

Surface passivation of GaN using aqueous solution



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ABSTRACT

The sulphur passivation of a free standing GaN surface was investigated by employing an aqueous (NH₄)₂S solution. Scanning tunnelling spectroscopy revealed that treatment with (NH₄)₂S results removal of native oxide and formation of sulphide monolayer on top of the GaN surface. The removal of surface density of states is more effective in 30 sec ammonium Sulphide passivation than 90 sec and above. We present the passivation mechanism of an (NH₄)₂S treated (0001) GaN surface. It is also found that sulphide treatment can passivate nitrogen, gallium vacancies and forms the bonding with gallium and nitrogen. The stability of protective layer was observed by rising the sample temperature (up to 200 OC).

Keywords: Sulphur, passivation, ammonium, GaN.

Introduction

The study of surface and interface properties of semiconductor physics has to be considered one of the most important fields of the research¹. The characteristics of semiconductor devices mainly depend on the surface properties of the semiconductors. Atoms on the top surface of the semiconductor material are incompletely bonded with the neighbouring atoms. These open bonds create new states within the forbidden gap so called surface states. These states increase the surface recombination velocity there by reduces device performance².

Recently, there is an immense interest in wide band gap (WBG) semiconductors, whose technology was developed from past three decades and continues its progress in these days, many researchers focused on surface and interface studies of these materials. Especially GaN (E_g=3.4 eV) and SiC made applications possible those which are unattainable with Si and GaAs, due to its better physical properties such as low intrinsic carrier concentration, high temperature stability, mechanically stable, high saturation velocity and high electrical breakdown³⁻⁴.

Moreover, this is a direct wide band gap semiconductor. There are potential applications such as operation in high temperature, space applications and the applications which are relevant to modern life light emitting diodes (LEDs) are a more efficient and energy saving, the blue laser

diode allows an increase in the density of data writable on or readable form DVDs. GaN based high electron mobility transistors (HEMT) are excellent candidates for high temperature, high power, high frequency, low noise and radiation hard applications⁵.

Despite these excellent properties GaN suffers from the absence of native oxide passivating layer as compare to the native silicon oxide on the silicon surface. Therefore, in the absence of passivation native oxide layer, the large density of surface states on the GaN surface will pose a major problem in the development of GaN based devices. This led us to study and understand the surface/interface properties of these wide band gap semiconductors⁶.

The present work is the evolution of surface density of states of free standing GaN under ammonium sulphide passivation technique and how the passivating layer protects the formation of the native oxide as a function of temperature by scanning tunnelling spectroscopy (STS).

Experimental

2" inch diameter and 300 micron thick free standing GaN wafer was commercially used in the present study. The first step is to follow the cleaning procedure. This is very useful for surface passivation. Firstly, the samples undergo the organic cleaning after that, samples dipped in Ttrichloro ethylene for 5 minutes followed by IPA cleaning. Ultrasonic bath of these samples carried

out for 60 sec. Next step to remove the native oxide using 1:1 (HCl: DI) solution for 1 min and rinse the sample in DI water for 20 sec. Passivation of the samples using ammonium sulphide have been elucidated in this work.

Results And Discussion

Sulphide Passivation mechanism The freshly prepared GaN surface have large number of dangling bonds, these bonds creates a large number surface states within the band gap, this is bottom nice for device applications. The real surface exposed to the atmosphere is very complex and is not a well-defined system. In case GaN wurtzite structures each Ga atom is coordinated by four nitrogen atoms. Conversely, each nitrogen atom is coordinated by four Ga atoms. At the surface of GaN forms gallium oxide, with different stoichiometric⁷⁻⁸.

To reduce the surface density of states and form new stable state surface, passivation was needed. The passivation on the semiconductor surface remove the native oxide which present on the surface and forms a protective layer on top of the surface, it resist the further oxidation. At the surface of GaN forms Gallium oxide with different stoichiometric. This oxide is removed by dipping sample in 1:1 (HCl: DI) solution for 1 min and rinse the sample in DI water for 20 sec. Now transport the sample into ammonium sulphide solution, it forms a sulphide layer on top of GaN surface. The mechanism involved in the formation of sulphide layer too complex to explain. There are various types of mechanisms occurring at the (0001) surface of the GaN. Sulphur forms a bonds with Ga and nitrogen in different stoichiometric. It also replaces the Ga or nitrogen vacancies⁹⁻¹⁰.

According to the reported data for bond strengths, Ga-O (487 KJ/mol) bond energy is more than the Ga-S (361 KJ/mol) bond and N-O (174KJ/mol) bond energy is less than the N-S (318 KJ/mol). In case of GaN, only Ga-O bond is strong and N-O bond weaker than N-S bond. So the surface reoxidation is slower because it will limited by O replacing S in Ga-S. Nitrides form more stable protecting surfaces. Another important point is that, nitrogen is volatile, elemental N forms N₂ molecules and desorbs¹¹⁻¹². Moreover, the sulphide solution itself typically etches the material during treatment, like native oxides. From the

above mechanisms we conclude that ammonium sulphide treatment on GaN surface gives much stable and protecting surface. The X-ray diffraction (XRD) measurement is used to verify the crystal structure of the sample (see fig.1).

