

Reduction of Chlorinated Solvents in GaAs Manufacturing

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ABSTRACT

Chlorinated solvents have been used historically in the semiconductor industry for applications such as photoresist removal and surface treatments. However, in recent years, this class of solvents has undergone increased scrutiny, especially from customers in the European Union, leading to a need to find environmentally safer alternatives. Gallium arsenide, in particular, can be subject to surface changes or surface degradation after wet chemical processing, making the selection of replacement chemistries critical. This paper discusses an approach taken successfully to replace chlorinated solvents in some wet clean processes in a GaAs manufacturing facility, specifically focusing on those processes that have been used for pHEMT fabrication. The primary requirement for the success of this project was that the change in wet chemistry would not introduce any parametric changes for existing device technologies. The chosen methodology included surveying a range of chemistries by testing parameters that are predictors of future performance, such as surface contact angles, surface roughness, and material etch rates, followed by selection of solvents and subsequent processing and testing of qualification wafers. Results from all stages of this assessment are presented, including parametric data from fabricated devices and the outcomes of associated DOEs. Potential pitfalls and sources of problems are also discussed.

INTRODUCTION

Semiconductor device fabrication relies on the use of wet chemicals in a number of areas, including photoresist removal, oxide removal, metal liftoff, and various other cleaning and polymer removal steps. Hard-baked, ion-implanted, or negative resists can be particularly difficult to remove, requiring aggressive strip chemistries. There are a variety of formulations that are effective for these applications; however, some of the traditionally used chemistries contain chlorinated solvents. For these chlorinated solvents, there is an increasing risk of ownership due to the associated environmental issues. In addition to the increased costs of disposal, there has been an industry trend

to move away from the use of these solvents, resulting in the discontinuation of some formulations. Also, customers in the European Union are increasingly requiring the use of environmentally safer alternatives; failure to comply with these standards represents a potential loss of business.

Finding replacement chemistries for these chlorinated solvents can be particularly challenging in GaAs manufacturing. Surface degradation and surface changes can be induced by chemical cleaning processes [1-4]; these effects can be increased through galvanic corrosion once ohmic contact metal has been formed on GaAs and both the metal and the GaAs are exposed to the wet cleaning solution [1, 3-4]. Some solvents can attack and degrade the exposed metal contact layers, as well. These reactions may be sensitive to the moisture content of the solvents [3], resulting in process variability and frequent replacement of chemical baths. Most importantly, changes to the GaAs surface due to wet cleans early in the process flow may also interact with downstream processing, changing device performance.

This paper presents findings from the replacement of chlorinated solvents in some wet clean processes used in GaAs pseudomorphic high electron mobility transistor (pHEMT) fabrication. Although the use of chlorinated solvents affects many steps of the process flow, this paper will focus primarily on results related to the replacement of solvents early in the process flow.

METHODOLOGY

Prior to processing qualification wafers, a range of potential replacement chemicals was surveyed; parameters that were believed to be predictors of future performance were tested. These parameters included surface contact angles, surface roughness, and GaAs etch rates. Viable solvents were selected based on the results of this preliminary testing and qualification wafers were processed using the preferred replacement chemistries; critical parameters for the qualification were identified and results from the qualification wafers were compared with those obtained from wafers processed using the standard flow and chlorinated solvents. During the completion of this study, interactions were discovered between cleans at various points in the processing; these interactions were investigated through the use of design of experiments (DOEs).

EXPERIMENTAL

Preliminary Testing

Surface contact angles were evaluated by measuring, with a goniometer under high magnification, the angle of contact between the GaAs surface and a water droplet on the surface of the wafer; the angles were measured on bare GaAs substrates, immediately after processing through each selected wet chemical clean. Surface roughness was characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM); these measurements were completed on device quality substrates with complete pHEMT epitaxial structures. The relative etch rate of GaAs in the various solvents was evaluated by comparing the change in sheet resistance, before and after processing, of silicon-implanted GaAs substrates; the sheet resistance was measured using a contactless sheet resistance probe manufactured by Leighton Electronics.

Process Qualification

Qualification lots containing device quality material were processed through all steps of a standard pHEMT flow. At the appropriate wet clean steps, the lot was split between processing with the chlorinated solvent and processing with the replacement chemistry. Cleanliness of the surfaces was evaluated through optical and SEM inspections. Parametric data were collected through in-line testing of process control monitor (PCM) structures and through DC and RF testing of device structures.

The device results described here focus primarily on solvent cleans that were completed early in the process flow; specifically, the described solvent cleans were completed after isolation implant to remove implant-hardened resist. At this stage in the processing, the ohmic contacts had been formed but the gates had not yet been patterned and the surface was not passivated with nitride.

