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## DEEP STATES AND SURFACE PROCESSES IN GaAs GROWN BY MOLECULAR BEAM EPITAXY

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**Résumé.** - Nous avons utilisé les mesures de DLTS pour étudier l'influence des conditions de croissance sur les pièges à électrons désignés par M1, M2, M3 et M4 présents dans le GaAs élaboré par EJM dans un domaine de températures de 520°C à 650°C. Pour un rapport As : Ga de 5:1, les concentrations de M1, M3 et M4 tombent de 2 décades pour des températures de croissance passant de 520°C à 650°C, tandis que M2 a un comportement plus complexe et est le piège principal dans les couches déposées à 650°C. A une température de croissance fixée à 550°C, les concentrations de M1 et M4 diminuent quand le rapport As:Ga augmente alors que les concentrations de M2 et M3 augmentent. Les concentrations de M1 et M4 sont également réduites d'un facteur de 25 quand Pb ou l'hydrogène interagissent avec la surface pendant la croissance. Nous concluons que M1 et M4 sont reliés, bien que n'étant pas le même centre, et peuvent être associés à une lacune As. M2 et M3 sont des entités différentes, reliées ni à M1 ni à M4.

**Abstract** - We have used DLTS measurements to study the influence of growth conditions on the electron traps designated M1, M2, M3 and M4 which occur in MBE GaAs grown in the temperature range 520°C to 650°C. At an As:Ga ratio of 5:1 the concentrations of M1, M3 and M4 fall by two decades for growth temperatures increasing from 520°C to 650°C, whereas M2 has a more complex behaviour and is the dominant trap in 650°C grown layers. At a fixed growth temperature of 550°C concentrations of M1 and M4 fall with increasing As:Ga ratio whereas concentrations of M2 and M3 increase. The concentrations of M1 and M4 are also reduced by a factor 25 when Pb or hydrogen interact with the surface during growth. We argue that M1 and M4 are related, though not the same centre, and may be associated with As vacancies. M2 and M3 are different entities, neither of them related to M1 nor M4.

**Introduction** - In this paper we report an investigation of the influence of growth conditions on the concentrations of four deep states observed in n-type GaAs grown by molecular beam epitaxy at temperatures above 520°C. The samples were grown in ion pumped systems fitted with vacuum interlocks for sample transfer. The deep states were observed by DLTS capacitance measurements using Al Schottky barrier diodes fabricated on n-on-n<sup>+</sup> epitaxial layers.

Nine different deep states have been reported in the upper half of the band gap in MBE GaAs grown at around 540°C [1]. Our measurements on a large number of samples have shown that four of these states, designated M1, M2, M3 and M4 [1], are found reproducibly in n-type MBE GaAs grown under the appropriate conditions in four different systems, both diffusion pumped and ion pumped and for Sn and Si doping. This paper will concentrate on the behaviour of these four states.

We have measured the emission rates ( $e_n$ ) of M1, M2, M3 and M4 as functions of temperature at low electric fields where there was no detectable shift in DLTS peak position with bias. Making a careful comparison with trap signatures in ref. [2], using only those data on low doped samples where field enhancement of  $e_n$  should be small, we conclude (in common with ref. [1]) that the levels M1 - M4 do not

correspond to levels in electron irradiated material. We also conclude that M1, M3 and M4 do not correspond to known traps in VPE layers. The data for M2 is close to L9 in VPE material [2] and these traps may have a common origin.

We take the view therefore that, with the possible exception of M2, the principal levels in MBE GaAs are characteristic of the growth process, and may take the form of complexes involving chemical impurities [1]. We therefore expect that their concentrations are determined by the surface processes which control the growth of the layer. With this view, we have investigated the influence of growth temperature, As:Ga ratio, As species and adsorbates on the concentrations of the 'M' levels.

