Photoelectrochemical Capacitance-Voltage Measurements in GaN

C.E. STUTZ,[1] M. MACK,[1,2] M.D. BREMSER,[3] O.H. NAM,[3] R.F. DAVIS,[3] and D.C. LOOK[4]

1.—WL/AAD, 2241 Avionics Circle, Wright-Patterson AFB, OH 45433-7322. 2.—WL/AAD Palace Knight co-located at University of California, Santa Barbara, CA 93106. 3.—North Carolina State University, Raleigh, NC. 4.—University Research Center, Wright State University, Dayton, OH 45435

Photoelectrochemical etching of GaN, using a KOH solution and a 325 nm wavelength UV laser, has been used to obtain carrier concentration depth profiles. The photoelectrochemical capacitance-voltage measurements are supported with conventional depletion mode capacitance-voltage, secondary ion mass spectroscopy, and Hall measurements. The data show that steps in carrier concentration profiles can be accurately reproduced.

Key words: Carrier concentration depth profile, GaN, photoelectrochemical etching

INTRODUCTION

The last few years have witnessed a flurry of work on the development of GaN material for use in high temperature transistors and blue lasers. In order to fabricate these devices efficiently, new fabrication and characterization techniques need to be developed. Several groups have worked on the development of wet etching GaN material at room temperature.

Pearton et al.[1] reported the wet etching of GaN using 30–50% $NaOH/H_2O$. Minsky et al.[2] reported on the wet etching of GaN using $HCl:H_2O$ (1:10) and 45% $KOH:H_2O$ (1:3) under the illumination of a 325 nm laser. Lu et al.[3] used a buffered solution of tartaric acid and ethylene glycol along with illumination by a Hg lamp that produced 365 and 405 nm light.

Recently, Kocha et al.[4] have shown that it is possible to make surface capacitance-voltage (C-V) measurements on GaN with electrolytic solutions used as a Schottky barrier contact. Several solutions of various pH values were examined and the authors indicated a linear Mott-Schottky plot for all pH values shown. The flatband voltage varied from about –1.5 V to –0.85 V for pH values of 14 to 2, respectively.

DISCUSSION

In this work, we show that it is possible to both etch and make C-V measurements down through a sample in order to ascertain the carrier concentration depth profile of n-type GaN with carrier concentrations of 5×10^{16} to 1×10^{19} cm^{-3}. (Similar work attempted on p-type GaN has been unsuccessful so far.) The GaN material used was grown via the metalorganic vapor phase deposition process, producing 2–2.5 μm thick layers with various silicon dopant levels on silicon carbide and sapphire substrates. The photoelectrochemical capacitance-voltage (PC-V) measurements are conducted in a modified Bio-Rad PN4200 system under both depletion and etch modes. The original light source and optics are removed with the light source being replaced with a 325 nm UV laser. The laser beam diameter is about 1.1 mm, which passes through optical filters to an electrochemical cell described by Blood.[5] The cell window is replaced with a sapphire disk so that the UV light passes through to the solution and hits the sample, which is pressed against a 1 mm diameter sealing ring to retain the solution. The Schottky/etching solution used in our experiment is 1M KOH.

The basic carrier concentration vs depletion depth C-V measurement modulates a small voltage («1 V) and uses the following equations to determine a depletion depth Wd and carrier concentration N:

$$W_d = \frac{\varepsilon A}{C_m}, \quad (1)$$

$$N = \frac{C_m^3}{q\varepsilon A^2 \frac{dC_m}{dV}}, \quad (2)$$

where the dielectric constant $\varepsilon = 9.5 * \varepsilon_o$ for GaN, A is

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the Schottky area, C_m is the measured capacitance, q = 1.6×10^{-19} C, and $\dot{V}$ is the modulated voltage. The etch depth W_e is the integration of the measured etch current over time

$$W_e = \frac{M}{zF\rho A}\int Idt \quad (3)$$

where M is the molecular weight of the semiconductor, z is the semiconductor valency, and is 3 for GaN. F is the Faraday constant, ρ is the density of the semiconductor, I is the measured etch current, and dt is an increment of time. Therefore, the total depth (X) in a profile is $W_d + W_e$.

