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COMPOSITION FLUCTUATIONS IN III-V SEMICONDUCTORS

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ABSTRACT - Electron microscopy studies have previously revealed the presence of fine scale (10nm) variations of contrast within III-V compound semiconductor epilayers. Using a pulsed laser atom probe it has been possible to study the microchemistry of these layers at very high resolution. This study has shown that in epilayers of GaInAs, AlInAs and GaAlInAs there are variations of up to 10% in composition. In the GaAlInAs system the epilayer is seen to cluster towards small regions of GaInAs and GaAlAs. Preliminary experiments using a position-sensitive atom probe have confirmed that the composition variations can be further quantified using three dimensional microanalysis techniques.

1. - INTRODUCTION

Contrast fluctuations, generally assumed to be composition related, have been observed in transmission electron microscopy studies of epitaxially grown layers of III-V semiconductor alloys. These fluctuations would be expected to have an adverse effect on both the optical and electrical properties of the layers [1]. The variations within the epilayers are thought to occur as a result of attempting to grow the layers at compositions lattice-matched to their substrates. The required compositions often lie within a miscibility gap at the growth temperature, which may give sufficient driving force to induce phase separation [2].

The contrast variations have been observed to be present on two different scales; a coarse scale variation, typically of several tens of nanometers [3], and a finer scale variation of a few nanometers [4]. It has been suggested that both of these variations in contrast are a result of strain modulations in the epilayer material [5]. The coarse variation is a consequence of specific growth conditions, i.e. growth must occur within a miscibility gap for the contrast to be observed. The fine scale variation has been suggested to be present in all layers of III-V alloys as a consequence of statistical fluctuations in the distributions of atoms having different covalent radii but this has not yet been confirmed directly [6]. The coarse scale fluctuation has proved amenable to STEM microanalysis, and has been confirmed to be associated with a variation in composition [6], however the finer scale variation is too fine to permit analysis by electron microscopy microanalytical techniques. To carry out microchemical analysis on these fluctuations it is necessary to make use of the higher spatial resolution capability of the atom probe.

The conventional atom probe has been shown by many authors to be suitable for the analysis of fine scale chemical variations in a wide range of metallurgical systems, and the pulsed laser atom probe has been used in the microanalysis of a variety of bulk semiconductor materials [7,8]. The development of specimen preparation techniques appropriate to semiconductor epilayers [9] has now made it possible to apply atom probe microanalysis to the study of compositional homogeneity in III-V epilayers.

2. - EXPERIMENTAL TECHNIQUE

The pulsed laser atom probe has been used to study four ternary alloy and one quaternary III-V alloy all grown on indium phosphide substrates. The epilayers were all grown at compositions at (or close to) that required to lattice-match the epilayer to the substrate. The growth conditions, and nominal compositions, of the samples studied are shown in Table I.

A number of the samples were studied using dark field transmission electron microscopy to confirm the existence of the fine-scale variations in the samples used, examples are shown in figure 1. Recent work [6] has suggested that the fine-scale variation is present in all III-V alloys, and this is in agreement with the observations on the specimens available for this investigation.

Atom probe specimens were produced from each of the samples listed in Table I using the technique described by Liddle et al [9]. In order to detect fine scale chemical variation, it is necessary to perform detailed statistical analysis on the raw data produced during the experiment. The first stage of analysis was to establish the presence of deviations from chemical homogeneity. In heavily decomposed materials the compositional variation can be seen visually, however where the level of decomposition is slight and the components have similar compositions it is much more difficult to establish the presence of any variation.

