Surface Reaction of Undoped AlGaN/GaN HEMT Based Two Terminal Device in H⁺ and OH⁻ Ion-contained Aqueous Solution
(Tindak Balas Permukaan Peranti Dua Terminal HEMT AlGaN/GaN di dalam Larutan Akuas Mengandungi Ion H⁺ dan OH⁻)

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ABSTRACT

Gallium nitride is considered as the most promising material for liquid-phase sensor applications due to its chemical stability and high internal piezoelectric polarization. In this work, the sensing responses of undoped-AlGaN/GaN two terminal devices upon exposure to various pH levels in aqueous solution (a mixture of HCl and NaOH) as well as their possible sensing mechanism have been investigated. No reference voltage or gate voltage is applied. The changes in drain-source current, I_{DS} as a function of pH level were evaluated. In the acidic region, there was an almost linear change in I_{DS} where I_{DS} decreased with the increase in pH level. Hence, the translated channel resistance increases with the pH level. High H⁺ ion concentration at low pH level which corresponds to the large net positive potential on the surface leads to the enhancement of the flow of electrons in 2DEG channel. As the pH level was increased towards neutral point in the acidic region which corresponds to the increase of OH⁻ ion concentration, the net surface potential on the surface starts to be dominated by negative potential. As a result, the 2DEG channel starts to deplete which resulted in the increase of channel resistance. The estimated current and resistance change for sensing area of 1 mm² and drain-source voltage, V_{DS} of 1- 6 V are in the range of 2.16-80.1 mA/pH and 154.6-500.5 kΩ/pH, respectively. However, the linear decreases of I_{DS} were not continuously observed in the basic region where OH⁻ ions were dominant. The I_{DS} levels were high, showing that the flows of carriers in 2DEG channel were enhanced again. The resistance was low and almost constant in the basic region. It seems to be resulted by the formation of thin $Ga_{(x)}O_{(y)}$ layer on the AlGaN surface contributed by the interaction of OH⁻ with the Ga-face surface. Hence, the net potential on the AlGaN surface seems to be dominated again by the net positive surface potential.

Keywords: Gallium nitride; liquid sensor; two terminal devices

ABSTRAK

Galium nitrida (GaN) adalah bahan yang menjanjikan bagi aplikasi penderia cecair disebabkan ciri kestabilan kimianya dan juga kualiti dalaman polarisasi piezoelektrik. Di dalam kajian ini, tindak balas pengesanan peranti dua terminal struktur HEMT AlGaN/GaN terhadap pelbagai nilai aras pH dalam larutan akuas (campuran HCl dan NaOH) serta mekanisme penderiaannya dikaji. Tiada voltan rujukan atau voltan get digunakan. Perubahan arus salir-punca, I_{DS} sebagai fungsi aras pH dinilai. Di dalam rantau asid, perubahan I_{DS} hampir linear dan I_{DS} berkurang dengan kenaikan nilai aras pH. Oleh yang demikian, rintangan saluran yang ditaksirkan meningkat dengan kenaikan nilai aras pH. Kepekatan ion H⁺ yang tinggi pada aras pH rendah merujuk kepada keupayaan positif yang tinggi pada permukaan, mendorong kepada peningkatan aliran elektron dalam salur 2DEG. Semakin tinggi aras pH ke arah titik neutral di dalam rantau asid yang merujuk kepada peningkatan kepekatan ion OH⁻, keupayaan bersih permukaan mula didominasi dengan keupayaan negatif. Kesannya, salur 2DEG mula merosot dan mengakibatkan peningkatan rintangan salur. Anggaran perubahan arus dan rintangan bagi kawasan penderiaan bersaiz 1 mm² dan voltan salir-punca, V_{DS} bernilai 1- 6 V adalah dalam julat 2.16-80.1 mA/pH dan 154.6-500.5 kΩ/pH. Walau bagaimanapun, penurunan linear I_{DS} diperhatikan tidak berterusan di rantau bes dengan ion OH⁻ adalah dominan. Aras I_{DS} yang tinggi menunjukkan aliran pembawa di dalam salur 2DEG meningkat kembali. Rintangan adalah rendah dan hampir tidak berubah di dalam rantau bes. Hal ini mungkin berpunca daripada pembentukan lapisan tipis $Ga_{(x)}O_{(y)}$ di atas permukaan AlGaN yang berpunca daripada interaksi OH⁻ dengan permukaan muka-Ga. Seterusnya, keupayaan bersih di atas permukaan AlGaN kelihatan didominasi semula oleh keupayaan permukaan positif.

