Electrical Characteristics of GaN-based Metal-Oxide-Semiconductor (MOS) Structures

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Abstract

Gallium nitride (GaN) has attracted considerable interest for electronic device applications at high temperature environment with high power conditions. The large lattice mismatch and the large thermal expansion coefficient difference between the GaN film and silicon substrate makes it difficult to get film of high quality and suitable for the metal-oxide-semiconductor (MOS) devices. However, deposited films can be subjected to different fabrication processes to exhibit good electrical characteristics. In this paper, we report on the fabrication and characterization of MOS capacitor based on GaN grown on silicon substrates at low growth temperatures (200°C and 600°C). The roughness, morphology, composition and crystalline quality of the GaN films were determined by atomic force microscopy (AFM), scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX) and x-ray diffraction (XRD) measurements. The fabricated MOS structures were characterized using capacitance-voltage (C-V) measurements.

1. Introduction

Wide band gap, nitride-based semiconductors have recently attracted much attention, mainly because of their tremendous potential for applications in high power and high frequency devices. GaN films used in the mass production of such devices are grown by metalorganic chemical vapor deposition on sapphire and SiC substrates. However, they are limited in size and still rather expensive. Attempts to grow GaN on substrates like Si or quartz, which are available at low cost and large areas have resulted in highly defective films [1]. An extremely interesting application of integration with Si technology is the development of Si/GaN metal-oxide semiconductor (MOS) capacitor.

Amorphous (a-GaN), microcrystalline (μc-GaN) or polycrystalline (pc-GaN) gallium nitride (GaN) films have the advantage that they can be produced more cheaply and on large substrates and it has been shown theoretically that amorphous films could have a large, state-free band gap [2]. Amorphous, microcrystalline and nanocrystalline GaN grown by reactive sputtering have been reported [3,4,5].

The metal–insulator–semiconductor (MIS) or MOS structures consist of a semiconductor substrate covered by an insulator layer (such as SnO_2, SiO_2). MOS structures could be fabricated either with thin dielectric layer ($d \leq 50$ Å) or thick dielectric layer ($d \geq 50$ Å). These structures essentially constitute a capacitor which stores the electric charge by virtue of the dielectric property of insulator or oxide layers. Due to its importance in Si technology, the insulator/semiconductor (such as SnO_2/Si, SiO_2/Si) interface and associated defects on its neighborhood have been extensively studied in the past four decades [6].

Dielectric layers in the dice technology play many important functions such as: passivation of semiconductor surface, selection of semiconductor regions in doping processes, electrical insulation of selected structures of semiconductor device and protecting the device from environmental hazards [7]. On the other hand, insulating dielectric films are used as gate dielectrics in MOSFET structures, as insulating layers in multilevel interconnects, as capacitor dielectrics in dynamic random access memory (DRAM), in thin film transistors (TFT), as intermetal insulators in detector and sensor applications, or for solar energy devices. Requirements on these films are high breakdown field strength, high resistance, low leakage currents and low defect density [8].

Studies of MIS structures using GaN have been performed with deposited SiO_2 and Si_3N_4 acting as the gate insulator. Casey et al. [9] produced a MOS capacitor using remote-plasma-enhanced chemical vapor deposition (RPECVD) of SiO_2 on epitaxial n-GaN. The study indicated a flat band voltage of –2.35 V, which corresponds to a fixed positive charge of approximately 10^{12} cm^{-2}.

Present work reports on the characterization of GaN films grown on Si (100) substrates at low growth temperatures by electron cyclotron resonance (ECR) plasma assisted metalorganic chemical vapor deposition (PA-MOCVD) and fabrication of MOS capacitors based on these films.

2. Experimental

The GaN films under study are grown on Si (100) substrates by ECR PA-MOCVD at 200°C and 600°C. Details of the growth apparatus and procedures have been given previously [10]. Atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) were used to determine the surface morphology and to analyze the contents of the GaN film. X-ray diffraction (XRD) was used to assess the structure of the deposited layers.

The oxide layer deposition was prepared by using spin-on of SiO_2 glass. After SiO_2 film deposition, a 200°C anneal for 1 hour was done. Then, aluminium was deposited as gate contacts on dielectric layer and ohmic back contact on Si substrate by vacuum evaporation. The fabricated MOS structure was characterized using capacitance-voltage (C-V) with computer aided measurement system (Keithly Instrument with ICS Software).

