PULSED LASER ATOM PROBE ANALYSIS OF III-V COMPOUND SEMICONDUCTORS

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PULSED LASER ATOM PROBE ANALYSIS OF III-V COMPOUND SEMICONDUCTORS

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Abstract - The pulsed laser atom probe has been shown to give stoichiometrically correct analyses of GaAs and InAs. Temperature rises under pulsed laser irradiation are investigated and the generation of As cluster ions is found to be primarily due to field evaporation at elevated temperatures. Preliminary results on the analysis of ternary materials is presented, showing local composition variations in a GaAlAs layer.

1 - INTRODUCTION

Detailed information on the microchemistry of semiconductor materials and interfaces is of crucial importance not only from a technological viewpoint but also for obtaining fundamental information on device operation. This is especially the case for the complex chemistry of compound semiconductors. In particular the performance of heterojunction devices (such as GaAlAs/GaAs lasers) and the properties of low dimensional structures are dependent on nanometre composition variations.

Early atom-probe work on III-V compound semiconductors showed that these materials could not be analysed accurately using voltage pulses. Materials studied included GaAs and GaP [1,2]. It was found that analyses by this method indicated compositions outside the range expected for these materials, typically being Ga deficient. The observed stoichiometry was also found to vary according to the conditions of analysis (e.g. background gas pressure) [3]. It appears that either surface migration [3] or preferential evaporation [4] of Ga atoms is responsible for the inaccuracy. In either case, conditions for reliable atom probe analysis for the materials must be obtained before studies of more complex systems (interfaces, ternary materials) can be performed with confidence.

The pulsed laser atom probe (PLAP) [5] has already been used to study native oxides on silicon and the SiO_2/silicon interface [6]. We have previously shown that the PLAP gives stoichiometrically correct analysis of GaAs and InAs [7] (figure 1). In this paper we show that during PLAP analysis of these materials, the peak temperature is in the range 270-300K and that the atomic depth resolution of the atom probe is not seriously impaired by laser heating. We also present the first atom probe analysis of a ternary material, $Ga_{1-x}Al_xAs$.

2 - INSTRUMENT

The PLAP used in the main part of the work has been described elsewhere [8]. Laser pulses are produced by a JK Lasers Nd:YAG system, used in the frequency doubled mode (λ = 532nm). This generates 5ns pulses of ~1mJ into an unfocussed $1mm^2$ beam and gives a mass resolution $M/\Delta M \approx 800$ FWHM for W^{3+} ions. Some of the work was carried out on an older instrument, also previously described [9].

3 - TEMPERATURE RISE

Kellogg has described a variety of methods by which the peak specimen temperature in the PLAP can be estimated [10]. These include the use of evaporation field and charge state variations with temperature. Additionally, we have found a variation in the extent of As cluster ion formation with the temperature at which field evaporation occurs. There is some evidence showing a similar effect for P-containing materials, indicating that this technique of estimating specimen temperature is applicable to a wide range of III-V compound semiconductors.

We have used InAs as a model material to measure the variation of evaporation field, As charge state and extent of As cluster ion production with temperature. An InAs specimen was polished from a whisker by dipping in H_2O_2/H_2SO_4 solution at 60°C. This was then analysed in the atom probe, using voltage pulses, at a variety of specimen temperatures, yielding the results of figures 2-4. The data of figure 4 indicate that As cluster ion generation is due primarily to the temperature/field conditions under which evaporation occurs and not to any photoexcitation phenomena. Comparison of these curves with data from a PLAP spectrum allows the peak specimen temperature under laser irradiation to be estimated. In the case of the spectrum in figure 1, taken at a base temperature of 100K, the peak temperature is in the range 270-300K.

With a low peak temperature and a short duration laser pulse, it is expected that little surface diffusion will occur. If this were not the case, the spatial resolution of the PLAP would be reduced, impairing studies of atomic scale composition variations. A ladder diagram along the InAs [111] direction shows the PLAP analysis of individual planes (figure 5) although some blurring of this detail is seen due to the extremely close spacing (0.09nm) of alternate plane pairs. Here the resolution is limited by the size of the probe hole and is not improved by analysis at a lower temperature (using voltage pulses).