Kata kunci: Galium nitrida; penderia cecair; peranti dua terminal

INTRODUCTION

Many wide bandgap semiconductor materials especially gallium nitride (GaN), have been tested for their suitability as sensitive chemical sensors (Stutzmann et al. 2002). AlGaN/GaN heterostructures have been extremely useful for gas and liquid sensor due to primarily three reasons: a high electron sheet carrier concentration channel induced by piezoelectric polarization of the strained AlGaN layer (Pearton et al. 2006); the carrier concentration which strongly depends on the ambient (Chaniotakis et al. 2007; Eickhoff et al. 2003) and an opportunity of on-chip co-integration with signal processing and communication circuit to provide high speed transmission of the data (Hasegawa & Akazawa 2008). In addition, due to their low intrinsic carrier concentrations, wide bandgap semiconductor sensors based on GaN can be operated at lower current levels than conventional Si-based devices and offer the capability of detection up to 600°C (Muller et al. 2002). For these reasons, GaN-based high electron mobility transistor (HEMT) structures are versatile structures that may be used for a variety of sensing applications such as in spacecraft, satellite, homeland defence, mining, automobile, nuclear power and radar applications.

The study on the pH responses to n-doped AlGaN surfaces was reported by Kokawa et al (2006), utilizing three-terminal open-gated structure. The possibility of pH sensing using two-terminal undoped AlGaN/GaN HEMT was reported by Mehandru et al. (2004). The fabricated two-terminal device showed significant changes in current upon exposure of the open area to solvents (water, acetone and HCl) (Mehandru et al. 2004). Song and Wu (2006) have also reported the sensing responses of undoped AlGaN/GaN based two-terminal devices in polar liquids. There are some major works that study the effect of oxide layers on open-gated AlGaN/GaN HEMT devices (Kang et al. 2007, 2008). According to Kang et al. (2007, 2008) the possible sensing mechanism of pH and dipole moments to GaN and AlGaN surfaces can be related to the action between polarization-induced positive surface charges and ions in the electrolyte on the exposed region of GaN or AlGaN/GaN structures, which affect the surface charges of the devices. The change in the surface charge will result in the change in the carrier concentration of the channel causing a change in drain-source current, I_{DS}. As a result, changes in pH and dipole moments of the solution can be known by the relative changes in current. The major advantage of using two-terminal instead of three-terminal structure lies in a simple structure and measurement setup. However, the disadvantage of two-terminal device is that the channel may be hard to be completely pinched off. The advantages of undoped-AlGaN/GaN structures as compared with doped structures are lower gate leakage current, lower pinch-off voltage and less noise due to the absence of any donor in the AlGaN.

Recently, Podolska et al. (2010) reported that two-terminal (ungated) AlGaN/ GaN devices are sensitive to ionic concentrations in solutions rather than to the pH of the solution, with selectivity towards negative ions over positive ions. They have studied truely gateless four contact device configuration without a reference electrode.

The aim of the present study was to investigate the sensitivities of these ungated AlGaN/ GaN heterostructure devices in the mixed solution of NaOH and HCl. We observe the linear change of current and resistance in acidic region but unchanged current and resistance in the basic region. Based on the obtained results, we propose the model of surface reaction which relates to the variation of H^+ and OH^- ion concentration in electrolyte and their interactions with Ga-face surface.

EXPERIMENTAL PROCEDURES

In this work, the undoped-AlGaN/GaN heterostructure (Al fraction: 25%) grown on 430 μm-thick sapphire substrate by metal organic chemical vapor deposition (MOCVD) was used. From Hall measurement at room temperature, the carrier mobilities and the 2DEG sheet carrier density of AlGaN/GaN heterostructure were 1860 cm^2/Vs and 6.61×10^{12} cm^{-2}, respectively. The heteroepitaxial growth of the group III-nitrides on sapphire substrate allows the application of simple planar device structures (Edgar & Liu 2002). The following AlN buffer layer is necessary as it dramatically improves the surface morphology and crystalline quality of the following undoped-GaN layer (Edgar & Liu 2002). For the AlGaN/GaN structure, those two adjacent layers form a two-dimensional electron gas (2DEG) in between.

