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Novel Sensor Applications of group-III nitrides

M. Eickhoff, O. Ambacher, G. Steinhoff, J. Schalwig[1], R. Neuberger[1], T. Palacios[2], E. Monroy[2], F. Calle, G. Müller[1] and M. Stutzmann

Walter Schottky Institute, Technical University Munich, Am Coulombwall, D-85748 Garching, Germany
[1]EADS Deutschland AG, IRT/LG-MX, P.O. Box 800465, D-81663 Munich, Germany
[2] ISOM and Dpto. de Ingeneria Electronica, ETSI Telecomunicación, Univ. Politécnica de Madrid, 28040 Madrid, Spain

ABSTRACT

The present paper gives an overview over different sensor applications of GaN thin films and AlGaN/GaN heterostructures. The response of Pt-GaN Schottky diodes towards hydrogen and hydrogen containing gases is analysed and their gas sensitivity is characterized from room temperature up to 600°C. In addition, the sheet carrier density of a two dimensional electron gas confined at the heterointerface in AlGaN/GaN high electron mobility transistors (HEMTs) is shown to be significantly influenced by changes in the electronic properties of the device surface. This effect is successfully exploited for the realization of ion detectors and sensors for fluid monitoring based on AlGaN/GaN HEMTs with non-metalized gate areas. Promising possibilities of fabricating monolithically integrated sensor devices for wireless signal transmission are demonstrated by the realization of SAW devices on epitaxial AlN-films.

INTRODUCTION

In addition to their high temperature and high frequency capability in electronic devices, wide bandgap semiconductors like silicon carbide, diamond or III-nitrides exhibit material properties which make them promising materials for sensor applications in harsh environment. In the case of III-nitrides, which due to their band gap variability are up to now mainly considered for optoelectronic applications [1], recent experiments have shown their capabilities in solar blind UV-detectors [2] and piezoresistive sensors for dynamic pressure sensing [3,4]. The present work gives an overview over the main experimental observations concerning other sensor applications of GaN layers and HEMT devices based on undoped AlGaN/GaN heterostructures as well as first attempts to understand and exploit the physics behind those phenomena for optimization of the sensor response. In the second paragraph gas sensitive devices based on Pt-GaN Schottky diodes are described. These sensors are shown to respond to hydrogen and various hydrogen containing gases like hydrocarbons. Similar devices have been realized before using other semiconductor materials, for example Si-MOS structures with catalytic Pd-gates [5] or SiC-MOS structures with Pt-gates [6]. Due to the spontaneous and, in the case of pseudomorphic growth, piezoelectric polarization of III-nitrides, a polarization induced two dimensional electron gas (2DEG) is formed at the heterointerface of AlGaN/GaN heterostructures. The corresponding sheet carrier density turns out to be highly sensitive towards any manipulation of the electronic state of the device surface, which is described in the third paragraph. This sensitivity gives rise to various sensor applications such as ion detectors or sensors for polar fluid detection, which are described in detail. In addition surface acoustic wave (SAW) devices have been realized with AlN layers grown on sapphire substrates. The performance of SAW filters for microwave frequencies is discussed, including an outlook on the promising possibilities of monolithically integrated smart sensors for wireless signal transmission based on group-III nitrides.

GAS SENSORS

Gas sensitive MOS-devices based on silicon with catalytically active palladium gates have first been reported by Lundström et al. in 1975 [5]. In case of a thick, continuous gate those devices work as selective hydrogen sensors. In order to allow the detection of more stable molecules like different hydrocarbon species, MOS-sensors based on silicon carbide with catalytic Pt gates have been realized later [6]. These sensors have been shown to operate up to temperatures of 800°C [7]. Recently, Pt-GaN Schottky diodes have also been shown to be sensitive to the presence of hydrogen and different hydrocarbons [8,9].

