

Si-interdiffusion in heavily doped AlN-GaN-based quantum well intersubband photodetectors

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We demonstrate the effect of rapid thermal annealing on heavily Si-doped AlN/GaN quantum wells. After 1000 °C annealing during 5, 10, and 20 min, the dominant effect was interdiffusion of Si rather than intermixing between the Al and Ga atoms. Both their original value and the magnitude of the changes after annealing reveal that intersubband absorption and photovoltage are related to two different optical transitions as follows: absorption occurs in the 1 to 2 intersubband transition, whereas photovoltage is due to a subsequent process from the 1 to 2 and the manifold of 2 to higher order transitions.

Impurity interdiffusion and quantum well (QW) intermixing are two versatile techniques which have seen widespread use in many semiconductor based technologies. They are used for the fabrication of high quality stripe lasers,^{1,2} nonabsorbing mirror sections of Fabry–Perot lasers,³ and also for the fabrication of photonic integrated circuits.^{4–6} Many different semiconductors have shown similar effects with specific temperatures for each material system, be it GaAs/AlGaAs, GaP/InGaAsP, or even GaN/InGaN. In the early days, most experiments were performed on GaAs/AlGaAs-based superlattices (SLs).^{7,8} The heavy Si-doping led not only to diffusion of the impurity atoms into the non-doped areas, but also to an intermixing of atoms in the barrier and well materials. Pioneering work was performed in the mid-1980s by Holonyak and co-workers who investigated many different configurations of SLs and dopings. In the early 1990s, Marsh looked at several techniques to establish intermixing at certain sections of a stripe laser.³ Some of this work was taken over by groups at the XEROX Palo Alto Research Center (USA) (Ref. 1) and the Paul Scherrer Institute (Switzerland).^{4–6} The former institution fabricated side-by-side laser diodes with quaternary cladding and QW layers, while at the latter, fabrication of GaAs/AlGaAs-based photonic integrated circuits forming a double Michelson interferometer was realized. In the late nineties, McCluskey succeeded in the complete intermixing of p-doped InGaN/GaN QWs at very high temperatures of 1300 to 1400 °C.⁹ Finally, Wierer *et al.*¹⁰ at Sandia National Laboratories found in 2010 that intermixing of heavily n-doped metalorganic vapor phase epitaxy (MOVPE) AlN/GaN material could already take place at 1000 °C. However, in contrast to Hofstetter *et al.*,¹¹ they measured absorption curves only, and they did not investigate electrically active material. In this letter, we report a systematic study of heavily Si-doped AlN/GaN-based SLs which were subject to anneals at 1000 °C for 0, 5, 10, and 20 min. Interestingly, no intermixing at the interfaces was found, whereas interdiffusion of Si seemed to be quite heavy already at these relatively low temperatures.

Its effect on the intersubband (ISB) absorption and photovoltage is discussed.

For the fabrication of these devices, we deposited a 40 period SL with 15 nm thick undoped AlN barrier layers and 1.5 nm thick heavily n-doped ($[Si]=5 \times 10^{19} \text{ cm}^{-3}$) GaN QWs on 1 μm thick AlN-on-sapphire templates using plasma-assisted molecular beam epitaxy (MBE).¹² The growth was performed at intentionally low substrate temperature (720 °C) in order to achieve AlN/GaN interfaces which were as sharp as possible. Nevertheless, a small amount of quantum dot like localization cannot be completely ruled out. The sample was cut into four smaller pieces, which were all characterized in the same way. We polished the back and two parallel 45° facets, so that each sample formed a multipass waveguide. The distance between the two parallel facets was held at exactly 2 mm while the rectangular sample was roughly 10 mm long. For photovoltage measurements, we added two parallel metal stripes of $2 \times 0.8 \text{ mm}^2$ which ran from facet to facet. Details on the photovoltage fabrication and measurements can be found elsewhere.¹² A simulation of the conduction band structure using the software “calculeband” (developed by the University of Neuchâtel) showed that it consisted of isolated states rather than minibands [see calculated wave functions in Fig. 1 (left)]. The annealing of the samples was performed in a hydride vapor phase epitaxy (HVPE) reactor under NH_3 atmosphere at 1000 mbar pressure. The rise time from 850 to 1000 °C was 5 min, and the fall time from 1000 to 850 °C was 10 min. This procedure gave a certain transient error which resulted in an apparent 1 min shortening of all annealing times.

