The Effects of Chemical Treatment and Storage Time on the Surface Chemistry of Semi-Insulating Gallium Arsenide

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Abstract

The steps used to prepare semi-insulating Gallium Arsenide (SI-GaAs) surfaces for subsequent processing can have a profound effect on process line yields. This work explores the effect of acid/base treatment and storage time has on the surface chemistry of semi-insulating gallium arsenide. Distinctions are drawn between "freshly-processed" wafer surfaces and substrates prepared and stored over time. Specific points addressed include examination of pre-epi native oxide composition, wettability, and thickness. It is shown that although the oxide thickness increases slightly over time, the chemical bonding of the uppermost surface layers remains in an unstable condition.

Introduction

Semi-insulating Gallium Arsenide (SI-GaAs) substrates are used to manufacture many varieties of monolithic microwave integrated circuits (MMICs). These MMIC devices find predominate use in wireless communications satisfying control and amplification functions. The wireless communications market is extremely price sensitive. Manufacturers of MMIC devices must focus intensely on process yield to minimize cost. The processes used to fabricate MMIC devices are either based upon ion implantation or epitaxial growth to create electrically active regions on the insulating substrate. In both device technologies, the GaAs surface is critical in determining the device performance and process yield. MMIC device fabrication utilizes numerous wet chemical steps. The behavior of the GaAs surface can strongly influence the results obtained from these processing steps.

Experimental

SI-GaAs substrates, 100 mm in diameter, were prepared from ingots grown by a High-Pressure Liquid Encapsulated Czochralski (HP-LEC) process utilizing in-situ synthesis from elemental gallium and arsenic. All starting materials were of greater than seven nines purity. The material produced by this process typically has a resistivity between 1-4x10^7 ohm-cm with an electron mobility greater than 7000 cm^2/V-s. The polished substrates were prepared using standard processing techniques. The substrates were polished using a two step process. The first step is a chemo-mechanical polish utilizing standard colloidal silica with $NaOCl^-$ as an oxidizer. This is primarily a stock removal process designed to remove residual damage from preceding mechanical operations. The final polishing step is primarily chemical in nature, again using dilute $NaOCl^-$ as an oxidizer.

Subsequent to polishing, the SI-GaAs substrates were immersed in one of two common GaAs wafer treatments: diluted NH_4OH (28% by weight):H_2O (1:10) or HCl:H_2O (1:1) for various times. The substrates were then rinsed in an overflow rinse system using de-ionized water (18 Megaohm) followed by a dry cycle utilizing heated nitrogen in a spin drier. The rinse time was used as a variable in some of the experiments.

The surfaces of the wafers were then characterized utilizing numerous techniques to investigate the effects of wafer pre-treatment and storage condition.

Contact Angle: The contact angle of a sessile drop of de-ionized water on the GaAs substrate surface was determined by measuring a silhouette image of the droplet. The image was recorded with a computerized video system and viewed on a monitor. The system, a VCA-3000, was manufactured by Advanced Surface Technology Products, Inc. The contact angle (ϕ) is defined as the angle between the substrate surface and tangent to the droplet surface at the substrate/droplet/air tri-junction as shown A large contact angle reflects a hydrophobic surface while a low contact angle reflects a hydrophilic surface.

X-Ray Photoelectron Spectroscopy /Electron Spectroscopy for Chemical Analysis (XPS) Spectra were collected using a Phillips PHI 5600 XPS system utilizing a small spot (<10µm) X-ray beam to generate the photoelectrons. Utilizing this semi-quantitative technique, the presence and concentration of organic and inorganic species on the surface of the GaAs substrate could be determined.

Spectroscopic Ellipsometry: The oxide thickness on the GaAs wafer surface was mapped with a J.A. Woolam Company M-2000 fast spectroscopic ellipsometer system.

