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The Mechanism of Charge Flow and Electric Current in Porous GaN Thin Films during Photo Electrochemical Etching

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Abstract: In this work nano-porous structures of n-GaN was fabricated using simple photoelectrochemical etching techniques. The electrolyte was H2SO4:H2O2 under direct current density of 5 mA/cm2 for 30 min. Scanning electron microscopy (SEM) has been used to studied the morphology, the size, and the shape of the pores of n-GaN nanostructures. The mechanism of charge and current flow in photoelectrochemical etching process was investigated deeply. The electrical and chemical behaviour of the electrolyte-GaN junction has been studied. The energy diagram of an n-GaN and the electrolyte was used to illustrate the charges flow mechanism. A simple model depend on two parallel plate capacitors was used to understand the etching mechanism at the GaN electrolyte interface. This mechanism was confirmed by J-t curve.

Keywords: GaN thin film, photoelectrochemical etching, etching mechanism, porous.

1 Introduction

Recently, GaN-nanostructures have been widely studied, due to their physical and chemical properties relative to those of bulk structures [1, 2]. One of the famous types of GaN-nanostructures was porous GaN thin films, which present high surface area and enhanced the optical and electric properties of GaN thin films. This enhancement opens a wide range of application such as optoelectronics to chemical and biochemical sensors [3,4,5,6,7]. Photo-electrochemical etching (PEC) was the simple techniques to synthesis porous GaN nanostructures [8,9,10,11,12,13,14]. Some advantages of the PEC etching in comparison with other methods are; can be fabricated at room temperature, less damages in the film structures, simple experiment equipment and process, and low cost. The main factors that affect the electrochemical etching are the electrolyte, electric current and illumination lights. The role of these variables is very important to understand the etching mechanism.

In PEC etching GaN is immersed in chemical electrolytes and build GaN-electrolytes junction like metal-GaN junction. The main issue in the GaN-electrolytes junction is the charge transfer between a solid and a liquid solution. Then the mechanisms of transferring of electric charge through the (PEC) etching is still controversial and it needs more investigated. In addition, the study of porous GaN is still in the early stage; many fundamental properties are still not clear. The study of the details of the electrochemistry of semiconductors in fact is very complex and sometimes poses a great mystery to condensed matter researchers. The complexity is mainly what occurs in the solution and at the solution/semiconductor interface. A quantitative analysis is a great challenge, even for the simplest systems [15,16,17].

In this work we investigate deeply the chemical and electric mechanism of etching (PEC) of GaN films. In addition, the transfer of charge and electric current through the GaN-electrolyte junction was discussed. A simple capacitor charge and discharge model was used to explain the photoelectrochemical etching mechanism. Finally, the J-t curve used to confirm this model. This paper is organized as follows. In Section 2, we describe all experimental steps in detail. In section 3, we discuss the mechanism of charge flow and electric current in porous GaN thin Films during

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photoelectrochemical etching depend on the experiment results. Finally, we summarize our results in section 5 as conclusions.

2 Experimental details

In this work commercial Si doped n-GaN thin films grown on sapphire substrates were used. The thickness (d) of GaN layer was 7µm. The carrier concentration was $n = 1x10^{17}$ cm^{-3} obtained by Hall measurements. After cleaning the samples Aluminum was then partly evaporated on the face of GaN thin films using thermal evaporating system. By using a Teflon homemade cell, we fixed the GaN sample as an anode and Pt wire as a cathode. The electrolyte was a mixture of aqueous sulphuric acid H_2SO_4 and H_2O_2 3:1 by volume. For the electrochemical etching process, we used constant current density $J=5mA/cm^2$ supplied by a programmable current source (model Keithley 220) for duration 30min under UV illumination. After the etching, the samples were rinsed in deionized water, and dried in ambient air. The sample surface morphology was characterized by scanning electron microscopy (SEM) (JOEL JSM-6460LV).

