Functionalised AlGaN/GaN Heterostructures for Electronic Saccharide Sensing

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***Abstract* – A novel field-effect sensor device based on functionalised AlGaN/GaN heterostructure was developed for sensing of various saccharides in solutions. Device was functionalized with a boronic acid chemical receptor, a thiol group and alkane chain linker. Electrical measurements on fabricated devices were performed to demonstrate their response to buffered saccharide solutions (fructose, galactose and glucose) of varying concentrations. The obtained results provide basis for the development AlGaN/GaN-based electronic sensor devices incorporating boron receptor chemistry.**

***Index Terms* – GaN, AlGaN, sensors, HFET, saccharide.**

I. INTRODUCTION

In recent years there has been large interest for use of GaN based structures for various electronic and optical devices for telecom and solid-state lighting markets. However, AlGaN/GaN heterostructures have also shown great potential for field-effect based electronic chemical and biochemical sensors [1,2,3]. In these structures formed two dimensional electron gas (2DEG) at the interface between the AlGaN and GaN layers provides high density carriers confined near the surface, which has been widely exploited for RF device applications. Together with excellent chemical and thermal stability of these materials this makes them good candidates for variety of chemical sensing applications.

To functionalize GaN structures various approaches were explored, typically silane [4] and alkene [5] groups were involved to create a linker between receptor and surface. However, both these approaches have limitations, requiring additional extensive processing or indirect bonding to surface via less stable oxides. On other hand, thiol based attachment is known to provide straight-forward bonding either directly to semiconductor surfaces or on thin gold films [6, 7] and is a possible alternative to existing methods.

In-situ detection and analysis of saccharides is of great importance for a variety of domestic and medical applications. However, accurate, reliable and cost-effective electronic saccharide sensors are not readily available. Typically, electronic saccharide sensors are fabricated via the immobilisation of a specific enzyme [8]. However, such devices suffer from high fabrication costs and complexity as well as reduced stability of the finished devices [9]. Alternatively, boronic acid receptors have been shown to bind to saccharides effectively via covalent interactions in aqueous media [10,11,12].This lead to development of non-electronic fluorescence sensor approaches based on carbohydrate sensing “click-fluor” [13].

In this paper, we present a novel electronic saccharide sensor structure using boronic acid functionalised AlGaN/GaN heterostructure and thiol linker for proof-of-concept demonstration of specific chemical sensors based upon field-effect device structures.

II. EXPERIMENTAL DETAILS

AlGaN/GaN heterostructures were grown on Si(111) substrates by metal organic chemical vapour deposition. Thickness of GaN layer was about 2.5 µm, covered with 20 nm of $Al_{0.25}Ga_{0.75}N$ layer. Square die of 0.5 x 0.5 cm were cleaved from the wafer. Standard Ti/Al/Ti/Au ohmic contact pads, separated by 2mm, were deposited by e-beam evaporation through a shadow mask and then annealed at 850 °C for 30s under nitrogen ambient. Subsequently, a NiCr/Au layer was deposited in the space between contacts to allow receptor attachment and act as a Schottky gate. On each die a pair of identical devices was fabricated, to act as a reference and a functionalised active sensor device. Devices were mesa-isolated via scribing.

Reference device was fully masked as was the most of active device structure, apart of rectangular functional area between ohmic contacts. Die was then placed in a 5 mM solution of prepared by chemical synthesis boronic acid thiol (BAT) product in ethanol for 24 hrs. Mask was then removed and contact angle measurements were used to confirm functionalisation of the prepared surfaces.

III. RESULTS AND DISCUSSION

Figure 1 shows a schematic diagram of a device structure, receptor and thiol linker (BAT) and functionalisation steps. In comparison to organosilane functionalisation [4], thiol based method benefit from much simpler chemistry and fewer fabrication steps, and can be used to bond receptors to thin gold layers or directly to the surfaces. While alkene based linkers are also offer a simple pathway for GaN fuctionalisation [5], the method relies on use of hydrogen terminated GaN surface, which is very unstable and have very limited life time.