In this work, PC-V measurements are made at carrier frequencies from 1 to 10 kHz. A large conductance is noticed for frequencies up to 6 kHz in these samples, as seen in Fig. 1. Measurements made at 10 kHz showed little or no conductance. This observation agrees with the impedance spectroscopy results of Kocha et al.,[4] who noticed a low frequency time constant that they attributed to surface states. All PC-V measurements in this work are made at low bias and 10 kHz.

Several samples were evaluated by various C-V measurement techniques, along with Hall effect and secondary ion mass spectroscopy (SIMS), as shown in Table I. The C-V measurements used in this work include mercury probe C-V, Electrochemical C-V (depletion mode), and PC-V (etch mode). The MB series of samples are grown with a 1000Å AlN buffer followed by a 1 μm unintentionally doped GaN layer and a 1 μm silicon doped GaN layer on a silicon carbide substrate. All of the C-V data are in good agreement with Hall measurements and within error of the SIMS measurements, which claim an error of plus or minus 40%. The SB sample had an 0.5 μm unintentionally doped GaN buffer, followed by an 0.5 μm highly silicon doped GaN layer and a 1.5 μm lower silicon doped GaN layer at the surface on a sapphire substrate. The gas flow rate during the growth of the highly doped silicon layer was ten times higher than for the lower silicon doped layer. The Hall effect assumed a total thickness of 2 μm and measured a mobility of 261 cm^2/V s at 300K.

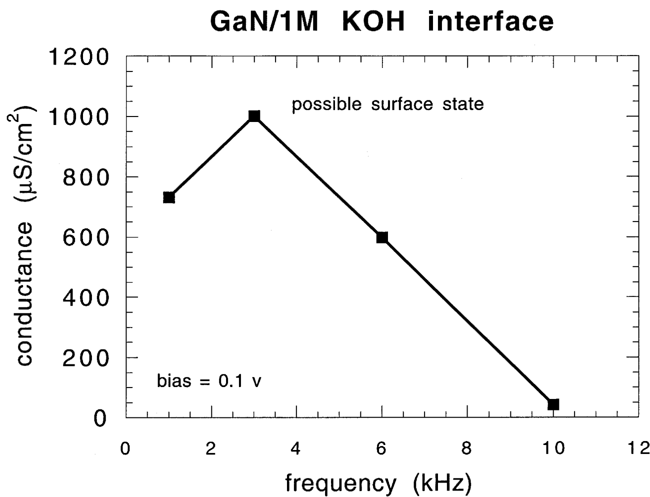

Fig. 1. Conductance vs bias for frequencies varying from 1–10 kHz.

The 1M KOH solution etched the GaN layers reasonably well (etch rate was about 1.0–2.0 μm/h, depending on light intensity) and showed excellent Schottky characteristics. The solution also avoided the problem of surface charge accumulation under high bias conditions, which was seen for higher KOH concentrations over a period of time in some samples. For example when a 5×10^{16} cm^{-3} sample was exposed to a high enough voltage (>3 V) for several minutes, the surface charge would increase so that a carrier concentration in the mid 10^{18} cm^{-3} was measured. The reason for the charge accumulation at high concentrations of KOH is not clear, but may be due to ionic movement, oxide formation, trapping effects or dislocations as discussed by Morrison.[6]

An example of an etched GaN layer on a sapphire substrate is shown in Fig. 2. Since the layers pass visible light it is possible to see how the etchant stopped at the GaN/sapphire interface. The darkened area is the top of the etched hole and the dark line circling beneath is where the etch stopped on the sapphire. The stylus step profile shows how vertically the sidewalls were etched, while the bottom of the sample is very smooth. The lines running through the dark area are optical reflections and are not an indication of sample roughness in this case.