3. Results and discussion

The transparent GaN thin films exhibit smooth surface morphology as revealed by SEM mesurements. The presence of Ga and N in the samples are confirmed by EDX measurements. The root mean square (rms) surface roughness, measured by AFM on a 2×2 μm^2 scan area were 4.95 nm (600°C sample) [11] and 1.86 nm (200°C sample).

The x-ray diffraction (XRD) spectra of the GaN layer grown on Si substrates are shown in Figure 1. The pattern for film grown at 200°C only reveal substrate peaks at 33.4° and 69.6° which correspond to Si(200) and Si (400) planes respectively. No x-ray diffraction peak corresponding to the crystalline phase of GaN was detected, suggesting an amorphous structure. For the GaN film grown at 600°C, weak peak was observed at 34.6° which corresponds to (0002) hexagonal wurtzite crystalline GaN. X-ray diffraction peaks for GaN should be observed at around 32.3°, 34.6° and 36.8° which correspond to $(10\bar{1}0)$, (0002) and $(10\bar{1}1)$ planes of the hexagonal crystalline GaN. The absence of strong and sharp GaN crystalline peaks and a broadening centered at the crystalline region for films grown at 873K could be an indication that these films are a mixed phase of crystalline and amorphous structure. This is probably a signature of the microcrystalline phase for GaN. The crystallite (grain) size determined by the Scherrer method is about 167 nm, thus confirming the microcrystalline structure of our films [11]. Additionally, previous photoluminescence measurements performed at low temperatures (9K-12K) for films grown on silicon at 923K revealed a broad "blue" emission band centered at 391 nm (3.17 eV). In contrast, films grown below 200°C which is amorphous in structure exhibited a broad "green" emission centered at ~510 nm (2.40 eV) [10]. Weak broad band lower energy emissions centered at 430 nm (2.88 eV) were observed for films grown at 600°C [11]. All of these spectra do not exhibit sharp near band edge emissions at 357 nm (3.47 eV) commonly observed for epitaxial GaN films grown on sapphire by MOCVD. It should also be noted here that this single broad band emission characteristic is similar to that observed for a-SiC:H and μc-SiC:H [12]and also nano-crystalline GaN (nc-GaN) deposited on quartz substrates by reactive sputtering [4].

The capacitance-voltage (C-V) characteristic of the fabricated MOS structures are shown in Figure 2. The minimum capacitance, $C_{\min}$ can be expressed by:

$$C_{\min} = \frac{C_{ox} C_s}{C_{ox} + C_s} \qquad (1)$$

where C_{ox} is the oxide capacitance and C_s is the semiconductor capacitance. Using the experimental values obtained for $C_{\min}$ and C_{ox}, C_s is determined to be 7.79 pF and 11.51 pF for MOS structures based a-GaN (200°C sample) and μc-GaN (600°C sample) respectively.

The surface charge potential, ϕ_{fn} is given by:

$$\phi_{fn} = V_t \ln\left(\frac{N_d}{n_i}\right) \qquad (2)$$

where V_t is thermal voltage, N_d is density of donor impurity atoms and n_i is intrinsic concentration of electrons. Using equation (2), the surface charge potential, ϕ_{fn} were deduced to be -1.39 V (200°C sample) and -1.41 V (600°C sample) based on V_t value of -0.0259, N_d values of 4.06×10^{13} cm^{-3} (200°C sample), 9.00×10^{13} cm^{-3} (600°C sample) and n_i value of 2.0×10^{-10} cm^{-3}. The intrinsic carrier concentration, n_i is 2.0×10^{-10} cm^{-3} for GaN at room temperature with an electron density of states effective mass, $m_n^* = 0.2m_o$, a hole density of states effective mass, $m_p^* = 1.0m_o$ and an energy gap of 3.4 eV [13].

The maximum surface charge width, $x_{d\max}$ can then be calculated using

$$x_{d\max} = \left\{\frac{4\varepsilon_{GaN}\phi_{fn}}{eN_d}\right\}^{\frac{1}{2}} \qquad (3)$$

Here ε_{GaN} is the permittivity of GaN which is equal to 8.41×10^{-13} Fcm^{-1} and e is the electronic charge. From equation (3), the maximum surface charge width, $x_{d\max}$ is calculated to be 8.48×10^{-4} cm (200°C sample) and 5.74×10^{-4} cm (600°C sample).