RESULTS AND DISCUSSION

Preliminary Testing

Effect on surface contact angle was examined for a range of wet clean processes, including solvent blends, pure solvents, acids, and bases. Table 1 shows the results of this testing. Not all of the selected chemistries were suitable for the removal of implant-hardened resist; however, this range of chemicals was selected to baseline the effect of different chemistries and as part of the larger project to remove chlorinated solvents from all fabrication processes. Solvent blends A, B, C, n-methyl-2-pyrrolidone (NMP), and the combination of NMP/Solvent C were capable of stripping implant-hardened resist; solvent blends A and B were both chlorinated solvents and were both chemicals that were being replaced.

Surface contact angle was used as one predictor of the surface state of the wafer post-clean; the surface state can affect resist adhesion, as well as etch rates, in subsequent processing. It was desirable to find a replacement chemical that would have a similar contact angle to that of the

chemical being replaced; however, the contact angle was not the only factor considered and the final selection of replacement chemistry was based on a combination of this and other data.

TABLE 1
CONTACT ANGLE OF WATER DROPLET ON GaAs SURFACE,
MEASURED POST-SURFACE CLEAN

| WET CLEAN CHEMISTRY | CONTACT ANGLE |
|--------------------------------|---------------|
| Solvent Blend A | 21.9 |
| Solvent Blend B | 19.1 |
| Solvent Blend C | 52.8 |
| Solvent Blend D | 36.8 |
| NMP/ Solvent Blend C | 57.0 |
| NMP | 27.1 |
| Tetrachloroethylene | 39.0 |
| Xylene | 37.5 |
| Acetone | 53.8 |
| Methanol | 23.8 |
| Isopropanol | 47.3 |
| Ammonium Hydroxide | 44.3 |
| Dilute (10:1) HCl | 57.5 |
| Positive Resist Developer (AZ) | 46.7 |
| DI Water | 42.1 |

The relative etch rates of GaAs in solvent blends A, B, C, and NMP were also studied. The amount of etching can be an important factor in the selection of wet chemicals for GaAs processing since the GaAs surface is particularly susceptible to chemical attack [1-4]. There is considerable evidence indicating that etching of GaAs is enhanced at the boundary between ohmic metal and GaAs and that this corrosion of the surface may affect subsequent device parameters and product yield [1, 3-4]. The use of chlorinated solvents A and B, resulted in etching and enhanced corrosion near the ohmic contacts; these solvents were also observed to attack metal layers containing nickel. The typical change in sheet resistance observed after 10 minutes of processing in solvents B and C is shown in Figure 1 as a function of the

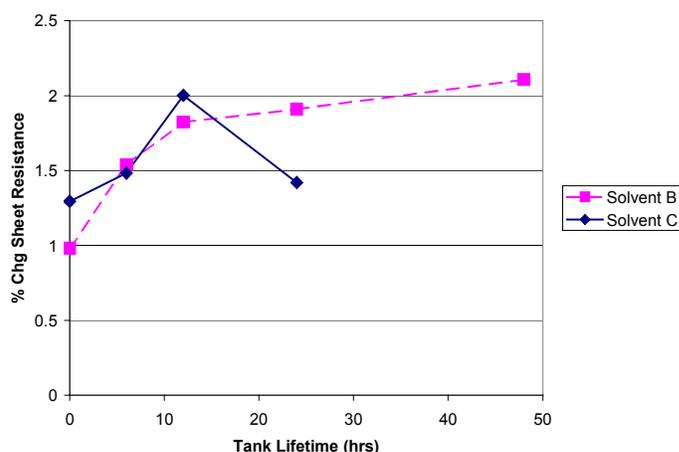


Figure 1: Change in sheet resistance of silicon-implanted GaAs substrates as a function of process tank lifetime. Data are shown for solvent blends B and C.

lifetime of the chemical bath. Although not shown on the graph, solvent A exhibited similar behavior to solvent B, while processing in NMP did not result in any appreciable change in sheet resistance and, therefore, no significant etching of the GaAs surface. As can be seen in Figure 1, the change in sheet resistance for solvent B, in particular, was a function of the lifetime of the chemical bath. In order increase stripping efficiency, these solvents are heated to 80-100°C; the increase in etch rate over time is believed to be due to moisture condensation occurring within the heated chemical tanks. The addition of water to cleaning solutions has been shown to enhance corrosion of the GaAs surface [3]; Figure 2 shows the results of adding controlled amounts of DI water to chlorinated solvent blend B. Replacement of these chlorinated solvents is expected to improve process stability, as this will reduce corrosion of the GaAs surface and eliminate variability due to the condition of the process tanks. Use of non-chlorinated solvent blend C or NMP was also found to eliminate the attack of nickel-containing metal layers.