Figure 3 shows an example of a PC-V measurement compared with SIMS data. The PC-V was run two times on the same sample several millimeters apart at an etch current of about 1.5 mA/cm^2. Two different layers of silicon doped GaN material can be seen using the PC-V. The lower doped layer at the surface is about 1×10^{18} cm^{-3} while the more highly doped layer is about 1×10^{19} cm^{-3}. The two measurements tracked fairly well to a depth of 1.5 μm, where it appears the etch became quite rough. Upon further inspection an etch pattern was noticed when another sample had its

Table I. Comparison of Carrier Concentrations by Different Measurement Techniques ($\times 10^{17}$ cm^{-3})

Sample	Hall	Hg-Probe C-V	Depletion EC-V	PC-V	SIMS
MB-224	4	4	4	4	6
MB-228	20	18	20	20	—
MB-229	100	100	—	—	—
MB-231	0.5	0.5	0.5	0.5	—
SB970310	20	—	—	10	6
(2 layers)				100	50–60

etch stopped before the sapphire substrate was reached. The etch depth variation on that sample was in the range of a 0.5 μm. The roughness seemed to reflect the UV laser beam profile, which negated any correlation with etch pits. Also, a stylus surface scan was run on a virgin piece of GaN epitaxial material before any etch was made and variations of up to several hundred angstroms were noticed. These variations may be due to the large concentration of material defects found in GaN material.[7] The SIMS data show a much sharper interface between the two doped regions with the carrier concentrations being around 6×10^{17} and 6×10^{18} cm^{-3}. Note that the ratio of 10 in the carrier concentration is seen for both the PC-V and SIMS measurements, as expected from the gas flow rates of the of the dopant. Also, SIMS shows a sharp drop in concentration at the interface between the 6×10^{18} cm^{-3} layer and the buffer layer. This may also be due to the roughness of the etch.

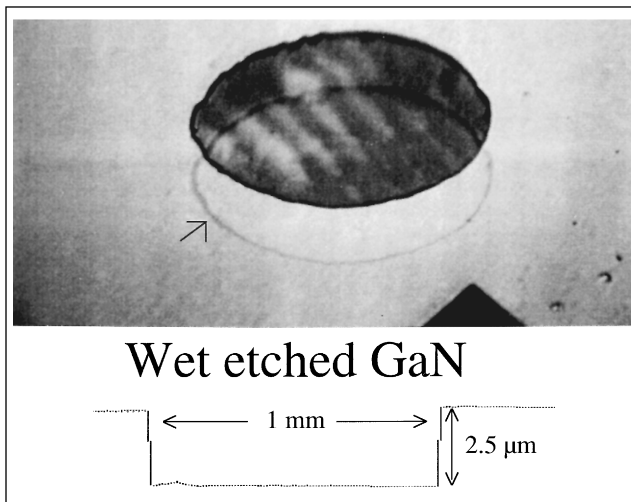

Fig. 2. An example of wet etched GaN using a 325 nm laser and 1 M KOH electrolyte.

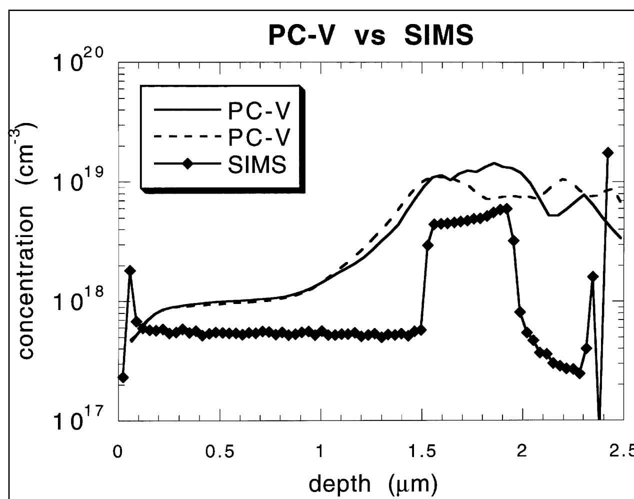

Fig. 3. Comparison of PC-V and SIMS measurements for carrier concentration vs depth profile.

CONCLUSION

We have shown that it is possible to make C-V measurements while etching GaN material. The data agree with conventional C-V, Hall effect, and SIMS measurements. The PC-V concentration measurement is correct within error, but etching roughness due to virgin material surface conditions and system etching variation can cause depth problems. It is expected that improvements in etching should be possible.

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