# Storage conditions for high-accuracy composition standards of AlGaAs

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AlGaAs epitaxial films were stored under different environmental conditions and the resulting surface oxidation and contamination variations measured with several analytical techniques. Auger depth profiles confirmed that contamination had been confined to within approximately 10 nm of the surface for all specimens stored in controlled environments for over three years. We also performed an atomic force microscopy study on a multilayer structure, measuring the height of the oxides formed in air. Surface contamination was examined in more detail with time-of-flight secondary ion mass spectrometry and x-ray photoelectron spectroscopy. Surface oxides changed over time, and could be altered by sputtering. Sputtering was particularly effective in removing hydrocarbons. Based on these results, AlGaAs reference films for $x < 0.4$ should remain stable for at least five years if stored in either nitrogen or vacuum environments, with allowance for periodic handling in air.
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## I. INTRODUCTION

AlGaAs compounds are known to be sensitive to oxygen contamination, particularly when the specimens are epitaxial layers with high mole fractions of Al. In this article, we report on a controlled study of the effects of different storage environments, including $N_2$, vacuum, and short-term exposure to room air, on epitaxial structures of GaAs and AlGaAs. Our primary goal was to determine acceptable storage conditions for composition standard specimens for epitaxial layers of AlGaAs. The data here show that with reasonable care, surface contamination can be kept to a minimum for storage periods of at least three years. Conventional surface science methods, such as Auger depth profiling and x-ray photoelectron spectroscopy (XPS), demonstrated that contamination was limited to oxide and hydrocarbon species, within the detection limits, and confined to within 10 nm of the surface. Storing specimens in vacuum or $N_2$ led to a reduction in oxide contamination, but incidental exposure to air was not damaging except for a specimen containing pure AlAs.

The detailed nature of the surface contamination and its alteration through sputter cleaning were examined with time-of-flight secondary ion mass spectrometry (TOF-SIMS). Because TOF-SIMS can detect species present at less than 0.01 at. % on the surface, the scans contain a large amount of data that can lead to an overall impression of high contamination levels. The dominant species detected in the positive ion mode, however, were elemental Ga and Al. Before sputtering, these species represented approximately 50% of the ions detected, and after sputtering this figure increased to around 90%. The dominant As-containing species in the scans are oxides, but this observation probably reflects the fact that As prefers to form clusters when in vapor form. Furthermore, these clusters may remain neutral and therefore escape detection. The relative intensities of the various molecular species are interesting for the insight they give into the surface chemistry of the oxidation and hydrocarbon accumulation.

## II. EXPERIMENT

All specimens were grown with molecular-beam epitaxy at substrate temperatures between 580 and 600 °C. Growth was initiated with a thermal oxide desorption followed by GaAs buffer layer approximately 0.4 to 0.6 $\mu$m thick. All layers were lightly doped with Si to an approximate atomic concentration of 0.1 to $2 \times 10^{17}$ cm$^{-3}$. Detailed descriptions of the wafer structures are given in Table I. For Wafer L1, the Al mole fraction in the various $Al_xGa_{1-x}As$ layers was set by varying the relative duty cycle between $Al_{0.5}Ga_{0.5}As$ and AlAs or GaAs with a 2 nm periodicity. For Wafer L2, the Al flux was varied to achieve different mole fraction except for the $x=0.9$ layer, which was grown with alternating AlGaAs and AlAs similar to layers in L1. Al mole fraction $x$ was determined from growth rate measurements to an uncertainty of 0.015 based on reflection high-energy electron diffraction intensity oscillations.[1]

Pieces of Wafer L2 were stored under a variety of conditions and examined with TOF-SIMS immediately after growth and then again after storage for 24 months. The surfaces of the specimens were intentionally scratched with a scribing tool; however, no anomalies were visible near the scratches, even when viewed with scanning electron microscopy. Three storage environments were used: A storage box with continuous $N_2$ purge ("$N_2$ box"), a sealed vessel filled with $N_2$ ("$N_2$"), and a sealed vessel evacuated to less than 10 Pa ("Vac"). The $N_2$ and vacuum vessels went through five cycles of evacuation and repressurization with clean nitrogen before being left in the appropriate final state. Specimens that were placed in the $N_2$ purge box were located near the

