Optimization of (In)GaN Heterostructures for Sensing Applications

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Herein, the optimization of (In)GaN heterostructures for chemical sensing is presented. The metalorganic vapor phase epitaxy (MOVPE)-grown sensor consists of an In$_x$Ga$_{1-x}$N quantum well (QW) placed close to the surface of a GaN substrate with a thin GaN cap layer on top. The photoluminescence (PL) wavelength of this QW is sensitive to surface potential changes and thus its optical signal is used as sensor response. Simulations are performed with nextnano to improve its sensitivity. Sensor parameters such as the cap layer thickness $d$, QW thickness $L_z$, background buffer layer doping concentration $N$, and indium concentration $x$ of the QW are varied. It is found that a thin cap layer, together with high background doping and medium QW thickness, is ideal. The indium content does not show a strong influence on sensitivity. The trends found in the simulations are mostly confirmed in real-world experiments performed in a chemical sensing setup, yet quantitative deviations exist.

1. Introduction

For many years, III-nitrides have attracted strong research interest and already found their application in devices such as visible and UV light-emitting diodes (LEDs), laser diodes, and high-power electronics.[1,2] The extraordinary chemical stability of GaN has led to interesting applications in aggressive environments, such as corrosive, high-temperature, or biological environments.[3–5] Among others, our group has focused on possible sensing applications of GaN and its ternary alloy InGaN.[6–9]

The surface potential of a semiconductor is reactive to material that may be adsorbed chemically or physically on the surface. In our studies, we focus on the reversible adsorption of molecules on the surface of an (In)GaN heterostructure to use the change in surface potential to get quantitative information on the amount of molecules adsorbed. The underlying process is the quantum confined Stark effect (QCSE): An internal electric field in a quantum well (QW) leads to an inclination of the conduction and valence band edges and thus to a reduced effective bandgap (see also Figure 1). The surface potential influences the near-surface band bending of the semiconductor, which ranges deeper (up to a few 100 nm) into the material. The resulting electrical field induces a change of the QCSE within the QW, and the resulting shift in PL emission can be used as a sensor signal. In other simulations we showed[10] that the energy shift $\Delta E$ increases with higher electric fields within the QW (Figure 2). Therefore, we benefit by using polar InGaN QWs for sensing as they inherently exhibit a piezoelectric bias.

The wavelength shift depends on structural parameters, such as the QW position within the sensor (cap layer thickness $d$), the QW thickness $L_z$, or its indium content $x$. Moreover, the band bending, which directly influences the internal field in the QW, is altered by the background doping $N$ within the semiconductor. The amount of wavelength shift per amount of adsorbate on the device is called the sensitivity.

To save experimental effort and cost, a 1D model of the sensor was built within nextnano,[11] a commercially available semiconductor device simulation tool. Nextnano performs a recursive calculation of Poisson’s and Schrödinger’s equation to receive a static model of the sensor structure (see example in Figure 1, left, middle). The static solution then gives the localized wavefunctions for electrons $|\psi_e\rangle$ and holes $|\psi_h\rangle$ within the QW and their energy levels $E_e$ and $E_h$. Nextnano then is used to output all possible transition energies $\Delta E = E_e - E_h$.

The sensor surface was defined as a Schottky barrier with variable barrier height $\Phi_B$. Different groups found the value of $\Phi_B$ to be around 0.7 eV for GaN.[12–14] Following the results of Lian and Xing,[15] we suggest that our structures undergo a surface potential reduction of 0.2 to 0.5 eV upon laser excitation in our sensing experiments. To simulate the adsorption of molecules on the sensor surface, we reduce $\Phi_B$ by an additional 0.4 eV down to 0.1 eV. This induces a reduction in the effective recombination energy of the electron and hole wavefunctions, which in turn leads to a redshift in PL. The surface shift value from 0.5 to...
0.1 eV proved to give wavelength redshifts similar to experimentally observed shifts for deionized water and isopropanol. For the model of the sensor, a 2 μm GaN layer was assumed, which can be considered infinitely thick and unstrained for the sake of calculations. An InₓGa₁₋ₓN QW with a thickness Lz and indium content x was placed close to the surface of the device covered with a GaN cap layer of thickness d (see Figure 1, top left).

