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An Optimised Method for ZnO Sacrificial Layer Lift-Off on GaN Substrates

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Abstract: This study investigates the optimisation of the sacrificial layer epitaxial lift-off process using ZnO grown on GaN substrate. The aim of the study is to achieve efficient ZnO removal while preserving the integrity of the GaN layer. Previous studies [1] have identified two major challenges: the declining dissolution rate of ZnO in HCl solution without regular refreshment and the mechanical deformation of the GaN layer during the lift-off process (the GaN layer tends to crack and curve when directly transferred to glass substrate due to stress release during ZnO dissolution). This research establishes mathematical relationships between 0.1mol/mL to 2mol/mL concentration of HCl and ZnO dissolution rate, as well as between the thicknesses of GaN and ZnO layers. These relationships are crucial for preventing GaN layer defects during the ZnO stripping process.

Keywords: epitaxial, sacrificial layer, ZnO, GaN, heteroepitaxy

1. Introduction

Epitaxial layer stripping technology has emerged as a critical breakthrough in heterogeneous integration, enabling the development of next-generation electronic and photonic devices. Epitaxy plays a vital role in various fields, from semiconductors and optoelectronics to sensors, remote epitaxy and van der Waals epitaxy [2]. Traditionally, epitaxial growth occurs on substrates with compatible crystal structures. However, heterogeneous integration enables growth on dissimilar substrates, which is particularly beneficial for wide bandgap semiconductors and 2D materials [3]. This method involves growing a sacrificial layer [4], distinct from both the substrate and epitaxial material, which is later dissolved to release the epitaxial layer. Alternative methods such as laser lift-off (LLO), mechanical lift-off and thermal stress lift-off are also available [5-7].

In this study, ZnO is chosen as the sacrificial layer due to its easy dissolution in acidic solutions and close lattice constant with GaN. The research focuses on two main challenges: the nonuniform dissolution of the ZnO layer causing uneven stress distribution and the mechanical failure of the GaN layer. The goal is to establish the relationship between solution concentration and the ZnO dissolution rate at room temperature for uniform etching. Additionally, the optimal thickness ratio between GaN and ZnO is investigated to prevent GaN cracking during the lift-off process. The paper includes the theoretical background of the work, the methodology of the research, the results, process implementation, applications and conclusion.

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2. Theoretical Background

ZnO and GaN are both significant materials in optoelectronics and electronic devices. They have a closed lattice constant and high band gaps. To reduce defects on interfaces, these two materials can be combined to achieve multifunctional devices.

ZnO has a hexagonal wurtzite structure, which belongs to the *P6₃mc* space group [8]. It has high hardness and mechanical stability, with its lattice constant a=3.250 Å c = 5.2 Å [9] and which the parameter for GaN is a = 3.19 Å, c = 5.18 Å [10] for 300K. Through the probability of the lattice mismatch formula below we calculate that the δ is less than 2%, which means that, although there is a slight mismatch, it can still perform well.

$$\delta = \frac{|a_{ZnO} - a_{GaN}|}{a_{GaN}} \times 100\%. \quad (1)$$

This property allows them to match well, with reduced defects when applied to heteroepitaxial growth. In epitaxial growth, due to lattice mismatch and the difference of thermal expansion ecoefficiency, which for ZnO is $\alpha_{ZnO} = 4.75 \times 10^{-6} K^{-1}$ and for GaN is $\alpha_{GaN} = 5.59 \times 10^{-6} K^{-1}$, there is stress produced by ZnO when deposited on GaN. Consequently, there are two types of stress introduced by the ZnO layer [11]. One is lattice mismatch stress and the other is thermal residual stress. Details on these will be illustrated later in this paper.

However, during experiments the external chemical reaction environment has an influence on the ZnO film, that is dissolution.

Putting ZnO materials in hydrochloric acid HCL involves an acid-base reaction. The following is the reaction equation:

$$ZnO + 2HCl \rightarrow Zn^{2+} + H_2O + 2Cl^- \quad (2)$$

A solution of zinc chloride was formed with the dissolution of ZnO.

Generally, the factors affecting the dissolution of ZnO include the temperature concentration of the acid solution and the defects of ZnO; however, the main factors are temperature and concentration.

