InGaN Heterostructures as Optical Transducers for Hydrogen Sensing

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GaN/InGaN quantum wells were investigated as optical transducers for the detection of hydrogen. The heterostructure sensors were grown by metal organic vapour phase epitaxy and later covered by a thin layer of Pt by electron beam evaporation. The quantum well photoluminescence is sensitive to changes in the sensor surface potential and this characteristic is used as the detection principle. With the adsorption of hydrogen at the Pt/GaN interface, downward near-surface band bending results in an increase in the quantum-confined Stark effect producing a red-shift in the luminescence. A reduction in photoluminescence intensity is also observed due to the separation of the electron and hole wave functions. Some samples have shown opposite trends based on different surface treatments and those result are under investigation. Further studies are in progress to see whether this phenomenon also allows the detection of hydrides such as hydrogen sulfide, an important gas present in the human breath for early detection of diseases.

1. Introduction

Group-III nitrides have well known material properties that make them suitable for applications in biochemical sensing [1–4]. Specifically, GaN has the capacity to operate at high temperatures hence it can be used to realize Schottky diode and field effect transistor (FET) gas sensors which can be used in harsh environmental conditions [5–7]. Due to its surface being highly electrochemically stable [7, 8], GaN can also be applied in the field of biochemical sensors in liquid electrolytes [9–12]. The material also has good optoelectronic properties that can be utilized in the creation of novel sensors which produce an optical readout signal. Since this optical signal can be processed remotely the sensor can be used in situations where destructive chemicals would make electrical contacting a complicated endeavour.

GaN based gas sensors investigatd in this study work on the principle of near-surface band bending due to the adsorption of gas or biomolecules at the sensor surface. This produces a change in the surface potential and the Fermi level pinning. N-doped GaN in air has been reported to have a near-surface upward band bending of about 1 eV [13]. This somewhat compensates the quantum-confined Stark effect (QCSE) present due to internal stress in the near-surface GaInN quantum well (QW). When a reducing agent like hydrogen gets adsorbed at the sensor surface it produces downward band bending since it donates an electron to the semiconductor surface [14]. This results in an increase of the QCSE and a red-shift in the PL emission of the QW, while an oxidizing agent which accepts an electron from the surface will induce a blue-shift [15].

This study is concerned with characterizing GaN/InGaN QW grown on optically transparent sapphire substrates and capped by a thin Pt layer for selectivity purposes. Chemically induced changes to the surface potential alter the PL emission of the QW. This effect is then used to demonstrate hydrogen gas sensing by inducing a change in the PL wavelength and intensity.

2. Experimental Details

The semiconductor heterostructures investigated in this work were grown in Aixtron AIX200/RF, a commercial horizontal flow metal organic vapour phase epitaxy (MOVPE) reactor. Ammonia (NH_3), trimethylgallium (TMGa), trimethylaluminum (TMAl), triethylgallium (TEGa), and trimethylindium (TMIn) are the precursors for the epitaxial growth. Ultra-pure hydrogen and nitrogen act as carrier gases. Growth takes place on a 2 inch *c*-oriented 0.2° off m-axis double-side polished (DSP) sapphire wafer. Firstly, a 10 nm thick AlN nucleation layer is grown for better quality GaN growth. This is followed by an undoped Ga-polar GaN buffer layer with a thickness of about 2 µm. Then a series of samples with a single 3 nm thick InGaN QW was grown with a GaN capping layer of different thickness, i.e., 3, 6, 9 and 15 nm at the top (Fig. 1). Another series with higher background doping concentration ($\approx 1 \cdot 10^{18}\,\mathrm{cm}^{-3} - 1 \cdot 10^{19}\,\mathrm{cm}^{-3}$) of the GaN buffer layer was also investigated, as simulation results had shown better sensitivity with higher carrier concentration [16]. To functionalize the sensor surface for hydrogen detection, a layer of Pt with thickness of 3, 6 and 9 nm was grown on top of these samples using electron beam evaporation.