3 Results and Discussion

Figure 1(A, B) shows the scanning electron microscopes of the morphology of the as-grown and porous GaN sample. The as-grown GaN possessed a smooth surface morphology Fig. 1(A). While the porous GaN sample Fig. 1(B) has different rough structures. There are many pores with variable sizes between 30 to 90nm. To understand the conditions that cause these structures on the GaN surface, the mechanism of formation GaN-electrolytes junction will be studied. The key to understand this mechanism is by studying the electrochemical reaction and the energy structures at the GaN-electrolytes junction.

The energy diagrams of an n-type GaN electrode and the electrolyte are shown in Fig.2 (A) without contact. When a GaN sample is immersed into the electrolyte, the GaN electrode-electrolyte interface energy band diagram resembles a semiconductor-metal interface. Thus, a Schottky contact is formed as shown in Fig.2 (B) like metal-GaN junction. The extent of the band bending is quantized by the Schottky barrier height φ_B, which is defined as the energy difference between the conduction

band edge at the GaN-electrolyte interface and the equilibrium Fermi level, as shown in Fig.2 (B).

$$\varphi_B = E_c - E_f \tag{1}$$

The main issue in the GaN-electrolytes junction is the charge transfer between a solid and a liquid solution. The species which prefer to donate an electron are called reducing species (Ered), those which prefer to accept an electron are called oxidizing species (Eox). Pairs of reducing and oxidizing species are called redox couples. For a solution containing one dominant redox couple it is convenient to define an "effective Fermi level" Eredox similar to the solid [18].

For n-GaN at open circuit Fig. 2 (A) the Fermi level is higher than the effective Fermi level (E_{redox}) of electrolyte. Because the electrolyte contains strong oxidizing species, then the electrons will flow from n-GaN to the electrolyte and thus the Fermi level moves down until it aligns with the Fermi level of electrolytes and reach the equilibrium ($E_F=E_{redox}$) when GaN and electrolyte in contact Fig. 2 (B). This transfer of electrons bends the bands upwards and creates a layer near the n-GaN surface that is depleted of electrons; this area of electrons named depletion layer. This depleted region, similarly to Schottky barrier in p-n junction, is called space charge region (SCR), but there are some differences here spatially in the electrolyte side .

There are three major charge layers formed on the electrolyte side: space charge layer near the GaN surface (I), wide range layer (II), and a very thin layer near the Pt wire as shown in Fig. 3 (A). For more analysis we consider these three charge layers as capacitors connected in series, with capacitance C_I, C_{II} and C_{III}. The capacitance of the wider second layer is very small compares to other two capacitance, then it can be neglected and it works as reservoir of ions for other two layers. The capacitance of these capacitors can be considered as a parallel plate capacitor connected in series described by [19]:

$$C = C_I C_{III} / (C_I + C_{III}) = \kappa \varepsilon_0 A / (d_I + d_{III}) \tag{2}$$

where C is the capacitance, κ is the dielectric constant for the electrolyte, d is the thickness of the layer and ε_0 is the vacuum permittivity.

On the solid side (GaN surface), the charge can arise in three forms: an accumulation of free charge, free charge trapped from the solid onto surface states, and adsorbed ions. Due to the wide band gap of GaN, and the valence band (V_B) energy of GaN is -6.66eV relative to vacuum, so holes cannot be obtained by the V_B of GaN to oxidize GaN [20]. Then we need to illuminate the sample with light energy larger than energy gap, and also, need to applied an external electric potential to push electrons and holes to the surface of semiconductor [21]. Then the depletion layer or space charge layer is formed on the GaN side with width W. If a depletion region is considered, then the surface charge density in the SCR layer is equal to q x N_d, where N_d is the doping concentration in the n-type semiconductor. The depletion region is a strong function of GaN conductivity and the applied bias potential.