The fixed oxide charge per cm^2, N_f is defined as

$$V_{FB} = V^o{}_{FB} - \frac{eN_f}{C'_{ox}} \qquad (4)$$

where V_{FB} is the flat band voltage, $V^o{}_{FB}$ is the ideal oxide flatband voltage which is given by the difference between the work functions of the Al gate electrode and the work function of the GaN, C'_{ox} is the capacitance of the oxide per unit area. From the C-V curves, the threshold voltages and flat band voltages for the 200°C sample and 600°C sample were deduced to be -4.95 V and -4.01 V ; and 1.72 V and -0.65 V respectively. Using equation (4), if the work function of Al is taken as 4.1 eV and the work function of GaN is taken as 4.1 eV [14], then the calculated value of the fixed oxide charge density, N_f is 2.72×10^{10} cm^{-2} (200°C sample) and 2.82×10^{10} cm^{-2} (600°C sample), indicating a slight increase of the N_f value with increasing GaN growth temperature.

The fabricated MOS structures based on amorphous and microcrystalline GaN films revealed similar values of N_f, but less than the value obtained for MOS structure based on epitaxial GaN [9]. Typical values reported with the remote plasma SiO_2 on Si are 4-6×10^{11} cm^{-2} [13]. These results are encouraging for further investigation of MOS capacitors based on low temperature GaN films, which includes nanocrystalline GaN (nc-GaN).

4. Conclusion

Al/SiO_2/GaN MOS capacitors based on unintentionally doped n-type amorphous GaN and microcrystalline GaN grown on Si substrates have been successfully fabricated and characterized. The values of fixed oxide charge density, N_f determined from capacitance-voltage (C-V) measurements were 2.72×10^{10} cm^{-2} and 2.82×10^{10} cm^{-2} for MOS capacitors based on GaN grown at 200°C (a-GaN) and 600°C (μc-GaN) respectively. Structural analysis of these GaN films showed that these transparent films exhibited smooth surface morphology as revealed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements.

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Figure caption

Figure 1. XRD pattern of GaN grown on Si (100) at (a) 200°C and (b) 600°C

Figure 2. Capacitance-voltage characteristics of fabricated MOS structures based on GaN grown at (a) 200°C and (b) 600°C