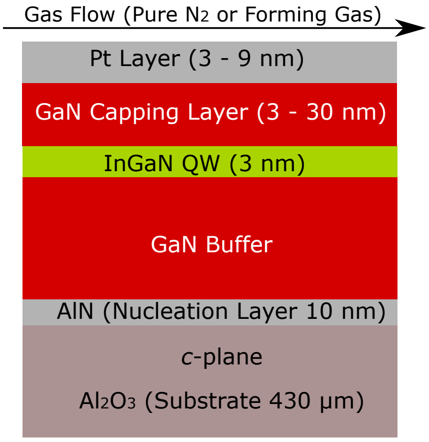

Fig. 1: InGaN/GaN semiconductor heterostructure. Capping layers of different thickness were used for these measurements.

For the optical characterization of the QW, a photoluminescence setup (Fig. 2) was built specifically for gas sensing measurements. It consists of a sealed chamber with a sample holder used for backside excitation of the sample through a glass window with AR coating. The chamber is connected to a gas mixing apparatus which is in turn connected to nitrogen and forming gas (95 % nitrogen and 5 % hydrogen mixture) supply, forming gas being used as a source of hydrogen. The PL emission changes in response to the cyclic switching of ambient gases and is recorded continuously. A blue laser with a wavelength of 405 nm is used for the excitation of the QW with PL emission around 465 nm, and the read-out of the PL spectra is performed through the same path as the excitation. A dichroic mirror with a cut-off wavelength of 425 nm separates the excitation from the PL signal. Finally a monochromator in combination with a CCD camera is used to spectrally resolve and record the QW emission signal.

