

GaAs Surface Preparation for Thin Films Deposition Using Sodium Hypochlorite

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ABSTRACT

Preparation of Gallium Arsenide (GaAs) surfaces, prior to a thin-film deposition, serves the prevailing functions of lowering defectivity, contamination removal and promoting adhesion. When native oxides, metallics or particulates are a concern, the common GaAs clean includes a dilute acid (HCl, HF) or base (NH₄OH). When adhesion is the primary concern, the GaAs surface may need to be roughened in order to increase the exposed surface area. This etching is generally achieved using an oxidizing chemistry (H₂O₂) in conjunction with an acid or base (HCl, NH₄OH). Unfortunately, a number of oxidizing chemistries are often too strong or unstable to be useful in particular processes, such as metal adhesion. Sodium Hypochlorite Bleach (NaOCl) is an oxidizing chemistry that attacks GaAs and is also fairly stable as a diluted solution. The condition of the resulting surface is an indication of process control and effectiveness and is measured using reflectivity.

The purpose of this paper is to discuss the use of active scientific investigation to systematically define and implement changes to a critical NaOCl surface preparation process. Opportunities for improvement of the process were discovered through process stability and manufacturability issues. A hypothesis was formulated and focused on the theoretical breakdown of the bleach during the process. The NaOCl solution degraded at a very fast rate and allowed for only 3 hours of processing per bath, with low statistical process capability (SPC). The investigation began with a literature search into the breakdown mechanisms associated with NaOCl. Following the theoretical stage, wet chemical experiments were conducted in a laboratory. The results of the lab work proved that the breakdown mechanism discussed in research literature was occurring in the existing process. Additionally, this data was verified through experiments in the factory. Process improvement work was completed using experiments in the factory. This work included recipe alteration, bath preparation changes, chemical storage improvements, and in-tool chemical containment improvements. The results of this scientific investigation are improvements involving: a 40% decrease in qualification frequency, 83% decrease in cycle time, 300% SPC improvement, 50% cost decrease, 100% elimination of reworks, and 1200% improvement in bath-life.

This paper concludes with a discussion on future process improvements with NaOCl as well as applications of the lessons learned to other processes that use unstable chemistries. The work discussed in this paper is an example of the successful application of the scientific method and active research used to determine a root cause and solution for a critical process issue.

Introduction

The surface preparation process that this paper discusses is a multiple iteration process that uses HCL and NaOCl. During this process, the wafers are exposed to HCL to remove native oxides, while the NaOCl is used to oxidize and smooth the exposed GaAs. The final iteration of HCL is to ensure all oxides have been removed. In order to determine if the wafers were processed correctly, samples out of each lot are measured for correct reflectivity. The reflectivity percentage determines the roughness of the GaAs surface.

The process that prompted this change was rather cumbersome. The old process started with the preparation of an unstable and delicate NaOCl bath; including the qualification test, this first step could take up to approximately 80 minutes. Prior to the improvements, this process took 30 minutes per run and required a new bath to be mixed every four hours. A simple calculation based on the above numbers shows that each bath was only applicable for about four process runs. Due to all these limitations, research was conducted to make this process more robust.

Background

Bleach has a storied chemical past. In 1787, the French Chemist Berthollet discovered bleach's ability to whiten textiles and in the late nineteenth century Louis Pasteur discovered the disinfectant properties of sodium hypochlorite. Bleach can be defined chemically as a strong oxidizing agent. Hypochlorites or peroxides often supply the oxidizing power. Commonly known bleaching agents include calcium hypochlorite, hydrogen peroxide and sodium hypochlorite. Sodium hypochlorite is regularly used as a germicide in water treatment, a medical disinfectant and a common household cleaner and disinfectant [1]. Sodium hypochlorite is a strong electrolyte that completely dissociates in solution. It then works by decomposing to liberate nascent oxygen, which is much more active than ordinary oxygen gas [2]:



Sodium hypochlorite is considered concentrated in a 5-7% solution and is commercially sold as such [3]. At a pH of 11 or above it is highly stable. However, there are

several factors that lead to the chemical's degradation; including changes in temperature, foreign metals, and exposure to air. Temperature and air exposure, specifically carbon dioxide in the air, are the two primary concerns in the GaAs preparation process [1]. Since the process was ran at ambient temperature, a hypothesis was developed stating that the primary factor in the breakdown of the bleach was air exposure due to turbulent agitation during the process. This hypothesis was reached through a literature search into the breakdown mechanisms associated with NaOCl.

This degradation was inherent in the process because the recipe called for over 4 minutes of reclaimed bleach as well as a constant recirculation of the chemistry in the equipment tank. Based on this hypothesis, a project was developed with specific goals to improve bath life and reduce run-to-run variability while keeping the current reflectivity controls.

The first step in the project was to recreate the process conditions in the laboratory. Both pH and concentration of the NaOCl were analyzed under varying concentrations and agitation conditions. Concentration was determined using an iodometric titration [4] and pH was determined using a meter. The agitation was created using a magnetic stir bar and those techniques were the determining factor in confirming the hypothesis. When the solution was stirred evenly (Figure1), the concentration and pH stayed relatively constant. However, when the solution was mixed vigorously (Figure2), the pH and concentration dropped drastically. This turbulent agitation infused air into the mixture and better replicated the process conditions in the fab. The degradation data can be viewed in Figures 3 and 4.