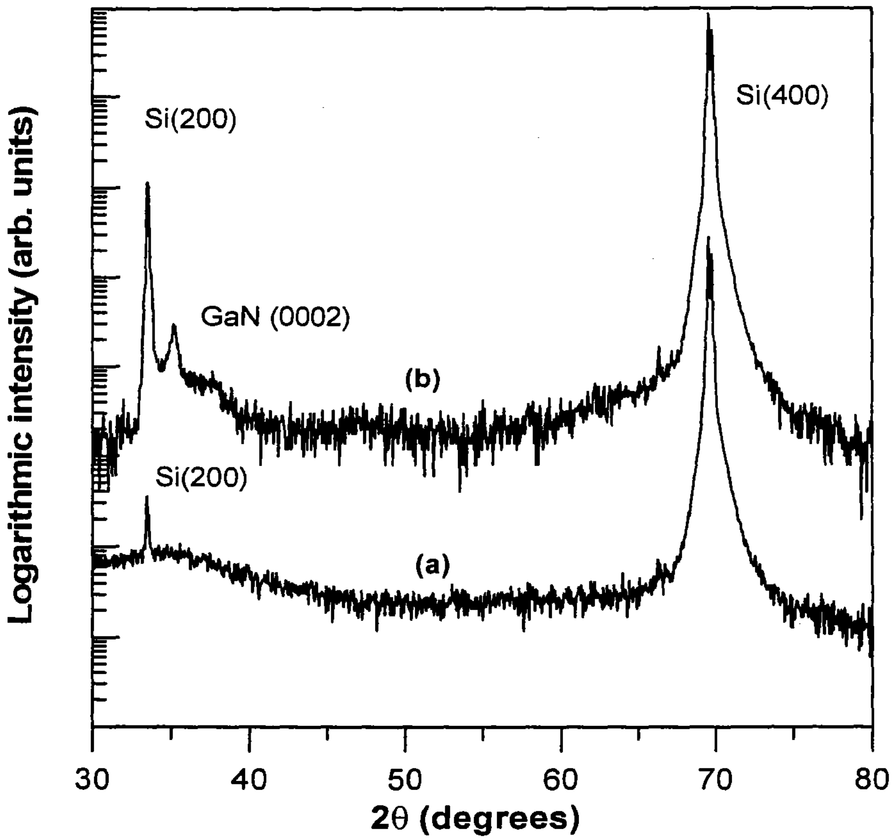

Figure 1. XRD pattern of GaN grown on Si (100) at (a) 200°C and (b) 600°C

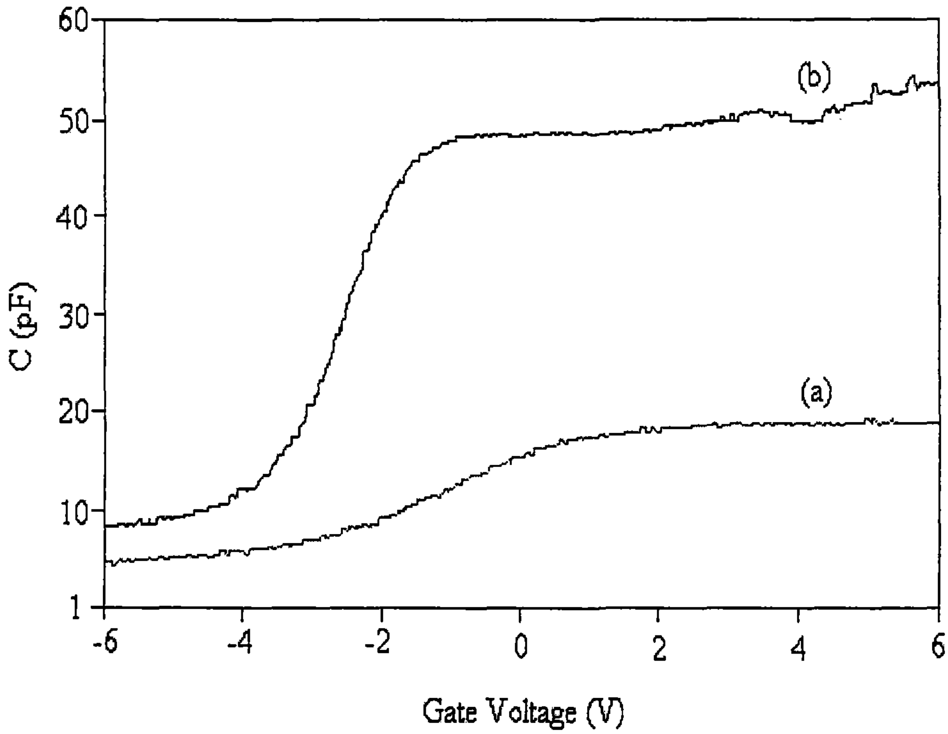

Figure 2. Capacitance-voltage characteristics of fabricated MOS structures based on GaN grown at (a) 200°C and (b) 600°C

Reversible barrier height changes in hydrogen-sensitive Pd/GaN and Ni/GaN diodes

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KEYWORDS: GaN; Gas-sensor; Schottky diodes; Hydrogen detection

Abstract

In this paper, Schottky contacts of Pd and Ni film were deposited on n-GaN using thermal evaporation, and annealed at 600°C for 1 hour. The forward current of Pd/GaN and Ni/GaN Schottky diodes is found to increase significantly upon introduction of H_2 into a N_2 ambient. Analysis of the current–voltage characteristics as a function of temperature showed that the current increase was due to a reduction in effective barrier height probably caused by a decrease in metal work function upon absorption of hydrogen. The introduction of 2 percent H_2 into a N_2 ambient was found to lower the effective barrier height of Pd on GaN by 70~160 meV over the temperature range of 25 to ~325°C and that of Ni on GaN by 90~170 meV over the range of 170 to ~400°C. The magnitude of the changes increased with temperature due to the high diffusivity of H_2 into the sample as observed by other researchers on Pt/GaN. The changes in barrier height were completely reversible upon restoration of N_2 ambient.