Effect of Surface Treatment: NH_4OH and HCl

Wafers were immersed in dilute ammonium hydroxide or hydrochloric acid, rinsed for 1 minute and spun dry. The contact angle of a de-ionized water droplet on the surface of the wafer was measured immediately upon removal from the dry cycle (t=0). The results are presented in Figure 1. The two treatments exhibit radically different behavior. The surface of the base-treated wafers resulted in a very hydrophilic surface (low contact angle). In most cases the contact angle approached zero rapidly during the initial measurement. This indicated that a very unstable and reactive surface has been formed. On the other hand, the acid treated surfaces exhibited hydrophobic behavior (high contact angle) and remained stable over the time of measurement.

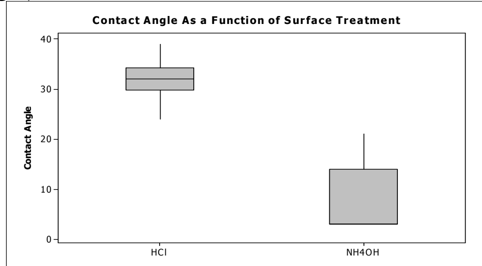

Figure 1 Contact Angle as a Function of Surface Treatment (t=0 minutes). The range of the boxes indicates the 1-σ spread in the experimental data.

Additional contact angle measurements of the acid and base treated wafers were made as a function of rinse time. The results are plotted in Figure 2. The NH_4OH and HCl treated surfaces are found to behave in a very different manner. It is found that the contact angle of the de-ionized water drop on the HCl treated wafers is in the range 30-35 degrees and is independent of the rinse time for rinse times as long as 1000 minutes. In contrast, the ammonium hydroxide-treated wafers are hydrophilic when rinsed for one minute after treatment. A strong relationship between contact angle and rinse times is observed with NH_4OH treatment. .

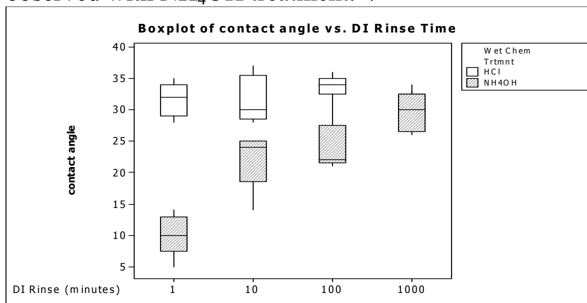

Figure 2 The contact angle of NH_4OH and HCl treated surfaces at t=0 as a function of post treatment rinse time in de-ionized water. The plotted points represent the mean of five individual wafers measured at each experimental condition.

The contact angle is observed to increase with rinse time. After 1000 minutes of rinse time, the contact angle of the NH_4OH-treated wafers became similar to that of the acid-treated wafers The surface chemistry of NH_4OH and HCl treated wafers were investigated with X-Ray Photelectron Spectroscopy (XPS). Figure presents XPS spectra of SI-GaAs substrates treated with HCl (a) and NH_4OH (b) followed by a 3 minute de-ionized water rinse. Measurements were made shortly after chemical treatment. Analysis of the XPS data requires de-convolution of the spectra into its constituent peaks: Ga_{GaAs}, As_{GaAs}, Ga_2O_3, Ga_3O_5, As_2O_3, As_2O_5. The concentration of each species was estimated from the product of the peak height and the FWHM.

