Gas Sensing Using InGaN Quantum Wells

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Chemical stability and inertness of GaN and InGaN make them suitable candidates for gas and biosensing applications in chemically harsh environments. Unlike conventional III-nitride based sensors with electrical readout, we focus on heterostructures which can be read out purely by their photoluminescence signal remotely. These semiconductors are particularly sensitive to changes in surface charges. In this initial study, InGaN quantum wells grown on GaN buffer layers are used for gas sensing measurements and the knowledge acquired from these experiments will be applied to the development of highly sensitive optical analysis of gases present in human breath.

1. Introduction

GaN is well established as a general lighting and lasing applications semiconductor material. In recent years it has also attracted interest from the scientific community for other applications such as gas and biosensing [1–3]. The material is chemically stable and inert, has good optoelectronic properties and is biocompatible [4, 5]. For biosensing the polarity dependent piezoelectric properties are expected to be extremely useful [6]. GaN also has a large bandgap and the highest occupied and lowest unoccupied orbitals of many biomolecules match very well with it [7]. Typically gas and biosensors are electrical devices, transistors and Schottky diodes [8], in which the adsorption of molecules changes the surface Fermi level pinning and hence the electrical conductivity. A near-surface upward band bending is observed with the creation of a depletion zone for n-doped semiconductors. More complex nanostructures have also been researched due to their high surface-to-volume ratio and low power consumption. However, these structures require intricate fabrication processes and also sophisticated contacting methods. Even then the contacts are vulnerable in wet chemical environments.

III-nitride based semiconductors on the other hand can be read out optically completely avoiding the drawbacks of electrical contacting making the structures stable against destructive chemicals. The adsorbates on the surface of such structures modify the optical photoluminescence (PL) response which can be investigated remotely. In this study a label-free approach towards gas sensing is presented, with a particular focus on gases present in the human breath. The PL response of a planar near-surface InGaN quantum well (QW) with different GaN capping layer thickness in the presence of different gases is studied.

2. Experimental Details

A commercial horizontal flow metal organic vapour phase epitaxy (MOVPE) reactor Aixtron AIX200/RF is used for the semiconductor heterostructure growth. Ammonia (NH_3), trimethylgallium (TMGa), trimethylaluminum (TMAl), triethylgallium (TEGa), and trimethylindium (TMIn) are used as precursors. Nitrogen and ultra-pure hydrogen are used as carrier gases. First, a 10 nm thick AlN nucleation layer is grown on a c-oriented double-side polished sapphire wafer followed by a nominally undoped Ga-polar GaN buffer layer with a thickness of about 3 µm. Then a single 3 nm thick InGaN QW is grown with a GaN capping layer of different thickness, i.e., 3, 6, 9, 15 and 30 nm at the top (Fig. 1, left). For the optical characterisation of the QW, a micro-photoluminescence setup with a sealed chamber connected to a gas mixing apparatus was used. The changing PL spectra in response to the cyclic switching of ambient gases is continuously recorded. A HeCd laser (325 nm) is used for the excitation of the QW PL and both the optical excitation and the read-out of the PL spectra is performed from the top. A monochromator in combination with a liquid nitrogen cooled CCD camera is used to spectrally resolve and record the QW emission signal.

3. QW Photoluminescence Response to Gas Molecules

The adsorption of gas molecules on the surface influences the near-surface InGaN QW PL emission. Within the GaN bandgap the Fermi level is pinned to the surface states present in high density when no surface modification is done. For n-doped GaN in air, upward band bending of 1 eV has been reported [9] which induces a depletion zone for majority charge carriers (i.e., electrons) near the surface. The length of the depletion zone (W_d) is dependent on the carrier concentration in the bulk crystal and the surface potential as described by

$$W_\mathrm{d} = \sqrt{(2 \cdot \epsilon_\mathrm{s} \cdot \psi_\mathrm{s})/(q \cdot N_\mathrm{d})} \; . \tag{1}$$