1.Introduction

The detection of hydrogen and hydrocarbon gases is necessary for applications such as combustion control and leak detection. Gas sensors have been fabricated on a number of semiconductors using catalytic metals as the gate in metal–insulator–semiconductor MIS devices or as the metal contact in Schottky diodes [1]. Hydrogen or hydrocarbon gases are dissociated by the catalytic metals in these sensors, and hydrogen atoms diffuse to the device interface. It is presumed that a dipole then forms, lowering the effective work function of the metal and changing the electrical characteristics of the devices. High temperature operation and long term stability are important requirements for gas sensors. Hydrocarbons are dissociated by catalytic metals only at elevated temperatures, making it necessary for hydrocarbon gas sensors to be operated at these temperatures. Gas sensors based on Si cannot be operated above about 250°C, prohibiting them from being used as hydrocarbon detectors or for other applications requiring high temperature operation. On the other hand, semiconductors with wider bandgaps retain their semiconducting properties at higher temperatures and can therefore be operated as gas sensors at higher temperatures.

To make such gas sensors, a catalytic metal such as Pd or Ni may be used in either a capacitor or a Schottky diode device that is stable at the desired operating temperature. SiC is a wide-bandgap semiconductor that has been investigated for gas sensing applications [2-7]. Pt–SiO –SiC gas sensors have been operated at temperatures as high as 800°C by adding a TaSi layer to the device structure improving the stability of the Pt layer [4]. Schottky diode gas sensors have advantages over MIS devices in their ease of fabrication, eliminating the need for the growth or deposition of an insulator layer, and in their sensitivity, since the diode reverse current varies exponentially with barrier height. Schottky diodes on SiC have been investigated for hydrogen gas sensing but displayed poor thermal stability [8,9]. Pd Schottky contacts on SiC have been observed to react at temperatures as low as 425°C, forming Pd silicides [8]. Although hydrogen detection was possible after this reaction, the electrical characteristics of the Pd–SiC Schottky diodes had changed considerably.

GaN is a wide-bandgap semiconductor ($E_g = 3.4$ eV) that shows great promise for electronic devices operating at high temperatures. In this paper we report on measurements of the forward current-voltage (I-V) characteristics of both Ni/GaN and Pd/GaN Schottky diodes in N_2 and 10% H_2 in N_2 ambient at different temperatures. The presence of hydrogen in the ambient is found to have lowered the effective barrier height of Pd on GaN by 70~160meV in the temperature range 25 to ~325°C and of Ni on GaN by 90~170 meV in the temperature range 170 to ~400°C. The changes are larger as temperature increases, consistent with more effective catalytic cracking of the H_2.

2. Experimental

The n-type GaN epilayers on sapphire with carrier concentration of 3×10^{17}cm^{-3} were used in this study. Clean surfaces were prepared by the following procedure. Prior to the metal deposition, the native oxide was removed in the NH_4OH: H_2O (1:20) solution, follow by HF: H_2O (1:50). Boiling aqua regia HCl: HNO_3 (3:1) was used to chemically etch and clean the samples. A rectifying contact of either Pd or Ni was deposited by thermal evaporator (Edward 306) at base pressure of at least 5×10^{-5} Torr onto the GaN through a metal mask. After deposition the samples were annealed under flowing argon gas environment in the furnace at 500°C for 6 minutes, and the film was cleaned and dried for 1 h at 80°C. The sensitivity tests were carried out in a homemade testing chamber. Before the measurement, the sample was pre-heated by heating it to 500°C and cooling it to 50°C. This step was repeated three times before starting film characterization in order to clean the sample from water vapour. Measurements were performed at temperatures from 25-500°C in flowing gas ambients of N_2 or 2% H_2 in N_2. Current-voltage (I-V) measurements were performed to the as deposited and samples annealed, where the I-V behaviour of each of these conditions were compared for different gases and different temperatures.