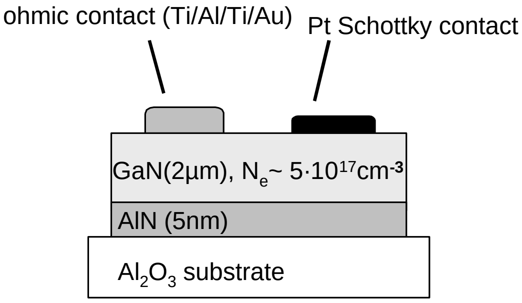

Fig.1: Hydrogen sensitive Schottky diode with catalytic Pt Schottky contact

In this paragraph we report on the sensitivity of Pt-GaN Schottky diodes with N-face and Ga-face polarity towards hydrogen and various other gases. The structure of the investigated samples is schematically shown in Figure 1. The Schottky diode is made from a 2µm Si doped GaN layer ($N_e \approx 5\cdot10^{17}cm^{-3}$) grown by plasma induced molecular beam epitaxy (PIMBE) as described elsewhere [10].

The Schottky contact is realized by a thermally evaporated catalytic Pt-film with a thickness of 30nm. The measured forward and reverse current as a function of the applied voltage in an 4% oxygen ambient at room temperature is shown in Figure 2. It is also shown that for a molecular hydrogen concentration of 1% both the forward and reverse current significantly increase already at room temperature. This variation in the current is attributed to a decrease in the Schottky barrier height due to the presence of hydrogen. The voltage shift at a fixed reverse current is the sensor signal to be evaluated. At a device temperature of 400°C this effect is much more pronounced, as at such elevated temperatures the Schottky contact becomes completely ohmic as a result of hydrogen exposure. For both temperature regimes the observed effect is reversible, however, the regeneration time of the device decreases with increasing device temperature. These observations strongly suggest that atomic hydrogen, which results from the dissociation of molecular hydrogen at the Pt-contact and adsorbs at the Pt-GaN interface, is the origin of the detection mechanism.

The observation of a Temkin-isothermal behaviour of the sensor signal as a function of hydrogen partial pressure (not shown) further corroborates this suggestion. Lundström et al. [11] have shown that this kind of relationship is observed when the heat of adsorption for atomic hydrogen at the metal semiconductor interface linearly decreases with the number of occupied adsorption sites.

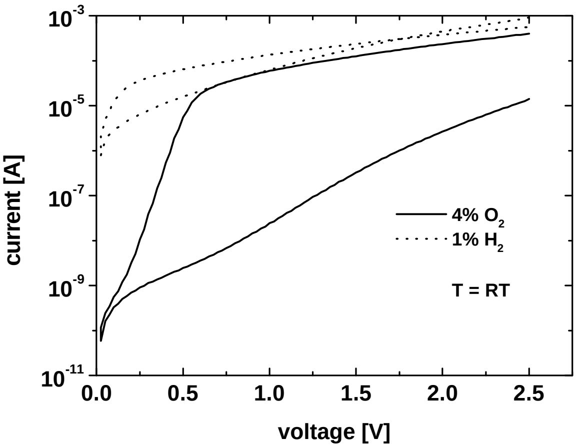

Fig.2: Forward and reverse current of a Pt-Schottky diode in oxygen atmosphere (solid line) and at the presence of hydrogen (dotted line) at room temperature.

Recent studies of the Pt-GaN system by elastic recoil detection analysis have shown an accumulation of hydrogen at the Pt-GaN interface as well as in the Pt-bulk and the Pt surface. Further investigations to quantify the number of electronically active adsorption sites are in progress.

