Scanning Microscopy

Volume 8 | Number 4 Article 3

12-22-1994

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Recommended Citation
Lowes, Theodore D. (1994) "Observations on Interactions Between Metal Clusters and III-V Semiconductor Substrates," *Scanning Microscopy*: Vol. 8 : No. 4 , Article 3.
Available at: https://digitalcommons.usu.edu/microscopy/vol8/iss4/3

Scanning Microscopy, Vol. 8, No. 4, 1994 (Pages 773-780) 0891-7035/94$5.00+.25
Scanning Microscopy International, Chicago (AMF O'Hare), IL 60666 USA

OBSERVATIONS ON INTERACTIONS BETWEEN METAL CLUSTERS AND III-V SEMICONDUCTOR SUBSTRATES

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(Received for publication May 27, 1994 and in revised form December 22, 1994)

Abstract

Interfacial reactions between deposited indium and gallium metals with GaAs(001) substrates are discussed. After Knudsen cell molecular beam epitaxy (MBE) deposition, samples were annealed in ultrahigh vacuum (UHV) and examined by *ex situ* electron microscopy. The resulting microstructure was compared to the microstructure of GaAs(001) substrates without metal deposition. It is shown that significant interactions occur between the deposited metal and substrate and that the final microstructure is consistent with the model for thermal decomposition of III-V compound semiconductor substrates.

Key Words: Compound semiconductor substrates, metals, interactions, decomposition.

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Introduction

The studies of clustering on surfaces from both theoretical and experimental approaches can be powerful predictors of surface phenomena as outlined recently by Zinke-Allmang *et al.* (1992). Some examples of information obtained on issues at the fundamental level include: identification of the dominant growth process (e.g., ripening versus coalescence), growth dynamics including power law scaling, self similarity, and activation energies and precursors for surface diffusion.

One major driving force for this field of research is the desire to produce smaller and more densely packed electronic devices while still maintaining an acceptable level of reliability. Fundamental knowledge garnered by theoretical and experimental investigations of clustering on surfaces has played and continues to play an essential role in the continued development of thin film growth as applied to electronic devices. Contributions include predictions of thin film stability and the development of new materials systems.

One class of electronic material used extensively in a wide variety of devices is the III-V compound semiconductors. In order to manufacture electronic devices, thin films must be grown at elevated temperatures where III-V substrates have a tendency to decompose. Previous work involving GaAs and InP at elevated temperatures examined the process of thermal decomposition in detail for these III-V compounds stressing the role of surface clusters (Lowes and Zinke-Allmang, 1993, 1994). In this paper, the interaction of deposited metal clusters with GaAs(001) substrates at temperatures typically used for thin film growth is presented. The detailed evolution of microstructure for these systems is presented and some potential consequences for thin film growth are discussed.

Experimental

Samples approximately 1 cm x 1 cm in size were cleaved from polished (001) oriented wafers. For all samples, a standard two step preparation procedure prior to molecular beam epitaxy (MBE) deposition was used: (**i**) *ex situ* chemical treatment of polished wafers to form a well defined oxide and, (**ii**) thermal oxide removal under ultra high vacuum (UHV) conditions (base pressure $\leq 2 \times 10^{-10}$ torr) in an MBE growth chamber. Samples were mounted on molybdenum holders with indium metal and heated radiatively. The temperature was constant to within ±1° and accurate to within ±10°. Temperature was monitored with a thermocouple located near the specimen that had been previously calibrated against a thermocouple placed at the specimen position.

In this study, indium and gallium metal were deposited onto cleaned GaAs(001) wafers using standard Knudsen effusion cells. Typical deposition rates for this work were 1 monolayer/minute. The amount of material deposited expressed as equivalent coverage in monolayers (ML) was determined from Rutherford backscattering spectroscopy (RBS) using ^{4}He ions at 3 MeV. *Ex situ* sample analysis was done by scanning electron microscopy (SEM) and plan-view transmission electron microscopy (TEM) with energy dispersive X-ray analysis (EDXA). TEM sample preparation was performed by single sided chemical thinning with a fresh solution of 1% bromine in methanol by volume at room temperature. The thermal history of samples was as follows unless otherwise stated: 150°C for 5 minutes (degassing), 475°C for 10 minutes (temperature equilibration), 600°C for 15 minutes (oxide removal), cooled to below 150°C, metal deposition, and a post deposit anneal.