Here ϵ_s is the absolute dielectric permittivity, ψ_s is the surface potential, q is the elementary charge and N_d is the doping concentration [10]. Figure 1 (right) shows the energy band diagram of an n-type semiconductor with upward band bending resulting in the depletion of electrons and accumulation of holes in the region. The QW near the surface experiences this electric field and as a consequence the effective bandgap is changed, an effect known as the quantum-confined Stark effect. Moreover, the QW grown on the polar c-plane also suffers from the internal piezoelectric fields which tilts the QW energy band in the opposite direction to the surface-induced band bending. Any adsorbate on the surface accumulating negative charges will increase the near-surface band bending for an n-doped material while on the other hand a reducing agent will have the opposite effect. So for oxidising agents a blue-shift in the emission due to the reduced tilt in the QW energy band is expected while an increase in the overlap of electron–hole wave function should also improve the radiative recombination probability.

The QW should be positioned in the region with a large potential gradient, i.e., close to the surface, for maximal spectral shift. However, due to lowering of the barrier height, there is an increased probability of the carriers tunnelling out of the QW and non-radiatively

recombining at the surface or in the bulk. This could potentially lead to a loss in the PL intensity. Under these circumstances a compromise might be necessary between high sensitivity in terms of a wavelength shift and high signal-to-noise ratio for such a sensor.

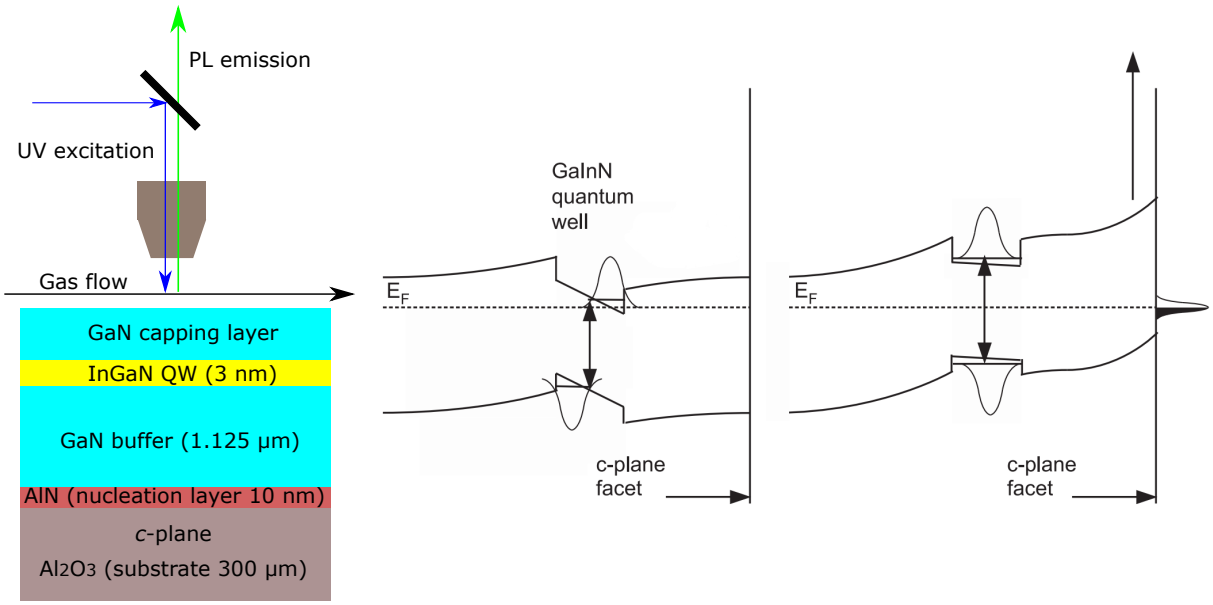

Fig. 1: Micro-PL setup schematic for front-side UV excitation of the InGaN QW (left). Capping layers of different thickness were used for these measurements. Band structure for GaN/InGaN heatrostructure without and with near-surface band bending after adsorption of oxidising agent (right) [1].