The sensor response towards various gases has been investigated as a function of device temperature for GaN of both N-face and Ga-face polarity (Figure 3 and 4). The increase of the sensitivity at low and medium temperatures mirrors the increasing efficiency of the dissociation process at the surface of the catalytic metal. Due to enhanced desorption from the surface, the sensitivity starts to decrease again when the temperature exceeds a critical value, which is a characteristic quantity for the combination of the gas to detect and the catalytic metal. The devices also show a significant sensitivity towards non hydrogen containing gases. This effect has been attributed to the spill-over of different reaction by-products which adsorb on the semiconductor surface due to porosity of the catalytic metal layer [12]. If the catalytic metal forms a continuously closed layer, the sensor selectively responds towards hydrogen and hydrogen containing gases such as different hydrocarbons. This strongly suggests the use of these devices for exhaust gas monitoring in automotive applications. However, further studies of the semiconductor-metal interface have to be carried out to ensure a detailed chemical and physical understanding of the basic detection mechanisms of gas sensitive GaN-based Schottky diodes.

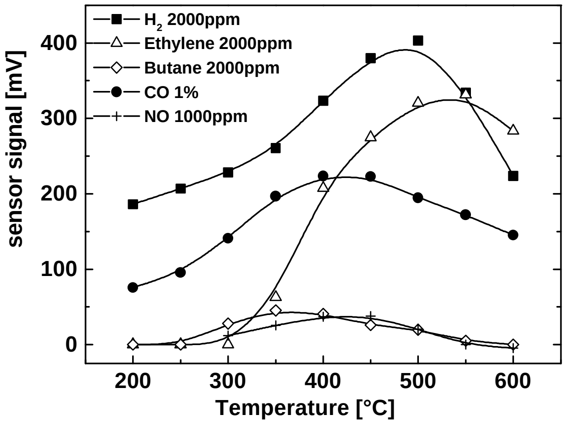

Fig.3: Temperature dependence of the sensitivity of a Ga-face Pt-GaN Schottky diode towards hydrogen and different hydrocarbons.

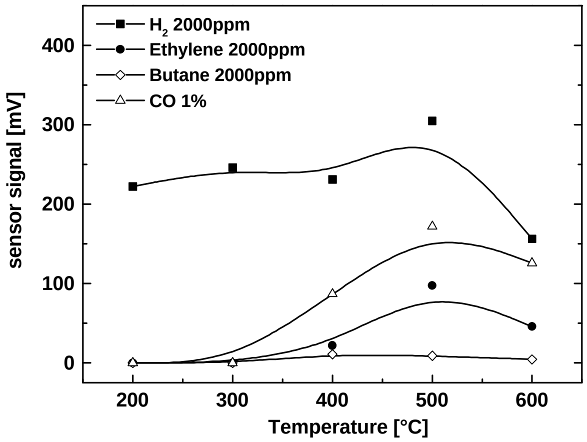

Fig.4: Temperature dependence of the sensitivity of an N-face Pt-GaN Schottky diode towards hydrogen and different hydrocarbons

SURFACE SENSITIVITY OF AlGaN/GaN HETEROSTRUCTURES

The gas sensitivity of the above mentioned GaN Schottky-based diodes is caused by the catalytic metal which forms the Schottky contact and, thus, is qualitatively similar to the same sensitivity observed in Si or SiC Schottky diodes with the same metal. However, the pyroelectricity of the III-nitrides gives rise to a different sensing mechanism which has not been investigated so far.

Due to the presence of spontaneous and piezoelectric polarization in a strained AlGaN/GaN heterostructure, a polarization induced two dimensional electron gas (2DEG) is formed at the heterointerface, which exhibits a discontinuity of the macroscopic polarization. This discontinuity causes a positive localized interface charge which is compensated by free electrons, forming a layer of mobile interface carriers with sheet densities of up to $2 \cdot 10^{13}$ cm^{-2} [13]. Up to now, the exact mechanism which leads to the formation of the 2DEG and the source of the corresponding electrons are not completely clarified. Independent of these questions, the global charge neutrality of an AlGaN/GaN heterostructure has to be guaranteed. Consequently the total charge of the 2DEG has to be compensated by a positive charge of the same amount. For instance, according to the surface donor model, this positive charge as well as the electrons in the 2DEG is supplied by ionization of surface donors [14]. Another possibility is that the polarization induced ionic surface charge is compensated by adsorbed species from the ambient, leading to a positive sheet charge on the surface (Fig.5). In both cases manipulation of the surface charge or the surface potential leads to a variation of the sheet carrier density in the 2DEG, which results in a modulation of the channel current when the source-drain voltage is kept constant.