Results and Discussion

The motivation for the present study was to evaluate the extent of cluster/substrate interactions for clusters generated by deposition and annealing as compared to substrate decomposition at elevated temperatures. In order to facilitate the discussion of the present data, it is useful to review the evolution of microstructure and cluster/substrate interactions in the temperature range where substrate decomposition occurs due to the preferential loss of the group V component.

Figure 1 is an scanning electron micrograph of the (001) surface of GaAs and InP after annealing for short times at temperatures greater than the decomposition temperature. The important features of these micrographs are the various sized metal clusters (up to 30 μm in diameter), cluster free regions that are lower in height compared to the substrate surface (i.e., depressions, see "R" in Fig. 1), and a significant fraction of facetting (≈ 10% of clusters) consistent with the preferential etching tendencies of III-V compound semiconductors (Takebe *et al.*, 1993).

The evolution of the microstructure shown in Figure 1 starting from a fresh surface is as follows. At elevated temperatures regions of an excess group III element develop and nucleate clusters locally where group V atoms have desorbed from the surface predominantly as diatomic molecules. As more group V species leave the surface, the excess concentration of group III atoms increases, and clusters grow through surface diffusion and ripening dominated by the Gibbs-Thompson effect. However, early on in the development of micrometer sized clusters, the dominant process by which clusters increase their volume changes to a process involving interactions with the substrate.

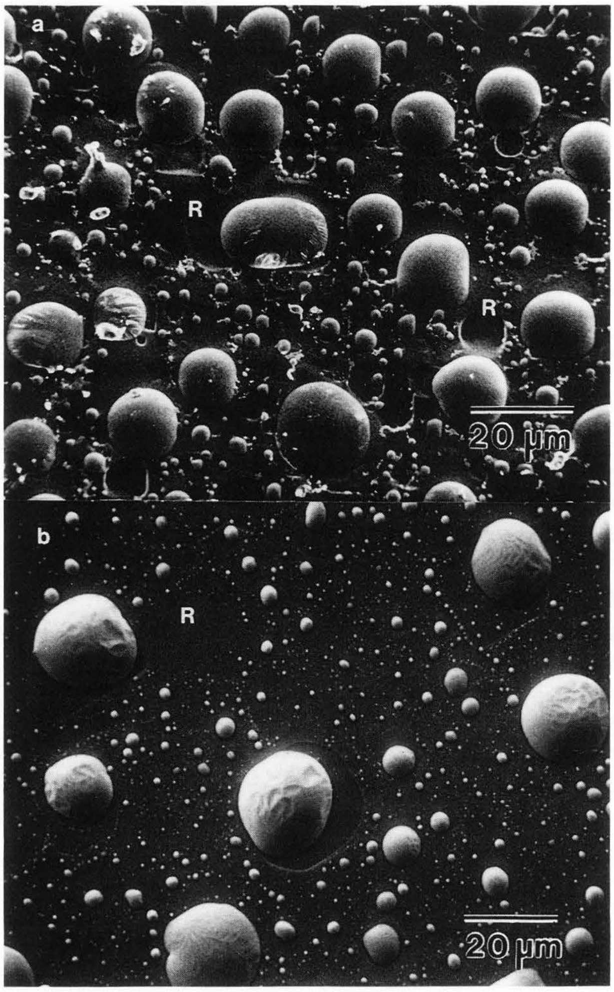


Figure 1. Scanning electron micrographs of (**a**) GaAs(001) after thermal treatment in UHV at 680°C for 15 minutes; and (**b**) InP (001) after thermal treatment in UHV at 500°C for 10 minutes.