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TABLE I. Wafer descriptions.

| Wafer name | Al mole fraction(s) $x$ | AlGaAs thickness | GaAs spacers (if multilayered) | GaAs cap |
|---|---|---|---|---|
| AL30 | 0.30 | 3 $\mu$m | ⋯ | None |
| AL62 | 0.62 | 3 $\mu$m | ⋯ | 5 nm |
| AL100 | 1.00 | 3 $\mu$m | ⋯ | 5 nm |
| L1 | 0.20 to 0.90 | 50 nm each | 200 nm | 100 nm |
| L2 | 0.18, 0.41, 0.70, 0.90 | 100 nm each | 200 nm | 400 nm |

back of the box, and the box door was opened about once or twice per day as part of normal laboratory use. For storage within the two sealed vessels, specimens were placed in both vented polypropylene wafer carriers ("poly"), and glass Petri dishes ("glass"). Before loading with specimens, carriers and glass dishes were cleaned with acetone, isopropanol, and water, and then allowed to dry. The specimens in the $N_2$ box were in nonvented polypropylene wafer carriers. A sixth specimen was stored in a transparent hard-plastic box on a silicone gel membrane with medium tack sold for transporting semiconductor specimens. In addition, the specimen examined just after growth was stored in air ("Air") in a polypropylene carrier and re-examined after the 24 month storage period. In the six months between the TOF-SIMS and XPS measurements on this specimen set, the specimens were maintained under a high vacuum.

Wafers AL30, AL62, and AL100 had been stored in the purged $N_2$ box for 43 months before the Auger spectroscopy measurements. The specimens had been exposed to 10 to 20 h of room air prior to being loaded into the vacuum analysis chamber. Two of these specimens, "AL30 Air" and "AL62 Air," were then stored in polypropylene carriers in air for an additional eight months before re-examination with TOF-SIMS. Specimens from all three wafers that had been stored only in the purged $N_2$ box (for a total of 51 months) were also examined with TOF-SIMS. An additional specimen from Wafer AL100 was stored in air and began to show signs of surface decomposition within one month. The decomposition began as small blisters that grew in size and density over time, growing to a size around $100\times 300\ \mu m^2$ and covering about one-quarter of the surface area after six months in air.

TOF-SIMS is a mass spectrometry method with high sensitivity to surface layers and excellent mass resolution. For these experiments, the mass resolution was $M/\Delta M = 6600$ at $^{28}$Si. The intensity of peaks from scan to scan was reproducible to about 10% for peaks with more than ten counts. In general, surfaces with higher concentrations of hydrocarbons and surface oxides had a higher ion yield than the cleaner surfaces. In order to maintain a picture of the relative concentrations of the different species within a scan, the scan counts were normalized to a total of 100 000 counts. The TOF-SIMS data were acquired using a $^{69}$Ga source operating at 25 keV. The background pressure in the TOF-SIMS chamber was about $4\times 10^{-7}$ Pa$(3\times 10^{-9}$ Torr). Spectra were first collected from the as-received surface over an area of $100\times 100\ \mu m^2$. A single dc sputter cycle was then performed over a larger area $(150\times 150\ \mu m^2)$, and additional spectra acquired from the central region. The ion dose did not exceed $10^{12}$ cm$^{-2}$ for spectra taken prior to the dc sputter cycle. A new area of the sample was used for each series of spectra and sputter cycles. The average depth of the sputtered craters was 3 nm as measured by a profilometer. Separate scans were taken for positive and negative ions, covering a range up to at least 600 amu, for a total analysis time of 100 s. Because $^{69}$Ga ions were used for sputtering and producing the ion counts, we display only peaks containing $^{71}$Ga in the plots that follow, unless otherwise noted. This precaution was not critical, however; the Ga peaks were distorted by less than 1% from the standard terrestrial isotope distribution, indicating that Ga implantation and collection of Ga atoms from the ion beam were negligible.