4. Experimental Results

Gas sensing experiments were performed using a single 3 nm thick InGaN planar quantum well. In order to investigate the influence of the capping layer thickness on the sensitivity of the sensor, layers of different thickness were grown. With the HeCd laser front-side excitation of the QW, a PL signal from the different samples is observed at around 2.6 eV. By changing the thickness of the capping layer from 3 nm to 30 nm, a blue-shift of about 90 meV is observed (Fig. 2). This shift might be a result of strong near-surface band bending compensating the internal piezoelectric polarisation effects. Another possible reason for the blue-shift is the desorption of indium during the longer capping layer growth at slightly higher temperature.

To measure the influence of surface gases on the QW emission, first nitrogen and oxygen were used and the results for PL peak energy variation are shown in Fig. 3 for two different capping layers i.e., 3 and 30 nm. Oxygen atmosphere is expected to increase the upward surface band bending and increase the overlap of the electron–hole wave function. A clear peak emission shift is visible when switching from nitrogen to oxygen and the PL intensity is also affected (not shown here). However, the sensitivity of the sensor decreases considerably after the first cycle, as is evident from the energy variation, pointing to the

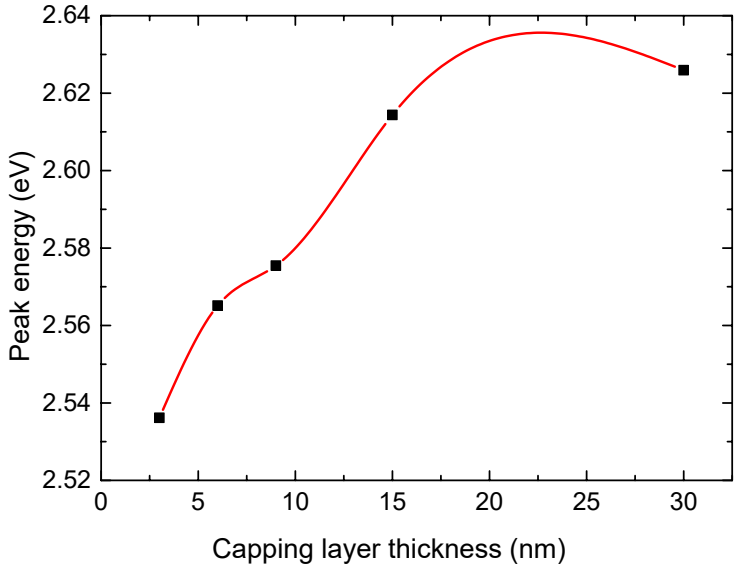

Fig. 2: Peak emission energy of InGaN QW structures with different GaN capping layer thickness, a blue-shift with increasing cap thickness is observed.

formation of an oxide layer on the surface. The thinner capping layer with 3 nm showed higher sensitivity compared to a thicker layer with 30 nm showing shifts of about 28 meV and about 0.5 meV, respectively. These results confirm simulation results presented in [11].

