Pre-photolithographic GaAs Surface Treatment for Improved Photoresist Adhesion During Wet Chemical Etching and Improved Wet Etch Profiles

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Abstract

Results of several experiments aimed at remedying photoresist adhesion failure during spray wet chemical etching of InGaP/GaAs NPN HBTs are reported. Several factors were identified that could influence adhesion and a Design of Experiment (DOE) approach was used to study the effects and interactions of selected factors. The most significant adhesion improvement identified is the incorporation of a native oxide etch immediately prior to the photoresist coat. In addition to improving adhesion, this pre-coat treatment also alters the wet etch profile of (100) GaAs so that the reaction limited etch is more isotropic compared to wafers without surface treatment; the profiles have a positive taper in both the [011'] and [011] directions, but the taper angles are not identical. The altered profiles have allowed us to predictably yield fully probe-able HBTs with 5×5 µm emitters using 5200 Å evaporated metal without planarization.

INTRODUCTION

Photoresist adhesion can play a critical role in the outcome of a wet etch and the subsequent yields of electrical and optical devices. There are many factors which can contribute to the adhesion of photoresist to a semiconductor substrate. However, there is very little information specific to gallium arsenide available in the open literature and methods common to silicon such as hexamethyldisilazane (HMDS) pre-treatment may not be effective on GaAs [1]. Additionally, the surface of GaAs is difficult to control and can be sensitive to seemingly minor process conditions such as the length of time a wafer is rinsed with water [2].

To our knowledge there is only one reference which cites the use of a pre-coat native oxide etch on GaAs to improve adhesion [1]. The referenced study suggests that the pre-coat treatment is promising based on water droplet contact angle experiments, and the adhesion is verified after the photoresist develop step. There are no references citing the use of pre-coat treatments for adhesion during wet etching nor on the observed effect on wet etch profiles, which are commonly attributed to the GaAs crystallographic structure and properties of the etchant.

BACKGROUND: PROCESS CHANGES

Two major process changes were made to our historical etch process which necessitated this work. First, we switched from Clariant AZ4330 photoresist to Shipley SPR220-3. We have found that the latter resist has better spin uniformity and resolution, but its adhesion to GaAs is slightly inferior to AZ4330. Second, we migrated our wet etches from a manual immersion based process to an SSEC 3300 spray etch system. While potentially yielding better etch uniformity and repeatability, the spay etch system can be a harsh test of photoresist adhesion and under the wrong circumstances can lead to process failure such as that shown in Figure 1 which depicts a typical device from one of the first lots to encounter the spray etch system.

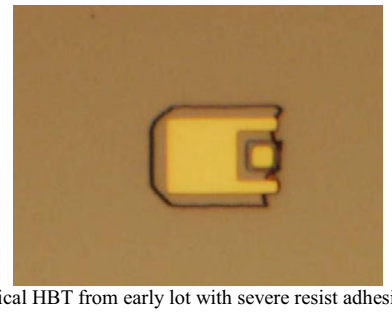

Figure 1: Typical HBT from early lot with severe resist adhesion failure after partial processing.

WET ETCH PROCESS

The initial lithography process served as a control for the studies described later. The lithography consisted of an HMDS vapor prime at 140C, a 5 kRPM coat for a 2.2µm film, and 115 °C, 90 second soft-bake on a Suss Microtec ACS200 coat/develop track. Samples were then exposed with an ASML PAS5000/55 i-line projection stepper (dose =

370mJ/cm^2), post-exposure baked for 90 seconds at 115 °C and spin-developed in Tokyo Ohka Kogyo and Co. NMD-W (2.38 % TMAH) developer for one minute. They were then post-develop baked at 120 °C for two minutes and oxygen plasma descummed for one minute in a Tepla 300 Barrel asher. The descum is a 200 W, 750 mTorr plasma with nitrogen and oxygen flow rates of 500 sccm and 10 sccm respectively. Normally, the samples rest horizontally on a metal platen during the descum.