Auger spectroscopy depth profiles were taken with a 5 kV 20 nA primary electron beam that was rastered over an area of approximately 400 $\mu m^2$. Sputtering was done with a 3 keV $Ar^+$ beam at 15 $\mu A/cm^2$ at a rate of $50\pm 10$ nm/min. The XPS data were taken with Al radiation of 1486.6 eV, a pass energy of 188 eV, and a take-off angle of 60° with respect to the sample plane. Atomic concentrations were derived from numerically integrated peak areas of the Ga $2p^{3/2}$, the As $3d$ doublet, O $1s$, and C $1s$ photoelectron lines. The data analysis for both Auger and XPS was performed with elemental sensitivity factors in the software provided by the instrument manufacturer. The relative accuracy of these concentration determinations was 5%.

## III. RESULTS

As a first measure of oxidation rate and its dependence on Al mole fraction, Specimen L1 was cleaved to expose a fresh surface perpendicular to the growth direction and scanned with atomic force microscopy (AFM) in tapping mode. The difference in height between the AlGaAs stripes and the surrounding GaAs layers is plotted for two total air exposure times in Fig. 1. As expected from studies of native oxides of AlGaAs,[2] the oxide height increases with Al mole fraction in a highly nonlinear fashion, and the higher mole fractions show that oxide growth continues even after 24 h of air exposure, though at a slower rate. The data indicate that specimens with $x\leqslant 0.4$ can tolerate several hours of air exposure without developing thick oxide layers.

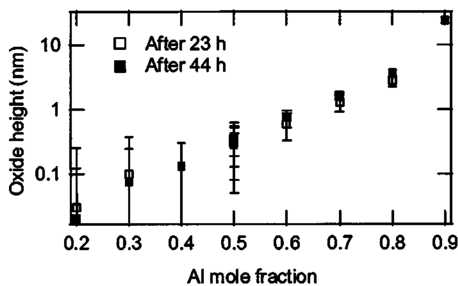


FIG. 1. Oxide height measured with AFM for layers of various Al mole fraction following a fresh cleave of Specimen L1 and two cumulative air exposure times of 23 and 44 h.

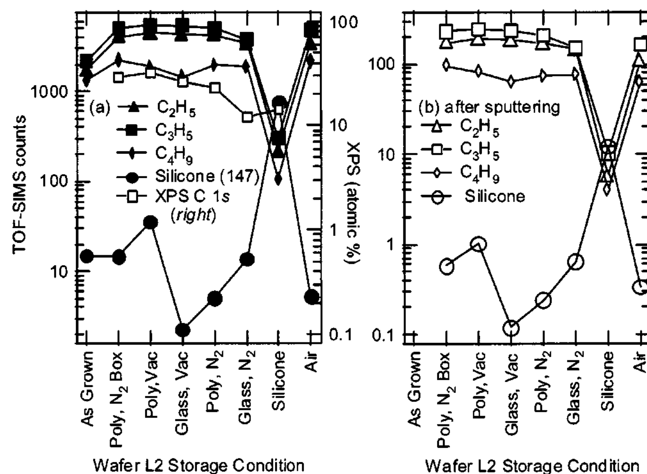


FIG. 2. TOF-SIMS counts for various representative hydrocarbon species (a) before and (b) after sputtering to 3 nm. Note that vertical axis ranges differ by a factor of 20. Silicone oils are indicated by a fragment peak at 147 amu. The lines connecting the points are included as a guide for the eyes. Storage time was 24 months.