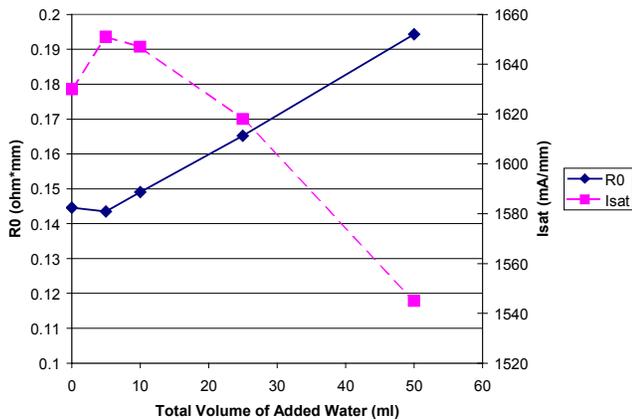


Figure 2: Effect of water content on the contact resistance and Isat values of devices processed through solvent blend B. Controlled amounts of DI water were added to the solvent tank; after each addition, a wafer was processed through the solvent clean and contact resistance and Isat values were measured. The total volume of the tank was 14 liters.

Process Qualification

One indicator of galvanic corrosion of GaAs adjacent to the ohmic contacts is the contact resistance and the corresponding un-gated saturation current (Isat), measured between the ohmic contacts. Figures 3 and 4 show the contact resistances and the Isat values, respectively, measured on PCM structures of process qualification lots prior to gate channel formation. As can be seen, these results indicate that there is an effect due to the type of solvent clean used. Solvent blend B, in particular, exhibits higher contact resistances and lower measured saturation currents; these results were correlated to increased etching in the region of the ohmic contacts.

Another important aspect of the process qualification was an examination of the changes in Isat values that occurred during formation of the gate structure. The pHEMT gate is

defined through the use of a dual recess process; Isat is measured prior to recess and after each subsequent recess

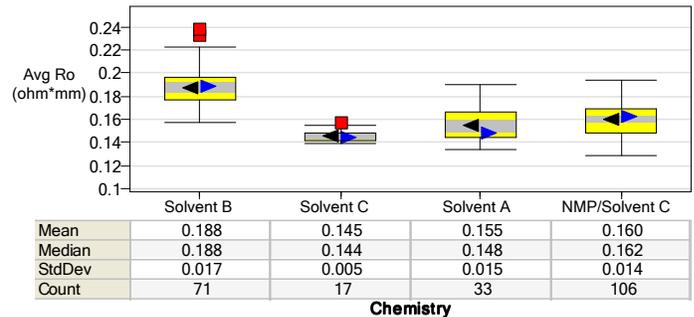


Figure 3: Effect of solvent clean chemistry on ohmic contact resistance, measured prior to gate channel formation.

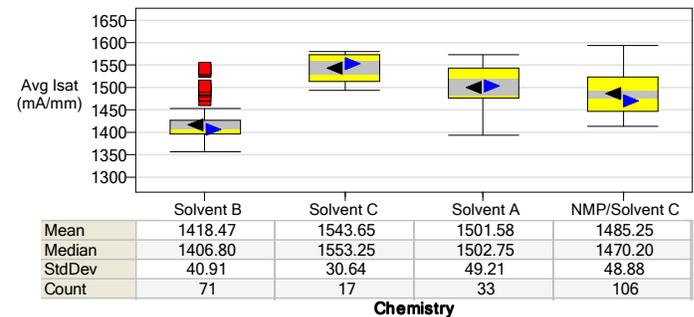


Figure 4: Effect of solvent clean chemistry on saturation current, measured prior to gate channel formation.

step. Changes in wet cleans can affect the recess process through increased etching of GaAs next to the ohmic contacts, as has been described previously in this paper, and through changes in the surface state of the GaAs substrate. The first recess etch, “wide” recess, is an iterative process, based on the measured Isat value; since corrosion next to the ohmic contacts will result in a lower measured Isat value, less etch steps will be required to meet the target value. This will change the profile of the gate channel and, consequently, will lead to differences in DC and RF parameters. Changes to the surface state, such as the amount and type of oxide remaining on the surface prior to recess etch, will also affect the Isat values measured during the recess process. Some non-chlorinated solvents, such as NMP, are effective at removing resist residue; however, these solvents may not remove oxides in the same manner as some chlorinated solvent blends. Residual oxides on the surface can interact with subsequent processing to roughen and pit the surface; this roughened surface may not etch uniformly during the recess process [5]. Figure 5 shows Isat values measured prior to the second recess etch, “narrow” recess; differences in wet cleans prior to wide recess have resulted in different Isat values at narrow recess. As part of the qualification, it was important to select chemistries that would minimize these differences.