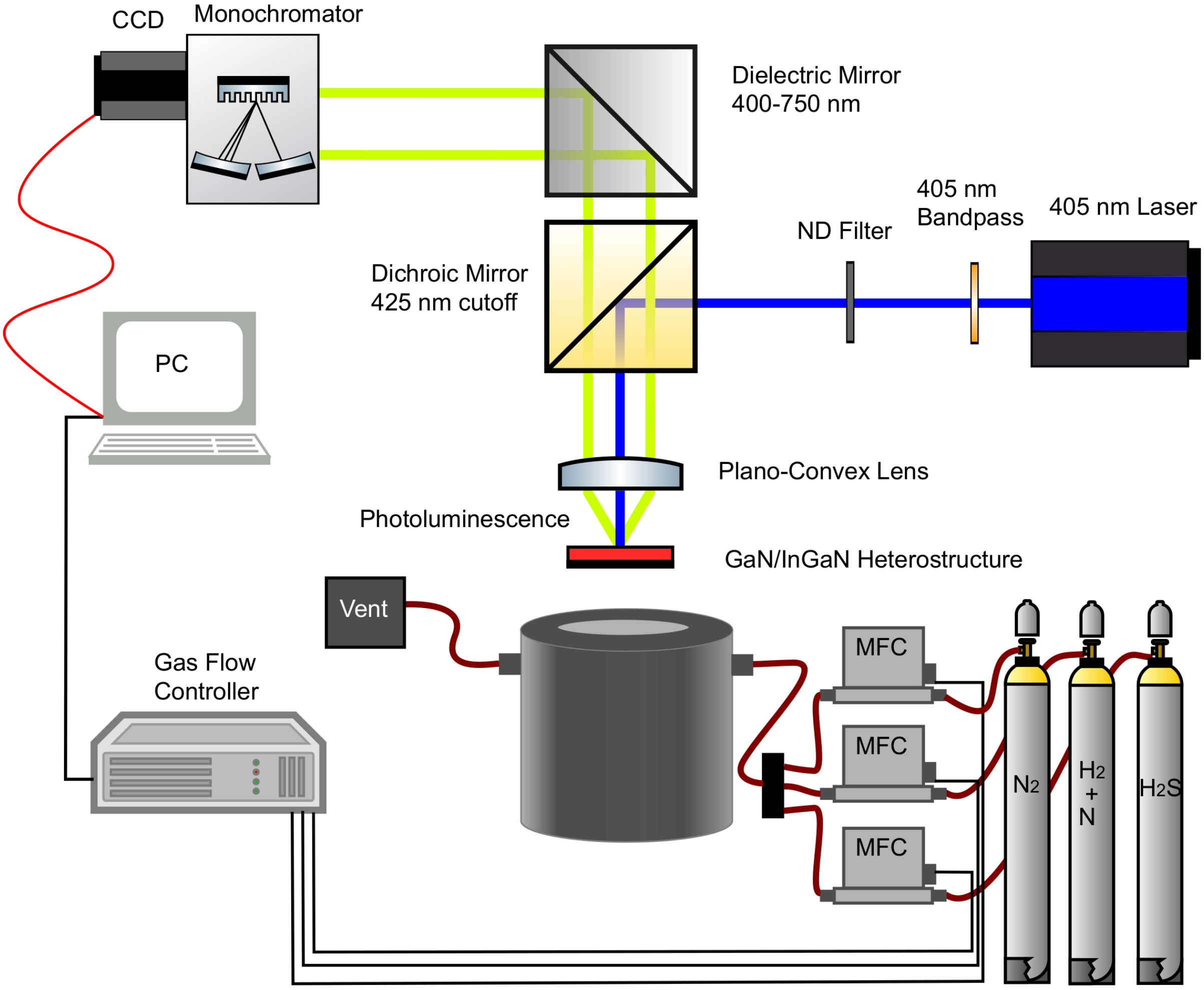

Fig. 2: Optical gas sensing setup: A blue laser is focused onto the GaN/InGaN heterostructure through an optical system consisting of a plano-convex lens and a dichroic mirror which separates the laser and the PL emission. A dielectric mirror reflects the collimated PL emission into a monochromator. The sealed chamber is connected to a gas mixing setup with a supply of nitrogen, hydrogen and hydrogen sulfide.

3. Gas Sensing Results and Discussion

Gas sensing was performed first for the planar single InGaN quantum well samples. The parameter investigated in this case was the thickness of the GaN capping layer as that has a direct impact on the responsiveness of the sensor. The influence of gases on the

QW emission was measured by alternatively letting pure nitrogen and then hydrogen (in 95 % nitrogen) flow through the gas chamber in intervals of 2 min. Hydrogen being an electron donor will induce a downward near-surface band bending for n-GaN, increasing the QCSE. Stronger QCSE produces a red-shift in the PL emission along with a reduction of the electron–hole wave function overlap resulting in lowered intensity.

Earlier simulation and experimental results reported in [17] have shown a higher sensitivity with a thinner cap layer. However, the PL emission intensity of samples with thin cap layer suffers considerably with the deposition of a Pt layer. It is assumed that the smaller barrier results in tunnelling transport of electrons out of the QW towards the metal-coated surface. Further investigations will be done to optimise the cap layer thickness where the PL intensity is still measurable.

In Fig. 3 the sensor response of a sample with 15 nm GaN cap with different Pt layer thickness is plotted. When switching from nitrogen to hydrogen a red-shift along with a decrease in PL intensity is observed the mechanism for which is described above. Ignoring the one spike when switching from hydrogen to nitrogen with the 3 nm Pt, the sensor response does not seemingly change much with the thickness of the metal layer for a single QW sample. It remains between 3–6 meV here and in several other measurements. The result for the intermediate thickness of 6 nm have shown some inconsistency and are being investigated further.