Figure 1



Figure 2

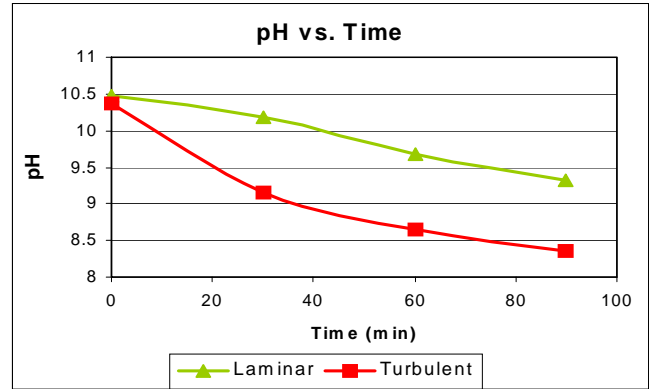


Figure 3

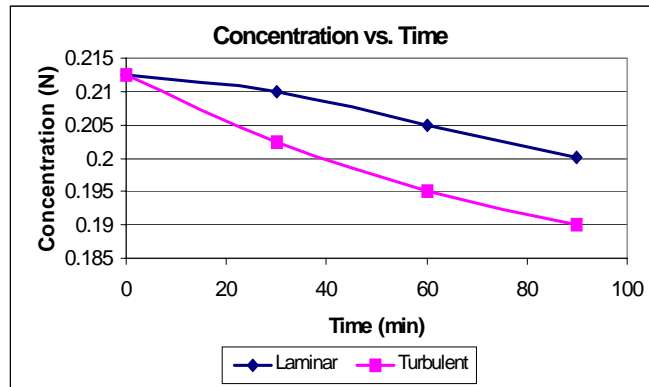


Figure 4

With the knowledge that vigorous agitation caused the swift and drastic degradation of the chemistry, the next step was to develop a process in which the agitation could be limited. The original process involved several steps of reclaimed bleach that would be pumped from the tank, to the process chamber, onto the wafers, and then back into the tank. This reclamation of the chemistry was the direct cause of the process instability. In order to eliminate the reclamation steps, two methods were investigated. The first was an aspirated NaOCl sent directly to drain after coming in contact with the wafers. This method could not be optimized due to high across-wafer reflectivity variation as seen in the below graph (Figure 5).

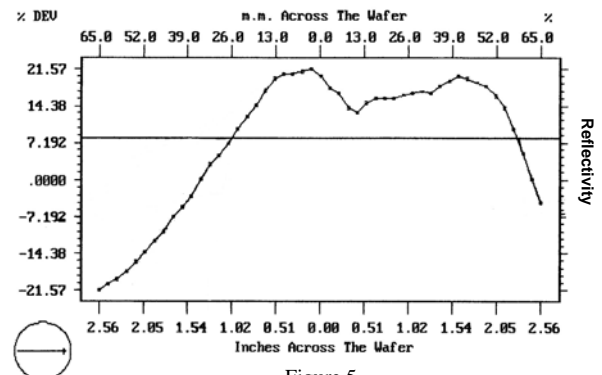


Figure 5

Since the aspirated process proved insufficient, the work turned to redesigning a fully pumped process. The first step was to design a bath that could sufficiently roughen the wafers without using a considerable amount of chemistry. The target time was approximately 15 seconds of chemical exposure with the full amount of chemistry pumped to drain. At a flow rate of 2 gpm, that equals to ½ gallon per run. Due to bleach’s low cost, this amount of chemistry to drain was acceptable. Below is a chart showing concentration versus reflectivity (Figure 6).

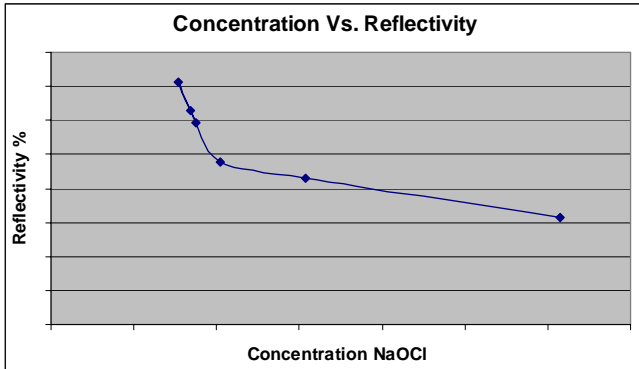


Figure 6

Bath life tests were then conducted on the chosen bleach concentration. The results showed that if the bath were allowed to sit in the tank and neither recirculated nor reclaimed, the bath would degrade linearly and last up to 48 hours with minimal effect on reflectivity. In comparison, the previous method’s reflectivity would go out of control within three hours. See the chart below for the bath life study (Figure 7).

