 4. Summary

We have characterized four $In_{0.176}Ga_{0.824}P_{1-y}N_y$ ($y = 1.5\%$–8.7%) alloys grown on GaP(001) substrates via metalorganic vapour phase epitaxy using the SPS technique. The band gap transition energies of $In_{0.176}Ga_{0.824}P_{1-y}N_y$ ($y = 1.5\%$–8.7%) alloys are determined by fitting the SPV spectra. The results indicate that the incorporation of small amounts of N into $In_{0.176}Ga_{0.824}P$ changes the nature of the fundamental optical transition from an indirect-gap transition in $In_{0.176}Ga_{0.824}P$ to a direct-gap transition in $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloys. This finding is quite similar to the previous reports on GaPN alloys, where there is an N-induced transformation from indirect to direct band gap. Our results also indicate a nitrogen-concentration-dependent band gap bowing effect for these materials. The parameters that describe the temperature dependences of $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloys are similar to those of InGaPN films grown on GaAs substrates and smaller than that of GaP. This has been attributed to the incorporation of nitrogen into the InGaPN alloys.

## Acknowledgment

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