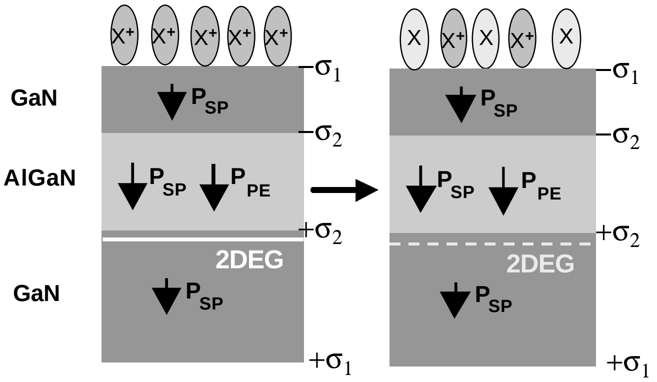

Fig.5: The compensation of the polarization induced surface charge $-\sigma_1$ of a Ga-face GaN/AlGaN/GaN heterostructure is partially neutralized by incident negative ions. This leads to a decrease in the sheet density of the 2DEG

As a consequence of these considerations it should be possible to manipulate the channel current of a HEMT device by an incident flux of positive and negative ions onto the non-passivated gate area or by variation of the work function due to screening in polar liquids. In the following these effects will be demonstrated and possible applications of AlGaN/GaN HEMT devices as ion detectors or for fluid monitoring are illustrated.

Ion sensitivity

AlGaN/GaN heterostructures were grown by plasma induced molecular beam epitaxy (PIMBE) on sapphire substrates. Initial deposition of an AlN nucleation layer lead to Ga-face polarity of the heterostructure, which consisted of a 2µm undoped GaN buffer layer and a strained $Al_{0.3}Ga_{0.7}N$ layer with a thickness of 30 nm. A 3 nm GaN capping layer was deposited on top.
The ohmic source and drain contacts were formed by a Ti/Au metalization system, whereas the gate area (1x3mm^2) was kept non metalized and unpassivated. Except for this area the entire sample was sealed with silicon glue to avoid direct charge transfer from the incident ions to source and drain contacts. Positive and negative ions were generated in ambient atmosphere by a high voltage cascade plasma spray ionizer which allowed ion fluxes up to 10^{13} cm^{-2}s^{-1}. Either positive or negative ions were directed towards the sample under investigation and the modulation of the channel current caused by the incident ion flux was monitored. Figure 6 shows the observed current voltage characteristics of the HEMT device.
In the initial state a 2DEG with a sheet carrier concentration of 1.2x10^{13} cm^{-2} is detected about 34 nm beneath the sample surface by CV-profiling, leading to a channel resistance of 3.8 kΩ. An

incident negative ion flux onto the gate area results in an increase of the channel resistance by nearly four orders of magnitude to 22 MΩ. Exposure of the gate area to a positive ion flux decreases the channel resistance to 3 kΩ.

These observations indicate that compensation of the positive surface charge, which balances the sheet carrier density confined in the 2DEG, by negative ions depletes the channel almost completely. In contrast, a positive ion flux enhances the already existing compensating positive surface charge by providing additional adsorbed charge of an amount which is of the same order of magnitude as the already existing charge and, therefore, leading to a comparably small decrease in the channel resistance.