To enhance the flow of electron an external electric potential will be applied. To applied external potential to make reverse bias, (Al) evaporated on the GaN surface as an ohmic contact. In this case n-GaN connected as a positive anode in the closed circuits. The energy band bends in the upward direction, and a potential well for holes is formed, and hence

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the hole moves towards the interface, while the electron moves to the interior of the GaN films. This increased the depletion rate of electrons from the GaN

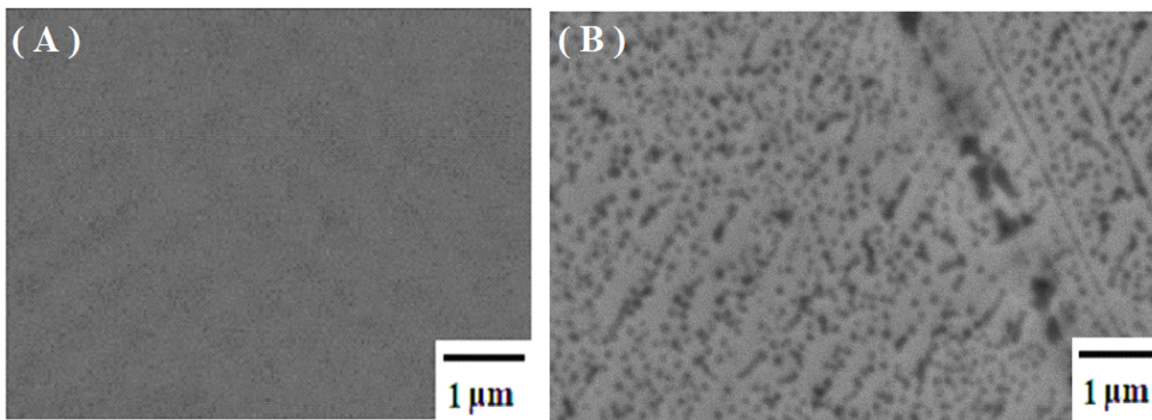

Fig. 1: GaN SEM images of the (A) as-grown and (B) porous films.

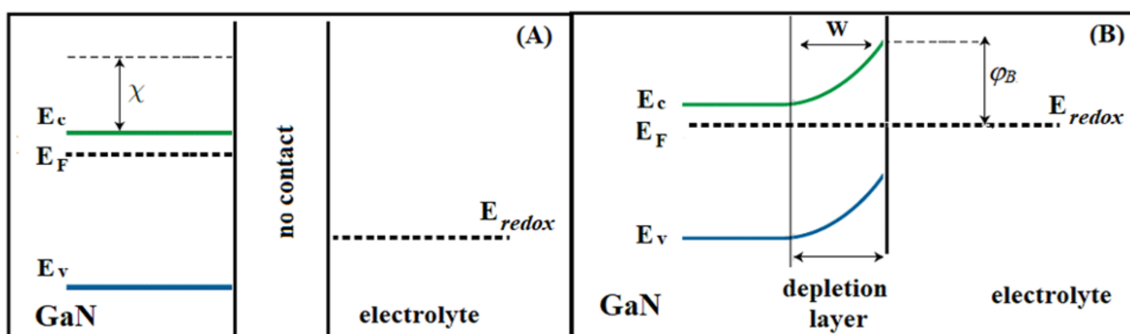

Fig. 2: Energy band diagrams for the n-GaN-electrolyte junction. (A) without contact (Not in equilibrium), (B) with contact (in equilibrium).