3. Result and discussions

Figure 1 shows forward I-V characteristics from the Ni/GaN diodes at two different temperatures (25 and 300°C) in both N_2 and 2% H_2 in N_2 ambients. There is a shift of ~1V at 25°C and ~1.3V at 300°C in the forward bias needed to maintain a current of 1.5mA. This shift is indicative of a change in Schottky barrier height, Φ_b which is related to the work function of the Ni Φ_m and the electron affinity χ_s of the GaN through the relation

$$\Phi_b = \Phi_m - \chi_s = eV_{bi} + \xi \qquad (1)$$

where e is the electronic charge, V_{bi} the built-in potential and ξ is the position of the Fermi level in the GaN bandgap. The decrease in barrier height is therefore a result of a change in the Pt work function. Such changes in work function due to absorption of hydrogen have previously been reported for a number of refractory metals (8). Similar results are shown in Figure 2 for the Pd/GaN diodes in which the bias needed to maintain a particular forward current are larger than for the Ni/GaN.

The shifts in forward bias occur at higher measurement temperatures. This is consistent with the greater catalytic cracking efficiency for H_2 of Ni relative to Pd. Other considerations such as the long term thermal stability of the metal on GaN would also come into play if the primary application of the devices was hydrogen gas sensing at elevated temperature. In this case, it would be necessary to compromise some degree of sensitivity for the added thermal stability of metals. Values for schottky barrier heights were extracted from the relationship

$$J_F = A^{**}T^2 \exp(-\frac{e\phi_b}{kT})\left[(\frac{eV}{nkT}) - 1\right] \qquad (2)$$

where J_F is the forward current density at voltage V, A^{**} is the Richardson's constant for n-GaN (24 $A \cdot cm^{-2} \cdot K^{-2}$), T the absolute measurement temperature, n the ideality factor and k is Boltzmann's constant. Table 1 shows the extracted changes in Φ_b upon switching from measuring under a N_2 ambient to measuring under a 2% H_2 in N_2 ambient. The absolute values of Φ_b were 0.65eV at 200°C for Pd and 0.68eV at 150°C for Ni, within the ranges reported previously for these metals in n-GaN. The decreases in Φ_b for both metals, caused by the decrease in metal work functions upon exposure to a H_2-containing ambient, are responsible for the increased forward current when H_2 is introduced.

Table 1. Change in Φ_b when switching from N_2 to 10% H_2 in N_2 ambient as a function of measurement temperature

SAMPLE	T (°C)	$\Delta\Phi_B$ (meV)
Ni/GaN	170	-90
Ni/GaN	400	-170
Pd/GaN	25	-70
Pd/GaN	325	-160

Fig.3. shows the time response of Pd/GaN at different temperatures upon switching the gas introduced into the enclosure from N_2 to 2% H_2 in N_2. The diffusion of hydrogen through the Pd contact layer is not the limiting factor in the time response of the diodes, but rather the mass transport of gas into the enclosure as we have observed by altering the introduction rate. The time response of the output current at 2V signal of the element on varying the atmosphere at different operating temperatures is shown in Fig.

3. It could be found that the output current increased sharply in the primary stage when hydrogen was just introduced into chamber, and then developed to a state of gradual increase. In the early stage, a sudden temperature rise on the Pd catalyst side would take place due to the initiation of the hydrogen-oxidization reaction. With the progress of the reaction, the rate of temperature increase becomes low as it approaches its final equilibrium value. We believe that diffusion similarly, the initial recovery of the characteristics after introduction of the initial N_2 ambient is most likely dominated by removal of hydrogen atoms from the Ni/GaN or Pd/GaN interfaces. These results demonstrate the ability of both samples diodes to perform as rapid, sensitive gas sensors over a broad range of temperature.

4. Conclusion

In conclusion, electrical measurements of the barrier height of Ni/GaN and Pd/GaN diodes during exposure to hydrogen-containing ambients shows a decrease in effective barrier height for both metals relative to the values measured in pure N2 ambients. The observed barrier height lowering is due to the creation of a dipole layer at the metal-GaN interface, as reported previously reported by other workers. The time response of the diodes is limited, with the intrinsic response due to changes in the interfacial OH-dipole layer being very rapid.

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Figure caption

Figure 1. Forward I-V characteristics from Ni/GaN diodes measured at 25 and 300°C in N_2 or 2% H_2 in N_2 ambients.

Figure 2. Forward I-V characteristics from Pd/GaN diodes measured at 50 and 350°C in N_2 or 2% H_2 in N_2 ambients.

Figure 3.Time response of Pd/GaN, sensors upon changing from pure N_2 to 2% H_2 in N_2.