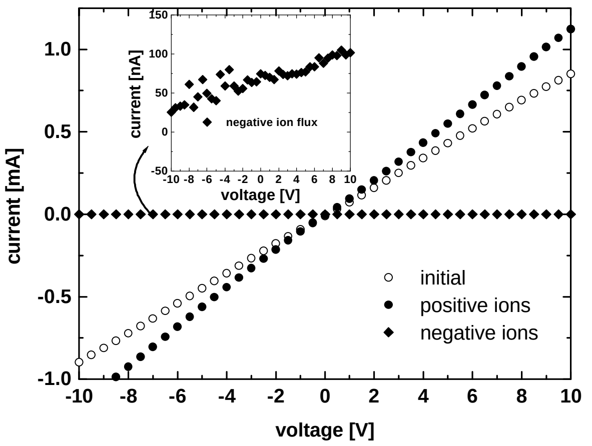

Fig.6: Current-voltage characteristics of a GaN/Al$_{0.3}$Ga$_{0.7}$N/GaN heterostructure in the initial state and after directing a positive or negative ion flux onto the unmetalized gate area. The insert shows a magnification of the I-V curve during negative ion flux.

Figure 7 shows the time dependence of the channel current upon switching positive and negative ion fluxes on and off at a constant source/drain voltage of 10 V. It can be seen that sudden exposure of the gate area to positive/negative ion flux leads to an immediate rise/drop in the channel current, whereas the relaxation back to the initial state takes place with a significantly larger time constant. Cyclic changes between the initial, depleted and accumulated state (no ion flux, negative ion flux, positive ion flux) were performed with complete relaxation to the initial state, indicating that no irreversible processes such as ion damage, formation of surface traps or surface oxidation contribute to the observed sensor response.

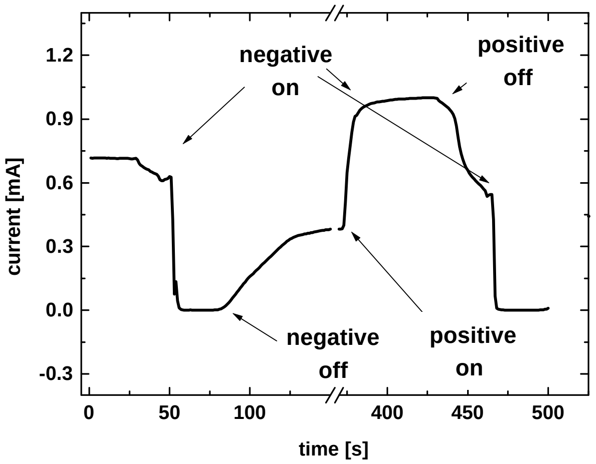

Fig.7: Time response of the channel current after switching on and off fluxes of negative or positive ions towards the sample surface.

Sensitivity to polar fluids

The adsorption of polar molecules on the surface of semiconductors leads to a corresponding variation of the surface potential [15]. In the case of an AlGaN/GaN HEMT structure, this will give rise to changes in the sheet carrier density of the 2DEG.

An identical sample structure as for the ion experiments described above was used. To study the influence of polar fluid molecules on the electric characteristics of the device, the non passivated gate area was immersed in different polar fluids. The resulting variations of the current voltage characteristics are shown in Figure 8. A decrease in the sheet carrier density due to interaction of the polar molecules with the polar GaN surface is observed, monitored by a drop of the pinch off voltage U_{PO} as well as a significant decrease of the saturation current.

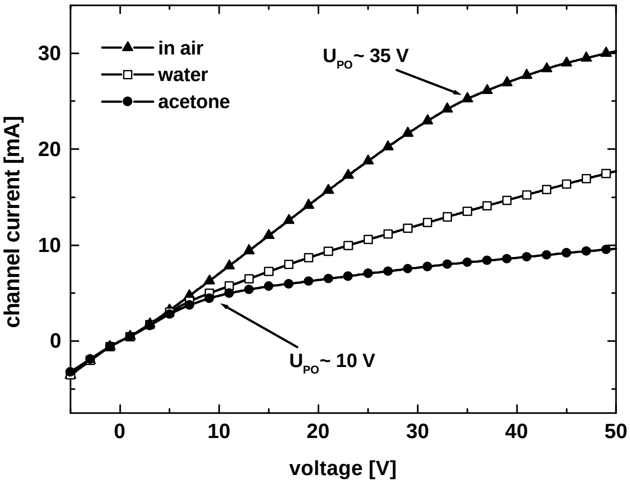

Fig.8: Changes in the I-V characterristics of an AlGaN/GaN HEMT structure due to the presence of polar fluids on the unpassivated bare gate area.