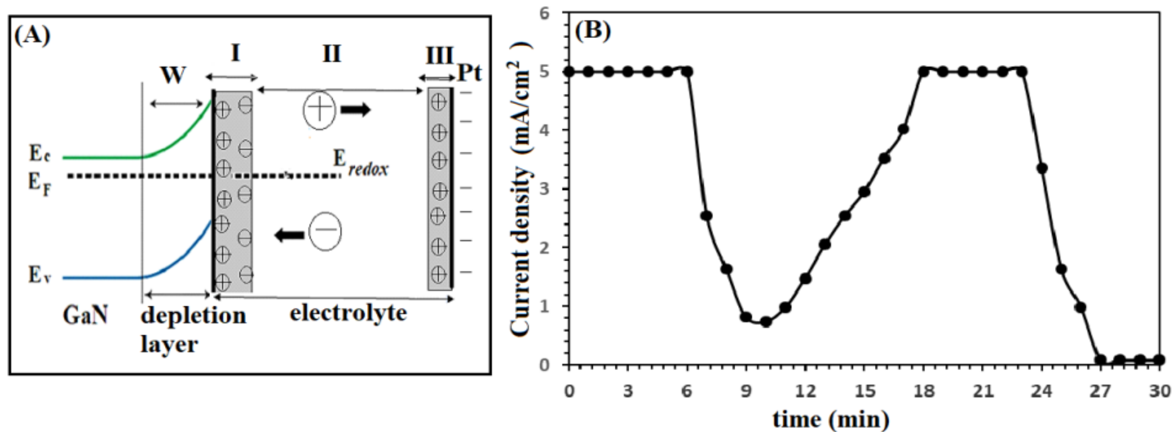

Fig. 3: Charge layers on GaN-electrolytes junction(A), and Current density vs time for GaN electrochemical etching process.

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surface. This current known as a reduction current. Photoelectrochemical etching (PEC) will be formed, after contact between GaN and electrolytes under UV-illumination by supported with external electric potential.

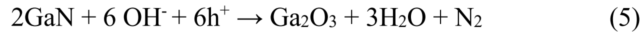
Figure 3(B) shows the J-t curves, five characteristic regions can be identified in the curve: constant current flowing for 6min, fast decreasing of the current for 4min to reduce 90% of its initial maximum value, increasing in the current to reach the same initial maximum value in 8min, then it returns to the initial constant value for 6min and finally reduce fast to zero for 4min. This behavior of the current may be suggesting the etching mechanism on the GaN surface. When the GaN and the electrolyte become in contact, many layers of charge will be formed as a capacitor, these capacitors start charging until reach the maximum value of charge within the first stage (6min) in fig. 3(B). In this stage the positive ion of Ga^+ accumulated on the surface of GaN films and have a free bond then it became react with oxides in electrolyte to form Ga_2O_3 for 4min, and this form an insulator layer in the surface of GaN thin films. At this stage the circuit become like open circuit and no charge will be reach the surface then the behavior inversed and the Ga_2O_3 will be dissolved in the electrolyte and produce a small charge exchange between electrolyte and GaN surface, then the current become increased until all the oxide layer dissolved for 8min. At this stage the capacitors lost their charges, then the circuit become closed and start charging for 6min in second cycle like the first starting cycle with same time. Finally, the capacitor reaches to the maximum charging while the current reduces due to the oxide layer on the GaN surface and in this stage the second cycle of etching start. In this experiment, the etching process required two cycles, the number of cycles depend on the thickness of GaN.

In the electrochemical reaction, the total current flowing in the external circuit equals the charge consumed in the reactions at the anode and the cathode. Thus, hydrogen is evolved at the Pt cathode, to which electrons flow from the external circuit, as shown below :

$$H_2O_2+2H^+\rightarrow 2H_2O+2h^+ \quad (3)$$

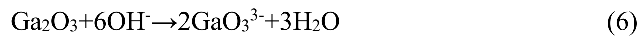
$$2H_2O(l)+2e^-\rightarrow 2OH^-+H_2(g) \quad (4)$$

The two-cycle shown in fig. 3(B) can be used to illustrate the mechanism of the photoelectrochemical etching process. As first step, an oxide layer is formed on the GaN surface (charging process). This formation of oxide layer come from the reaction between holes in the valence band and oxidants in the electrolyte, which governed by equation [22]:



$$2GaN + 6\,OH^- + 6h^+ \rightarrow Ga_2O_3 + 3H_2O + N_2 \quad (5)$$

Thus, only if the resulting oxide is soluble in the electrolyte is the semiconductor surface etched.
Then the oxide layer is dissolved in the electrolyte (discharging) as a second step:



$$Ga_2O_3+6OH^-\rightarrow 2GaO_3^{3-}+3H_2O \quad (6)$$

In the second cycle the same two steps will be repeated; formation and dissolved with the same period like first cycle. Both holes Ga^+ and OH^- ions take active parts in the etching of the GaN. It has been observed that bubbles are often found near the surface of the sample during PEC etching, which may come from the release of N_2. In addition, the photoelectrochemical etching current decreased gradually due to the increasing oxide thickness. During the chemical etching, bond exchange proceeds simultaneously between undissociated molecules and the surface atoms in the solution. Chemical bonds between the surface atoms and the bulk atoms are broken while new bonds are formed between Ga and O_2 and move to the solution.