Figures 1(a) and 1(b) show the top view of fabricated device and the cross sectional schematic of AlGaN/GaN-based two-terminal device, respectively. The mesa pattern or channel was formed by conventional photolithography and reactive ion etching (RIE). The two ohmic contacts were formed by conventional photolithography, followed by electron beam deposition of Ti/Al/Ti/Au (20/50/35/50 nm) and standard lift-off technique. The ohmic characteristics of both contacts were obtained by alloying at 850°C in N$_2$ ambient for 30 s. 100 nm-thick SiO$_2$ layer was used to cover the contacts from being directly exposed to electrolyte during measurement. SiO$_2$ layer was deposited at 300°C using plasma-enhanced chemical vapor deposition (PECVD). The sensing area (dimension of 40 μm × 490 μm) was formed by etching out the SiO$_2$ layer using buffered hydrofluoric (BHF) solution that was defined by standard photolithography. Two samples with the same dimension named as device A and device B were used for sensing measurement.

For measurement, as shown in Figure 2, the device was mounted on a printed circuit board (PCB) where the copper lines were also covered with the PCB resist to prevent these copper lines from being exposed to the electrolyte. These two copper lines were connected to the source measure unit (SMU) so that the drain-source voltage, V_{DS} can be applied. The In wires made to connect the devices to copper lines as well as the ohmic contacts were covered with photoresist. The fabricated device was immersed in teflon beaker that
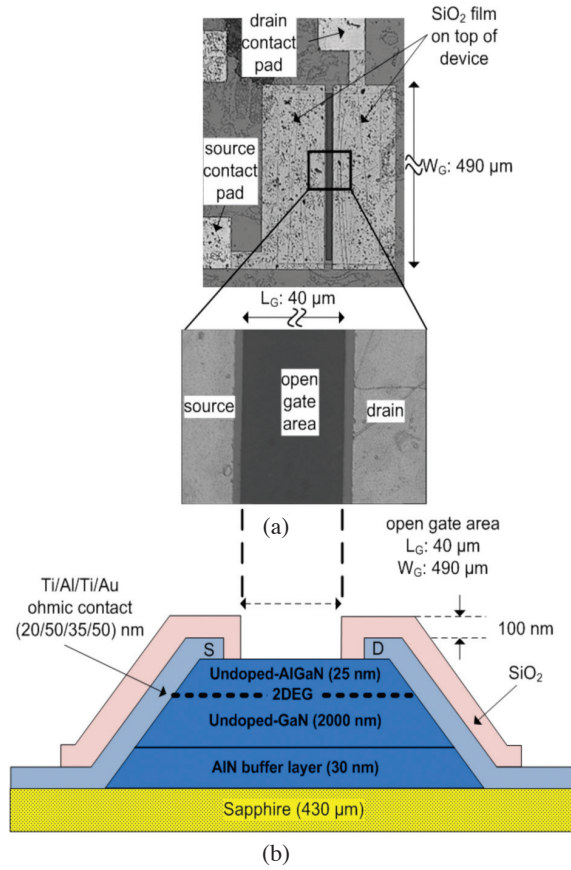
FIGURE 1. (a) Top view of fabricated device and (b) cross sectional schematic of AlGaN/GaN HEMT based two terminal devices
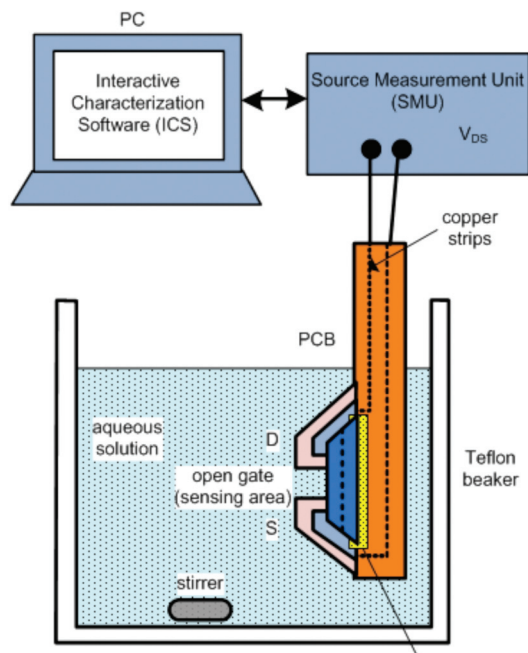

FIGURE 2. Schematic of measurement setup

contained an aqueous solutions with different pH values as the testing electrolytes. The I_{DS} was measured by interactive characterization software (ICS). All measurements were done at room temperature.