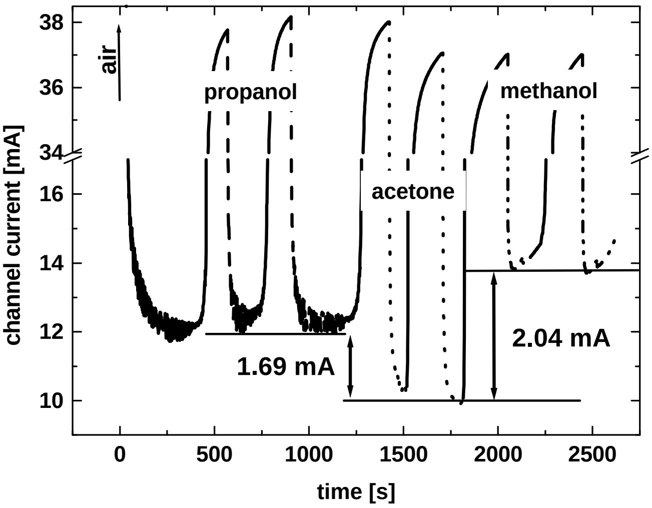

Fig.9: Time dependent changes in the channel current of a HEMT structure due to wetting of the gate area by different polar fluids.

Figure 9 compares the effect of three different fluids (methanol, isopropanol and acetone) as a function of time. In all cases, exposure to the polar liquid causes a drop of the channel current by a factor of approximately three, followed by a slow relaxation to the initial value after evaporation of the liquid.

As expected, acetone with the largest molecular dipole moment (2.7 Dy) leads to the strongest decrease in the sheet carrier density. On the other hand, isopropanol and methanol produce noticeable different sensor signals although they have a very similar molecular dipole moment of about 1.7 Dy.

A possible explanation for this discrepancy maybe the different molecular structure of these liquids. Although they exhibit a similar dipole moment, which results in a similar electrostatic dipolar interaction with the surface. Nevertheless the difference in the unpolar hydrocarbon structure leads to a different strength of van-der-Waals interaction. However, both van-der-Waals interaction and electrostatic dipolar interaction are weak in comparison to the thermal energy, which makes smaller molecules more likely to become misoriented with respect to the surface polarization fields of the uppermost GaN-layer. Consequently, as observed in our experiments, smaller molecules produce a smaller sensor signal in comparison to larger molecules with the same dipole moment.

As far as possible applications of the above mentioned effects are concerned, special interest has been focussed on the detection of contaminations in non-polar fluids. In preliminary experiments it was shown that the channel current of a HEMT device decreases monotonously with an increasing content of propanol when the gate area is exposed to a mixture of non-polar glycerol and polar propanol. Therefore, the sensor signal can be taken as a direct measure of the amount of polar liquid dissolved in an non-polar host [16]. This has a number of potential applications in industry, among which the detection of water contamination in hydraulic fluids is probably the most interesting one.

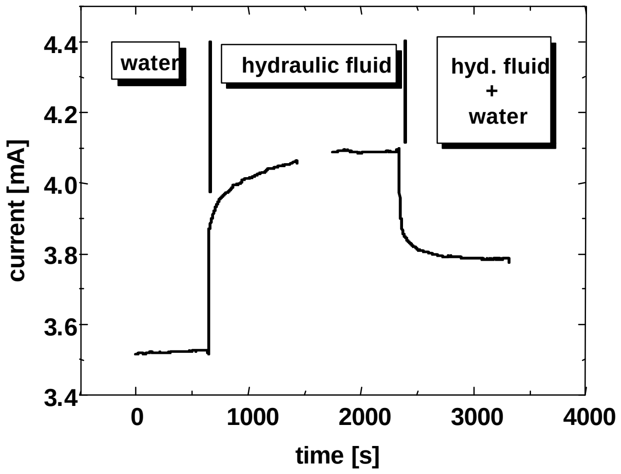

Fig.10: Channel current of a Ga-face AlGaN/GaN HEMT in water, hydraulic oil and an oil/water mixture with a water content of 10%.

