GaAs surface wet cleaning by a novel treatment in revolving ultrasonic atomization solution

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Abstract: A novel process for the wet cleaning of GaAs surface is presented. It is designed for technological simplicity and minimum damage generated within the GaAs surface. It combines GaAs cleaning with three conditions consisting of (1) removal of thermodynamically unstable species and (2) surface oxide layers must be completely removed after thermal cleaning, and (3) a smooth surface must be provided. Revolving ultrasonic atomization technology is adopted in the cleaning process. At first impurity removal is achieved by organic solvents; second, \(\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 10\) solution and \(\text{HCl} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 20\) solution in succession to etch a very thin GaAs layer, the goal of the step is removing metallic contaminants and forming a very thin oxidation layer on the GaAs wafer surface; \(\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1\) solution is used as the removed oxide layers in the end. The effectiveness of the process is demonstrated by the operation of the GaAs wafer. Characterization of the oxide composition was carried out by X-ray photoelectron spectroscopy. Metal-contamination and surface morphology was observed by a total reflection X-ray fluorescence spectroscopy and atomic force microscope. The research results show that the cleaned surface is without contamination or metal contamination. Also, the GaAs substrate surface is very smooth for epitaxial growth using the rotary ultrasonic atomization technology.

Key words: GaAs; cleaning; ultrasonic atomization

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1. Introduction

Cleaning is a key issue in epitaxial layers on GaAs based and Si based devices. Often, it limits the device in areas where the advantages of GaAs based diode lasers as compact, a wide choice of wavelengths, or the possibility to couple the beam into optical fibers, are otherwise compelling: where the reliability of Si based integrated circuits for the development of microelectronics, the main factor limiting device reliability and electricity peculiarity is the lustration of the wafer cleaning. A number of cleaning processes have been developed in the past with RCA\textsuperscript{[1]} to name probably the most influential one. Based on cleaning the wafer in an alkaline medium called first step and an acidic reactant with second step, the process induces an unfavorable effect on surface micro roughness and makes the oxide layer more compact and insulating. Thus further, mostly proprietary, processes have been created during the last decade. They concentrate on the removal of particles, organic, metallic contaminants stoichiometry and surface roughness by changing different etching mediums and/or cleaning methods.

For this purpose, various technological means have been applied as, for instance, a chemically clean method is that ultrasonically cleaned GaAs surface under running de-ionized water produced a damage free surface\textsuperscript{[2]}. The removal of native oxide and carbon contamination from the Si wafer by aqueous chlorine solutions\textsuperscript{[3]} or, more recently, with atomic hydrogen, treated the GaAs surface to obtain a stoichiometry surface\textsuperscript{[4]}. Unfortunately, surface roughness and contamination is unavoidable in nano-scale technology and the term “clean” is very subjective. A substrate with ideal electrical, chemical, and physical properties has not yet become available and new procedures are still needed.

This paper presents a novel approach for preparing metal-free surface, particle-free surface and oxide-free layers of the GaAs substrates by using revolving ultrasonic atomization solution and by using surface sensitive techniques: characterization of the oxide composition was done by X-ray photoelectron spectroscopy (XPS), metal-contamination was analyzed by total reflection X-ray fluorescence spectroscopy (TXRF) and surface morphology was observed by atomic force microscopy (AFM). In this paper, the process is detailed and results are presented on the performance of the treated GaAs wafer.

2. Experimental

2.1. Concept

The process development has been guided by several principles as follows. First, technical simplicity was mandatory implying the growth of the GaAs wafer and the use of standard
e-pi-semiconductor technology. Secondly, wafer cleaning has to be accomplished by a wet chemical process without employing energetic particles potentially damaging the wafer region. Cleaning has to concentrate on the removal of thermodynamically unstable species as arsenic, arsenic oxides, gallium oxides, carbon, oxygen etc. Their presence spurs gradual wafer surface degradation, eventually leading to damage. Thirdly, the cleaned wafer is measured with surface sensitive techniques: characterization of the oxide composition was done by XPS, metal-contamination was analyzed by TXRF and surface morphology was observed by AFM.