A schematic illustration showing the various processes that can contribute to an increased cluster volume including the cluster/substrate interaction is shown in Figure 2. The three processes are (**i**) diffusion of the group

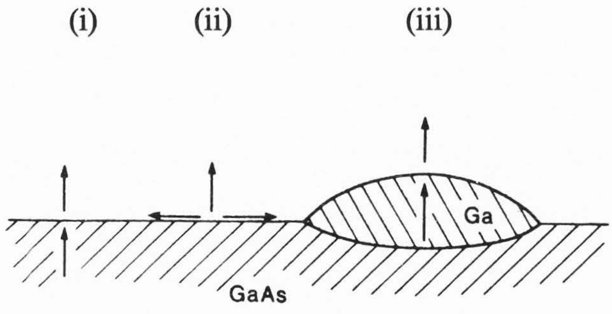


Figure 2. Schematic illustration showing the different possible desorption paths for the group V component: (i) bulk diffusion to the surface and desorption, (ii) surface diffusion of group III with group V desorption, and (iii) dissolution of the substrate at the cluster/substrate interface, diffusion of group V through the cluster and desorption from the cluster surface.

V component through the bulk and desorption, (ii) surface diffusion of the group III component to nearby clusters followed by desorption of the group V component and (iii) dissolution of the bulk crystal at the cluster/substrate interface, diffusion of the group V component through the cluster and desorption from the cluster surface. A detailed calculation comparing the three processes using published thermodynamic data for both GaAs and InP has been performed (Lowes and Zinke-Allmang, 1993, 1994). The calculations confirm that process (iii), where the metal cluster dissolves the substrate at the interface, is the fastest mechanism for group V desorption from III-V substrates. This mechanism is consistent with the observation that regions directly beneath clusters are recessed with respect to the substrate surface and confirms that the dominant process for cluster growth is through its interaction with the underlying substrate.

Therefore, after a stable nucleus is established and grows, it simultaneously decomposes the substrate forming etch pits down into the (001) surface. As the depth of the depression increases, the side faces of the depressions become exposed. As the side face area becomes significant, growth of the cluster accelerates in a lateral direction because the side plans have a greater etch rate than the (001) ground plane (Lum and Clawson, 1979). Etching at the cluster/substrate interface continues to supply group III metal to the growing cluster as group V desorbs from the cluster into the vacuum chamber.

Another mechanism for sudden dramatic increases in the volume of individual clusters is by coalescence. In the later stages of cluster growth, where the clusters are on the order of a micrometer in diameter, they can come in contact, join together to form one larger cluster and leave behind a cleared region that is depressed with respect to the height of the substrate surface (Fig. 1, "R"). It is precisely these coalescence events that reveal this complex interaction between a cluster and its substrate.

The remainder of this paper will focus on GaAs substrates and the interaction with MBE deposited metals. For these samples, it should be noted that at no time in the history of the sample did the temperature exceed the reported decomposition temperature of the GaAs substrate (≈ 650°C) (Jacob and Muller, 1984).

Examples of indium and gallium deposits on GaAs for various deposition and annealing conditions are shown in the scanning electron micrographs of Figure 3. Figure 3a is an example of indium deposited on GaAs and annealed at 455°C for 30 minutes. The clusters have an apparent bimodal size distribution and are irregular in shape with significant faceting and an apparently uniformly smooth substrate. Similar features are found for gallium deposited on GaAs with comparable deposition and annealing conditions. Figures 3b and 3c show the morphology of indium on GaAs annealed at 575°C and gallium on GaAs annealed at 585°C for 30 minutes each. One feature common to both of these samples is the substantial surface scarring that results in the formation of etch pits. The pits are on the order of 200 nm in size spaced approximately 500 nm apart with ≈ 2 x 10^8 pits/cm^2. The as supplied wafer etch pit density was less than 3 x 10^3 cm^{-2}. The surfaces of the corresponding control samples where GaAs did not have metal deposits or annealing were featureless as observed in the SEM. For comparable annealing conditions, GaAs with deposited metals exhibited surface pitting, yet GaAs, without deposition, showed no signs of pitting.