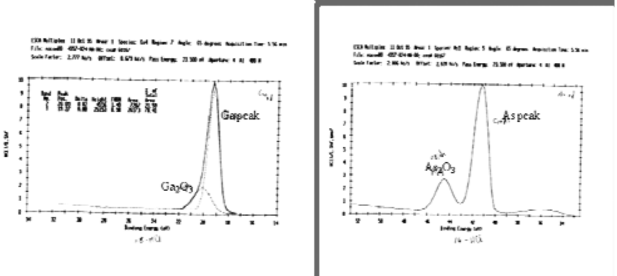

Figure 3a XPS Spectra HCl Treated GaAs surfaces. Time=0

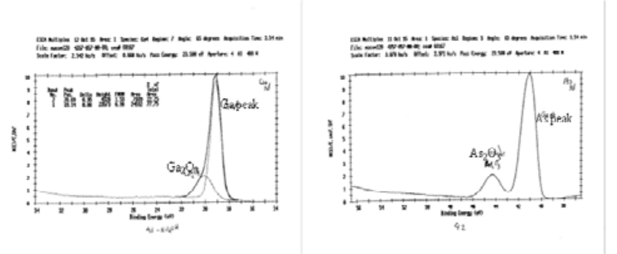

Figure 3b XPS Spectra of NH_4OH Treated GaAs surfaces. Time=0

Based upon this analysis, it is found that the oxide re-grown in de-ionized water after stripping in either HCl or NH_4OH has very similar chemical composition. It is found that the concentration of arsenic and gallium contained in oxide is very similar for both the ammonium hydroxide and hydrochloric acid treated substrates (Table 1).

Effect of Storage

GaAs substrates were treated with NH_4OH or HCl followed by a de-ionized water rinse for x minutes

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	Ga_{GaAs} (%)	Ga_{Ga2O3} (%)	As_{GaAs}(%)	As_{As2O3} (%)
NH_4OH	78.2	21.8	82.0	18.0
HCl	78.4	21.6	80.7	19.3

Table 1 Percent Gallium and Arsenic at surface of wafer contained in the native oxide vs bonded to the substrate

(x=1,10,100, and 1000 minutes) and spun dry in heated nitrogen flouroware, containers and divided into 2 groups: Packaged or vacuum-sealed vs. Un-packaged or no

vacuum-seal. Both groups of wafers were stored in a temperature and humidity controlled, class 10 clean room environment for the duration of the experiment. Wafers from both groups were removed after storing for 1, 3, 7, 14, 21 35, 42, 56, 70, 84, and 100 days. The contact angle was obtained as a function of storage time, storage method and treatment. The data for the NH_4OH- treated wafers as a function of storage condition and time is presented in Figure 4. Both HCl-treated and NH_4OH-treated substrates exhibited a dramatic increase in contact angle over time regardless of storage conditions. Wafers stored under either condition reach a contact angle of about 60 degrees after approximately 40 days in storage. At this point in time (35-40 days) the contact angle on the wafers that were stored with no-vacuum seal (un-packaged) began to decrease, approaching its original value. The contact angle of the vacuum-sealed (packaged) wafer surfaces appeared to stabilize at 60 degrees. After 100 days, there is some indication that the contact angle for the vacuum packaged wafers is beginning to decrease, following the behavior of the air stored.

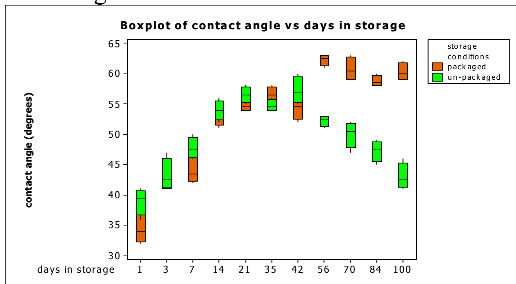

Figure 4. Effect of time on contact angle for NH_4OH-treated wafers under different storage conditions. Rinse time equals 10 minutes. The HCl-treated wafers are not plotted but behaved similarly.

After the 100 day storage period was complete, the sample wafers representing both storage conditions (vacuum and no vacuum-package) were analyzed by XPS to allow determination of the surface oxide composition. The results are presented in Figure 5. It is found that a significant change in surface oxide composition occurred during this storage period. It is apparent from this data that after the 100 day storage period, the oxide states of gallium and arsenic differed significantly when compared with figure 4.