As an example, the degradation of hydraulic fluids due to water contamination accelerates corrosion and thereby causes serious damage to the hydraulic actuator systems in aircrafts. A reliable and continuous measurement of the water content by means of an AlGaN/GaN HEMT device would lead to a significant reduction of maintenance costs while increasing the safety level. Figure 10 shows the different channel currents of a HEMT device in pure hydraulic fluid, pure water and in a mixture with a water content of 10% [16]. These results show that GaN-based sensors also hold great promise for this kind of applications.

SURFACE ACCOUSTIC WAVE DEVICES - INTEGRATION

In addition to their pyroelectric properties discussed in the content of sensor applications so far, III-nitrides also exhibit a large piezoelectric effect, which allows piezoelectric actuation of mechanical structures. In ternary $Al_xGa_{1-x}N$ alloys, the piezoelectric constants increase with increasing Al-content, which has lead to successful realization of SAW devices in the past [17]. Within those experiments, AlN layers were demonstrated to exhibit a very high surface acoustic wave (SAW) propagation velocity of about $4970ms^{-1}$, a high electromechanical coupling constant ($K^2 \approx 0.20\%$) and at the same time an almost negligible temperature coefficient of delay. Consequently, hexagonal AlN has been recognizes as an excellent material for the fabrication of low-cost SAW devices operating at microwave frequencies under harsh environmental conditions as for example elevated temperature or high doses of radiation. Figure11 shows the transfer functions of AlN-SAW filters grown by PIMBE on sapphire substrates. The interdigital transducers (IDTs) were structured by e-beam lithography with an electrode spacing of 1.5 µm and 1 µm corresponding to a SAW wavelength of 6µm and 4µm respectively [18]. Due to the high propagation velocity in the AlN layer and in the sapphire substrate, the measured center frequencies of the transfer function were 834 MHz and 1.24 GHz at effective propagation velocities of 5003 ms^{-1} and 4970 ms^{-1}. The increase in the propagation velocity with increasing wavelength is due to the higher propagation velocity of the sapphire substrate which becomes relatively more important for larger wavelengths, as the penetration depth of the acoustic wave into the sapphire substrate increases with increasing wavelength.

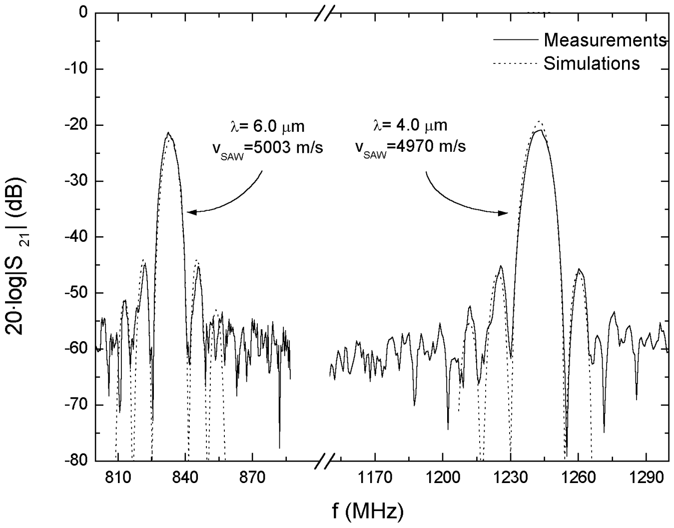

Fig.11: Transfer function of a SAW filter device on AlN grown by PIMBE on a sapphire substrate. The transfer functions for an IDT spacing of 1.5 µm and 1 µm are shown.