With our metalorganic vapor phase epitaxy (MOVPE) process in mind, where a constant doping for different growth conditions (buffer, QW, cap layer) is not easy to maintain, we assumed in our simulation that only the GaN buffer is doped, but that some diffusion of the Si atoms takes place into the QW and cap layers. Lin et al. observed Si diffusion up to 150 nm into their GaN layers upon thermal annealing from temperatures of 800–1000 °C for 2 h.[15] Even though our temperatures for QW and cap layer growth are at the lower end (≈800–820 °C), we still assume a substantial diffusion of Si into our top layers, as they are quite thin (10–32 nm). For simplicity, we introduced a linear decay of the Si concentration from the ending point of doping up to the sensor surface from the original doping concentration N down to 0, respectively.

The aforementioned structure parameters were varied in a multidimensional approach, where parameter boundaries were chosen within reasonable limits. The amount of wavelength shift was then analyzed as a function of the varied parameters.

### 2. Simulations by Nextnano

The first parameter to be varied in the simulations was the cap layer thickness d. The closer the QW is located to the surface, the stronger the interaction should be. Figure 3 shows several series of cap layer variations with different background doping levels. As expected, the trend shows a clear favor for thin cap layers, particularly for high doping concentrations around...
The sensitivity does not change much with cap layer thickness at low doping concentrations. This is a direct consequence of the long-range band bending (large Debye length) for low doping. For very high n-type doping levels, the absolute shifting potential is reduced. We attribute this to two main factors which go hand in hand: In the simulations we see that for high band bending (high background doping), the QW gets too close or even into the Fermi level, strongly increasing the number of carriers trapped inside. These carriers introduce a screening effect, which reduces the QCSE within the QW, thus reducing the possible shift (refer to Section 1 and Figure 2). Second, if the QW is too far inside the material (thick cap layer), for high doping it even stops being affected by the band bending completely, and the wavelength shift approaches zero.

Consequently, there is an ideal doping level for each cap layer thickness, the value of which increases for thinner cap layers (see Figure 3).

The next parameter being investigated is the QW thickness \(L_z\). For thicker QWs, the internal field builds up over a larger scale and thus increases the QCSE. Very thin polar QWs below 2 nm do not have a lowest bound state and are thus omitted. Figure 4 shows the wavelength shift for several series of QW thicknesses, again calculated for various doping levels. With increasing QW thickness, the potential wavelength shift rises continuously, even more so for higher doping levels. The highest doping level at \(1 \times 10^{19} \text{cm}^{-3}\) is an exception: It seems that here, even though the trend is still the same, a saturation begins and decreases the maximum obtainable shift compared to \(10^{18} \text{cm}^{-3}\). This is attributed to the QW reaching into the Fermi level; thus, screening reduces the effect of the QCSE. As the cap layer is kept constant at 3 nm, QW interaction via band bending is always present.

When varying the indium content of our QWs in the simulation, we observed that it only plays a minor role and thus was not examined in further experiments.

## 3. Experimental Verification

### 3.1. Methods and Procedures

All samples were grown in our horizontal flow MOVPE reactors (either AIX200/RF or AIX-200/4 RF-S). Precursors used for the growth process were trimethyl-aluminum (TMAl), trimethyl-gallium (TMGa), triethyl-gallium (TEGa), trimethyl-indium (TMIn), and ammonia (NH3). For buffer layer n-doping, silane (SiH4) diluted in hydrogen was used. The optical setup is described in detail elsewhere: a microfluidic system and a typical micro-photoluminescence setup. The microfluidic system is based on a multichannel active pump, electronic valves, and a liquid flow chamber with inlet and outlet silicon tubings. The on/off switching of the valves and pump is controlled automatically using a LabVIEW program. The flow rate of the chemicals was fixed to 500 mL min\(^{-1}\). The optical sensing studies were performed by exciting the QW from the backside using a blue continuous wave semiconductor laser of 405 nm (3.06 eV). This allows selective excitation of only the QW through the substrate and buffer. As testing analytes, isopropanol and deionized water (DIW) were flown cyclically over the sensor surface; the switching time between each liquid was 5 min. The benefit of using isopropanol and DIW as sensing reagents is their availability and low cost, compared to expensive biomolecules used in the other studies. Every 3 s, an optical spectrum was recorded. Each spectrum was fitted with three Gaussian functions, one of which represents the main QW PL emission, while the other two were fitted to the redshifted phonon replica. Two exemplary spectra are shown in Figure 1, right. For the evaluation, the centers of the fitted peaks were compared for the spectra of isopropanol and DIW. Due to the fit, the resolution was enhanced well below the spectrometer pixel resolution. The wavelength difference of the two spectra at the electrical switching points of the liquids was taken as data point for the diagrams below. Thermal effects on the sensor response originating from the temperature dependence of the bandgap can be excluded due to the relative nature of the sensing principle, thermal equalization of the setup before measurement, and their low impact of \(\approx 50 \text{pm} \text{C}^{-1}\) drift. A more detailed description of the measurements and analysis can be found elsewhere.