To explore the efficacy of controlled storage conditions, specimens from Wafer L2 were stored as detailed above for 24 months and examined with TOF-SIMS and XPS. As will be demonstrated, the surface contamination was confined to a very thin layer, and therefore was characteristic of the GaAs cap. The dominant peaks in the TOF-SIMS data were Ga and hydrocarbons in the positive ion spectrum, and $AsO_x$ and $GaO_x$ or $GaH_2O$ fragments in the negative ion spectrum. To assess the thickness of the contamination layer, each specimen was sputtered as described above, removing about 3 nm of material. Figs. 2 and 3 show a selection of hydrocarbon peaks and oxide peaks, respectively, both before and after sputtering. Overall contamination by hydrocarbons (Fig. 2) was inferred from the peak intensities for low-mass fragments of larger hydrocarbon molecules. These peak intensities were reduced by about a factor of 20 by the sputtering cycle. The XPS data for C 1*s* [right axis, in Fig. 2(a) only] confirmed that these peaks are representative of overall hydrocarbon contamination. Most specimens were similar in their degree and types of contamination. The "as-grown" specimen had noticeably less overall hydrocarbon contamination. (Data after sputtering were not available for the as-grown specimen.)

The specimen stored on silicone gel had a very strong peak at 147 amu, corresponding to $Si_2C_5H_{15}O$, one of the mass peaks associated with silicone. Although this particular peak is lower in intensity than the smaller hydrocarbon fragment peaks found on the other specimens, there are additional amine and hydrocarbon peaks associated with silicone oils that bring the total hydrocarbon mass to a higher value than for the other specimens. Silicone oils are widely used as release agents in molded plastics, in thermal pastes, and in vacuum lubricants. Although they have relatively low vapor pressures, they are not readily removed with common solvents (hexane being perhaps the most effective). The mass spectrum from the silicone storage specimen was distinctly different from all the others, implying that the silicone either displaced some of the other hydrocarbons or prevented them from accumulating in the first place. The detection limit for silicon from all sources (organic and inorganic) under the TOF-SIMS conditions used for this experiment is estimated to be between $10^{16}$ and $10^{17}$ atoms/cm$^3$. This implies that the Si concentration on the surface of the silicone storage specimen is between $3 \times 10^{19}$ and $3 \times 10^{20}$ atoms/cm$^3$. Many analytical methods will not be sensitive to the silicone contamination; there was no detectible Si peak ($<1$ at. %) in Auger spectroscopy for any of these specimens.

In contrast to the hydrocarbons, the oxide relative peak intensity either stayed the same or even increased after sputtering (Fig. 3). The oxide peaks for $AsO_x$ and $GaO_x$ are summations of peaks with $x=1$ to 3 and $x=1$ to 2, respectively. Storage in the vacuum led to the lowest amount of surface oxide, although the $N_2$ vessel and $N_2$ box environments also appeared acceptable. The difference between polypropylene containers and glass was not significant given the specimen-to-specimen variability. The specimens in the silicone storage environment had lower overall oxide peaks, but as discussed above, this specimen also had high hydrocarbon contamination. The XPS O 1*s* data indicated that oxygen, including oxygen from silicone oils, was highest on this specimen. The sputtering cycle did not affect the total $AsO_x$ peak intensities, but did lead to an *increase* in $GaO_x$ signals. The simplest explanation for this effect is that the sputtering cycle removed hydrocarbons and thereby exposed underlying Ga oxides.

Perhaps, the most surprising result was that the as-grown specimen had the highest $AsO_x$ peak intensities. This specimen also had the lowest hydrocarbon contamination, and both the XPS data and the TOF-SIMS data in Figs. 2(a) and 3(a) supported an inverse relationship between oxides and hydrocarbons. This could reflect either obscuration of the oxide by hydrocarbons or a tendency for oxides to be less reactive with hydrocarbons, a well-known phenomenon in metals.[3] Oxide species may also be transforming to bulk forms from the intermediate oxides[4,5] such as $GaAsO_4$. As shown in Fig. 3, the percentage of $AsO_3$ fragments (relative to total $AsO_x$) increases with greater exposure to air and is anomalously low for the silicone gel storage. The silicone gel may have protected the surface from oxidation, although at the expense of much higher hydrocarbon contamination. The