4 - ANALYSIS OF GaAlAs

Having shown that the PLAP gives reliable analysis of compound semiconductors, we have begun a study of composition variations in ternary and quaternary materials. These are normally grown as thin (1μm) epitaxial films on a planar substrate, but thicker films can be grown, which provide a suitable starting material from which PLAP specimens can be made. Figure 6 shows a spectrum of $Ga_{1-x}Al_xAs$ grown by unusually fast metallo-organic chemical vapour deposition (MOCVD) on a GaAs (100) substrate. A 50μm layer was cut into bars along the [110] direction and polished in H_2O_2/H_2SO_4 solution at 60°C. Although the layer has a nominal composition of $x = 0.1$, analyses of different specimens made from the layer shown widely different compositions, (table 1). A transmission electron microscope (TEM) study of the material shows 'band' contrast in the plane of the grown layer (figure 7) which is likely to be associated with these composition fluctuations. In quaternary material, InGaAsP, 'weave' contrast observed in TEM studies of these layers has been directly correlated with variations in stoichiometry due to spinodal decomposition [11]. We believe that the compositional differences observed in our

Ions			Al/Ga	(Ga+Al)/As	x
Ga	Al	As			
1923	375	2135	0.20 ± 0.01	1.08 ± 0.03	0.16 ± 0.01
1104	108	1182	0.10 ± 0.01	1.03 ± 0.04	0.09 ± 0.01
955	667	1417	0.70 ± 0.05	1.14 ± 0.04	0.41 ± 0.01

Table 1
Some examples of PLAP analyses of different specimens made from a 50μm GaAlAs layer

GaAlAs are due to changes in conditions during the rapid growth of this specially-produced layer. Any such variations in composition, even over a smaller range of stoichiometries, could have a profound effect on the electronic properties of device material. It is hoped that future work will allow direct correlation between specific contrast features observed in the TEM and the composition of these regions as determined by the PLAP.

5 - CONCLUSIONS

The PLAP has been shown to give reliable, quantitative analysis of III-V compound semiconductors, with peak temperatures during analysis of below 300K. The possibility of determining the composition from an ultra-microscopic volume of material makes this technique ideal for the study of stoichiometry variations in ternary and quaternary materials. With the atomic scale depth resolution of PLAP analysis, detailed characterisation of metal-semiconductor and heterojunction interface chemistry is also possible. The observation of local composition variations in a MOCVD-grown GaAlAs layer is an important first practical application of this approach to III-V materials.

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References

[1] Ohno Y., Kuroda T. and Nakamura S. Surf.Sci. 75 (1978), 689.

[2] Tsong T.T., Ng Y.S. and Melmed A.J., Surf.Sci. 77 (1978), L187.

[3] Sakurai T., Hashizume T., Jumbo A. and Sakata T., J.de Physique 45 (1984), C9-453.

[4] Nishikawa O., Nomura E., Kawada H. and Oida K., these Proceedings.

[5] Kellogg G.L. and Tsong T.T., J.Appl.Phys. 51 (1980), 1184.

[6] Grovenor C.R.M., Cerezo A. and Smith G.D.W., Proc. conf. on "Interfaces and Epitaxy", M.R.S. Boston, November 1984. In Press.

[7] Cerezo A., Grovenor C.R.M. and Smith G.D.W., Appl.Phys.Lett. 46 (1985), 567.

[8] Cerezo A., Smith G.D.W. and Waugh A.R., J.de Physique 45 (1984), C9-329.

[9] Smith G.D.W., Grovenor C.R.M., Delargy K.M., Godfrey T.J. and McCabe A.R., in "Proceedings of the 29th International Field Emission Symposium", ed. by H-O Andrén and H.Nordén (Almqvist and Wiksell International, Stockholm, 1982), p.283.

[10] Kellogg G.L., J.Appl.Phys. 52, 5320 (1981).

[11] Hénoc P., Izrael A., Quillec M. and Launois H., Appl.Phys.Lett. 40 (1982), 963.