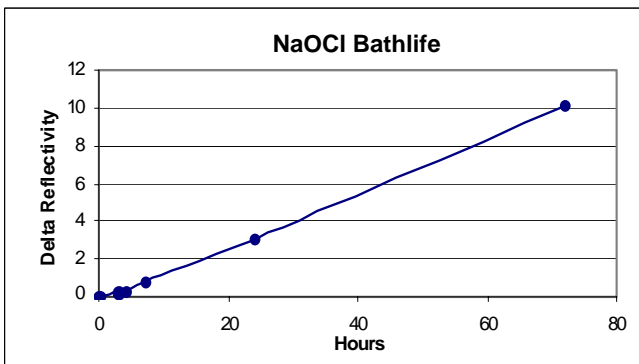


Figure 7

With the bath concentration, approximate chemical exposure time and bath life determined, the next step was to evaluate and decide on RPM, flow, and optimum chemical

exposure time. A design of experiment (DOE) was created to analyze for these variables.

The DOE conducted for this study showed that the new process parameters and bath mixture greatly improved variability from run to run. In addition, the reflectivity of each wafer was also very predictable and easy to control within Shewhart rules. Using the parameters defined in these experiments, a better, more predictable surface preparation process was developed.

Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) analysis were done to confirm the process changes did not deviate from the prior process (Figures 8 and 9 respectively). Recall that the goal of the new process was to improve the process without changing the final results.

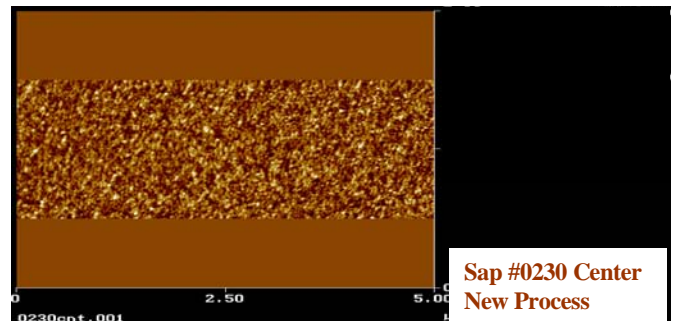


Figure 8

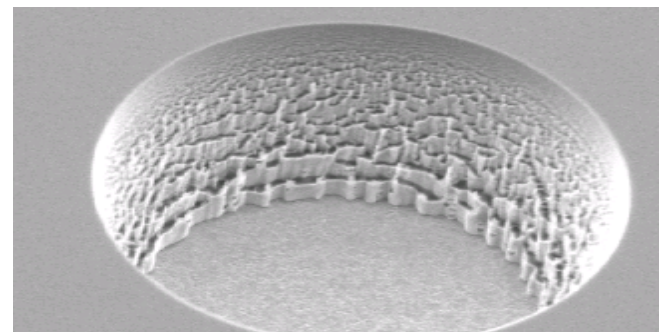


Figure 9

In addition to changes that needed to be made to the process parameters, other aspect of the process were observed to have made a difference to the resulting reflectivity of each wafer. For instance, based on the data from the control charts, a trend of higher reflectivity was observed during the summer months. This led to an inquiry about the difference in chemical production with each vendor. Since there were no notable production changes from the vendors, the investigation process dug deeper into what other parameters could be affecting the NaOCl. This exploratory work showed that there could have been a major issue with the storage conditions of the chemistry. The

extremely high temperatures of the Arizona summers were affecting the storage conditions for many of the fab's chemicals. After testing many samples of NaOCl, it was found that these hot conditions were actively degrading this chemical, in turn raising the pH and decreasing the bleach's effectiveness. This outcome substantiated the degradation mechanism described in the literature. Due to this discovery, the storage conditions have been considerably improved. The study also indicated that the pH of the NaOCl is a key factor when determining the proportions of this mixture and that a methodology would be needed to control the bath. The result of this find was a bath preparation chart. This chart indicates the amount of chemicals needed to make a proper bath based on a constant pH for the surface preparation process. The NaOCl ratio chart was statistically calculated and now plays an integral role in the bath preparation.

Conclusions

A quick comparison between the parameters and results of the old and new process shows that the application of the scientific method has helped to improve this surface preparation process greatly. Improvements for this process range from bath preparation to the controllability of the final product. Table 1 summarizes the list of improvements.

Table 1: Summary of Changes

| <u>Old</u> | <u>New</u> | <u>Improvement</u> |
|------------------------|-----------------------|--------------------|
| 30 minutes per run | 5 minutes per run | 83% reduction |
| 4 hour bathlife | 48 hour bathlife | 1,100% increase |
| 3 runs per bath | 6 runs per bath | 50% cost savings |
| 6 quals per day | 2 quals per day | 200% decrease |
| 18% reflectivity range | 9% reflectivity range | 100% reduction |

In conclusion, a mechanism of breakdown for NaOCl was discovered within the process: Leading to a new methodology of GaAs surface preparation. As of today, CS1 has attained improved cycletime, decreased qualification frequency, increased bath life, reduced run to run product variability, and generated a cost savings of 50% per run.

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