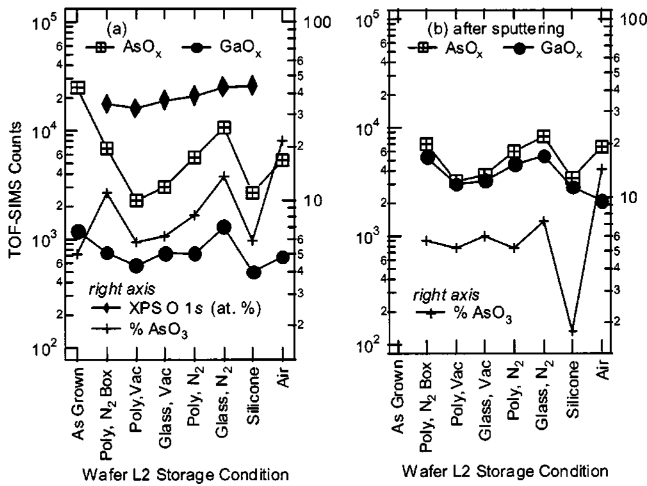


FIG. 3. TOF-SIMS counts for oxide species signals (a) before and (b) after sputtering. The percentage of the total $AsO_x$ counts represented by $AsO_3$ fragments is also indicated against the right axis.

increase in $GaO_x$ species after sputtering could be partially explained by the thermodynamically driven[6] conversion of $As_2O_3+2GaAs \rightarrow Ga_2O_3+4$ As. Because the $AsO_x$ peaks were still significant after sputtering, this oxide transformation cannot explain the entire increase in the $GaO_x$ species. We therefore conclude that the peak intensities following sputtering are the best measure of the overall degree of surface oxidation, because obscuration by hydrocarbons has been removed, but that further work is needed to assess the stability of oxide contamination.

The surface of L2 consisted of a relatively thick layer of GaAs, so we also conducted studies of Wafers AL30, AL62, and AL100 to see whether aluminum at or near the surface strongly affected contamination. The specimens were first examined with Auger depth profiling. The surface layers contained C concentrations between 17 and 25 at. % and O between 16 and 22 at. %, with all other contaminant elements being below the detection limit in broad survey scans. After the first sputtering cycle and its removal of $10\pm2$ nm of material, both the C and O signals had reached background levels.

Some of the details of these contamination layers are shown in the TOF-SIMS data in Fig. 4. The highest amount of surface Al was evident on Specimen AL30, and some Al had diffused through the 5 nm GaAs cap layers to the surface on AL62 and AL100. As shown in Fig. 4(a), the contamination with conventional hydrocarbons, represented by the $C_3H_5$ fragment peak, was similar for all specimens regardless of Al content. Storage conditions for the AL series specimens were not as well controlled as for Wafer L2, and the greater variability in the silicone and metal ion (not shown) signals suggests incidental contamination. As with the data discussed above for L2, the silicone appeared to be covering surface oxides, in that the $AsO_x$ and $GaO_x$ peak intensities followed an inverse trend relative to the silicone peaks. After sputtering [Fig. 4(b)], the silicone peaks were reduced to less than 1 count, the other hydrocarbon peaks fell to around 100 counts, and the surface oxides became the dominant contaminants. As would be expected, the specimens with more surface Al had higher $AlO_x$ peaks, represented in the figure