3. Experimental Methods

In this experiment, we should consider the size of the GaN substrate layer, due to the cost of the GaN substrate and the uncertainty of the initial experiment. Due to the difficulty of growing it [12], authors have introduced the method of preparing GaN nanostructure. We can apply a 1cm square substrate as a sample. Also, a smaller substrate is easier to control due to its reduced chance of bending or warping. In 2013 Wang Bin and his team discovered the relation between GaN size and wafer bowing on a sapphire substrate [13], which is shown in Figure 1.

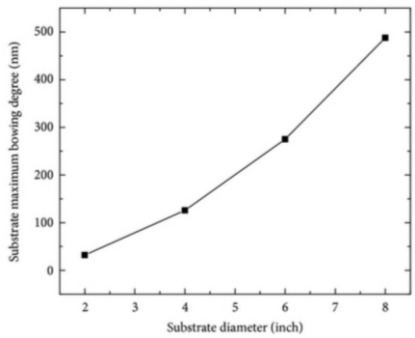

Figure 1: Relationship between GaN size and wafer bowing on sapphire substrate.

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Additionally, rough grinding, fine grinding, acid chemical mechanical polishing and alkaline chemical mechanical polishing can be used to clean the substrate [14]. Then, the method for deposition of the ZnO layer can be introduced (Figure 2). The ZnO layer is grown on the GaN substrate using pulsed laser deposition (PLD) [15].

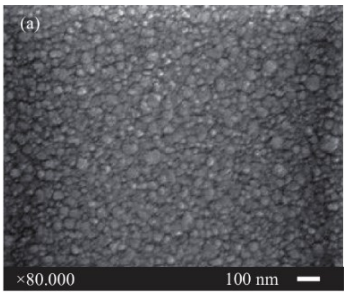

Figure 2: ZnO Electron microscope image.

This deposition method provides better control over ZnO thickness compared to CVD, allowing for consistent film preparation. To measure ZnO thickness accurately, X-Ray reflectivity (XRR) is used.

Following this, the stress of different ZnO layer thicknesses needs to be calculated and the definite thickness that the GaN can support needs to be determined.

3.1. Stress Calculation

This section illustrates that under static conditions the GaN can support the maximum thickness of the ZnO layer.

In this stress model, total stress consists of thermal expansion stress and lattice mismatch stress.

We should ensure the stress produced by the ZnO layer does not exceed the maximum bearing capacity of GaN, which means $\sigma_{total} \leq \sigma_{GaN,max}$

$$\sigma_{GaN,max} = min(\sigma_{fracture}, \sigma_{yield}) \tag{3}$$

$\sigma_{fracture} = 6 \sim 10GPa$ which is the fracture strength of GaN.

$\sigma_{yield} = 2 \sim 4GPa$ which is the elastic limit of GaN.

Firstly, we should determine the thermal expansion stress produced by different thicknesses of ZnO.

$$\sigma_{thermal} = \frac{\Delta\alpha \cdot \Delta T \cdot E_{ZnO}}{1-\nu_{ZnO}} \cdot \frac{h_{ZnO}}{h_{GaN}+h_{ZnO}} \tag{4}$$

Where $\Delta\alpha = \alpha_{ZnO} - \alpha_{GaN}$

E_{GaN}290GPa it's Young's modulus of GaN.

E_{ZnO} Young's modulus is 140GPa [16]

Where ν_{ZnO} is Poisson's ratio, $\nu_{ZnO} = 0.35$ [17]

h_{GaN} and h_{ZnO} are the thickness of the GaN layer and the ZnO layer.

Secondly, we should determine the stress introduced by lattice mismatch.

$$\sigma_{lattice(h)} = \sigma_{lattice0} \cdot f(h) \tag{5}$$

Where$\sigma_{lattice0}$ is initial stress, which can be calculated by:

$$\sigma_{lattice0} = \epsilon_{lattice} \cdot \frac{E_{ZnO}}{1-\nu_{ZnO}} \tag{6}$$

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$\epsilon_{lattice}=\frac{a_{ZnO}-a_{GaN}}{a_{GaN}}$ is the parameter of stress and $\epsilon_{lattice} \approx 1.88\%$

With the growth of thickness, when $h \leq h_{critical}, f(h)=1$. This occurs when the mismatched stress in the film does not relax; the main stress is an intrinsic feature and not related to thickness.

However when $h \geq h_{critical}, f(h) = e^{-\lambda(h-h_{critical})}$, $h_{critical}$ is critical thickness and λ is the stress attenuation coefficient, which can be derived from the XRD experiment.