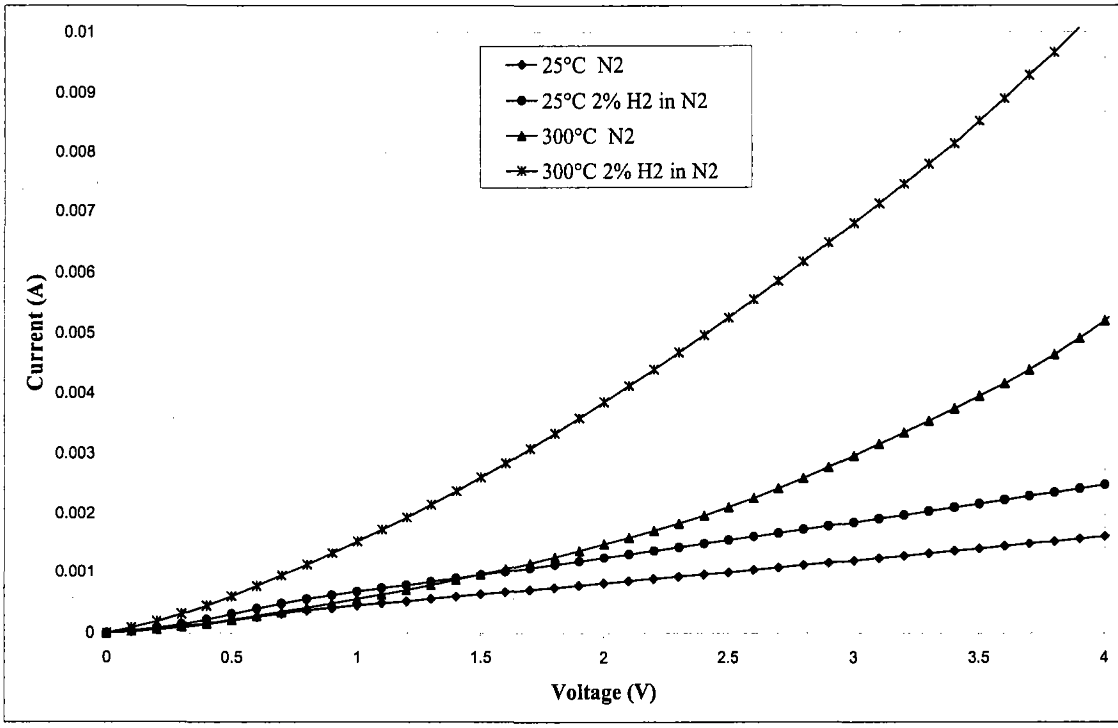

Figure 1. Forward I-V characteristics from Ni/GaN diodes measured at 25 °C and 300 °C in N_2 or 2% H_2 in N_2 ambients.