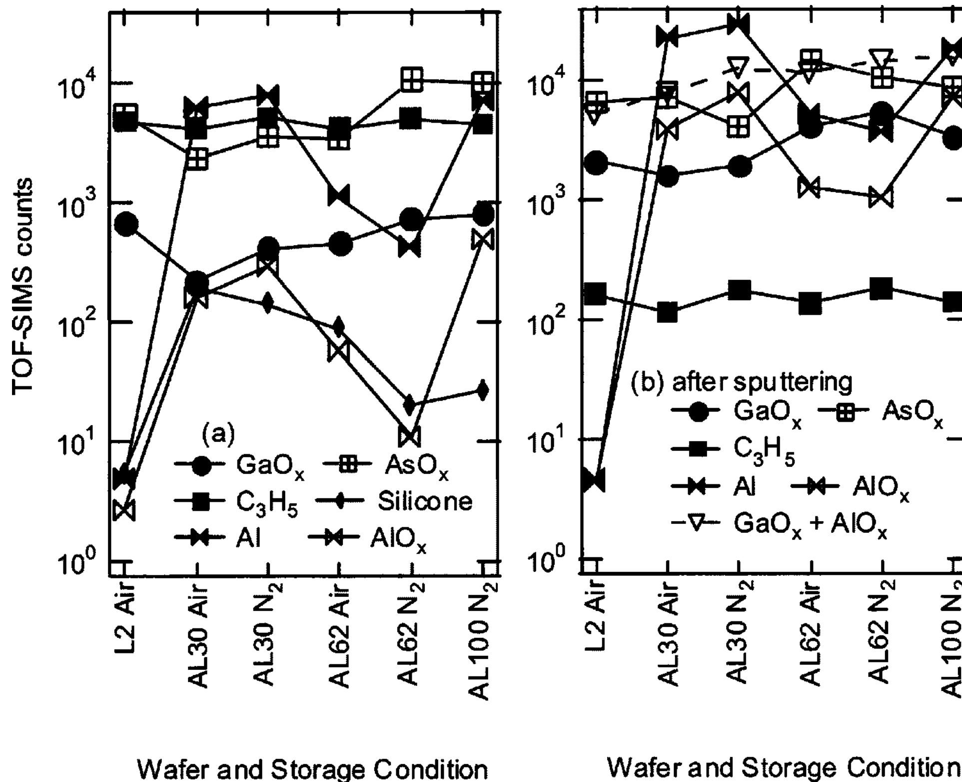


FIG. 4. TOF-SIMS counts for oxide, hydrocarbon, and Al species on specimens with Al near the surface, (a) before and (b) after sputtering. One data set from L2 is also included for comparison. The silicone mass peak was below ten counts after sputtering, and again was omitted from (b) for clarity. The $GaO_x$ counts were multiplied by 2.5 to include the contribution of $^{69}$Ga species.

by the sum of the two dominant Al oxide peaks, AlO and $AlO_2$. The total counts from the group-III oxide peaks (sum of $GaO_x$ and $AlO_x$) increased with Al content regardless of storage condition, but even on the specimens with the highest Al content, oxides comprised less than 20% of the ion count. We therefore find no evidence for extensive or deep oxidation in the AlGaAs specimens, except for the degradation of AL100 in air.

## IV. CONCLUSIONS

The GaAs and AlGaAs surfaces examined in this study were relatively clean, with hydrocarbon contamination mostly in the outer 3 nm and oxides persisting somewhat deeper but no more than 10 nm. Vacuum storage environments appeared to be effective at reducing oxidation, although the differences among vacuum, $N_2$, and medium-term air storage were small and appeared to be correlated with hydrocarbon contamination in a complex fashion. Incidental exposure to air was not much worse than these environments except for the specimen of pure AlAs with a thin GaAs cap. Using clean plastic tweezers and clean storage containers should minimize contamination by hydrocarbons and metals. Silicone gels added more contamination than the other environments and should be avoided for storage of standards.

The impact of the surface contamination layer on composition determination will depend on the surface sensitivity of the compositional analysis technique. For many analytical methods (dynamic secondary ion mass spectroscopy, electron microprobe, photoluminescence, and x-ray rocking curves), the sensitivity to a thin contamination layer is small and likely to cancel out in a comparison of unknowns and standards for analysis of Al mole fraction. When using methods with high surface sensitivity, such as Auger, XPS, and TOF-SIMS, both standards and unknowns will require some type of *in situ* cleaning, such as sputtering.

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