RESULTS

pH is a measure for acidity or alkalinity of a solution even though by definition it is a selective measurement of H^+ ion activity. In acidic region, the lower pH shows higher H^+ concentration while in the basic region, the higher pH shows higher OH^- concentration. In this study, a mixed solution of NaOH and HCl were used as the electrolyte. The pH of this solution is varied to specific pH values within the range of 2 to 12, monitored by pH meter.

Figures 3(a) and 3(b) show the changes of I_{DS} as a function of pH or ion concentration at certain V_{DS} values for device A and B, respectively. In the acidic region (pH<7), systematic changes in I_{DS} were observed in almost linear fashion for both devices, implying the existence of systematic surface potential change. However, in the basic region (pH>7), a very weak dependence was observed. Besides current responses, changes in resistance as a function of pH at certain V_{DS} values were also derived using simple Ohm's law relationship for both devices as shown in Figure 4. Resistance of 3.63 kΩ calculated from the open air-exposed measurement is also shown as reference. For both devices, since there is a linear reduction of the current with respect to pH in acidic region, the calculated resistance is also showing linear tendency. However, no increase of resistance was obtained when pH exceeds the neutral point. There was a drastic reduction of resistance and the values are almost the same at all pH levels in the basic region. Also, it was shown that the resistances measured at low pH of 2 - 4 and basic region are close to the resistance measured in open-air condition.

The estimated current and resistance change for sensing area of 1 mm^2 and V_{DS} of 1-6 V are in the range of 2.16-80.1 mA/pH and 154.6-500.5 kΩ/pH, respectively. Such values are considerably acceptable for this AlGaN/GaN two terminal device to be considered good enough in sensing the pH level in acidic region. However, such structure may not good for basic region due to small changes in I_{DS}. We believe that in order to create and maintain a systematic or continuous change of current in the basic region, the application of the third terminal i.e. gate voltage is necessary.

POSSIBLE MECHANISM

In the present study, we proposed that the net surface potential in the open area of the two-terminal device is simply and directly being altered according to the concentration of the H^+ and OH^- ions, leading to the modulation of I_{DS} as well as the resistance of the device. This evolution of net surface potential as the pH level is increased from 2 to 12 is discussed according to three main phases as illustrated in Figure 5.

At low acidic region (pH2~4: referred to phase 1), almost linear changes are observed in I_{DS} which decrease as the pH level increases, thus implying the increase in the resistance of the channel with increase in pH. At low pH, high H^+ concentration or large net positive potential on the surface leads to increase the flow of electrons in the 2DEG channel.

As the pH level is increased towards the neutral point (pH 4-<7: referred as phase 2), the net positive surface potential reduces and becomes dominated by the negative potential due to the increase in OH^- ion concentration. The 2DEG channel starts to be depleted by the net negative surface potential leading to the decrease of I_{DS} and the increase of channel resistance. These observations are consistent with the experimental observations reported by
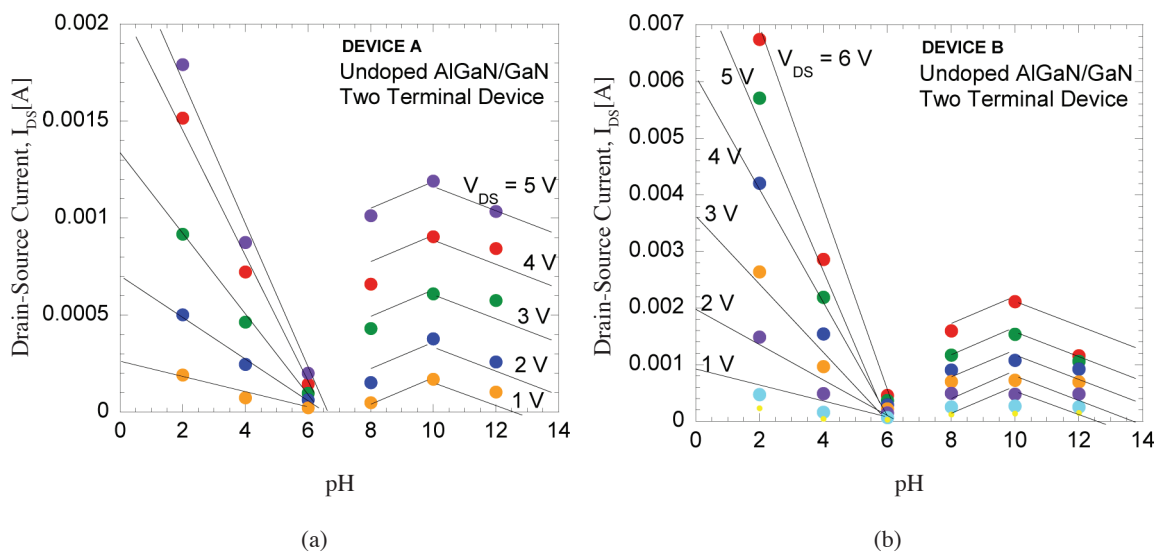