Up to now, there have been many papers on epi-ready wafer cleaning. However, there have been no reports on the making process of epi-ready wafer with revolving ultrasonic atomization. So, we report, for the first time, on the process of epi-ready wafer and the relation between chemical solution and performance of epi-ready wafer, and the particle-free, metal-free, oxides-free and very smooth surface that is achieved by this process.

2.2. Implementation

The ultrasonic atomization principle[5] is the use of ultrasonic transducer generated ultrasonic through atomization media transmit, to form surface tension waves at the gas-liquid interface, the liquid molecules interaction force was damaged by the ultrasonic cavitations effect and pulled out from the liquid surface forming a small droplet, at last the liquid was to be atomized in aerosol state. The small droplets produced by ultrasonic atomization have a low jet speed, so uniformly dispersed 2-4 μm droplets can be obtained[6,7], and the initial velocity of droplets is almost zero, the flow required for carrier gas is small, so the high density of the small droplet flow is easy to produce and is conducive to being transported and deposited. These ensure the solution concentration is homogeneous in the process of cleaning the wafer, and assure that cleaning the surface of the wafer achieves consistent results.

Rotary ultrasonic atomization refers to rotating the wafer at a high-speed by using mechanical means. Through continuous spurt ultrasonic atomization small droplets are sprayed to the surface of the wafer and achieve the purpose of cleaning the wafer by the process of the high speed rotate wafer method. This method uses the spurt liquid to dissolve contamination of the wafer surface by solution or chemical reaction, while using the centrifugal effect produced by high speed rotation to disengage the impurities dissolved in the liquid from the chip surface and timely, so that the wafer surface of the liquid can be maintained at a very high purity.

A clean and smooth surface means that there is no organic matter, particles, metals or native oxidation pollutants in the wafer surface. To achieve such a request, first of all, we have chosen organic solvents to remove organic contamination and thermodynamically unstable species on the surface of the GaAs wafer. Then we use NH₄OH : H₂O₂ : H₂O = 1 :1 :10 and HCl : H₂O₂ : H₂O = 1 :1 :20 solution in succession to etch a very thin GaAs layer; the goal of this step is removing the metallic contaminants and forming a very thin oxidation layer on the GaAs surface. At last we use NH₄OH : H₂O = 1 :5 solution to dissolve the oxidation layer of the GaAs wafer; the oxidation layer is composed of Ga₂O₃, As₂O₃ and As₂O₅. It is easy to form a reaction when making Ga₂O₃, As₂O₃ and As₂O₅ and NH₄OH solution together, so we generally use a NH₄OH : H₂O = 1 : 5 solution to remove the oxidation layer, and GaAs does not react with NH₄OH : H₂O = 1 :5 solution, so NH₄OH : H₂O = 1 :5 solution will not damage the surface of the GaAs wafer. At the same time, in an alkaline environment, GaAs surface can easily form a hydrophilic surface, so it is conducive to remove particles of the GaAs wafer surface.