Samples were then cleaned with 20 H_2O: 1 NH_4OH for 10 seconds (pre-etch clean) and etched in a 1 H_3PO_4: 4 H_2O_2: 45 H_2O solution. After photoresist strip, adhesion quality was determined by visual inspection with an optical microscope. A subjective adhesion rating was given to each wafer in the study with 10 being the best and 0 being the worst. Serpentine structures were particularly helpful in judging adhesion quality because they provided ample opportunity for adhesion failure in a relatively small viewing area. Figure 2 shows an example of such serpentine structures, illustrating one of the addressed failure modes.

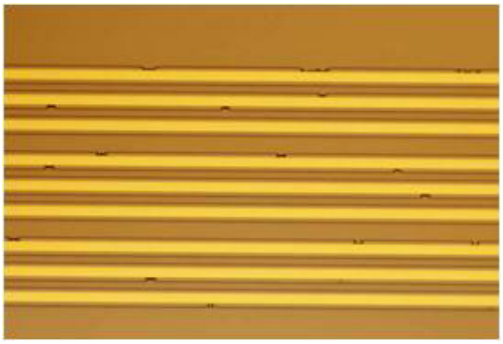

Figure 2: Serpentine structures viewed after the base-collector etch with no pre-coat treatment These image show a failure mode that is much more localized, but was also remedied by the pre-coat treatment.

INITIAL SPLITS

Prior to the resist adhesion DOE, process splits using manual, immersion-based etching of n-type (100) GaAs mechanicals (etch depth of ~2µm) were performed in order to study resist adhesion problems. The splits revealed that an added dehydration bake (120 °C for 10 min), and a higher post-develop bake (130 °C for 2 minutes) did little to improve adhesion compared to the control. A more aggressive, five minute, 600 W, 225 mTorr descum with O_2 flow rate of 600 sccm prior to the photoresist coat led to a degraded adhesion quality. Allowing the samples to sit for three days instead of etching immediately, degraded the adhesion for all the samples except for the 20 H_2O: 1 NH_4OH pre-coat treated sample. A pre-*coat* treatment of 20 H_2O: 1 NH_4OH for 10 seconds resulted in excellent adhesion. Additionally, a 10 H_2O: 1 HCl pre-*etch* clean for 10 seconds rather than the ammonium hydroxide based clean improved adhesion.

A surprising result of these initial splits was the profile of the (100) N-type GaAs wafers, which was tapered in both crystallographic directions when the 20 H_2O: 1 NH_4OH pre-coat treatment was applied as illustrated in Figure 3. The slope of the profile with the pre-coat treatment was ~50° when viewing the cross-section that is normally retrograde and ~40° when viewing the cross-section that is normally tapered.

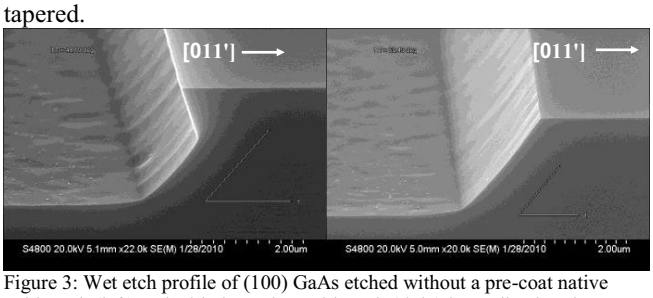

Figure 3: Wet etch profile of (100) GaAs etched without a pre-coat native oxide etch (left) and with the native oxide etch (right) immediately prior to coat. These samples were immersion etched.

RESIST ADHESION DOE

To further characterize and optimize the etch process, a resist adhesion DOE was performed. The etch depth was ~0.8µm and samples were etched in the spray etch tool the day after lithography.

An important process detail was the oxygen plasma descum of the samples which rested vertically in a quartz boat instead of horizontally on the metal grid. In comparing the control sample to other experiments, the use of the quartz boat likely significantly degraded adhesion under certain conditions because it thermally isolated the wafers allowing them to heat up during the descum. This resulted in a poor surface for resist adhesion. A second detail is the NH_4OH based pre-etch clean which took place in the spray etch tool, while the HCl based pre-etch clean was performed manually by immersion on an acid bench. The added spray pressure may have contributed to the poor adhesion observed when the NH_4OH based pre-etch clean was performed without any pre-coat treatment.