(a)

(b)

FIGURE 3. Changes in I_{DS} as a function of pH at certain V_{DS} values for (a) device A and (b) device B
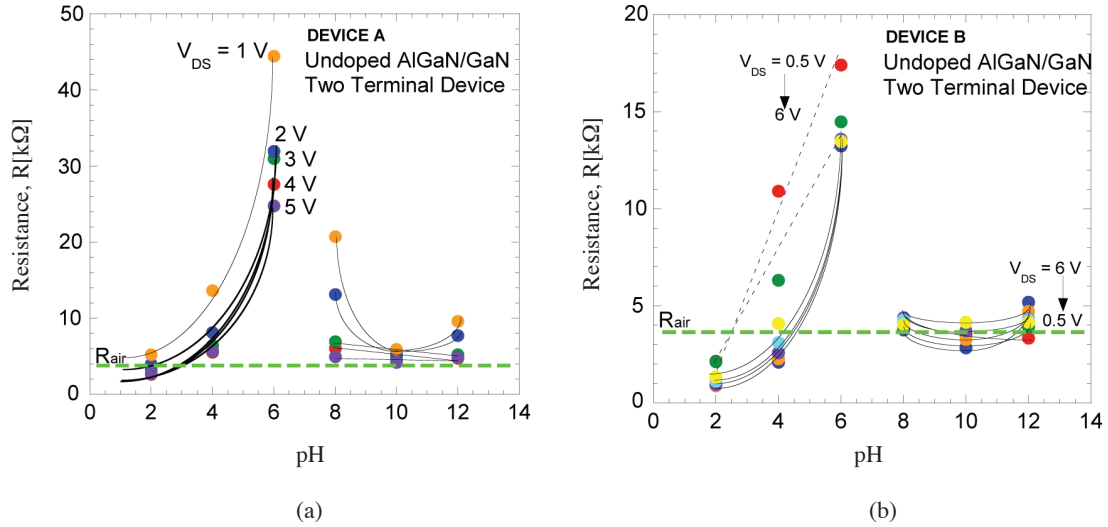
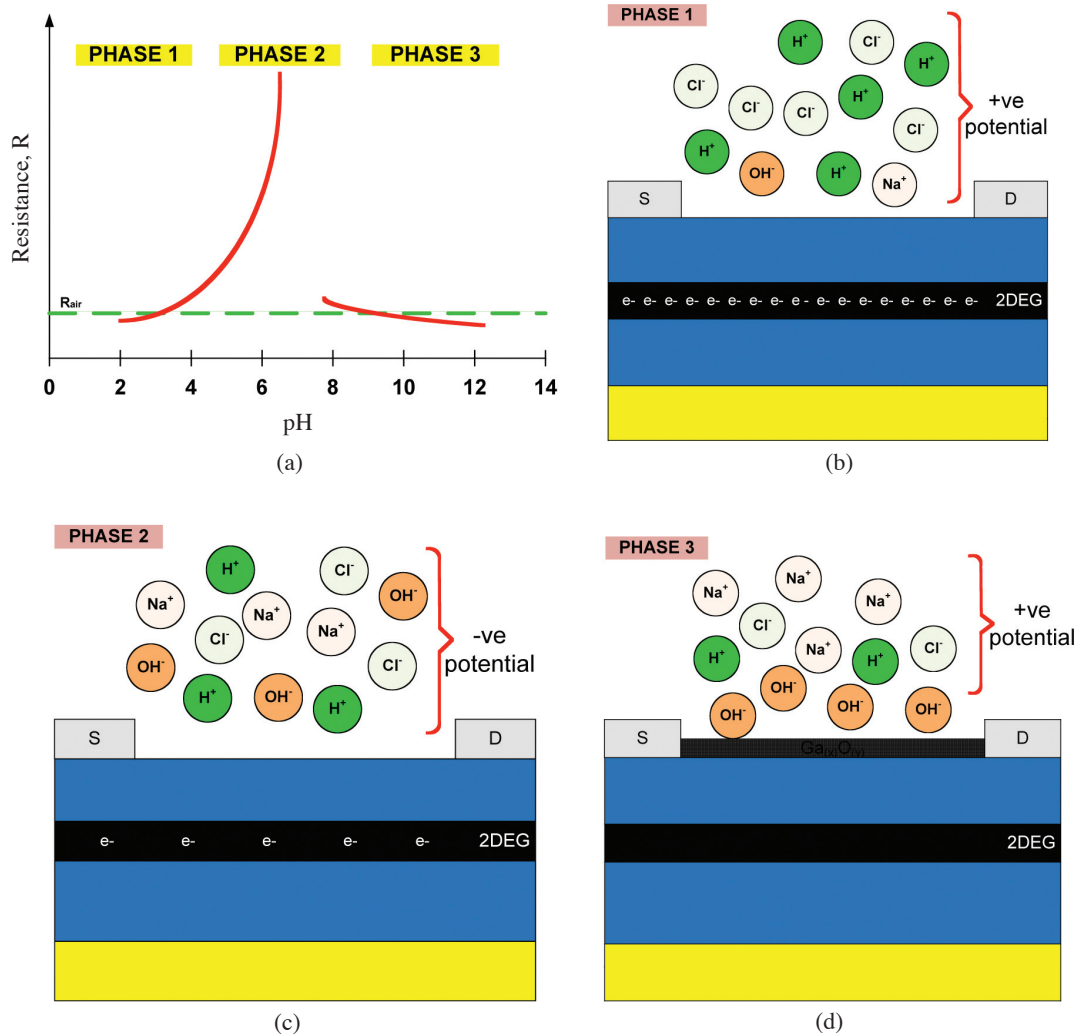FIGURE 4. Changes in resistance as a function of pH at certain V_{DS} values for (a) device A and (b) device B