3. Results and discussion

It is well known that the device performances and reliability of semiconductor laser and circuits are critically affected by the presence of chemical contaminants and particular impurities on the wafer surface. The objective of wafer cleaning is to remove any particular and chemical impurities from the semiconductor surface without damaging or deleteriously altering the substrate surface. There are several contamination types, such as molecular types, ionic types, and atomic types. Molecular contaminant films on wafer surfaces can prevent effective cleaning, impair good adhesion of deposited films, and form deleterious decomposition products. Ionic contaminants cause a host of problems in semiconductor devices. During high temperature processing, they may diffuse into the bulk of the semiconductor leading to electrical defects, and device degradation. Metallic contaminants, such as heavy metals, alkali metals, and light metals from the chemical and process, are especially detrimental to the performance of semiconductor devices. Metal contaminants on semiconductor wafer can lead to structure defects in vapor grown epitaxial layers and degrade the break down voltage of gate oxides. The results of residual metal contaminants on the surface of the GaAs wafer prepared with the revolving ultrasonic atomization solution wet chemical cleaning process measured by TXRF are summarized in Table 1. Many metal-impurities such as Fe, Ca, Al, Ti, Zn, and Mg are dissolved, to achieve a high-quality epi-layer, the wafer surface oxide layers must be easily decomposed during the epitaxy process, and a smooth surface is needed. Surface morphology was observed by AFM which is shown in Fig. 1, and the root mean square roughness of the surface determined on 2 × 2 μm² squares was equal to 0.163 nm. All oxides on the GaAs wafer surface e.g. As₂O₃, As₂O₅, Ga₂O₃, Ga₂O₅, if these oxides exist in the GaAs based semiconductor lasers, and those serve as nonradiative recombination centers and absorption, even lead to catastrophic optical damage. In the case of the final clean wafer, we measured a spectra of Ga3d peak and As3d peak before and after cleaning the GaAs wafer which are shown in Figs. 2 and 3. In the Ga3d spectrum, the XPS spec-

Table 1. Metal-impurities at the surface measured by TXRF according to the revolving ultrasonic atomization solution.

<table>
<thead>
<tr>
<th>Residual surface metal-impurities</th>
<th>Cu</th>
<th>Si</th>
<th>Cl</th>
<th>Fe</th>
<th>S</th>
<th>Au</th>
<th>Ti</th>
<th>Zn</th>
<th>Ca</th>
<th>Ni</th>
<th>Al</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before cleaning</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atoms at 1 μm²</td>
<td>2134</td>
<td>582</td>
<td>183</td>
<td>97</td>
<td>42</td>
<td>37</td>
<td>12</td>
<td>16</td>
<td>18</td>
<td>9</td>
<td>19</td>
<td>14</td>
</tr>
<tr>
<td>After cleaning</td>
<td>13</td>
<td>21</td>
<td>19</td>
<td>0</td>
<td>6</td>
<td>4</td>
<td>0</td>
<td>0</td>
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</table>
Fig. 1. AFM images of the GaAs substrate surfaces cleaned in revolving ultrasonic atomization solution. (a) Before cleaning. (b) After cleaning.

Fig. 2. XPS spectra of (a) Ga3d core levels and (b) As3d core levels in GaAs wafer before treated with revolving ultrasonic atomization solution.

Fig. 3. XPS spectra of (a) Ga3d core levels and (b) As3d core levels in GaAs wafer after treated with revolving ultrasonic atomization solution.

trum is dominated by peaks at 20.49 and 19.17 eV which are assigned as Ga oxide[8] and GaAs substrate[9], respectively. In As3d spectrum, the peaks at 43.97 and 41.01 eV are assigned as As$_2$O$_3$ and GaAs substrate, respectively[10,11]. The GaAs substrate surface cleaned with revolving ultrasonic atomization solution shows very little oxides in the GaAs surface, so the novel treatment technique can enhance GaAs based and Si based devices performance and prevent catastrophic optical damage.

4. Conclusion

For the first time a revolving ultrasonic atomization solution is used to clean a GaAs surface. This novel technique opens new outlooks on wet surface cleaning treatments for GaAs and silicon processing in production lines. In conclusion, we have succeeded in cleaning the metallic-impurity-free surface, particle-free surface, and oxide-free layer surface by using a revolving ultrasonic atomization solution. Cleaning in NH$_4$OH : H$_2$O$_2$ : H$_2$O = 1 : 1 : 10 and HCl : H$_2$O$_2$ : H$_2$O = 1 : 1 : 20 solution in succession to etch and NH$_4$OH : H$_2$O = 1 : 5 solution to remove the oxidation layer and with revolving ultrasonic atomization solution is the proper surface treatment to prepare GaAs substrates for epitaxial growth.

References


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