Experimental Measurements - The trap concentration,  $N_t$ , was calculated from the amplitude of the voltage transient  $\Delta V_0$  of a constant capacitance DLTS system using the equation

$$N_t = \frac{2 \epsilon \epsilon_0}{e} \frac{\Delta V_0}{\left[ \frac{x_2^2 - x_1^2}{\lambda} \right]}$$

where  $x_1$  and  $x_2$  are the depths below the surface at which the Fermi level  $E_f$  crosses the trap level  $E_t(x)$  during the trap filling period and reverse bias emission period respectively. The distances  $x_1$  and  $x_2$  were calculated as  $x_i = x_{di} - \lambda$  ( $i=1,2$ ) using the measured capacitance during filling and emission at each DLTS peak to give the corresponding depletion depths  $x_{di}$ . The transition region width  $\lambda$  should be calculated using the Gibbs Free Energy of each level, but in the absence of such data for the traps of interest we used the thermal activation energy as the best possible estimate. This will tend to overestimate  $\lambda$ . The trap filling time was long enough to establish steady state conditions. The quoted concentrations are the mean values of measurements on four diodes on each layer.

Figure 1 is a plot of the concentrations of traps M1, M2, M3 and M4 as a function of growth temperature for Sn doped layers grown in a Varian 360 system with an As:Ga ratio of 5:1. The layers were deliberately grown in a random sequence. At 650°C the levels M1, M3 and M4 were not observed above the detection limit of  $10^{13} \text{ cm}^{-3}$  for that sample; only M2 was observed. As the growth temperature was reduced values of  $N_t$  for M1 and M4 increased to about  $10^{15} \text{ cm}^{-3}$  at 520°C. The behaviour of M2 and M3 seems more complex: at 600°C M2 was not detected above the limit of  $5 \times 10^{12} \text{ cm}^{-3}$  whereas at lower temperatures M2 was clearly identified as a shoulder on the larger M1 peak. Lang et al [1] did not find M2 in material grown under As rich conditions at these temperatures.

Values of  $N_t$  as a function of As:Ga ratio at a fixed growth temperature of 550°C are shown in Figure 2. For M1 and M4  $N_t$  fell with increasing As:Ga ratio, whereas for M2 and M3,  $N_t$  increased. At a growth temperature of 650°C only M2 was detected and here  $N_t$  tends to fall with flux ratio such that, at 7:1,  $N_t(\text{M2}) < 2 \times 10^{12} \text{ cm}^{-3}$ .

Further evidence for the influence of surface processes on  $N_t$  is provided by studies of the effects of the arsenic species and adsorbates. We have already shown that growth with  $\text{As}_2$  molecules reduces the trap concentration compared with growth using  $\text{As}_4$  [3]. Figure 3 shows the effect of a flux of Pb or a hydrogen ambient during growth. These layers were grown at 530°C using  $\text{As}_2$  molecules and an As:Ga ratio of 2.5:1; they were doped with Si to give  $n \sim 2 \times 10^{16} \text{ cm}^{-3}$ . With a flux of  $2 \times 10^{15} \text{ Pb atoms cm}^{-2} \text{ s}^{-1}$  the surface reconstruction was changed from the usual As stable (2x4) pattern to a (1x2) pattern, and the concentrations of M1 and M4 were reduced by about a factor 25, though M3 was not strongly affected. No additional traps have been detected by optical DLTS in the lower half of the gap. The Pb flux provides a steady state surface coverage of about 0.1 monolayer [4], and no Pb has been found chemically in the layer above a detection limit of  $5 \times 10^{15} \text{ cm}^{-3}$ . A partial pressure of  $3.5 \times 10^{-6}$  torr of hydrogen during growth produces a similar reduction in trap content although the symmetry of the RHEED pattern is not changed from the usual (2x4) reconstruction. There is, however, a significant increase in the diffuse background intensity of the pattern.