The electrons and holes created in the space-charge region near the surface are transported by two mechanisms; drift under the influence of the electric field, and diffusion due to the carrier concentration gradient as shown in Fig. 4. The swept photogenerated holes are confined at the GaN-electrolyte interface due to the band bending. Finally, the etching rate is governed by the electron and hole dynamics at the interface, as schematically shown in Fig. 4 for an n-GaN electrode.

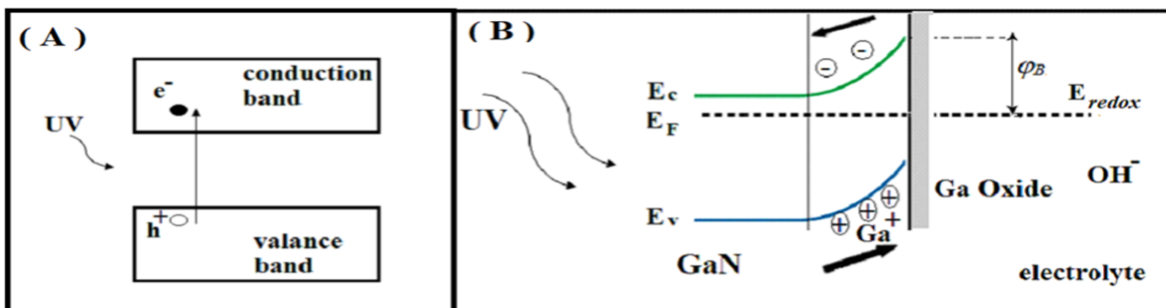


Fig.4: Electrons and holes dynamics on the n-GaN-electrolyte interface.

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One of the most important characteristics of porous GaN layers is their porosity (P), which is defined as the fraction of void in the porous structure. From the (J-t) curves Fig.3 (B) the average porosity ($P= V_p/V$) of the sample can be estimated [23]. The total volume of the semiconductor V is simply the product of the front surface area A and the film thickness d. The total 'void' volume produced by dissolution is $V_p = N\cdot V_0$ where N is the number of Ga-N pairs dissolved and V_0 is the volume of a single Ga-N pair in the GaN crystal lattice. V_0 is obtained from the lattice constants of hexagonal GaN: a = 3. 819A°, c= 5.185A° and $V_0 = a^2c\sqrt{3}/2$ and this gives the value of 4.566×10^{-23} cm^3. The variable N is Qint/eγ, where γ is the number of holes required to dissolve one Ga-N pair and Q is the integrated charge transferred during the course of the reaction, and equal to $Q=\int I\,dt$. Combining all the terms, we write

$$P_{av} = \frac{V_p}{V} = \frac{V_0 \int Jdt}{ed\gamma} \quad (7)$$

Where γ = 6 for GaN and d the thickness of GaN layer and it is 7μm in our samples. When the J-t curve (see Figure 3B) is integrated, one gets roughly 6.5 C cm^{-2}. One can obtain the value of the average porosity for the porous obtained in n-type GaN using Equation (4.5) in this sample. After substitute all values, the estimated average porosity is equal to 0.44.

4 Conclusions

In this work the interface contacts between n-GaN and electrolyte was discussed in details. The mechanism of charge flow across the surface was deeply studied. A simple model was used to explain the etching mechanism. In this model many charge layers were considered in electrolyte side and in solid GaN side. These charge layers arranged as a parallel plate's capacitors. When these capacitors are charged, Ga_2O_3 will be start to form, and when discharged, Ga_2O_3 dissolved and pores form on the surface of GaN. Charging and discharging process are confirmed by the J-t curve. Finely, the porosity was estimated from J-t curves.

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