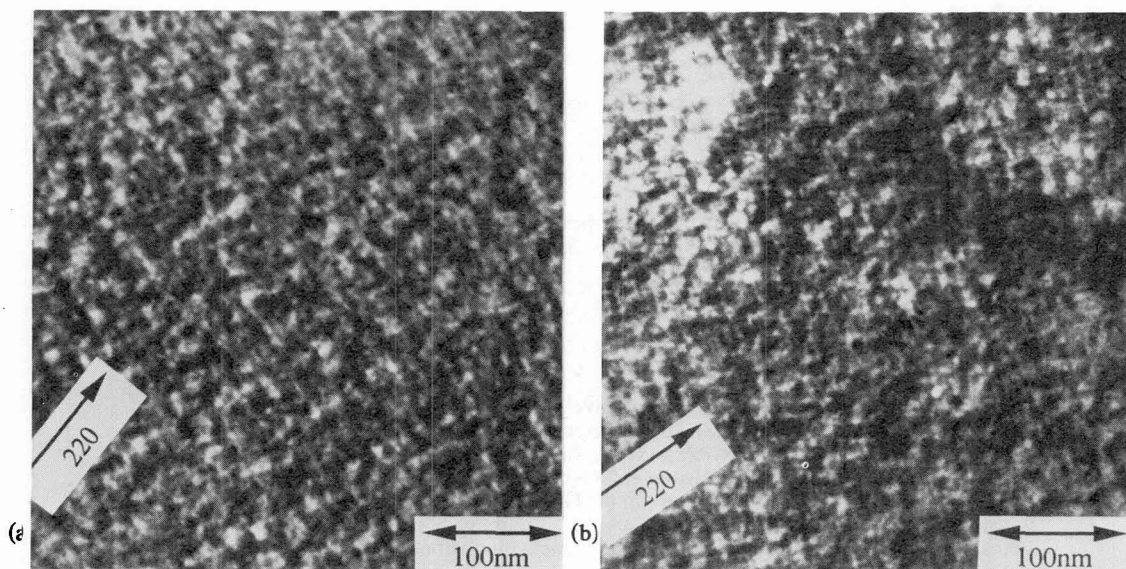


Figure 1. (220) Dark field TEM images showing the presence of fine scale contrast variation in the materials used in this study (a) GaInAs, (b) AlInAs,

TABLE I

Growth conditions and nominal composition of the materials used in this study

^a Low Pressure Metal Organic Chemical Vapour Deposition,

^b Atmospheric Pressure Metal Organic Chemical Vapour Deposition

Material	growth mode	growth temperature	nominal composition			
			Al	Ga	In	As
GaInAs#1	LP MOCVD ^a	650°C	-	0.47	0.53	1.00
GaInAs#2	LP MOCVD ^a	650°C	-	0.473	0.527	1.00
GaInAs#3	MOCVD ^b	600°C	-	0.47	0.53	1.00
AlInAs	LP MOCVD ^a	710°C	0.48	-	0.52	1.00
GaAlInAs	LP MOCVD ^a	680°C	0.16	0.325	0.515	1.00

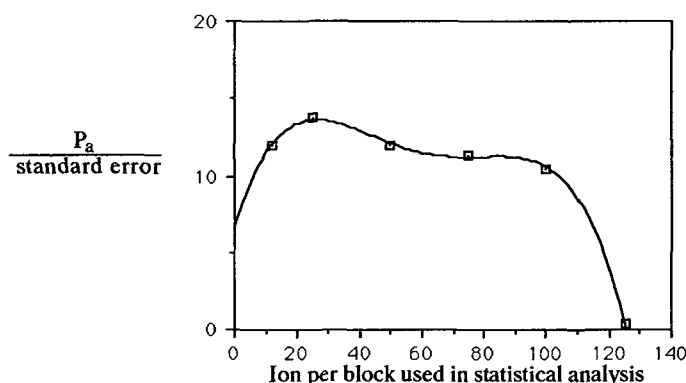
The analysis used to measure the presence of chemical variation in this investigation was demonstrated for both heavily and lightly decomposed materials by Godfrey et al [10]. This method attempts to fit a frequency distribution produced by summing a series of binomial distributions with sinusoidal probability amplitudes to the frequency distribution of the raw data. This yields a measurement of the amplitude of composition fluctuations (P_a), which characterizes the degree of decomposition. For example, a P_a value of 0.10 indicates a 10% variation in composition associated with the phase separation. The second stage of analysis was to establish the extent of clustering in the material. This can be established by performing autocorrelation analysis, as discussed by Hetherington and Miller [11].