The critical thickness of the film can be calculated by:

$$h_{critical} = \frac{b}{4\pi\epsilon_{lattice}} \tag{7}$$

b: norm of the dislocation Burgers vector. b= 0.32nm [18].

which means $h_{critical} \approx \frac{0.32}{4\pi \cdot 0.0188} \approx 1.36nm$

Finally, we can integrate the formula:

$$\sigma_{\text{total}} = \frac{\Delta\alpha \cdot \Delta T \cdot E_{ZnO}}{1-\nu_{ZnO}} \cdot \frac{h_{ZnO}}{h_{GaN}+h_{ZnO}} + \epsilon_{lattice} \cdot \frac{E_{ZnO}}{1-\nu_{ZnO}} \cdot f(h) \tag{8}$$

$$f(h) = \begin{cases} 1 & h \leq h_{critical} \\ e^{-\lambda(h-h_{critical})} & h \geq h_{critical} \end{cases} \tag{9}$$

From the equation $h = \frac{\lambda}{2\Delta\theta cos\theta_i}$ we can measure thickness by an XRR curve and then determine the relationship between stress and thickness. The equation will be verified in the result and discussion section.

Next, we will introduce the relationship between the dissolution rate and the solution concentration.

3.2. Dissolution Rate

As noted earlier, putting ZnO materials in hydrochloric acid HCL involves an acid-base reaction. The dissolution rate is related to the concentration of HCL liquid, which means it provides more H^+ ions to react with ZnO.

To determine the relationship between solution concentration temperature and reaction rate we can set up the following experiment. Firstly, we can apply 0.1 Mol/mL to 2 Mol/mL concentration of HCL liquid and then set the reaction temperature range from 303 K to 333 K. Secondly, for different thicknesses of the ZnO layer we can select 10 nm 50 nm 100 nm. As for the thickness control we use PLD, as mentioned previously. Then we can get different dissolution rates of different thicknesses of ZnO in different temperatures and HCL concentrates.

We can use the Arrhenius equation [19] and equations of concentration and dissolution rates to describe the relationship between the reactant temperature, the concentration of solution and dissolution rates.

$$k(h) = \text{Ae}^{\frac{-\text{RT}}{\text{E}_\text{a}}} \tag{10}$$

$$r(h,T,C_{HCL}) = k(h)e^{\frac{-RT}{Ea}} \cdot C_{HCl}n \tag{11}$$

$k(h)$ represents the constant of reaction velocity.

$r(h)$ represents the function between the dissolution rate and thickness.

A is a pre-exponential factor used to describe the frequency of product generation; it can be calculated by Coats-Redfern [20] and an equation can be used to fit the curve A.

R is the gas constant R=8.314J/(K·mol) [21].

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E_a is the activation energy, which is 39.626 kJ/mol [22]. This energy must be overcome by the reactant to have a chemical reaction. It represents the minimum energy for molecules to convert from their initial state to an active state.

C_{HCl} is the concentration of HCL. We set this parameter from 0.1 Mol/mL to 2 Mol/mL.

n is the reaction order. It represents the degree to which the reaction rate depends on the concentration of the reactant.

$$ln(\frac{\beta}{T^2}) = ln(\frac{AR}{E_a g(\alpha)}) - \frac{E_a}{RT} \tag{12}$$

Where β refers to the changing rate of heat in the experiment.

$g(\alpha)$ refers to the progress of the reaction. $g(\alpha) = 1 - \alpha$, where α can be determined by measuring the concentration of Zn^{2+} $\alpha = \frac{[Zn^{2+}]t - [Zn^{2+}]0}{[Zn^{2+}]\infty - [Zn^{2+}]0}$

4. Results and Discussion

Surface morphology analysis is performed using a scanning electron microscope (SEM) to examine the surface flatness, roughness and ZnO deposition quality. SEM provides high-resolution images to detect defects, ensuring structural uniformity and smoothness. Different ZnO thicknesses are prepared to explore the relationship between thickness and stress. The thickness values for GaN and ZnO are measured using XRR, as previously mentioned. Additionally, stress measurements are conducted for varying thicknesses to validate the stress formula.

It is possible to record the stress caused by each combination of GaN and ZnO to get the optimal thickness of the GaN.