During this qualification, a few interactions were discovered between the isolation resist strip and prior and

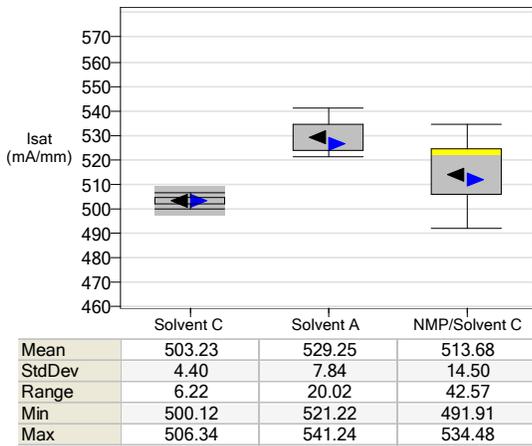


Figure 5: Average Isat values, measured prior to narrow recess, for qualification lots processed through solvent blend A, solvent blend C, and NMP/solvent blend C.

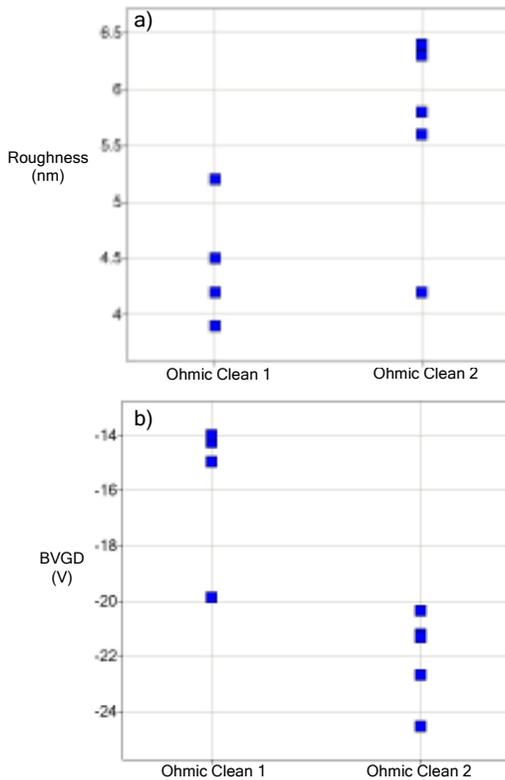


Figure 6: Two different cleans were used after forming the ohmic contacts and prior to completing the isolation resist strip. Figure a) shows the effect of these cleans on the surface roughness, as measured by AFM. Wafers processed using ohmic clean 2 are also the wafers that showed the largest difference in recess currents when processed through solvent clean C or NMP/solvent clean C during isolation resist strip. Figure b) shows the effect of these cleans on the gate-drain breakdown voltage measured at DC probe.

subsequent processing. Changes to cleans used prior to recess etch were found to interact with the isolation resist strip, resulting in differences in surface roughness and Isat values measured during recess etch; these differences, in turn, could be correlated to differences in DC parameters, such as

breakdown voltage. Figures 6a and 6b show results from a DOE that was completed to study these interactions. It is likely that these prior cleans also alter the surface state of the GaAs, affecting the manner in which material is etched during formation of the gate.

Subsequent processing through wet cleans can continue to enhance the corrosion adjacent to the ohmic contacts; the degree to which this occurs was found to be related to the solvent used for isolation resist strip. Table 2 shows the change in contact resistance for wafers processed through three different solvent cleans at isolation resist strip and then subsequently processed through a hydrochloric acid (HCl) clean after formation of the gate. Wafers processed through solvents A and B show a much larger shift in contact resistance than wafers processed through solvent C or the combination of NMP and solvent C.

TABLE 2
CHANGE IN CONTACT RESISTANCE MEASURED POST-ISOLATION CLEAN AND POST-HCl CLEAN

| Wet Clean Chemistry | Avg. Post-Isolation Ro (ohm*mm) | Avg. Post-HCl Ro, (ohm*mm) | Avg. Ro Delta (ohm*mm) |
|---------------------|---------------------------------|----------------------------|------------------------|
| Solvent A | 0.1335 | 0.3803 | 0.2468 |
| Solvent B | 0.1597 | 0.5153 | 0.3557 |
| Solvent C | 0.1429 | 0.1650 | 0.0221 |
| NMP/Solvent C | 0.1417 | 0.1604 | 0.0187 |

CONCLUSIONS

Removal of chlorinated solvents from GaAs manufacturing is motivated by the need to reduce process costs and to find environmentally safer solutions. The methodology used to replace some of these chlorinated solvents has been described and selected results from some of the qualification studies have also been presented. Replacement of these solvents presents a number of challenges due to surface changes and surface degradation induced by wet chemical processing of GaAs. However, these issues are also motivating factors for removal of more aggressive solvents from the process flow in order to reduce deleterious effect and lessen process variability. Reduction of these solvents requires careful testing of material parameters and evaluation of possible interactions in order to minimize changes in key device parameters.

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