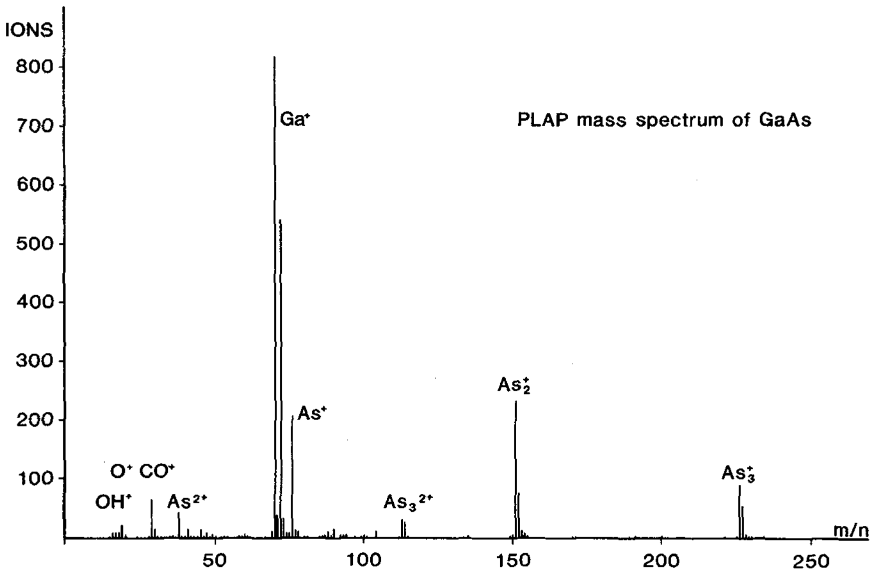
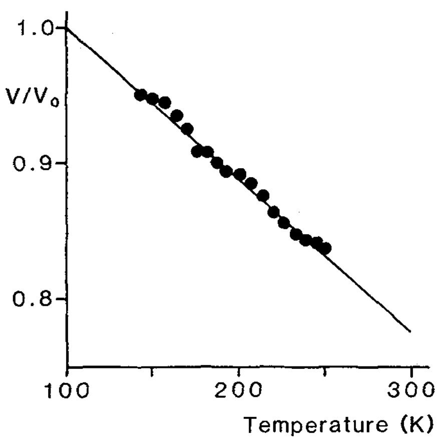


Figure 1. A typical PLAP spectrum from a GaAs specimen, yielding a stoichiometry of Ga/As = 0.99 ± 0.03.



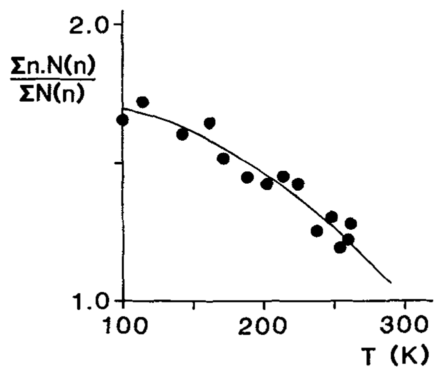


Figure 2. Variation of InAs pulsed evaporation voltage with temperature (normalised to value at 100K).

Figure 3. Mean As charge stage as a function of temperature for InAs.