3. - ATOM PROBE RESULTS

The results of the first stage of the study, for all five samples described above, are shown in Table II. This shows the measured (mean) compositions recorded during the experiments, and also the P_a and standard error (σ) values determined from the statistical analysis described above. The χ^2 test compares the sample distribution of the experimental data with the sample distribution of a binomial distribution which would be expected for a random (homogeneous) case. A χ^2 probability of less than 5% indicates the presence of a statistically significant deviation from a random distribution. In determining the P_a value it is necessary to consider a wide range of statistical sample sizes. The effect of varying this sample size is shown graphically in figure 2. This shows the variation of spinodal

TABLE II*Measured compositions, P_a values and χ^2 probability values showing degree of fit to model*

Material	measured composition			composition fluctuation	standard	$p(\chi^2)$
	Al	Ga	In	amplitude (P_a)	error	
GaInAs#1		0.476	0.524	0.110	0.008	< 0.1%
GaInAs#2		0.456	0.544	(0.040)	(0.025)	>10 %
				(0.071)	(0.024)	>10 %
GaInAs#3		0.483	0.517	(0.037)	(0.017)	<10 %
AlInAs	0.412		0.588	0.114	0.008	< 0.1 %
GaAlInAs	0.166	0.303	0.532	(Ga 0.030)	(0.017)	> 10 %
				Al 0.059	0.009	< 1 %
				In 0.070	0.012	< 1 %

*Figure 2. Variation of P_a -standard error ratio with statistical sample size for GaInAs#1*

amplitude, relative to standard error, with sample size for specimen GaInAs#1. The sample size was allowed to vary over the range 6 to 125. The spinodal amplitude can be seen to pass through a maximum, dropping off at small sample sizes as the statistical noise increases (and the standard error increases) and at large sample sizes as the decomposition gets smoothed out during sampling. All the samples studied varied in the same way, and the P_a values shown in Table II are from the maximum of each curve.

The need for statistical analysis to reveal the extent of the variations in composition can be seen by plotting composition profiles for the data. Two examples are shown in figure 3, in neither case is there any visual evidence for systematic composition variation revealed by P_a analysis.

In Table II we have quoted a single P_a value for each of the ternary samples, and three P_a values for the quaternary. The P_a values determined for both of the group III components in the ternaries will be the same. In the quaternary (which contains 3 group III components) there exists the possibility of different P_a values for each component. An attempt to look at the variation in group V components in a sample of GaInAsP proved to be unsuccessful since the analysis was dominated by the clustering effect of the group V components during the evaporation process [9].

As can be seen from Table II most of the variations in composition are quite small, compared to the estimates of standard error, indicating that the variation is near the limits of precision of the technique. In some case the P_a values determined are clearly statistically insignificant, but in other cases the values are significant. The value determined for the first GaInAs sample indicates a variation of the order of 11%, i.e. gallium content varies locally from 36% to 58% of the group III content (i.e. 18 to 29 atomic %), and accordingly the indium from 42% to 64% (21 to 32 at. %). However in the other two GaInAs samples studied the P_a values were not statistically significant. In the quaternary studied both the aluminium and indium content showed a significant variation from randomness, however the gallium content variation was below statistical significance.

The results of the second part of the investigation are shown in figure 4. This shows the auto-correlation plots for the gallium, indium and aluminium content in the GaAlInAs sample studied. The value of $R(1)$ on the Gallium plot indicates that no clustering is present, however in the cases of the aluminium and indium the first plot drops to a first minimum more gradually indicating the presence of clustering. The scale of the clustering is difficult to assess directly but is estimated from the auto-correlation plots as being of the order of 20 nm in both cases. Further information about the clustering can be obtained by constructing contingency tables [12]. The contingency table shown in Table III was calculated with a fixed block size of 1000 ions. Each block was classified as being rich or poor in each component, compared with the average content of that component in the sample. The presence of blocks containing greater than average levels of both components is indicative of co-segregation, whilst the presence of blocks containing high levels of one component and low levels of the other are indicative of segregation apart. In the case of the indium-aluminium contingency table it can be seen the number of blocks rich in indium but also low in aluminium is higher than would be expected, as is the number of blocks rich in aluminium and low in indium. This is indicative of the aluminium and indium tending to segregate away from each other, i.e. the epilayer tends to cluster to GaAlAs and GaInAs regions. This is consistent with the P_a analysis results shown in Table II.