ISB transmission measurements were performed using a Fourier transform infrared spectrometer. The measured spectra were normalized by a white light reference spectrum. Typical transmission measurements after annealing are shown in Fig. 2, where all the spectra have been normalized to 1. The 1 to 2 transition at 6200 cm^{-1} is always visible but gets weaker as the annealing time gets more prolonged. The small shoulder at higher energy, around 7200 cm^{-1} , is assigned to a manifold of transitions involving states 2 as well

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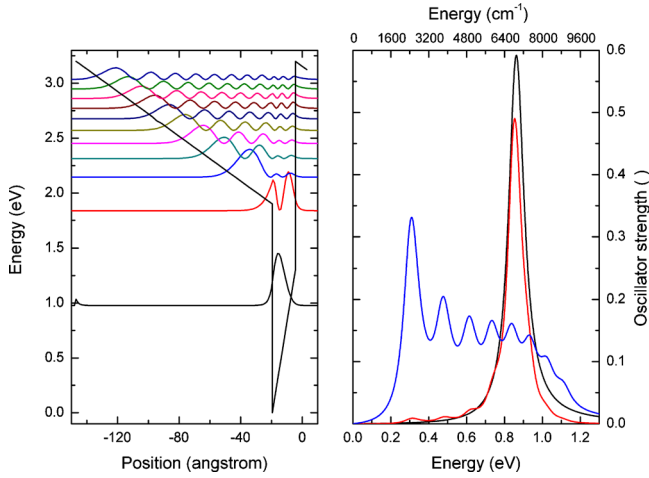


FIG. 1. (Color online) (Left) Schematic conduction band diagram with the different states of the sample having a 15 Å QW and 150 Å barriers. (Right) Absorption curves of the lowest (transition 1 to 2, black, singlepeaked response) and the next higher transition (manifold of states 2 to 3, 2 to 4, 2 to 5, etc., blue, multi-peaked structure). The absorption probability of the product is shown as red curve, and it peaks at 3×10^6 cm²/GW which agrees well to the experimental value.

as 3, 4, 5, etc. It starts to disappear already after 5 min annealing, and it is completely gone after 10 min.

The main (1 to 2) absorption drops from 63% at 0 min to 17% at 20 min, which corresponds to an absorbance going down from $\alpha L=1$ at 0 min to $\alpha L=0.16$ at 20 min. The fact that almost no change in position (per inverse centimeter) was seen even after 20 min of annealing indicates that the AlN/GaN interfaces remain unchanged, i.e., the AlN/GaN interdiffusion is negligible, which is consistent with McCluskey's result.⁹ Although they worked with p-doped and not n-doped material and GaN/InGaN instead of AlN/GaN, they could only observe strong intermixing after 15 min at 1300 °C. In contrast to Wierer's results¹⁰ (MOVPE material), our MBE-grown QWs have sharp QW/barrier interfaces,¹² which did not allow any intermixing at moderate temperatures like 1000 °C. However, strong interdiffusion of Si donors is responsible for the weakening of the absorption after 20 min of annealing. Under the action of the heating, the Si atoms which were initially located in the QWs only, get distributed among the entire period; including the barrier layers. Assuming that the Si atoms were not active as donors in the barrier layers, they can in this case occupy 15 nm instead of only 1.5 nm per period.