Another interesting feature of Figure 3b is the absence of indium clusters. Within the detection limits of scanning Auger spectroscopy and RBS, no indium was found on this sample. The explanation for indium no longer being on the GaAs surface is because of desorption. Significant desorption of MBE deposited indium from clean Si(001) takes place at temperatures greater than ≈ 450°C as measured by RBS (R. Barel, unpublished). Similarly, significant desorption of gallium from Si takes place at temperatures greater than ≈ 550°C (Mai, 1994).

In order to establish the role of deposited metals, annealing temperature and desorption in generating surface roughness and etch pits, the samples were examined in the TEM. A typical bright field micrograph of the sample shown in Figure 3b (In/GaAs) is shown in Figure 4. There are three distinct types of features of interest. Regions of dark contrast marked with "P" are indium precipitates as determined by EDXA. Neither Auger and RBS detected indium on this sample, however, it is apparent that the indium is highly localized.

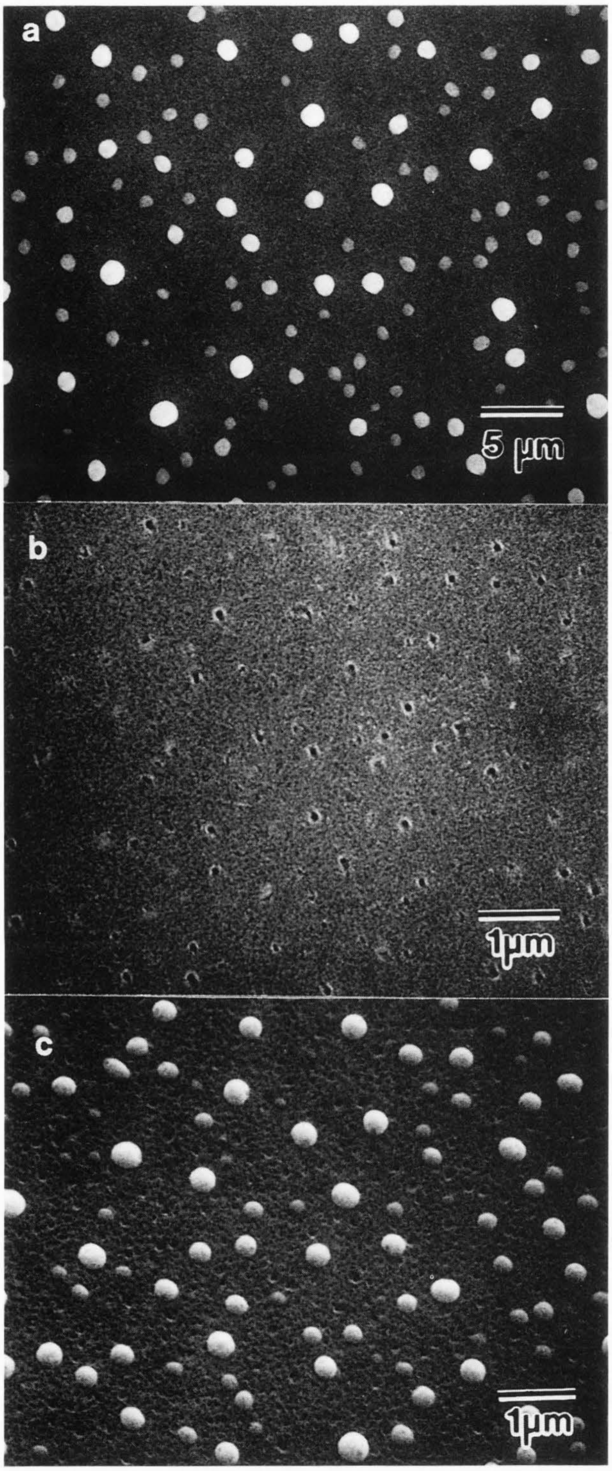
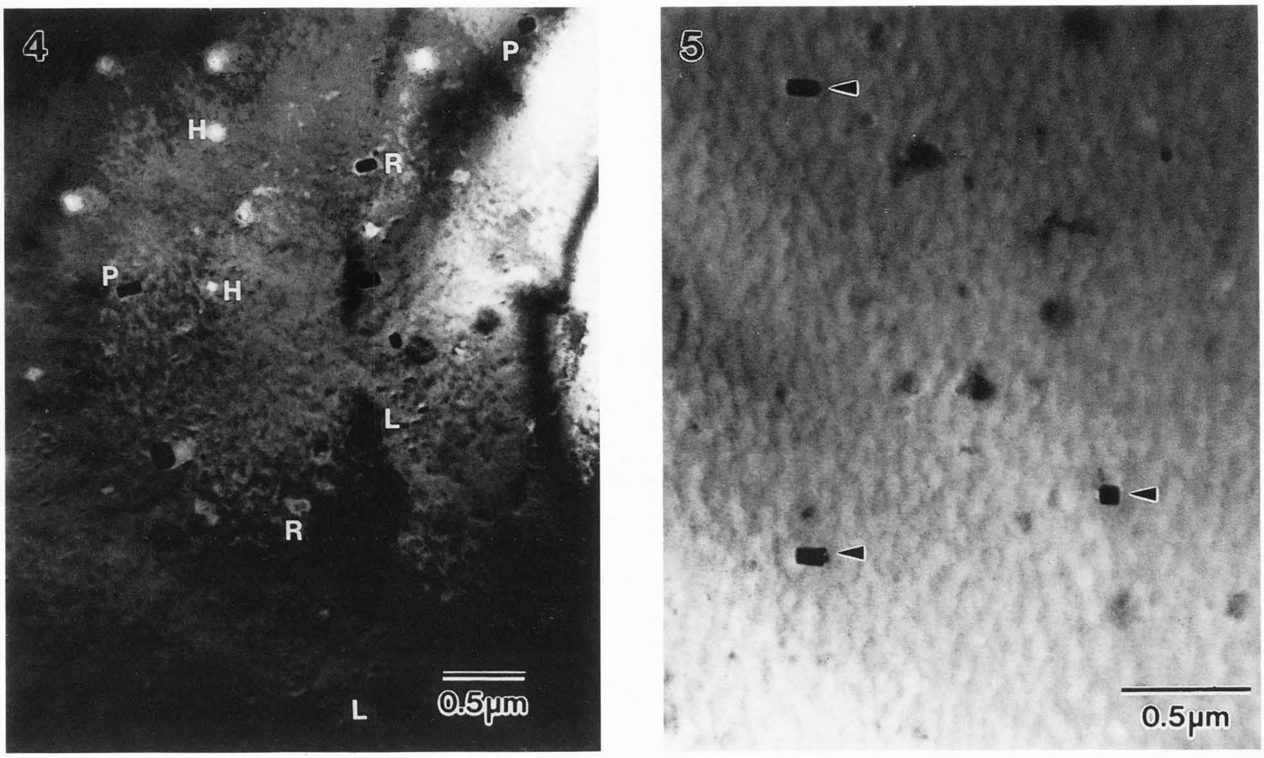


Figure 3. Scanning electron micrographs of GaAs(001) with metal deposits: (a) ≈ 30 ML of indium, annealed 30 minutes, 455°C. (b) ≈ 30 ML of indium, annealed 30 minutes, 575°C. (c) ≈ 60 ML gallium, annealed 30 minutes, 585°C (in this case, the angle between the surface normal and the incident electron beam is ≈ 45°).