The three factors considered in the 3x3x2 DOE were the pre-coat treatment (20 DI:1 NH_4OH, 10 DI:1 HCl, or none), the post-develop bake (120 °C for 2 minutes or none), and the pre-etch clean (20 DI:1 NH_4OH, 10 DI:1 HCl, or none). Table I details the levels for each factor and the resulting adhesion rating.

TABLE I
RESIST ADHESION DOE FACTORS AND RESULTS

Pre-Coat	Hard Bake	Pre-Etch	Rating
NH_4OH	Yes	NH_4OH	10
NH_4OH	Yes	HCl	9.5
HCl	Yes	NH_4OH	9.5
HCl	Yes	HCl	10
None	Yes	NH_4OH	0.5
None	Yes	HCl	10
NH_4OH	No	NH_4OH	10
NH_4OH	No	HCl	10
HCl	No	NH_4OH	8
HCl	No	HCl	10
None	No	NH_4OH	1
None	No	HCl	2
None	No	None	6.5

Some general observations from the DOE are that either of the pre-coat treatments will improve or maintain excellent adhesion when compared to identical processes without the pre-coat treatments. If no pre-coat treatment is applied, both a post-develop bake and HCl pre-etch clean must be performed in order to yield acceptable adhesion. Thus, the pre-coat chemical treatment enables greater flexibility in the fabrication flow.

The etch profiles of samples incorporating the pre-coat treatment from the DOE have a slight lip at the top of the mesa as evidenced in Figure 4. The lip could be explained by partial adhesion loss using the spray tool or the inability of the current spray etch process to remove material at the photoresist/GaAs interface. We are investigating methods to eliminate the observed lip.

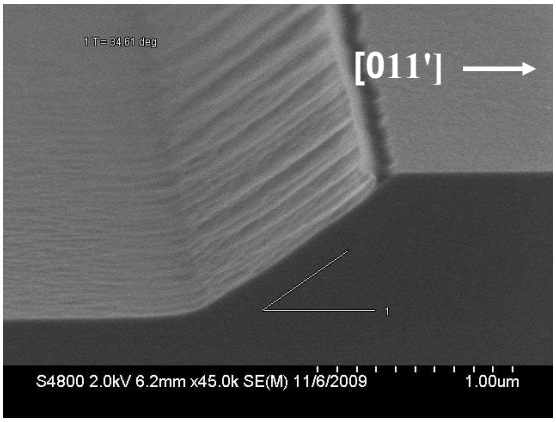

Figure 4: Sample with NH_4OH based pre-coat treatment and NH_4OH based pre-etch clean from the DOE.

HBT DEVICE LOTS

To further validate the use of the pre-coat treatment, process splits were performed on several device lots which used the spray etch process. In one such lot, two wafers were processed identically except one wafer incorporated a 20 DI: 1 NH_4OH pre-coat treatment prior to the base/collector etch lithography. To confirm the more isotropic etch profiles observed previously, we electrically probed 5x5µm emitter devices with evaporated 5200 Å thick first level interconnect metal routed in both crystallographic directions to bondpads. Without planarization, these devices typically have poor yields under most processing conditions since metal routed parallel to [011'] is unable to ascend the retrograde etch profile of the collector face. As expected, the electrical yield for these devices was 99% for the wafer with the NH_4OH based pre-coat treatment and 44% for the wafer having no pre-coat treatment. The difference in electrical yield is attributed to the altered profiles shown in Figure 5. More recent lots incorporating the pre-coat treatment have consistent electrical yields greater than 89% for these unplanarized devices enabling us to reliably fabricate and route small area HBTs without planarization.