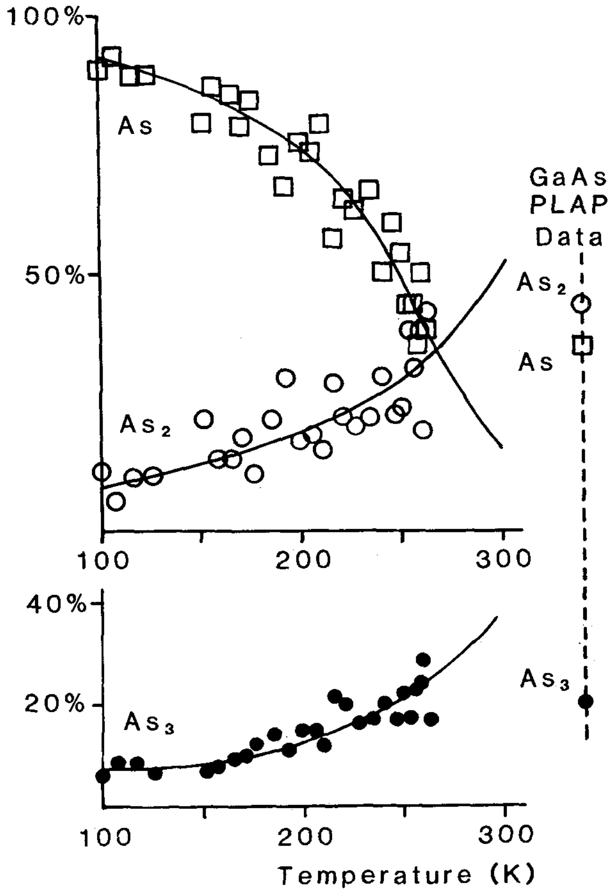


Figure 4. Variatiion in extent of As cluster ion formation with temperature. Also shown are data from the GaAs PLAP spectrum, figure 1, indicating a peak temperature during laser heating of about 280K.

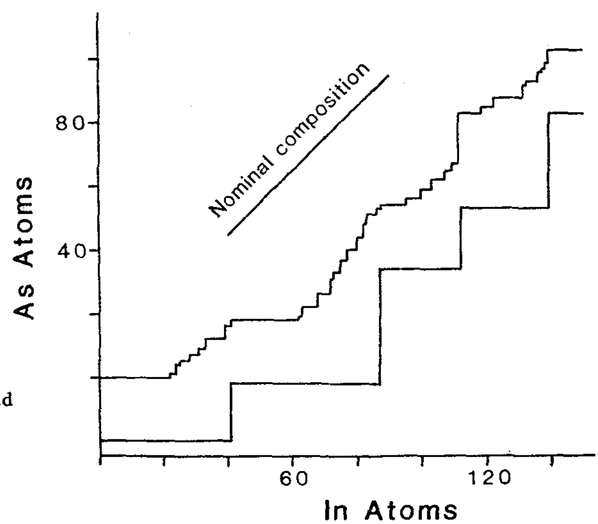


Figure 5. A ladder diagram obtained from PLAP analysis along the [111] direction in InAs.

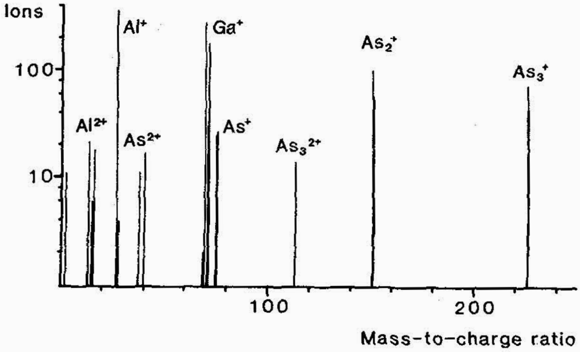


Figure 6. PLAP spectrum from a specimen made from a 50µm GaAlAs layer, indicating a local composition of $Ga_{0.58}Al_{0.42}As$.

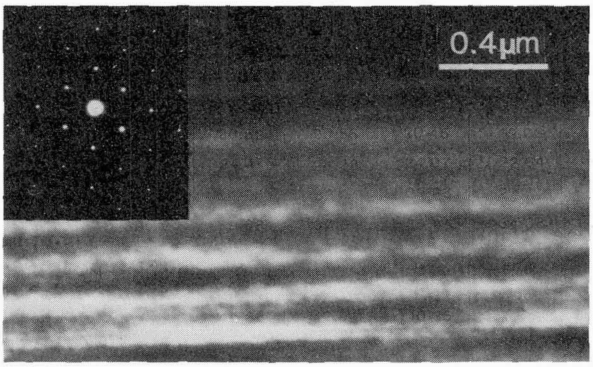


Figure 7. A dark field micrograph of a GaAlAs field ion specimen taken with the (400) spot excited. The linear features in the image are likely to be associated with composition variations in the growth direction as indicated by the PLAP analyses.