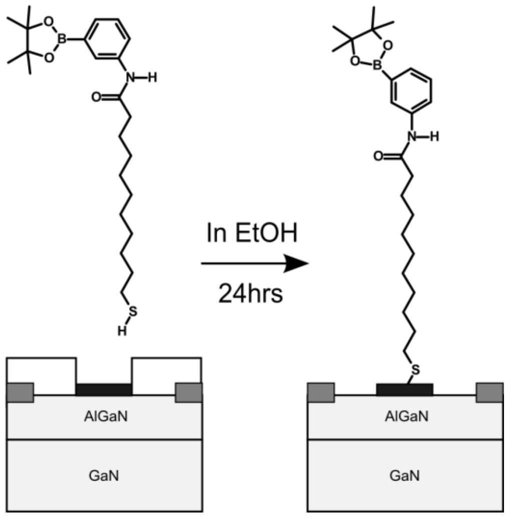

Fig. 8. Schematic diagram of a functionalised AlGaN/GaN sensor device. The BAT receptor molecule bonds to the gold layer between the Ohmic contacts.

Figure 2 displays measured sensor current, *I*, in the active functionalised device before and after exposure to analytes: a solution of 1M fructose in the buffer. Also given is a comparison with the reference device, which experiences only a negligible change in current in reaction to the analyte.

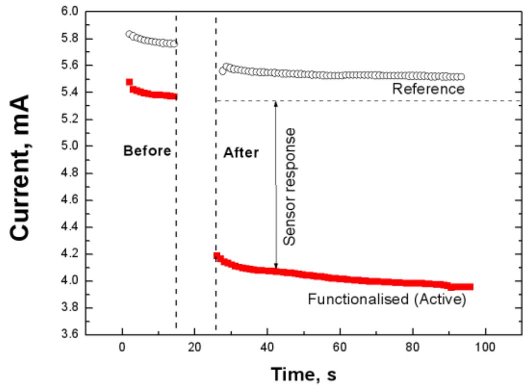

Fig. 2. Electrical response of reference and active devices exposed to 1M fructose solution. Time interval between 15 and 25 seconds corresponds to deposition of analyte (no electrical data).

Following confirmation of sensor activity, the device was exposed to buffered saccharide solutions of fructose, galactose and glucose with concentrations between 1M and 0.1M. The detected response was greatest for fructose, followed by galactose and glucose was the weakest, which follows the established stability order for simple boronic acids [12,14]. This result confirms that observed sensor response is due to specific interaction between the boronic acid and the saccharide molecule rather than some secondary interactions with one of the other groups present in BAT.

For all three analyte concentrations above 0.8M saturation behaviour was observed for the sensor device. In the low concentration region, only fructose can be reliable detected below 0.2M. Generally, despite non-optimised process parameters, sensitivity of the fabricated structures was compatible with non-electronic chemical method described in Ref. 13. During electrical measurements devices underwent several hundred cycles of analyte deposition and subsequent washing and cleaning without any significant loss in response, which suggest robust GaN surface functionalisation using thiol based linkers.

Necessary improvements in the low concentration detection limit (below 0.1 M) for sugars is essential for future applications of sensor devices and can be achieved via further optimisation of fabrication process and by modification in the BAT receptor design.

IV. CONCLUSION

Here we demonstrated a proof-of-concept for saccharide electronic sensor device based on AlGaN/GaN field effect structure. A novel approach of receptor design and functionalisation based on preassembled by chemical synthesis boronic acid receptor and thiol-alkane linker (BAT) allowed to achieve specific sensitivity of fabricated structure to different saccharide concentrations in solutions. This offers a way for robust and simple functionalising of GaN based structures not only for saccharide detection, but also by replacing boronic acid with other molecular receptors to a wider range of detected species.

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