Therefore, its presence could easily go undetected using techniques (like Auger and RBS) that cannot locally detect composition with a spatial resolution on the order of ≈ 100 nm. The indium precipitates are usually rectangular in shape with their edges aligned along <110> type directions of the substrate and are on the order of 200 nm in dimension. Larger precipitates exhibit an irregular shape with more than four sides (see "L", Fig. 4). A second feature type is regions of bright contrast. These regions are thinner than the surrounding substrate but they are not holes extending through the thickness of the foil. These etch pits are also rectangular, usually aligned along <110> directions and are on the order of 200 nm in size (see "H", Fig. 4). The third type of feature is a hybrid of the other two features. The characteristic of this type of feature is a dark indium precipitate centrally located within a bright halo (see "R" Fig. 4). For this case, indium precipitates reside inside the etch pits. Similar features are seen for GaAs with gallium deposits annealed above the gallium desorption temperature (not shown).

These three microstructural features are connected in the following manner. The largest multi-faceted indium precipitates are the remnants of micrometer sized precipitates seen in the SEM that have not completely desorbed. The features showing precipitates residing inside etch pits represent a snap-shot of precipitates at later stages of desorption. The fact that the precipitates have been identified as indium indicates that interactions between the cluster and substrate occur. Regions without any indium (see "H", Fig. 4) are yet later snapshots of the evolving microstructure where complete desorption has occurred leaving only the etch pit as evidence of its prior existence and interaction with the substrate. The ability to see these three features simultaneously indicates that significant interaction of deposited indium (and gallium) occurs with the underlying GaAs substrate.

Another interesting observation is that surface pitting seems to occur at much lower temperatures with metal deposits than without. However, when GaAs control samples (vis. one with only an oxide flash and another with the oxide flash and anneal) were examined in the TEM, evidence of substrate decomposition and etch pit formation was found. Bright field transmission electron micrographs of these two control samples are shown in Figures 5 and 6. Well-developed facetted gallium precipitates on the order of 100 nm are clearly evident in Figure 5 (arrowed). Other, less well-defined regions of dark contrast are believed to be gallium rich corresponding to decomposition regions at an earlier stage of evolution, etch pits were rarely observed. These data are direct evidence of decomposition of GaAs substrates at temperatures well below the decomposition temperature of 650°C.



Figures 4 and 5. Bright field transmission electron micrographs of GaAs (001). **Figure 4**. With ≈ 30 ML of indium, annealed 30 minutes, 575°C (as in Fig. 3b). Legend: "P" indicates indium precipitates, "L" indicates larger irregularly shaped indium precipitates, "H" indicates etch pits without indium precipitate, and "R" indicates etch pits with indium remaining inside. **Figure 5**. Annealed 600°C for 15 minutes for oxide removal. Arrows indicate gallium precipitates.

The GaAs sample treated for oxide removal with a subsequent anneal at 555°C is shown in Figures 6a and 6b. Once again, well developed facetted gallium precipitates are found (arrowed). In addition, larger irregularly shaped precipitates are present along with a significant number of facetted etch pits with small gallium precipitates inside (see "R", Fig. 6a). Figure 6b is a higher magnification image of a gallium precipitate inside an etch pit. The features found in Figure 6 are consistent with the expected evolution of the microstructure shown in Figure 5 considering an additional thermal treatment. Qualitatively, the number and size of gallium precipitates (i.e., decomposition sites) and the density of etch pits are significantly higher for samples annealed after the oxide flash treatment.

Contrary to the results of the SEM studies, GaAs substrates without metal deposits show evidence of surface scarring and etch pit formation. Moreover, the evolution of microstructure for samples with metal deposits and a subsequent anneal is identical to the evolution of microstructure in the case where the substrate thermally decomposes. For all cases discussed in this paper, cluster/substrate interactions occur. The explanation why etch pit formation was not observed in the SEM for samples with deposits having annealing temperatures below the metal desorption temperature is attributable to the absence of significant metal desorption as shown in Table 1. For GaAs with indium deposits annealed below 450°C and with gallium deposits annealed below 550°C, etch pits were not detected in the SEM.

Observation of the etch pits, which is direct evidence for the interactions, is not possible in the SEM unless the cluster is removed. If the cluster remains in place, it is not possible to see the underlying substrate to evaluate any interactions. One very simple way to remove the cluster is to desorb it from the surface. This was also true for the case of the thermally decomposed substrates shown in Figure 1. During a coalescence event, large clusters are removed from various regions of the substrate exposing the underlying surface, thereby revealing any prior cluster/substrate interactions.