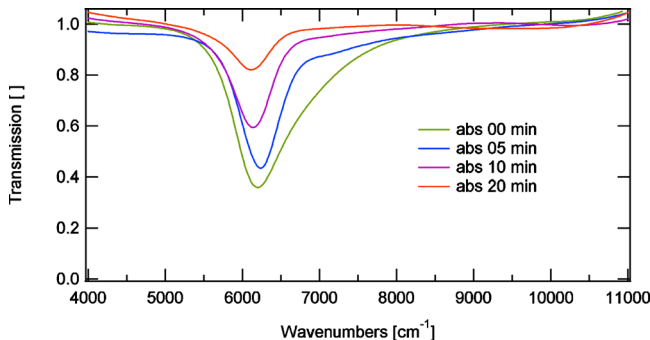


FIG. 2. (Color online) Optical transmission of the reference and the three intermixed samples. The strong absorption signal at 6200 cm⁻¹ is due to the 1 to 2 ISB transition while the 7200 cm⁻¹ shoulder is due to multiple ISB transitions.

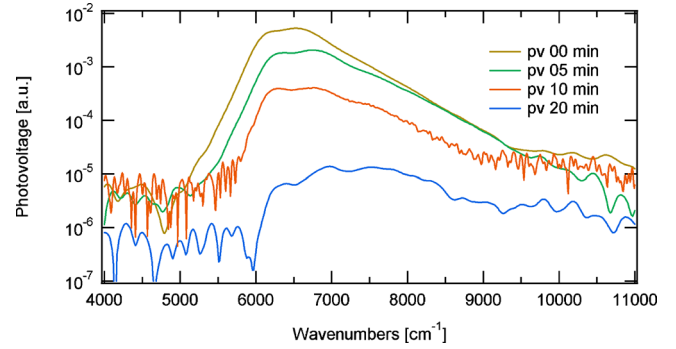


FIG. 3. (Color online) Photovoltage signals for the reference and the three intermixed samples. The peaks due to the different ISB transitions are clearly visible.

Figure 3 shows the room temperature ISB photovoltage spectra for the four different annealing conditions. This figure contains several evidences that the photovoltage is originated by a different transition than the absorption. First, the peak wave number of the photovoltage is rather high: between 6500 and 7000 cm⁻¹ instead of the 6200 cm⁻¹ of the absorption. Then, we see a pronounced multipeak feature, especially after 10 min of intermixing, which is related to the multiple absorption structure of the sample. We explain the observed effects as follows: All visible photovoltage structures are due to two photon resonance (product) between the 1 to 2 ISB transition at 6200 cm⁻¹ and the manifold between ISB peak 2 and 6 (5800 cm⁻¹), peak 1 and 2 (6200 cm⁻¹), peak 2 and 7 (6800 cm⁻¹), peak 2 and 8 (7600 cm⁻¹), etc. These noncoherent two photon resonances have been described before both theoretically and experimentally.¹³ They are also visible in the computed theoretical absorption curves in Fig. 1 (right). It is important to notice that the resonance condition between the 1 to 2 ISB transition and ISB peak 2 to manifold can always be maintained: in the latter, the peaks are spaced densely enough to pick the one with the best product between overlap and lateral displacement. One of the signatures of such resonances is an exponential behavior of the photovoltage signal strength with the number of carriers. Also if we look at the evolution of the photovoltage spectrum as a function of annealing, the lower order transitions (like 2 to 6 or 1 to 2) in photovoltage measurements disappear faster at long annealing times than the higher order transitions (like 2 to 7 or 2 to 8). This is consistent with the larger electron displacements of higher order transitions. The computed two photon absorption strength of the most prominent of these simulated transitions is 3×10^6 cm²/GW, which is close to the observed value.