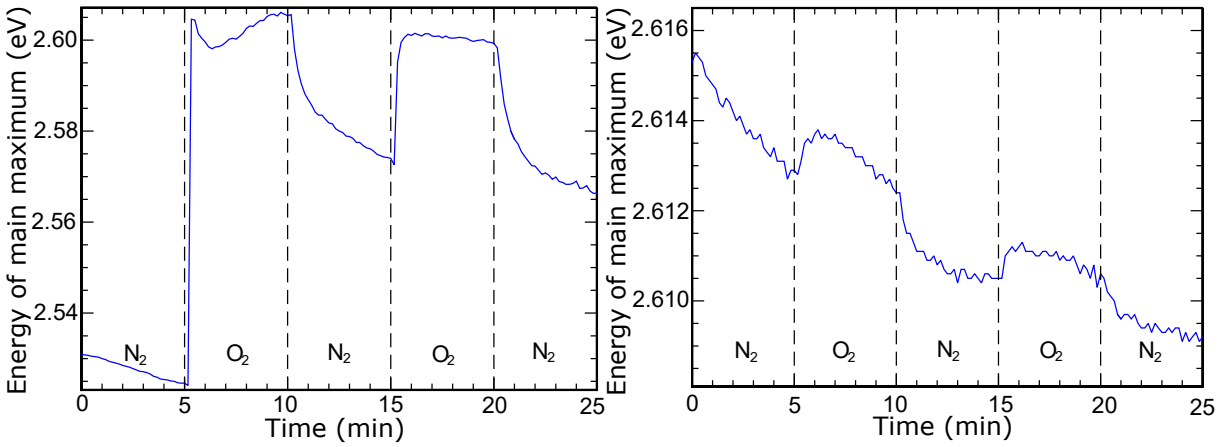

Fig. 3: Spectral shift of InGaN QW in nitrogen and oxygen when cyclically switched in 5 min intervals: 3 nm cap (left) and 30 nm cap (right).

The effect of hydrogen on the QW PL emission was also investigated. 5 % hydrogen in nitrogen was switched in place of oxygen and the PL emission peak position and intensity was recorded (Fig. 4). With hydrogen adsorption on the surface a blue-shift is observed again possibly due to the increased near-surface band bending. The reduction in sensitivity due to the oxidation layer is less severe in this case compared to pure oxygen. Although the emission energy is higher in hydrogen ambient, the intensity of the signal is decreased possibly due to the tunnelling of electrons out of the QW and

increased non-radiative surface recombination processes, although further studies need to be done to investigate this phenomena. The shift in energy seemingly is a more reliable sensor response as it is a direct result of the QW band situation. However, the intensity change could be used in combination with the energy change for more complex ambient environments carrying additional information about the gas to be detected.

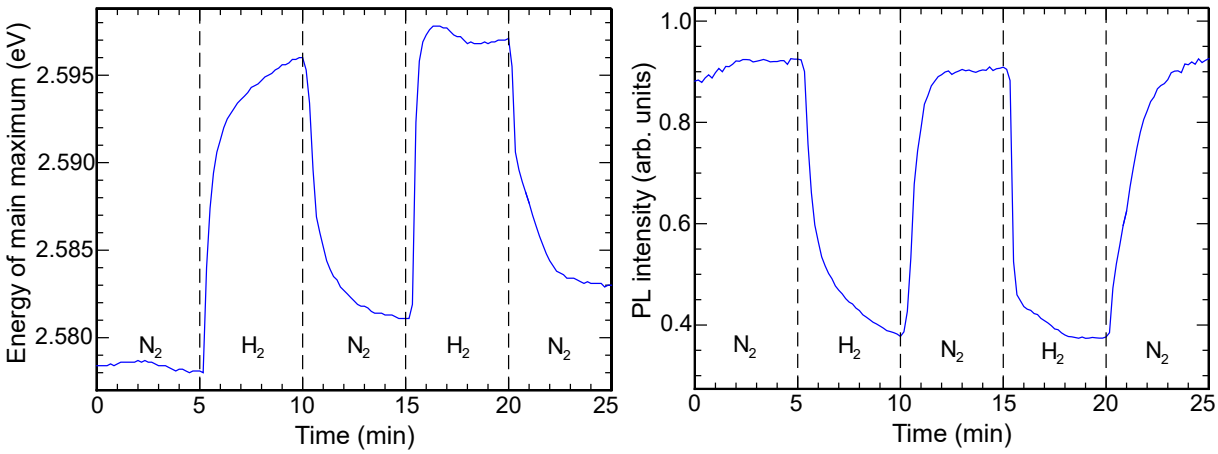

Fig. 4: (Left) Spectral shift and (right) intensity shift of an InGaN QW in nitrogen and 5 % hydrogen in nitrogen when cyclically switched in 5 min intervals.

5. Conclusion

Optical transducers based on GaN/InGaN heterostructures for the detection of gases have been realized for a proof of concept. Gas molecules on the surface of such sensors induce a spectral shift of the PL emission and a change in the signal intensity with the changing of gas molecules is also observed. Oxidising agents induce a blue-shift with a decrease in PL intensity while reducing agents induce a red-shift and an increase in the PL intensity. Further work is to be done towards functionalization of the surface to improve sensitivity and selectivity. These results are promising and could be useful in the development of high-sensitivity gas sensors with optical readouts.

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