

GaAs CORROSION UNDER OHMIC CONTACTS BY ELECTROCHEMICAL OXIDATION IN HBT DEVICE FABRICATION

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ABSTRACT

This paper presents a comprehensive study of GaAs corrosion happening adjacent to ohmic contact metal, often caused by GaAs degradation and subsequent electrochemical oxidation of the semiconductor material in wet chemical solutions. GaAs surface degradation, induced by chemical cleaning processes, ion-bombardment from dry etch processes and thin film deposition processes such as PVD and CVD, makes GaAs prone to electrochemical attacks. Ohmic contact metals put on these damaged surfaces will accelerate electrochemical reaction of GaAs, resulting in GaAs corrosion and poor device performances, if the chemicals used in these processes are not carefully chosen or the sequence of these process steps are not carefully designed. Processes to minimize GaAs corrosion are also discussed.

INTRODUCTION

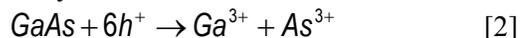
Metallization plays a very important role in fabrication of modern power amplifiers based on gallium arsenide (GaAs) heterojunction bipolar transistor (HBT) technology. There are many challenges in the metallization, including metal-metal inter-diffusion, metal-substrate inter-diffusion, metal corrosion, and substrate corrosion. Often these effects result in yield loss and create reliability problems. The effects of electrochemical etching on GaAs devices, particularly MESFET devices, have been discussed in the past [1-5]. The fabrication of PA devices relies on using photoresist to form patterns and using wet chemical strippers to remove it. Wet chemicals are also very frequently used in areas such as photoresist residue removal, oxide removal, and various other cleaning steps. GaAs surfaces, especially those near ohmic contacts, undergo electrochemical oxidation when exposed to these wet chemicals and subsequent DI-water rinse [5]. This oxidation occurs as a result of the difference in surface potential between GaAs and the ohmic contact. The metal enhances the GaAs oxidation and the resultant oxides are dissolved in the surrounding solution to cause

corrosion near the metal-GaAs interface. The metal-GaAs contact resistance rises as a result of the severe corrosion (even causing an open circuit) so that the functionality of the power amplifiers is adversely affected.

When a GaAs wafer, with a band gap of 1.42 eV, is immersed in electrolytic solution, the ohmic contact metal on it will behave like a cathode and the semiconductor will behave like an anode. At the metal surface, water is electrolyzed by electrons transferred from GaAs to the metal contact:



At the GaAs surface the following anodic oxidation occurs by holes in the GaAs valance band:



It's believed that the oxidation products will subsequently be dissolved in the aqueous electrolyte solutions such as HCl or NH₄OH and removed allowing the oxidation process to continue [6,7]. This also shows that, by forming an electrochemical cell with ohmic contact metal, GaAs can undergo anodic oxidation with just DI-water.

During the entire PA fabrication flow there are many dry etching steps as well as CVD/PVD steps that involve plasma processing or ion-bombardment to GaAs surface [8]. The resultant GaAs surface will be full of surface states and defect sites that make the surface prone to chemical attack/corrosion.

Corrosion affects devices with small ohmic contacts the most since corrosion happens at the boundary of metal and exposed GaAs. This limits the designers' abilities to design small electrical contacts in devices such as Schottky diodes and prevents further shrinkage of the total die size.

EXPERIMENTAL

Ni/AuGe collector metal is evaporated onto *n*-doped GaAs after a collector trench is etched. After alloy at 360 °C for a short period of time it forms an

ohmic contact on GaAs. Before evaporation, test wafers undergo a wet chemical pre-cleaning step to clean oxides off the GaAs surface. The ohmic contacts are patterned by photoresist, followed by normal liftoff process. The chemicals used in the pre-clean process step include either 6% HCl for 10 seconds or 2% NH₄OH for 30 seconds. Alloy process is done in a RTA oven for 30 seconds. The liftoff process is the industrial standard NMP liftoff, followed by DI-water rinse. TLM structures were created using a standard HBT transistor with a split collector, as shown in Figure 1. The collector contact size varies from 2×2 to 5×5 (μm²), including different orientations for collector contacts of the same size. These structures are connecting to bond pads via one level of metal interconnects. A thin layer of CVD-nitride is also deposited to evaluate the effects of nitride protection on the GaAs corrosion upon different chemical attacks in various process stages. The nitride thickness was also studied and a comparison was also made with silicon monoxide and PVD nitride. The electrical test is a simple 2-probe DC measurement that measures the resistance of the split collector.

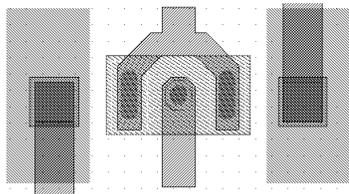


Figure 1 Split collector contact test structures.