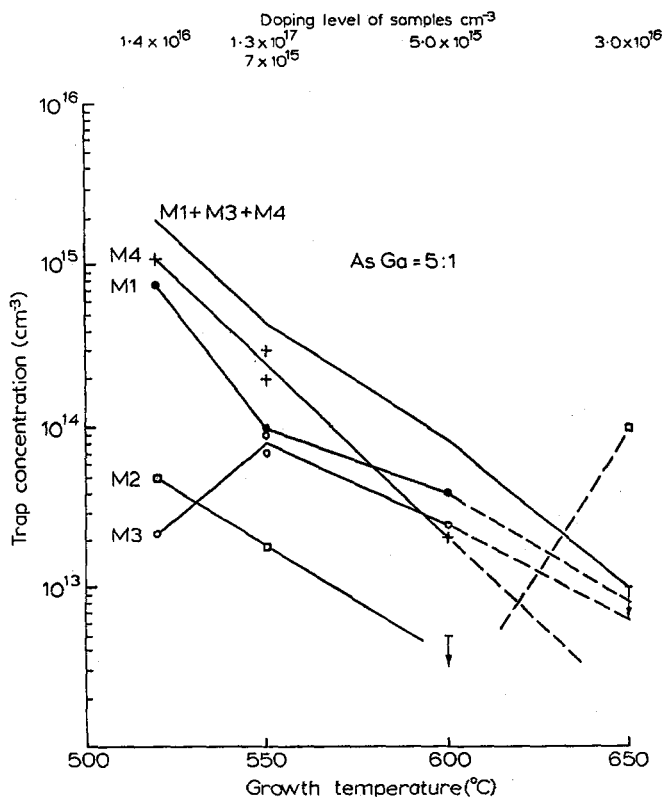


Figure 1 Plot of trap concentrations as a function of growth temperature for Sn doped n-GaAs MBE layers grown with an As:Ga ratio of 5:1. The carrier concentration of each sample is shown at the top of the figure.

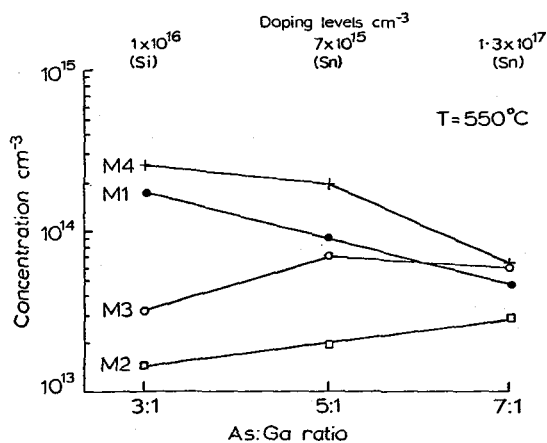


Figure 2 Trap concentration as a function of Ga:As ratio for Sn doped n-GaAs MBE layers grown at 550°C.

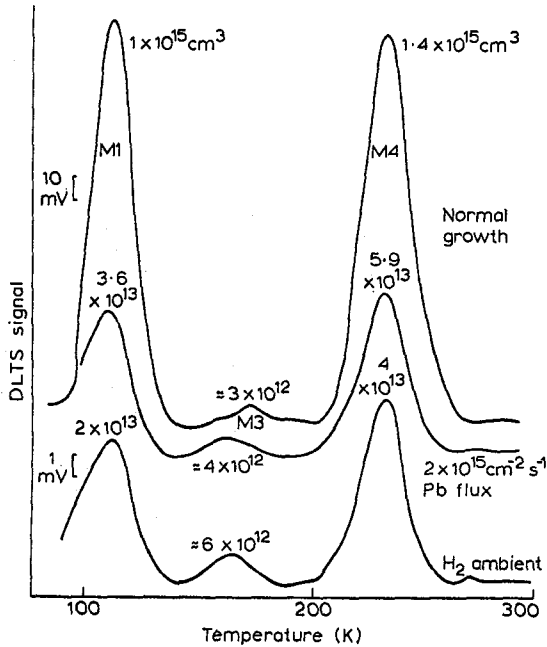


Figure 3 DLTS spectra for Si doped n-GaAs layers grown at 530°C and with an As:Ga ratio of 2.5:1. The upper spectrum is for normal growth, the lower spectra show the effect of Pb and hydrogen adsorbates.