The development of the position sensitive atom probe (POSAP) has made possible the development of three dimensional microchemical analysis techniques [13]. This type of analysis has been used on a AlInAs sample, similar to that used to determine the results shown in Tables I and II. Using three dimensional decomposition analysis methods described elsewhere [14] it has been possible to determine a P_a value for this material which is in good agreement with that obtained using the more conventional atom probe techniques described earlier. This provides the possibility of further characterising decomposition at fine scales, where analysis is made difficult by the extent of the probe area.

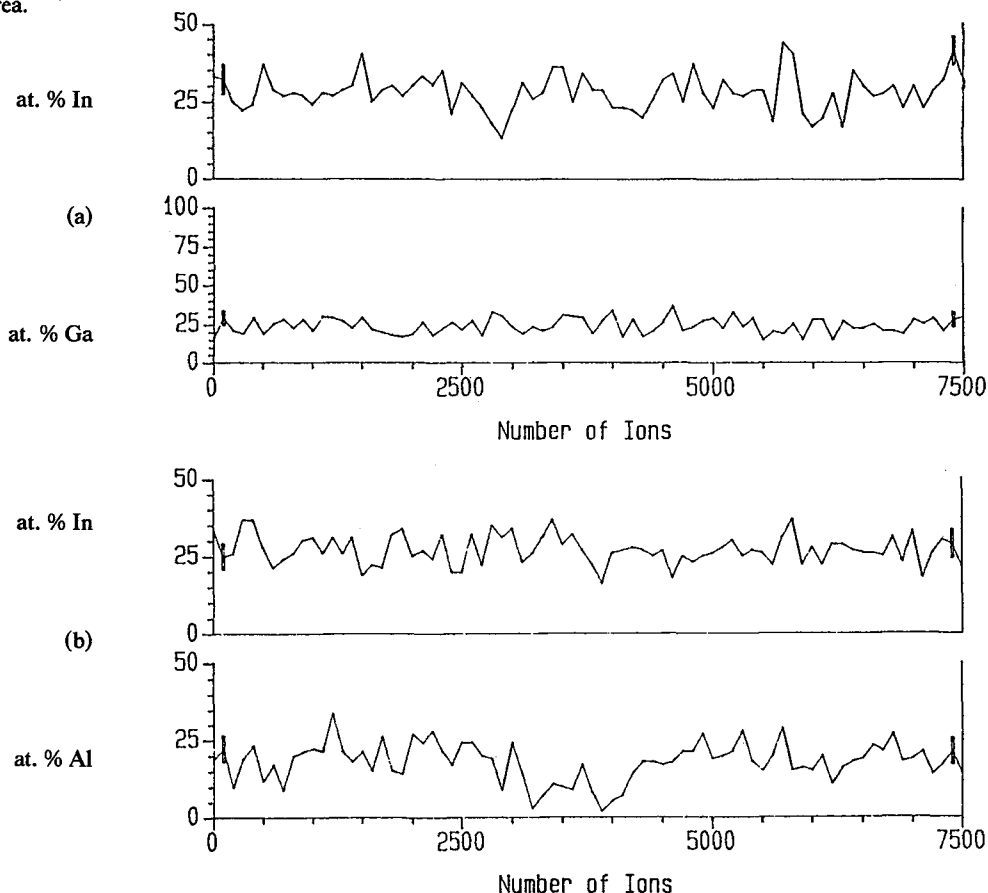


Figure 3. Atom Probe composition profiles from (a) GaInAs#1 and (b) AlInAs. The statistical scatter evident in these profiles makes it impossible to determine any composition fluctuations directly