### 3.2. Experimental Results

First, the position of the QW relative to the sensor surface was experimentally investigated by varying the cap layer thickness from 3 to 25 nm. The QW thickness \(L_z\) was fixed to 3 nm, and the indium content \(x\) was 12%. No SiH4 was introduced during the growth of this series; the samples are thus unintentionally doped (carrier concentration below \(10^{17} \text{cm}^{-3}\)). The resulting data are shown in Figure 5. For thick cap layers, the shift slowly rises with decreasing cap as predicted by our simulations for low doping concentrations (Figure 3). Thinner cap layers lead to a strongly increased sensitivity, although more resembling the trends predicted for higher background doping. To date, we cannot completely explain this behavior. Our model indeed might show limitations concerning the carrier distribution within the semiconductor layers, particularly during optical excitation.
After this, two doping series were grown, one with 4 and one with 8 nm cap layer thickness. For both thicknesses, four different doping levels were used; the QW thickness was kept at 3 nm. The doping was introduced shortly after the GaN nucleation and then continued for \( \frac{1}{24} \mu m \) up to 8 nm below the QW. Both cap layer thicknesses exhibit the highest shift at the same data point of \( \sim 10^{18} \text{cm}^{-3} \) (Figure 6). When taking into account the surrounding measurement points, however, it becomes clear that for 4 nm, the shift at \( \sim 10^{18} \text{cm}^{-3} \) is not substantially lower than the optimum, indicating a global maximum in between both doping concentrations. The opposite is true for the 8 nm cap: Here, the point of the second highest shift occurs at a lower doping of \( \sim 4 \times 10^{16} \text{cm}^{-3} \), thus hinting toward a global optimum at an intermediate doping concentration. This matches very well with the trends predicted in the simulations, although an exact quantitative match could not be reached. The observed trends could be confirmed in another measurement series with a 3 nm cap layer (not shown here).

Moreover, we have studied the impact of the QW thickness on the sensor’s performance. For this purpose, a series of 2.5, 3, 4, and 5 nm QW samples was grown by MOVPE. The GaN buffer layers were n-doped with \( \sim 10^{18} \text{cm}^{-3} \), whereas the cap layer thickness \( d \) was fixed at 4 nm. Figure 7 shows the trend of the wavelength shift obtained as a function of QW thickness through our DIW–isopropanol measurements. Again, the real measurements follow the expectations from the simulations.

4. Conclusion

To optimize our sensor structures, we systematically varied their structural parameters in simulation and experiment. The cap layer thickness \( d \), doping concentration \( N \), and QW thickness \( L_z \) showed great potential for sensor improvement, whereas the indium concentration of the QW did not. The wavelength shift was shown to increase when reducing the cap layer thickness in both simulations and experiments. Moreover, we found the existence of an optimal doping concentration \( N \) for a given cap layer thickness \( d \). Also, when varying the QW thickness, the samples followed the expected trend in terms of wavelength shift. To conclude, simulations helped us to predict trends in our sensor design and our sensor structures could be greatly improved in terms of sensitivity even though limitations exist in terms of quantitative predictions.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

chemical sensors, heterostructures, InGaN, simulation versus experiment
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