Discussion - First we discuss the behaviour of traps M1 and M4 which both show a reduction in  $N_T$  with increasing As:Ga ratio (figure 2). If we also speculate that the higher trap concentration in As<sub>4</sub> grown layers[3] is related to the higher concentration of unoccupied As surface sites arising from the As<sub>4</sub> pairwise interaction[5] compared to the As<sub>2</sub> dissociative chemisorption process[6] then these two experiments suggest that M1 and M4 are As-vacancy related.

This proposal appears to be at variance with the observed decrease in  $N_T$  with growth temperature (Figure 1) since the surface As vacancy concentration would be expected to increase at higher temperatures for a fixed incident flux. However it may be that the mobility of species on the surface is also an important factor. Alternatively, it has been found that annealing of Si<sub>3</sub>N<sub>4</sub> capped MBE GaAs layers in the temperature range 500°C to 600°C reduces the concentrations of M1 and M4[7], but it is not clear whether a similar bulk annealing process occurs during growth in the presence of excess As. The chemical concentration of some impurities in MBE GaAs decreases with increasing growth temperature[8] so if the deep state centres incorporate such an impurity this effect may also account for the data in Figure 1.

The concentrations of M1 and M4 are reduced by both Pb and hydrogen incident on the crystal surface during growth, although only Pb changes the RHEED pattern symmetry from an As-stable (2x4) reconstruction to a (1x2) pattern. It has also been suggested that Pb reduces the concentration of compensating species in p-type GaInP grown by MBE[9]. Direct chemical interaction of Pb with the defects responsible for M1 and M4 is thought to be unlikely because photoemission spectroscopy shows no

shift of the Ga and As 3d core levels in the presence of Pb, suggesting no significant chemical interaction between Pb and GaAs [10]. It therefore seems probable that the reduction in  $N_t$  for M1 and M4 is a consequence of some modification of the surface processes during growth. However, in view of the behaviour of the RHEED patterns, it is not clear whether Pb and hydrogen effect a reduction in  $N_t$  by the same mechanism, although photoemission experiments do show that both Pb and hydrogen quench emission from dangling As bonds on the (100) GaAs surface [10,11].

It has been suggested that traps observed in MBE GaAs grown at lower temperatures around 300°C are related to antisite As atoms [12]. This is unlikely to be the case for M1 and M4 produced at higher growth temperatures because their concentrations decrease with increasing As:Ga ratio. Our data suggests that M1 and M4 may be As vacancy related. There is certainly considerable evidence to suggest that M1 and M4 are of the same origin: both are influenced by Pb and hydrogen, they show the same dependence on As:Ga ratio, in many of our samples they are present in similar concentrations (see for example the data in Figure 1) and both are influenced by thermal annealing [7]. The capture cross sections ( $\sigma_n$ ) of M1 and M4 are greater than  $10^{-16}$  cm<sup>2</sup> and there is evidence that  $\sigma_n(M1) > \sigma_n(M4)$  (P. Blood, unpublished). It is unlikely therefore that these are two charge states of the same centre because the deeper state (M4) should be the more attractive to electrons and hence have the larger  $\sigma_n$ .

It is more difficult to speculate on the origins of M2 and M3, partly because M2 is present in only a few samples. We do not find that the occurrence of M2 is confined to the Ga-stable growth regime, as suggested by Lang et al [1], although at the growth temperature used in ref. [1] the concentration of M2 in our samples is a decade lower than the other principal traps. However M2 is the only trap observed at high growth temperatures where the surface population of As is small and this is in qualitative agreement with earlier work [1].

Our data suggests therefore that states M1 and M4 are related and that they may involve an As-vacancy though they are not different charge states of the same entity. States M2 and M3 are probably not directly related in view of their different behaviour at high growth temperatures, and they appear not to be related to M1 and M4.

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