For the case without metal deposits, etch pits were not observed in the SEM simply because they are at an earlier stage in their evolution compared to samples with deposits. Substrates without deposits have to first establish regions of excess metal before etch pits can develop.

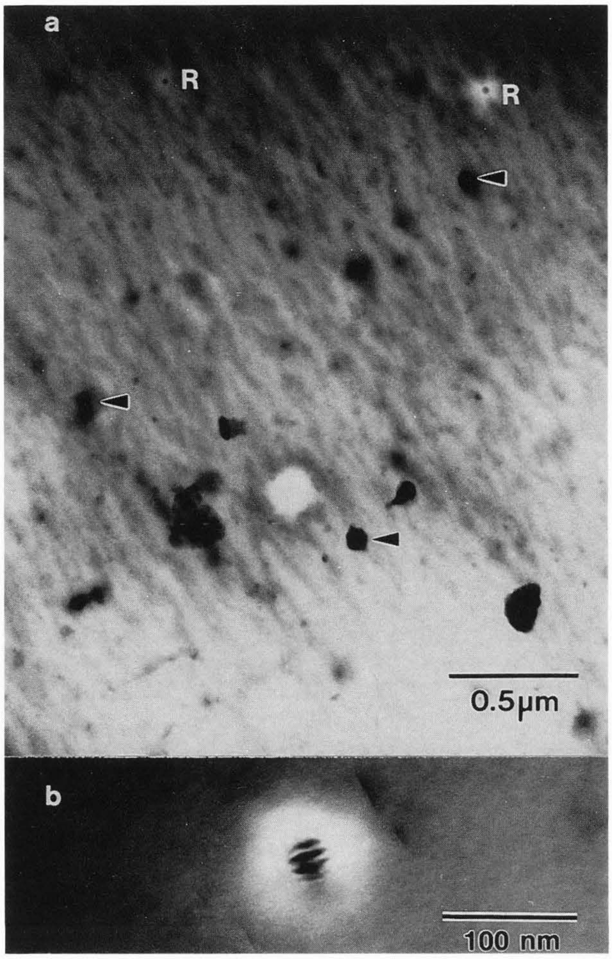


Figure 6. Bright field transmission electron micrograph of GaAs (001): oxide removed and annealed at 555°C for 30 minutes. (**a**) Arrows indicate gallium precipitates, "R" indicates etch pits with gallium precipitates inside. (**b**) Higher magnification image of a gallium precipitate inside an etch pit.

Conversely, samples with deposited metals effectively have a longer time at the annealing temperature for etch pit formation as excess metal is provided to the surface. This also accounts for the lower precipitate and etch pit densities found in the TEM for samples without metal deposits.

Summary

A detailed examination of the microstructure of MBE deposited indium and gallium with GaAs(001) clearly shows that the metal clusters interact substantially with the substrate. TEM evidence indicates that the mechanism responsible for the interaction is the same mechanism by which III-V compound semiconductors thermally decompose.

For annealing conditions that are routinely used for semiconductor substrate preparation and thin film overgrowth, significant interface roughening and alloying is likely to occur. Also, strong evidence is presented that the GaAs substrate thermally decomposes in a temperature range which extends to 50°C lower than the usually reported value of 650°C for thermal decomposition. This result should not be overlooked. Local substrate decomposition reported here on the order of 10's of nanometers can not be detected by the standard *in situ* characterization tools used in thin film growth including electron diffraction, Auger spectroscopy, and light scattering. Substrate anomalies of this kind are likely to have deleterious effects on subsequent processing steps for device fabrication.