RESULTS AND DISCUSSIONS

After the ohmic contact metal deposition process there are many steps in which the contact is exposed to wet chemical cleaning, including the NMP liftoff and 6% HCl cleaning before metal interconnect deposition and before nitride deposition. When the ohmic contact metal is submerged in these wet chemicals there will be an electrochemical cell formed between the contact and surrounding GaAs. The metal will behave like a cathode and the GaAs will behave like an anode and the circuit is complete by the chemical solution itself and the epitaxial layer of GaAs. The GaAs will undergo anodic oxidation and the oxidation products will be dissolved in the solution, resulting in physical material loss, as shown in Figure 2.

Untested wafers were also cross-sectioned to ensure that the corrosion was not test-related. Corroded ohmic contacts have much higher

resistance in electrical tests, regardless of the contact size. However, the smaller size contacts are affected more because the ratio of corroded area to the total contact area is higher. Table 1 shows the estimation of percentage of corrosion to total contact area, where the smaller contacts have much higher resistance and standard deviation.

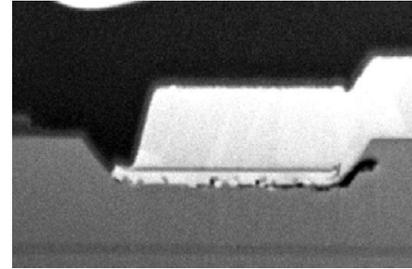


Figure 2 GaAs corrosion caused by electrochemical oxidation.

CC Size	Left Side	No Corrosion	Right side	Corrosion Width	Good Portion
2×2	1.0 μm	0 μm	1.0 μm	1.5 μm	25%
3×3	1.4 μm	0.2 μm	1.4 μm	1.0 μm	58%
3×5	1.4 μm	0.2 μm	1.4 μm	1.0 μm	81%
5×3	1.5 μm	2.75 μm	0.75 μm	0.75 μm	88%
5×5	2.5 μm	1.75 μm	0.75 μm	1.5 μm	80%

Table 1 Comparison of contacts with different sizes, based on estimation of corrosion area to total contact percentage ratio.

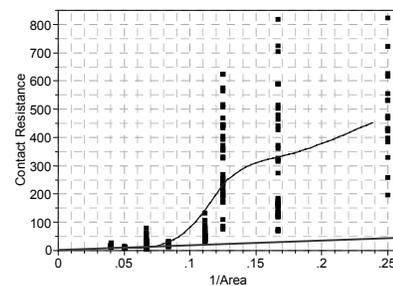


Figure 3 Resistance versus size plot for ohmic contacts with different sizes. Straight line indicates the theoretical values.

The electrical results are shown in Figure 3, where the calculated contact resistance is plotted against the reciprocal of the contact size. Theoretically it should be a linear curve, as depicted with the straight line. However, as the contact size decreases its resistance rises to much higher values because of the corrosion problem. This prevents the further shrinkage of the ohmic contacts, as well as the device size.

Numerous experiments were carried out to find the origin and nature of the GaAs corrosion. It is found that the corrosion happens after the ohmic contact has formed and after the contact is subjected to any of the surface protection processes, such as nitride deposition over the ohmic contact.

For GaAs to be corroded, or anodically oxidized, a number of electrons have to be transferred from GaAs valence band edge to the connecting ohmic contact, through the GaAs conduction band by electron tunneling between the conduction band and the ohmic contact [9]. Holes generated in the valence band will act like strong oxidants and oxidize the GaAs surface, as shown in Figure 4. Any process that can aid this electron hopping and tunneling will leave more holes in the valence band and thus enhance GaAs corrosion. Surface states will cause energy band to bend upwards for *n*-type GaAs so all the holes generated in the valence band will remain on the surface to cause corrosion on GaAs. Surface states will facilitate the electron hopping from valence band to conduction band [10]. GaAs corrosion under ohmic contacts may be related to surface property change of the GaAs itself, whether it ends with Ga or As, surface states and dangling bonds formation, which can happen during any of the process steps, such as etch, clean, and deposition.

The ohmic contact is formed by depositing Ni/AuGe onto *n*-doped GaAs and alloying it in rapid thermal process oven at high temperature. Prior to the metal deposition there is a wet cleaning step to etch the surface oxides so that an ohmic contact can be properly formed between the metal and the GaAs after RTA. Without this cleaning step the contact metal cannot be properly alloyed into GaAs and an ohmic contact cannot be formed so that the contact resistance is orders of magnitude higher. However, the higher resistance between the metal and the GaAs minimizes the electron tunneling and the GaAs corrosion is eliminated as a result.

The suppression of GaAs electrochemical etching by increasing the resistance between the exposed GaAs and the ohmic contact has been used in PHEMT manufacturing [3].

GaAs surface oxides form in a sequence of GaAs/As/Ga₂O₃/As₂O₃-Ga₂O₃ [11]. Both HCl and NH₄OH can remove oxides. However, using HCl will leave a thin film of As on the GaAs surface due to insolubility of As in HCl and preferential etching of Ga in HCl [6,7]. That will increase the density of surface dangling bonds and increase surface

states, causing band bending and GaAs corrosion. NH₄OH, on the hand, will dissolve As to expose a fresh GaAs surface. As shown in Figure 5, HCl-cleaned wafers have statistically higher resistance and worse standard deviation, compared to NH₄OH-cleaned wafers. These results are due to the GaAs corrosions under ohmic contacts, which was confirmed by FIB cross-section pictures.