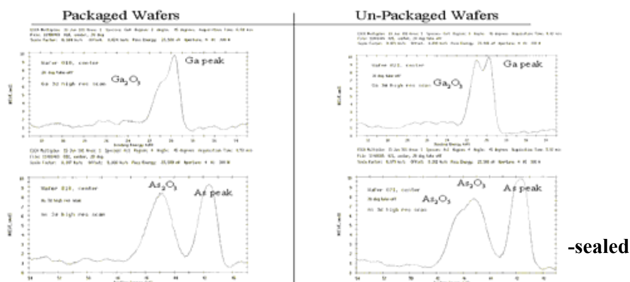

Figure 5. XPS spectra, t=100 days, Packaged or Vacuum-sealed wafers vs. Un-Packaged or No vacuum-sealed wafer storage.

The results of the XPS analysis on the 100 day storage period comparing the packaged (vac-sealed) vs. the un-packaged (no vac-seal) are summarized in table 2.

	Ga(GaAs)	Ga_2O_3	As(GaAs)	As_2O_3	As_2O_5
un-pkged or NO vac-seal	40.7	59.3	41.3	42.9	15.8
pkged or vac-sealed	59.2	40.8	46.0	51.4	2.6

Table 2. XPS data (Ga and As 3d peaks) showing the distribution of Gallium and Arsenic Oxide States at t=100 days (in Atomic Percent)

The stored SI-GaAs wafers were further characterized with variable angle wavelength elipsometry to estimate oxide thickness. Samples were measured several days after treatment, considered the as-processed condition, and t=100 days stored in both vac-packaged and non-vacuum sealed containers. The ellipsometry data (Figure 6- Figure 8) indicates that the thickness of the oxide of the as processed wafer is 15.2 Å. The oxide thickness of the packaged wafers stored "in air" (Figure 7) for 100 days grew to a mean thickness of 21.4 Å with a standard deviation of 1.14 Å. The oxide thickness of the vacuum-packaged wafers stored for 100 days (Figure 8) grew to a mean thickness of 18.6 Å with a standard deviation of 1.23 Å.

Results of the Variable Angle Spectroscopic Ellipsometry analysis are summarized in Table 3. Also listed are contact angle measurements for t=0 and t=100 for packaged (vac-sealed) and un-packaged (no-vac-seal) wafers.

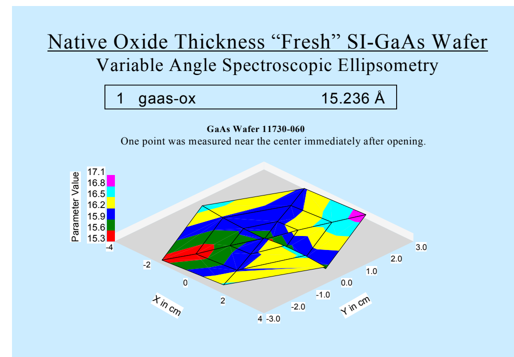

Figure 6 Native Oxide thickness of as-treated GaAs surface. The mean oxide thickness is found to be ~1.52 nm. (t=0 days)

Discussion

The data indicates that the surface of GaAs is highly active. The surface composition is a function of chemical treatment, storage condition and time. In considering the data, we will individually address the effect of surface treatments and wafers storage.

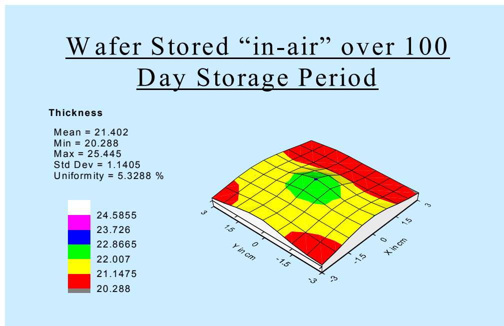

Figure 7 The native oxide thickness on a GaAs wafer after storage in air for 100 days. The mean oxide thickness is 2.14 nm.