Table 1. GaAs deposition and annealing conditions.*

Deposit	Anneal Temp. (°C)	Anneal Time (min.)	Etch Pits
NIL	---	0	no
	475	30	no
	555	10, 20, 30, 60	no
	585	30	no
Ga	575	30	yes
	585	10, 30	yes
In	300-425	10-60	no
	455	30	yes
	475	10	no
	500	30	yes
	555	20, 40, 60	yes
	575	30	yes

*GaAs substrates heated in UHV to 600°C for oxide removal, cooled to below 150°C, followed by deposition and a post-deposit anneal for the indicated temperatures and times. The SEM was the instrument used to determine the presence or absence of etch pits. Etch pits are observed in the SEM only in cases where the annealing temperature exceeds the desorption temperature of the deposited metal (450°C for indium, 550°C for gallium).

Acknowledgments

The author is grateful to M. Zinke-Allmang for valuable discussions. This project is supported through grants from the Natural Sciences and Engineering Council of Canada.

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Discussion with Reviewers

L. Schowalter: A particularly interesting aspect of the paper is the suggestion that the effects of thermal decomposition can be seen at temperatures substantially below 650°C. Although the paper does not explicitly state this, I presume that the author did not use an arsenic flux during the oxide desorption or annealing step. Would the author agree with the speculation that the decomposition that he sees at lower temperatures would have been eliminated if a proper arsenic flux had been maintained during the cleaning and annealing steps (as is standard practice in GaAs MBE)?

Author: An arsenic flux to prevent substrate decomposition was not used in the experiments reported in this paper. This was so that the probability of seeing a decomposition site would be high.

I do not think that total elimination of decomposition would take place even with an arsenic flux but rather I think that the severity (number and size of sites) of decomposition would have been substantially reduced. Features similar to those appearing in this paper are also seen by other groups who use a stabilizing arsenic flux at temperatures below 650°C.

G.C. Weatherly: GaAs and InAs form a complete range of solid solutions. Does the possibility of (In,Ga) As formation enter into the discussion of the reactions when GaAs is exposed to In at 575°C?

Author: Formation of a ternary (In,Ga) As solution is most probably occurring. I am planing to make some attempts to quantify this phenomenon. However, I do not think that this plays a significant role with respect to the details of the metal interaction with and subsequent decomposition of the substrate given the similarities between indium and gallium.

G.C. Weatherly: What is the origin of the contrast seen at the Ga precipitate in Figure 6b?

Author: I believe that the contrast is attributable to moire fringes due to overlapping unmatched crystal lattices, Ga and GaAs.

G.C. Weatherly: Can you elaborate on the remarks made in the summary about the implications for processing Group III-V substrates prior to thin film overgrowth? How do your annealing conditions compare to those used in semiconductor processing of GaAs or InP?

Author: The remarks made in the summary about implications for *in situ* processing prior to over growth were intended to heighten awareness of surface scientists and other interested researchers. The point is that most all of the standard *in situ* characterization tools in MBE growth facilities [i.e., low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED), Auger, X-ray photoelectron spectroscopy (XPS), etc.] provide data about the surface over a relatively long spatial scale or data is averaged over a large region. Standard techniques such as these may report "good" growth conditions when substrate integrity may have already been significantly compromised on an unresolved length scale as shown in this manuscript. *In situ* techniques can give a false sense of security.

Specifically, the message for these III-V systems is do not push the temperature limit of decomposition because decomposition may be happening and one may not be able to observe it. A more philosophical or general message is be aware of what is being measured and the limitations associated with the technique.

The annealing conditions used in this work are typical growth temperatures (400-600°C) and times (10-60 minutes) for these systems and (depositions rates of 1 μm/hr).

J.M. Gibson: The author stated that "etch pits are usually aligned along <110> directions", but this appears inconsistent with Figure 4.

Author: Some deviations from this crystallographic relationship between the etch pit and substrate occur, however, for the majority of cases the stated relationship holds.

J.M. Gibson: A bright feature in Figure 4 does not imply a "pit", because of the oscillatory aspect of diffracted intensity. Has the author confirmed this by tilting?
Author: The bright features were examined in various tilted configurations and the brightness seen in transmission is attributable to the absence of material, i.e., a pit. This is also confirmed by very little or no X-ray counts from a focused probe on such regions.