The successful realization of SAW devices on epitaxially grown AlN films opens the route for the preparation of monolithically integrated III-nitride sensor devices with wireless signal transmission. Among the above mentioned sensor concepts, those detection principles which result in variations of the sheet carrier density of the 2DEG in an AlGaN/GaN HEMT structure are the most promising ones in this respect. Such integrates systems would allow simultaneous growth of transistor structures for sensing or for electronic purposes together with SAW remote readout in the same material system. This would be a further step towards simplified fabrication of monolithically integrated sensor systems. Figure 12a shows a schematic drawing of such a SAW device for environmental sensing: The propagation characteristics of the SAW are strongly influenced by the carrier density in the 2DEG which is structured between the IDT structures for SAW excitation and reception. Similar sensor structures on silicon and other materials have already been realized and tested [19].

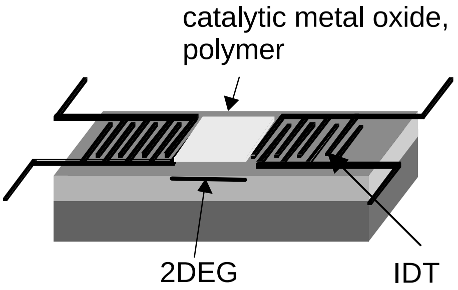

Fig.12a: Schematic drawing of a SAW device for sensor application.

The gate area of the HEMT device is the sensitive part of the device. It can be either unpassivated, unmetallized or uncoated in the case of ion detection or it can be covered by a gas sensitive metal oxide or polymer layer for chemical sensing. In each of these applications the sheet carrier density in the 2DEG is influenced by the environmental changes which are to be detected. This leads to changes in the propagation characteristics of the surface acoustic wave, which can be read out as a phase shift or attenuation between incoming and reflected wave (Fig.12b) or as a frequency shift in a closed feed back loop of an operation amplifier, which could also be monolithically integrated in the sensor/transmitter device.

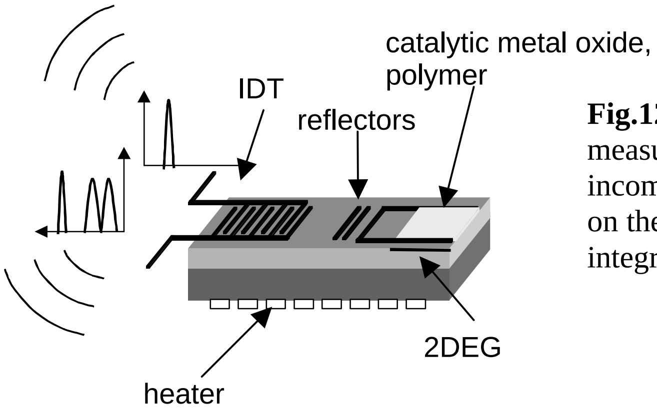

Fig.12b: SAW sensing device for measuring the phase shift between incoming and reflected wave depending on the sheet carrier concentration in the integrated HEMT structure.

CONCLUSION

Different kinds of III-nitride based sensors have been successfully realized. In addition to chemical sensors based on GaN thin films, AlGaN/GaN HEMT structures have been shown to be promising candidates for sensors in liquid or ion sensitive devices. In contrast to conventional ISFETs based on silicon technology [20], no gate coating is necessare, because of the polarization induced surface charges in III-nitrides, which give rise to a strong electrostatic coupling between the sheet carrier density in the 2DEG and the adsorbed polar molecules or incident ions on the unpassivated gate area. However, further work has to be done towards a more detailed understanding of the basic detection mechanisms and improvement of the reliability and reproduceability of these sensing devices.

Exploiting the strong piezoelectric effect in III-nitrides, SAW filters with center frequencies up to 1.2 GHz have been realized, motivating new concepts for monolithic integration of sensing elements, electronics and signal transmission. Based on the outstanding material properties of group-III nitrides these results allow the development of smart sensor concepts for mechanical, chemical and biological applications.

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