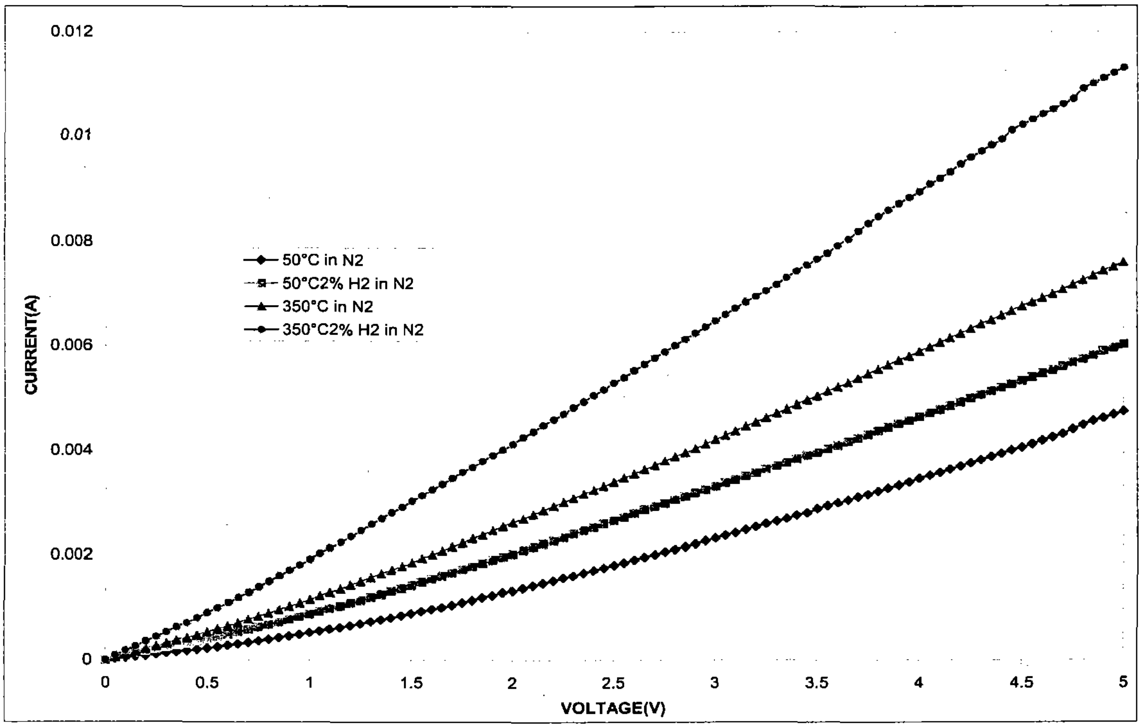

Figure 2. Forward I-V characteristics from Pd/GaN diodes measured at 50 or 350°C in N2 or 2% H2 in N2 ambients.

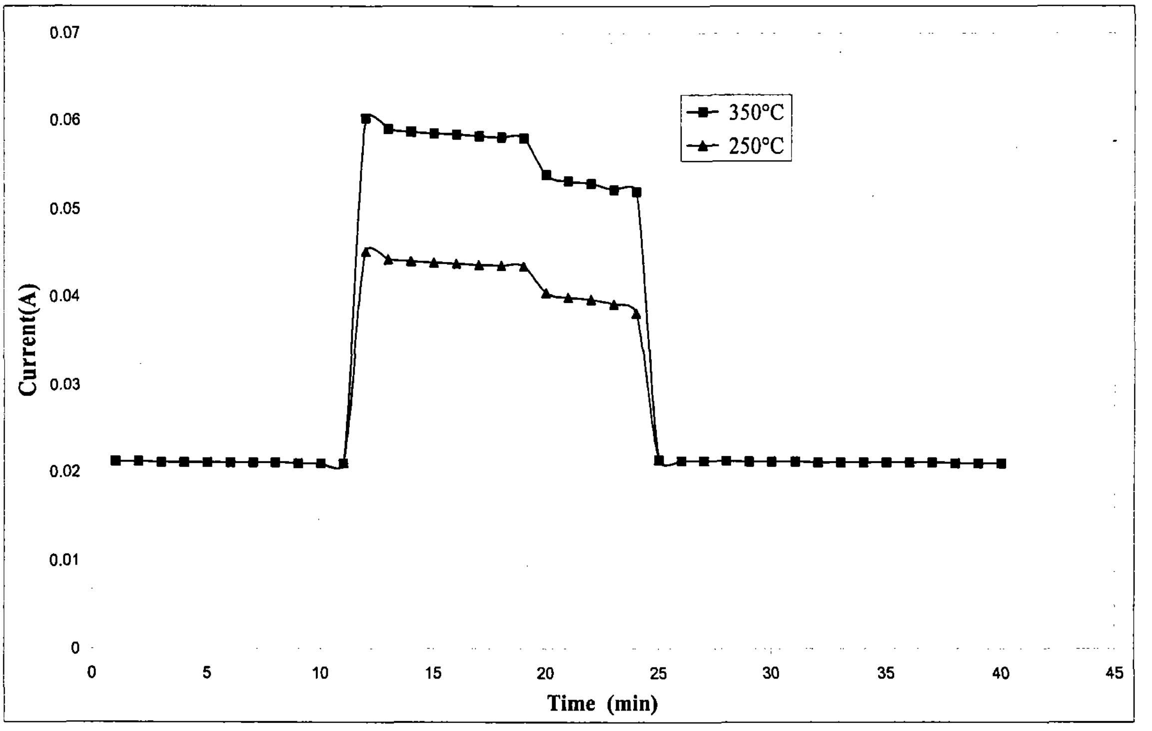

Figure 3.Time response of Pd/GaN, sensors upon changing from pure N_2 to 2% H_2 in N_2.