Furthermore, we used X-ray diffraction (XRD), which can help to analyse the stress and observe the full width at half maximum (FWHM) (Figure 1) to justify the quality and defects of the structure [23].

We start with stress. In the previous section we mentioned that alongside the growth of the ZnO layer, the stress increases. This is because stress in the film leads to changes in the interplanar spacing. This change can be detected by observing changes in the diffraction peak position $\Delta\theta$ using XRD.

$$\sigma = \frac{E_{ZnO}}{1+\nu_{ZnO}} \cdot \frac{tan\theta}{\Delta\theta} \tag{13}$$

We can compare different θ of ZnO thickness with the same thickness sample but not deposit on the GaN layer and calculate the difference to get stress σ. Figure 3 shows the maximum ZnO thickness that GaN can support under static conditions, with different GaN thicknesses applied to various experimental setups.

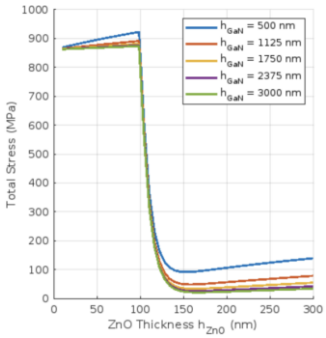

Figure 3: The relationship between different stresses introduced by different thicknesses of ZnO and match different thickness of GaN.

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X-rays scatter off regular atomic arrangements in a crystal, creating Bragg diffraction peaks due to constructive interference. By varying the X-ray angle and detecting diffraction intensity, we can analyse the crystal quality. The X-ray intensity versus ω forms a curve, where a smaller FWHM indicates better crystal quality. Figure 4 shows the quality of each growth temperature of ZnO [24].

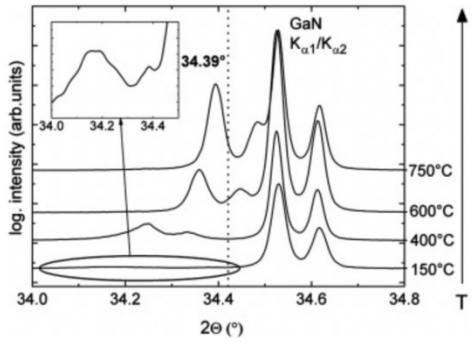

Figure 4a

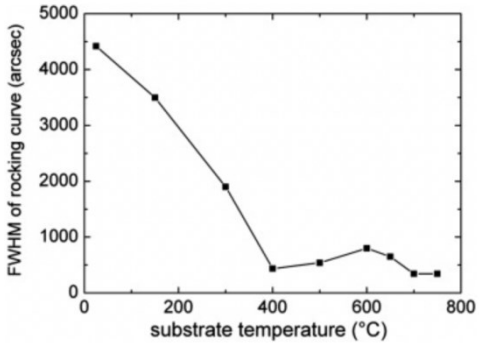

Figure 4b

Figure 4a shows ZnO-(0002)-peak with increasing substrate temperature (ZnO on GaN). Figure 4b shows FWHM of the ZnO-(0002)-rocking curve as a function of the substrate temperature (ZnO on GaN). 750 °C is the optimal temperature for deposition of ZnO.

To better understand the lift-off process, various characterisation techniques can be used. This section details the lift-off procedure, including HCl preparation, dissolution control and temperature monitoring. Firstly, different HCl concentrations are prepared to study their effect on the dissolution rate. A magnetic stirrer ensures uniform ZnO dissolution, while a pH meter monitors acidity. If acidity decreases, a precision pump adds HCl to maintain the desired concentration. A heating plate is used to control the reaction temperature throughout the process.

A Raman spectrum can be used for real-time monitoring of the dissolution process of ZnO [25]. Before the dissolution we recorded the Raman peak of ZnO as 437 cm^{-1} [26], with the dissolution of time the intensity of the characteristic peak will gradually weaken until ZnO is completely dissolute. In this way we can monitor without any contact or damage.