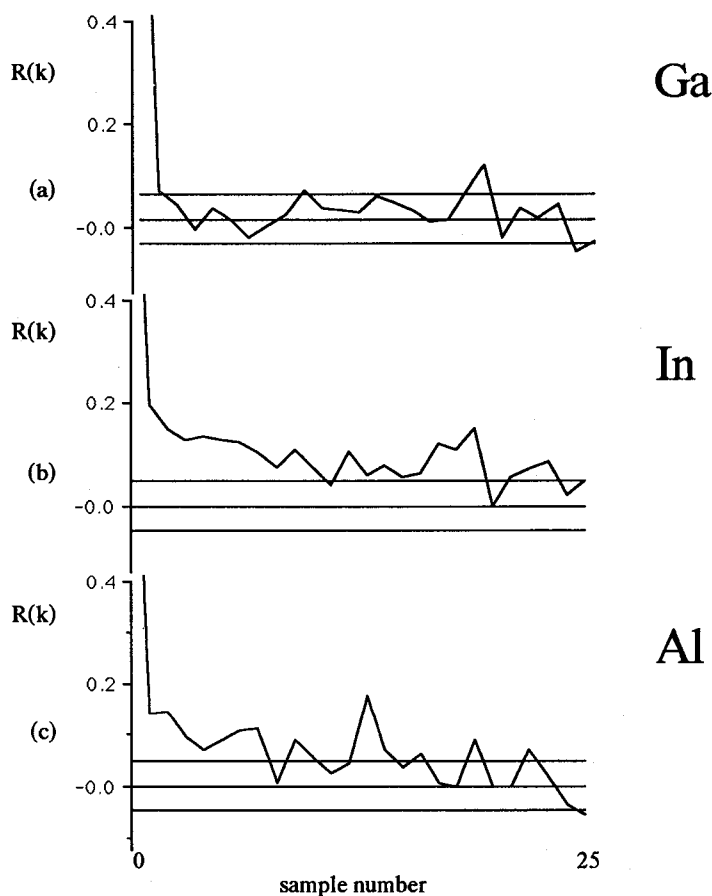


Figure 4. Autocorrelation plots for (a) Ga content, (b) In content and (c) Al content of the GaAlInAs sample

Table III

Contingency tables for Indium and Aluminium content of GaAlInAs determined with sample sizes of 1000.

(a) Number of blocks containing indicated levels of indium and aluminium - Observed values

		<u>Number of Indium ions in each 1000 ion block</u>	
		491 - 516	517 - 569
<u>Number of Aluminium ions in each 1000 ion block</u>	142 - 171	0	5
	172 - 186	5	1

(b) Number of blocks containing indicated levels of indium and aluminium - Expected values

		<u>Number of Indium ions in each 1000 ion block</u>	
		491 - 516	517 - 569
<u>Number of Aluminium ions in each 1000 ion block</u>	142 - 171	2.3	2.7
	172 - 186	2.7	3.3

χ^2 -value of these contingency analysis = 7.6,
probability of this distribution from a chemically homogeneous material (random) is <1.0 %

4. - DISCUSSION

The atom probe permits very high spatial and chemical resolution analysis to be carried out on small volumes of material. Whilst this makes it a suitable technique to study the fine-scale variation of composition of structure in epilayer materials, the volume of material sampled is however too small to permit any comment to be made on the nature of the coarse scale variations also observed in these materials.

There are two sets of conflicting results concerning the nature of the fine scale variation. The work of Norman and Booker [15] suggests that phase separation occurs to a point where it is detectable using transmission electron diffraction techniques. Conversely, the work of Glas [6] suggests that rather than a phase separation, driven by a miscibility gap, the fine scale contrast is the result of localized clustering. The work of Norman and Booker indicates the development of a much more regular structure than that of Glas.

The atom probe results presented here indicate that there is (in at least some cases) a statistically significant level of clustering present. The absence of any diffraction evidence would appear to be at odds with the results of Norman and Booker, however it is important to recognize that the samples used in their investigation had been produced at a much lower temperature than those used either in this investigation or that of Glas. The explanation of Glas, however, is consistent with the observations made during the present investigation. The extent of the variation from the average composition is quite dramatic, even in cases where the growth conditions are outside the miscibility gap, where the material is not expected to undergo any phase separation. The scale of the composition fluctuation revealed by autocorrelation analysis is consistent with the TEM observations of many authors.

It is hoped that by applying POSAP techniques and three dimensional statistical analysis methods that it will be possible to characterize the level of any phase separation or clustering in three dimensions in a wider range of materials. Preliminary investigations using these techniques have been very encouraging.

5. - CONCLUSIONS

This investigation has for the first time permitted ultra-high resolution chemical information on the fine scale structure of semiconductor epilayers to be determined. By using the intrinsic high resolution capability of the atom probe and detailed statistical analysis the epilayers have been seen to have composition variations of the order of 7-10%, this variation seems to be associated with the presence of fine scale clustering rather than with a miscibility gap driven phase decomposition.

6. - ACKNOWLEDGEMENTS

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