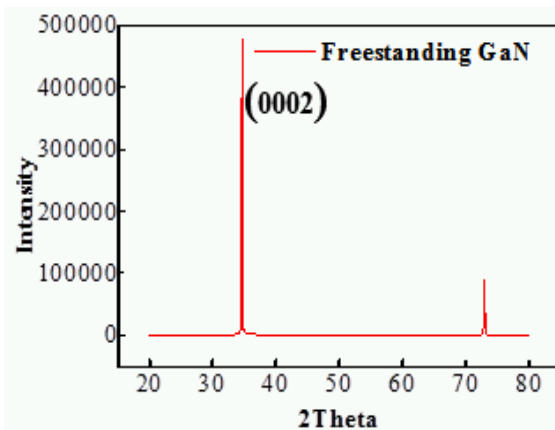


Figure. 1. X-ray diffraction for free standing GaN (0002) peaks shows the crystal structure of GaN. XRD data showed that the sample is GaN (0002) and peaks are exactly matched with JCPDF data. STM/S studies of freestanding GaN before and after passivation

Even in case of free standing GaN, the surface becomes oxidized before ammonium sulphide passivation. The thickness of native oxide is around 20 Å. The surface conductivity was much smaller than of the bulk. Due to these reasons we are unable to take surface morphology and voltage vs tunnelling current data for freestanding GaN sample before passivation treatment. These data showed in (fig. 2) taken after passivation. It was also showed that that native oxide is removed and protecting passivated layer is formed after passivation¹².

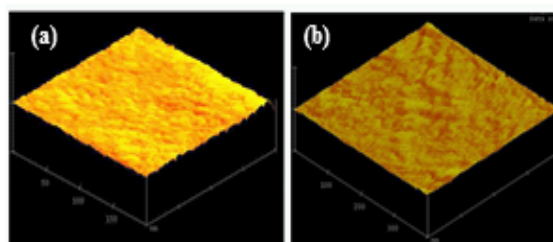


Figure. 2. (a) 200 × 200 nm GaN surface morphology at set point voltage 2.5 Volts and set point current 1 nA, after 90 sec ammonium sulfide

passivation, (b) surface morphology after 30 sec treatment.

The normalized differential conductance's Vs. Voltage curves for GaN samples at 90 sec and 30 sec ammonium sulfide passivation at room temperature shows the effective electronic passivation occurred in 30 sec sulfide treatment. From fig.3 it has also seen that 30sec passivation gives better results than higher passivation time.

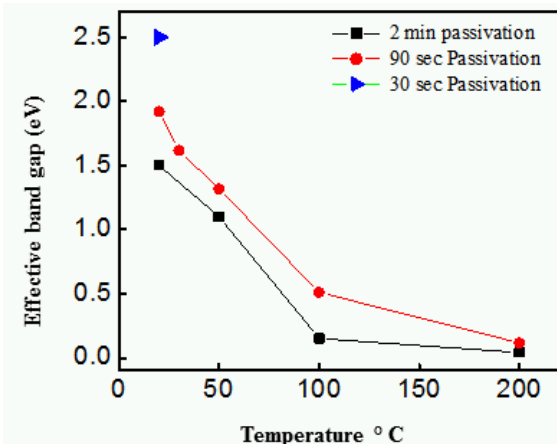
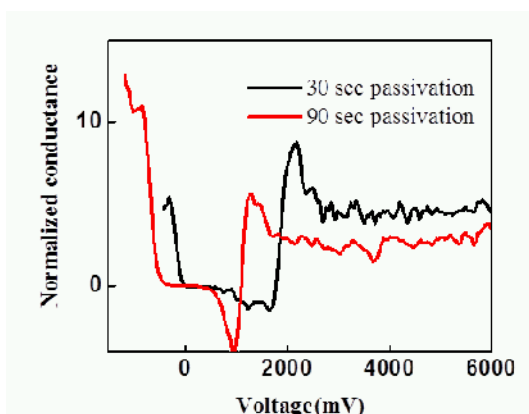


Figure. 3. Normalized differential conductance's Vs. Voltage curves for GaN single crystal samples at different ammonium sulfide passivation time at room temperature.

Figure. 4. The variation in effective band gap of free standing GaN sample surface vs temperature for the different passivation (ammonium Sulphide) times.

From the variation of effective band gap



vs temperature for the different passivation (ammonium sulphide) times of free standing GaN sample, we conclude that as increasing the passivating time, the surface becomes GaS instead of GaN [13]. The GaS is also direct wide band gap (2.5 eV at RT) semiconductor. The stability of protective layer was observed by rising the sample temperature.

Conclusions

From our experimental results on free standing GaN after passivation, we conclude that native oxide is removed and protecting passivated layer is formed after passivation. From the normalized differential conductance vs voltage curves, 30sec passivation gives better results than higher passivation time. The stability of protective layer

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