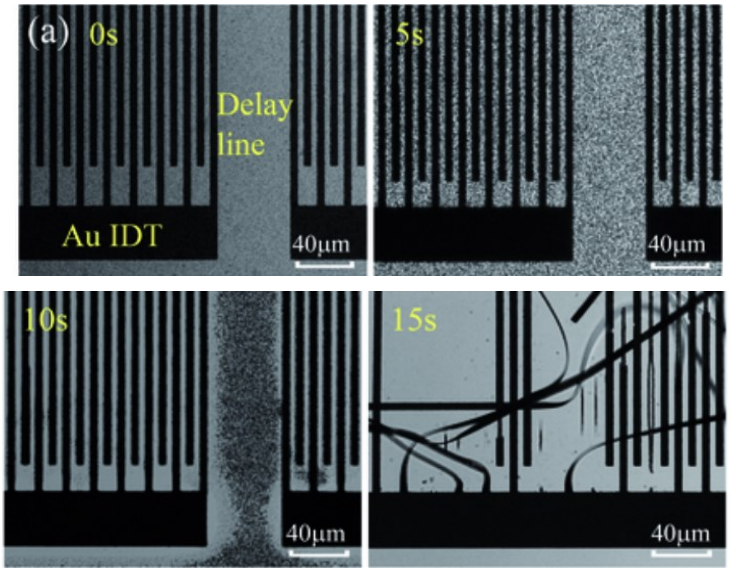

Figure 5: Optical images of different reaction times of ZnO devices in HCl solution [27].

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In this section, the results are discussed, focusing on the relationship between the HCl concentration and the ZnO dissolution rate. We use the Arrhenius equation and the concentration-dissolution rate equation to describe the relationship between the reaction temperature, solution concentration and dissolution rate.

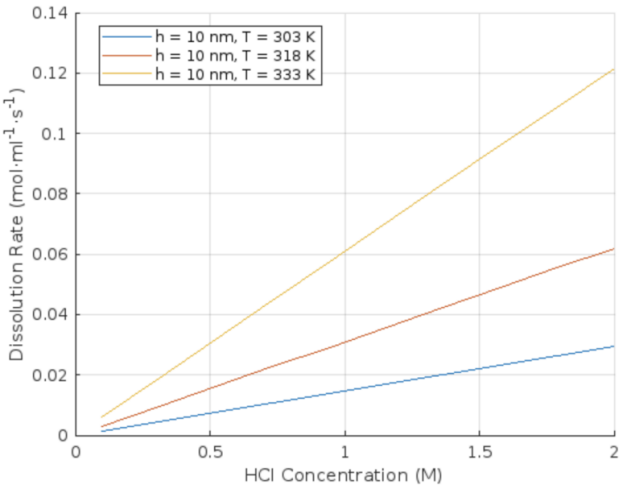

Figure 6: Simulation results of the dissolution rates with the same thickness of ZnO under different reaction temperatures. The dissolution rate is linear to the temperature.

5. Process Implementation

To optimise the process, we need to document the solution concentration, thickness, temperature and time for each ZnO and GaN thickness, ensuring minimal damage. Multiple repetitions of the experiment are necessary to ensure reliability and stability. Quality monitoring is essential for accurate results.

For industrial-scale applications, challenges include maintaining solution uniformity, controlling the concentration and temperature precisely and managing costs related to high-quality GaN, HCl solution and reaction devices. Costs can be reduced by recycling solutions and using automated systems. Environmental concerns, such as HCl waste disposal, can be mitigated by recycling the solution.

6. Applications and Future Prospects

This process reduces defects and damage to GaN, which is challenging and costly to prepare. Future research can focus on using more environmentally friendly solutions and improving the reaction rate. Additionally, exploring materials other than ZnO could enhance GaN layer stability, providing more material options for the semiconductor industry.

7. Conclusions

In this research we determine how to dissolute the critical thickness of the ZnO sacrificial layer without introducing defects to the GaN substrate, therefore improving the integrity of the GaN substrate. By using equation (8) mentioned previously, we can determine the optimal process parameter of the thickness of GaN and ZnO under different experiment needs. The reaction liquid concentration temperature and time can also be adjusted. This study aims to reduce the GaN material and cost of production.

The study does have limitations in its simulation of stress, due to its focus on theoretical analysis. This paper ignores the microstructural changes in the ZnO and GaN interface areas

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(such as interface slip and dislocations during oxide film growth. Another limitation can be seen in the dissolution process, where we didn't take the thickness effect into consideration, since the dissolution rate may not be a simple linear relationship, especially for a thicker film. In the future, to solve this, we can introduce the interface stress model to consider the contribution of microstructural changes on the interface to the stress. In addition, we can conduct a future experiment to determine the relationship between dissolution rate and thickness further. Finally, it is crucial to recycle the solution to protect the environment.

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