FIGURE 5. (a) Summary on three phases of changes due to ions presence in electrolyte causes the alterations of net potential of devices (b) Phase 1: H+ concentration is dominant in this phase. Thus, surface potential becomes positive. Current flow is enhanced and channel resistance becomes low (c) Phase 2: Presence of larger amount of OH- in solution causing negative potential. Channel begins to deplete, leading to low current flow and high resistance (d) Phase 3: OH- ions from NaOH will react with Ga-face surface and form gallium oxide layer on the top of sensing region. Accumulation of other ions from solution seems to create the net positive potential thereby, channel resistance will be lowered and almost similar to R_{air} (3.63 kΩ)

Neuberger et al. (2002). They reported that by exposing the sensing region of the surface to positive ions, the resistance of the channel reduces while increases if exposed to negative ions.

The further reduction of I_{DS} and the increment of channel resistance are not observed when the pH levels are increased in basic region (pH >7-12: referred as phase 3) where negative ions OH⁻ are dominant. However, large currents are obtained which becomes almost constant in the basic region which resulting in the decrease of channel resistance. In this case, we believe that the double layer is present on the surface of the semiconductor. The layer consists of the surface charge (positive charge) present on the AlGaN and the layer of counter ions (negative charge) present in the electrolyte next to AlGaN. The ions present in the electrolyte are adsorbed by the surface charges via electrostatic forces. As the concentration of negative ions is increased in the solution, the charge on the Ga-face surface would be neutralized by monolayer of ions of opposite charge (negative ions) to that of the surface. Thus, gallium oxide [$Ga_{(x)}O_{(y)}$] layer will form and the net surface potential becomes positive and the flow of current is enhanced.

CONCLUSION

In summary, as a result of systematic linear change of current and resistance in acidic range, so this undoped-AlGaN/GaN two terminal device is considered good enough to differentiate the pH level. However, this two terminal structure may not be good to be used to differentiate the pH level in the basic region due to the formation of the $Ga_{(x)}O_{(y)}$ layer contributed by the OH⁻ ions which results in the unchanged flow of current and resistance.

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