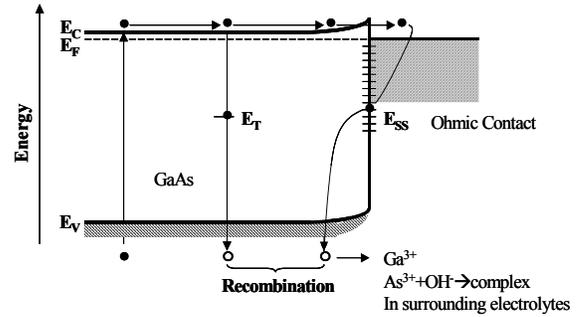


Figure 4 Schematic drawing of electron transfer and recombination paths in the ohmic contact/*n*-GaAs system.

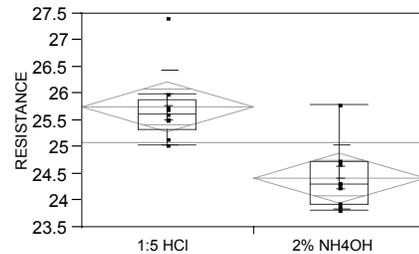


Figure 5 Comparison of ohmic contacts with different pre-cleaning processes.

For protection purposes, silicon nitride is normally deposited on the ohmic contact after its formation. During nitride deposition, by either PVD or CVD, GaAs surface is exposed to plasma bombardments that could potentially damage the GaAs surface [12]. SiO_x films will cause Ga out-diffusion and Si_xN_y films will cause As out-diffusion, even in the films as deposited [8]. The result of these out-diffusions is the high density of interfacial states and stresses, causing GaAs underneath these films to be prone to corrosion. This is especially true when these thin films have higher defect densities so that wet chemical can go through them to attack GaAs. Figure 6 compares resistance of ohmic contacts between PVD and CVD protection nitrides. Substantial RF power and longer time are used in the PVD process, resulting in more GaAs surface damage. This is reflected in the fact that ohmic contact resistance is 2 orders of magnitude higher for PVD nitride processes. In a

separated experiment, wafers were processed without the protection nitride (all other process steps were exactly the same). These wafers were tested and no corrosion could be found, indicating that the interaction between nitride or its deposition process and GaAs has a strong effect on the GaAs corrosion. Nitride thickness also plays a role in the GaAs corrosion. Thicker nitrides that have less intrinsic defects or cracks will prevent the wet chemical penetration and GaAs corrosion will be eliminated. Similarly, if the nitride density is increased, for example, using more lower frequency power during deposition, the resulting nitride will also protect the GaAs surface better and minimize the corrosion, as shown in Figure 7.

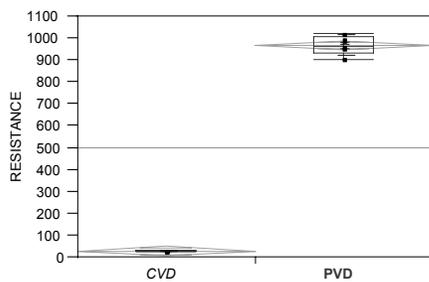


Figure 6 Comparison between PVD nitride and CVD nitride protection on ohmic contacts.

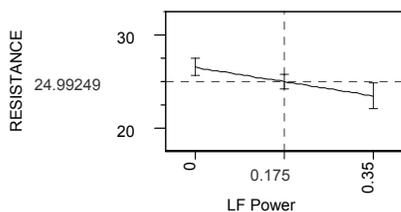


Figure 7 Comparison between CVD nitride protections with different low frequency power in deposition.

CONCLUSIONS

Besides the natural oxidation of GaAs in water or wet chemicals, GaAs corrosion can be greatly increased when ohmic contact metal is formed on GaAs and both the metal and GaAs are exposed to wet chemical solutions. The resulting high contact resistance is detrimental to HBT devices such as Schottky diodes. GaAs corrosion is strongly affected by surface damages which result from processes such as dry etch and deposition. Its surface states will cause energy band bending and make GaAs prone to corrosion. The interaction between GaAs and dielectric films also has strong

effects on GaAs corrosion. GaAs corrosion can be minimized or eliminated by carefully choosing wet chemicals for cleaning and etching processes. During any process steps the GaAs surface needs to be carefully protected, especially when exposed to wet chemical solutions.

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ACRONYMS

- HBT: heterojunction bipolar transistor
- GaAs: gallium arsenide
- RTA: rapid thermal annealing
- TLM: transmission line measurements
- FIB: focus ion beam
- CVD: chemical vapor deposition
- PVD: physical vapor deposition
- SiO_x: silicon oxide
- Si_xN_y: silicon nitride
- HCl: hydrochloric acid
- NH₄OH: ammonium hydroxide