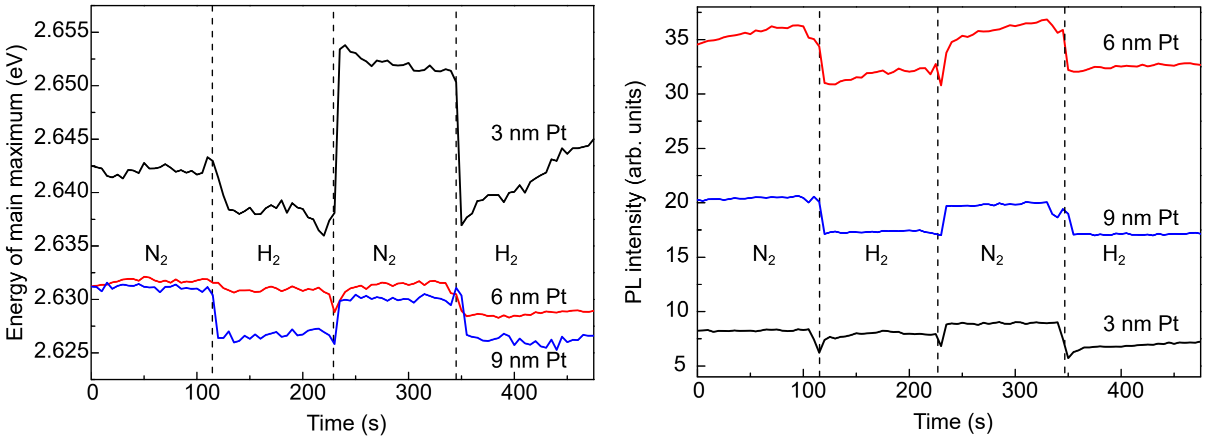

Fig. 3: The change in PL emission energy (left) and intensity (right) of a single QW sample with GaN cap layer thickness of 15 nm under nitrogen and hydrogen ambient. The gases were cyclically switched after 2 min intervals. A red-shift and decrease in PL intensity is observed when switching from nitrogen to hydrogen.

Simulation results [16] indicate a thinner capping layer along with higher background doping makes the sensor more sensitive. A series of samples with different doping ($\approx 1{\cdot}10^{18}\,\mathrm{cm}^{-3}$–$1{\cdot}10^{19}\,\mathrm{cm}^{-3}$) was grown and gas sensing measurements done for a comparison with simulated data. The results as seen in Fig. 4 show a nice correlation between the calculated (left) and the experimental (right) data. In both cases lower doping has a flatter response regardless of the cap layer thickness, while higher doping produces a large wavelength shift with a thin cap but the shift falls sharply with increasing cap thickness.

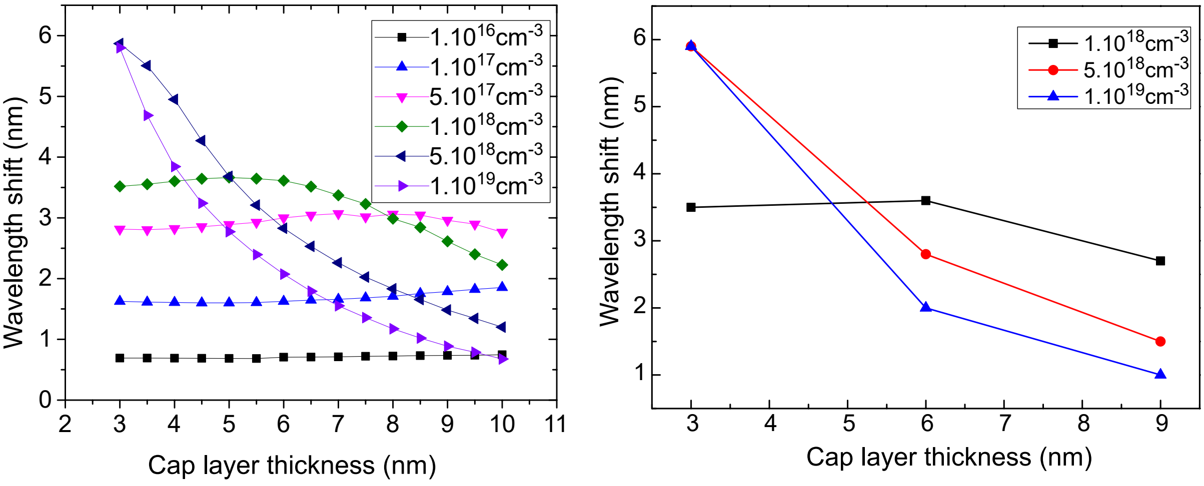

Fig. 4: Wavelength shift vs. GaN cap layer thickness. Simulation results have shown a larger wavelength shift with higher background doping concentration (left), this has experimentally been confirmed as samples with three different doping concentrations were grown and gas sensing performed, higher doping produced larger shift in emission wavelength (right).