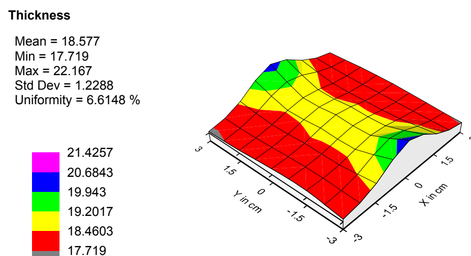

Figure 8 The native oxide thickness of vacuum packaged GaAs in a mylar bag. The mean oxide thickness is 1.86 nm. (t=100 days)

			Storage cond.	Storage cond.
technique	measurement	as-treated	pkged (vac-seal)	un-pkged (no vac-seal)
		t=0 days	t=100 days	t=100 days
sessile drop	contact angle	v. unstable	60.5 deg +/- 0.5%	39.2 deg +/- 2.7%
ellipsometry	oxide thickness	1.52 nm	1.86 nm	2.14 nm

Table 3. Summary of Surface Measurement of Wafers at t=0 and t=100 days under different storage conditions.

Surface Treatments

Two chemical treatments, NH_4OH:H_2O or HCl:H_2O, are used commonly in the GaAs industry to either "clean" or strip the oxide prior to subsequent processing steps. This type of treatment can be used in processes as diverse as prior to ion implantation or as a clean before gate recess etching.

The data (Figure and Table 1) indicates that composition of the oxide formed after emersion in either HCl or NH_4OH followed by rinsing in overflowing de-ionized water is essentially identical. This indicates that the oxide composition is primarily determined by the overflow rinse processes. After a 10 minute oxidation cycle in overflowing de-ionized water, the native oxide is approximately 15 nm thick. This oxide is composed primarily of Ga_2O_3 and As_2O_3 with no evidence of the presence of any significant concentration of other sub-oxide species.

Despite the similarity of the native oxide composition after treatment in HCl or NH_4OH solutions, the surface energy (contact angle) exhibits significantly different behavior. HCl results in a hydrophobic surface which is stable as a function of rinse time while the NH_4OH treated wafer is hydrophilic. The hydrophilic nature of the NH_4OH treated wafer changes as a function of both rinse time and exposure to air. We interpret these results within the context of hydrogen passivation of the surface. Dangling bonds at the surface of the wafer are satisfied by bonding with hydrogen donated from the HCl resulting in the hydrophobic nature of the surface. In the case of NH_4OH, surface bonds are not satisfied resulting in a highly reactive surface. The surface is hydorophilic, as it readily accepts the H_2O to lower the surface energy. As the dangling bonds are satisfied, the surface becomes more hydrophobic in nature as observed in figure 2

Wafer Storage

The surface of the GaAs wafers, regardless of surface treatment, is observed to change dramatically over time. Wafers stored both in air and in evacuated mylar bags are found to exhibit both large changes in contact angle (Figure 4) and significant changes in oxide chemistry (Figure 5). The only observed difference in the behavior of the vacuum packaged and air packaged wafers is the time constant associated with the evolution of the surface. In all cases, the contact angle reached a maximum of ~65° and then began to decrease. The XPS data indicates that over time, the concentration of Ga_2O_3 increased; increasing faster for the wafers directly exposed to air. No other Gallium sub-oxides were observed to form. In contrast, over time, As_2O_5 was seen to form in preference to As_2O_3 though the concentration of As_2O_3 also increased over its initial value. VASE measurements indicate that the native oxide increase in thickness as a function of storage time (Figure 8 and Figure 9).

Conclusion

The data suggests that the outermost atomic layers of SI-GaAs wafers are in constant flux and that the behavior of oxides on vacuum-packaged and unpackaged wafers evolve similarly during the initial period of approximately 40 days. After this point in time the oxide composition of the un-packaged wafers changes dramatically with very little change in oxide thickness. This study has also shown that the highly sensitive contact angle measurement technique is very effective at looking for subtle changes in surface properties. Knowledge of the evolving state of gallium arsenide surface oxides is of paramount importance for high yielding, production-worthy processing.