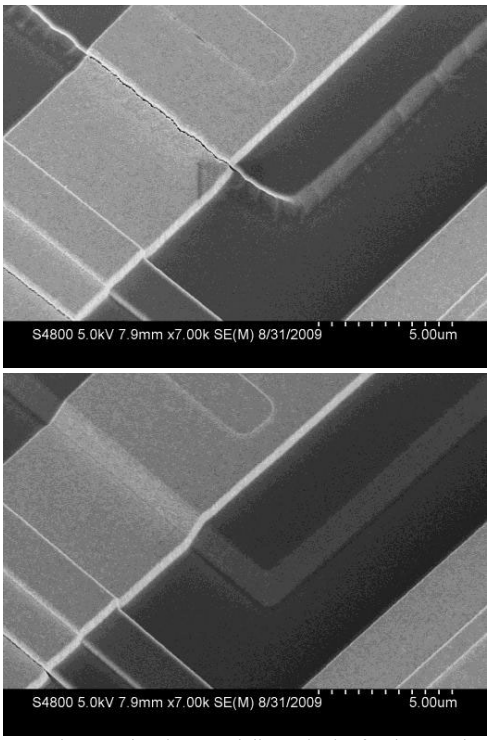

Figure 5: SEM images showing metal discontinuity for the sample with no pre-coat treatment (top) and smooth metal coverage for sample with pre-coat treatment (bottom).

Since it is the deepest etch in the process, the base/collector etch step is the most problematic for resist adhesion. Figure 6 illustrates bowing, a manifestation of poor adhesion, eliminated by the pre-coat treatment after the

base/collector etch for the same two wafers. The darkened outline on the right sample is an indication of the sloped profiles.

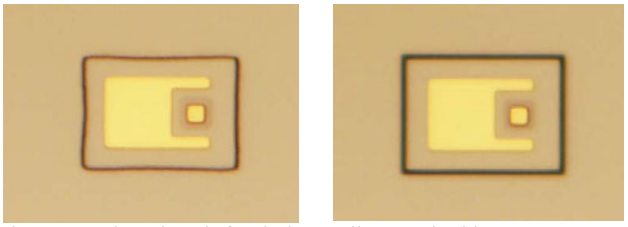

Figure 6: Devices viewed after the base-collector etch with no pre-coat treatment (left) and device with NH_4OH pre-coat treatment (right). The base mesa is designed to be 22×28.5 µm.

We were at first hesitant to adopt pre-coat treatments into our final HBT etch flow since visual observations showed that they slightly reduced the size of the top of etched mesas as illustrated in Figure 7. However, as shown in Table II, no major changes in electrical characteristics were seen in the two wafers discussed previously. The gain, for the pre-coat treated sample is larger but has a wider distribution - a possible affect that may require further investigation. I_{cbo} and $I_{ebo,}$ the leakage currents of the base-collector and emitter-base junctions are comparable for the two processes.

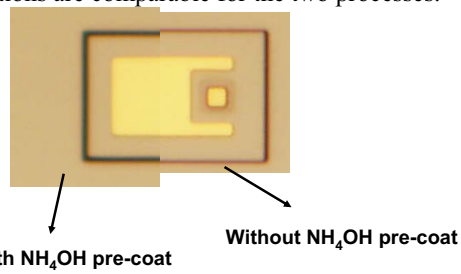

Figure 7: HBTs after the base/collector etch overlayed to show the difference in the mesa top width when a pre-coat treatment is used.

TABLE II
ELECTRICAL DATA COMPARING PRE-COAT TREATMENTS

Device: 5x5 HBT at first level interconnect		
Base Etch Pre-coat Treatment	**NH_4OH**	**None**
Mean Gain (Ic=3mA)	463	437
Std Dev Gain (Ic=3mA)	24.9	7.3
Mean I_{cbo} (A)	6E-10	5E-10
Std Dev I_{cbo} (A)	5.5E-10	3.1E-10
Mean I_{ebo} (A)	9E-10	1E-09
Std Dev I_{cbo} (A)	1.3E-10	1.6E-10

CONCLUSIONS

We have identified many factors which can influence photoresist adhesion to GaAs during wet etching. Results of a resist adhesion DOE indicate that excellent adhesion can be obtained by implementing a native oxide etch prior to lithography even under otherwise unfavorable adhesion conditions. This same pre-coat treatment also changes the etch profile of (100) GaAs indicating a dependency of the etch profile on the GaAs surface. The changes implemented as a result of this work have greatly increased visual and functional yields without significant changes in electrical performance. They have also allowed us to manufacture small area HBTs without planarization

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ACRONYMS

HBT: Heterojunction Bipolar Transistor
DOE: Design of Experiments