Up to now gas sensing was performed with single QW samples to keep the PL emission simpler to understand. However, since the emission intensity for a single QW when combined with a platinum layer becomes rather weak or even undetectable in some cases, a 5 QW sample was also tested. This sample was recently cleaned with Piranha solution and deposited with a Pt layer. Piranha etching hydroxylates the surface, the OH^- groups produce an upward near-surface band bending.

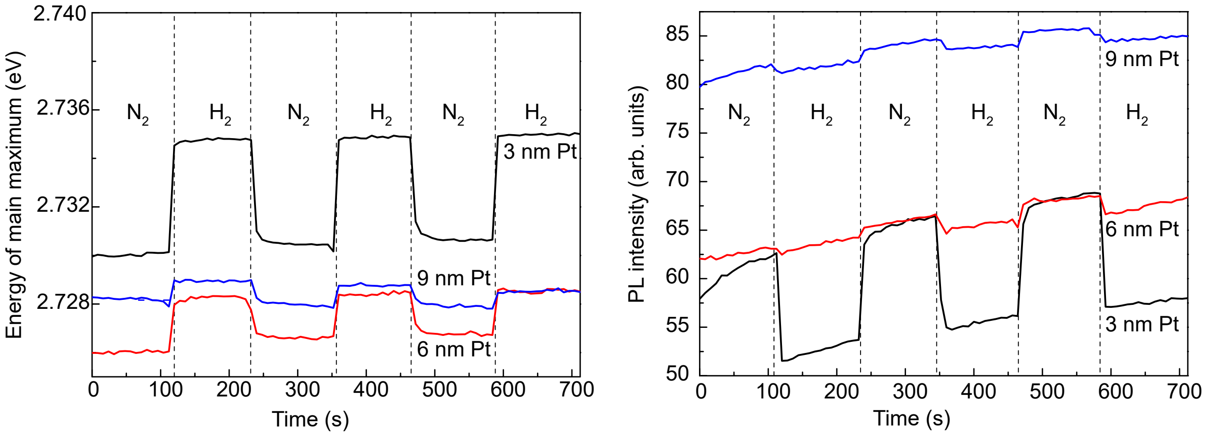

Fig. 5: The change in PL emission energy (left) and intensity (right) of a 5 QW sample with GaN cap layer thickness of about 9 nm under nitrogen and hydrogen ambient for different Pt layer thickness.

With the adsorption of hydrogen downward band bending should follow but instead of the expected red-shift a blue-shift is observed with a decrease in the PL intensity as seen in Fig. 5. This trend is not limited to the multiple QW but was also seen in single QW samples which have been freshly cleaned and deposited with Pt layer and tested within a day. Here time could be a factor in defining the sensing behaviour and will be investigated further.

The upward band bending counteracts the QCSE, so a blue-shift should also increase the radiation transition probability. However, the decreasing PL intensity points towards another mechanism counteracting the radiative recombination. One possible reason for this could be the enhanced tunnelling of photoexcited electron–hole pairs out of the QW, the reason for which is under investigation. This phenomenon will be verified with simulation data to better understand the bandgap changes under different conditions at the surface. However, in this case the thinner Pt layer of 3 nm gives the highest sensitivity compared to thicker layers a trend also seen in single QW samples which were cleaned with Piranha and tested for sensitivity soon after.

4. Conclusions

The effect of hydrogen adsorption on the surface of a GaN/InGaN heterostructure functionalized with a Pt layer has been investigated. For single QW samples, a red-shift and a decrease in the emission intensity is observed in accordance with an increase in the QCSE due to downward near-surface band bending. Thinner cap layer samples should in theory show higher sensitivity but suffer from increased tunnelling of the carriers to the metal-coated surface. Experimental data have confirmed theoretical calculations that higher doping concentration produces better sensitivity. Samples treated with Piranha solution form hydroxyl groups at the sensor surface and seemingly invert the sensor response to hydrogen by producing a blue-shift in emission. This phenomenon will be investigated further with accompanying simulations for a better understanding of the effects of surface chemistry on the GaN/InGaN bandgap emission. The results are nevertheless promising and the heterostructures will be improved to realize a highly selective and sensitive gas sensor.

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