In order to even better understand the carrier distribution between the first and the second ISB states, we present in Fig. 4, a plot with the peak absorbance and photovoltage as a function of the annealing time. Based on the simple theory that the occupation of the second ISB state is thermally activated by the energy difference between the two lowest states, we get

$$S_1/S_2 = \exp[N_1/N_2],$$

where S_1 and S_2 are the respective signal levels of the photovoltage, and N_1 and N_2 the carrier concentrations relevant for the absorption. We notice that the two curves agree well, as shown in Fig. 4. The absorbance and the logarithm of the photovoltage dropped by exactly the same amount, namely,

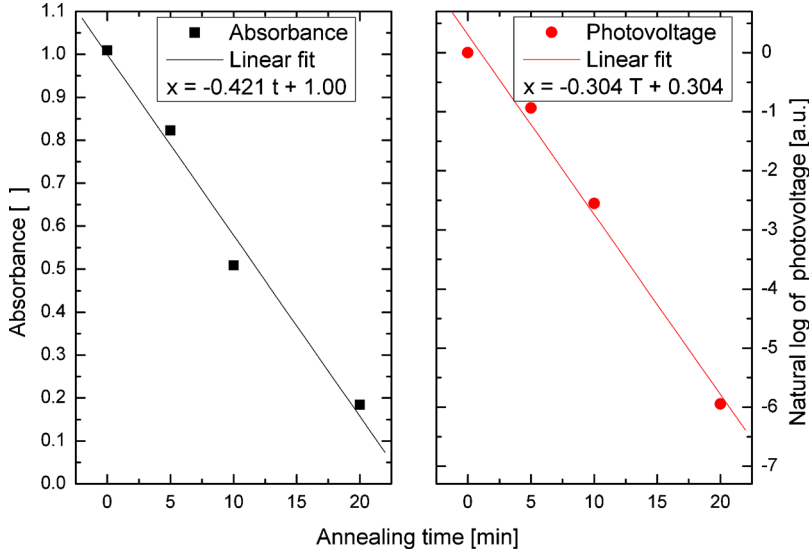


FIG. 4. (Color online) Comparison between absorbance out of the first ISB state and photovoltage out of the second ISB state. The very similar evolution of the two signals indicates that identical electron concentrations are involved in the two processes.

by a factor of 6 (or exactly a factor of 400 in photovoltage) when comparing the reference sample and the 20 min annealed sample. Having a linear relation in absorption and an exponential relation in photovoltage is by itself already an important indication for the different involved mechanisms of the two processes. The fact that they take place at slightly different energies strengthens this argument even further. From the absolute amount of absorption seen in the reference sample, we are also able to compute the amount of dopants present. We found a reference value of $7 \times 10^{19} \text{ cm}^{-3}$ which is in reasonable agreement to the nominal value. Based on the observation that a certain amount of quantum dotlike localization is nevertheless present in this sample, it is easily understandable that the second state is thermally occupied. Given the numbers, we conclude that at 0 K, the Fermi energy lies roughly 100 meV below the second state which is consistent with the observations in Fig. 4.

As illustrated by the two curves in Fig. 4, the absorbance and the logarithmic photovoltage have the same evolution. This is expected because the absorbance measures the carrier concentration above the first energy state, whereas the photovoltage is sensitive to the number of carriers in the second state. An exponential law governs the number of carriers in the second state when the concentration in the first one is known, and the relative distribution between the two energies remains constant. An interesting detail is the slight saturation effect at 0 min annealing time. As explained above, this is due to the time transients during the heating and cooling phase of the HVPE reactor.

In conclusion, we reported Si-interdiffusion in heavily doped AlN/GaN-based SLs by annealing at 1000 °C in NH_3 atmosphere. After 20 min annealing, there is no evidence of intermixing between the Al and Ga atoms. From ISB absorption and photovoltage measurements, we conclude that absorption and photovoltage involve different transitions.

While absorption probes the fundamental 1 to 2 ISB transition, the photovoltage is measured mainly on a manifold of ISB transition from 2 to higher states. As a result, only samples with a heavy enough doping and resonance between the three involved states, show photovoltage.

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