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Optical and electrical characterization of thick GaSb buffer layers grown on 2 in GaAs wafers

F. Royo[a], A. Giani[b], F. Pascal-Delannoy[b], L. Gouskov[b], J.P. Malzac[a], J. Camassel[a,*]

[a] *Groupe d'Etude des Semiconducteurs, Université Montpellier II and CNRS, 34095 Montpellier Cedex 5, France*

[b] *Centre d'Electronique de Montpellier, Université Montpellier II and CNRS, 34095 Montpellier Cedex 5, France*

Abstract

We have investigated the growth of thick, highly uniform GaSb buffer layers on 2 in GaAs substrates. We have found that ramping the temperature under an arsine flux optimizes the switching sequence between GaAs and GaSb. In this case, the large (about 8%) lattice mismatch which separates the Ga–As and Ga–Sb bond lengths is abruptly relaxed, and good quality GaSb can be homogeneously deposited. On such samples, the photoluminescence signal ranks as well (or even better) as that obtained for comparative homoepitaxial material; also, the electrical properties are among the best ever reported for GaSb grown by metal-organic chemical vapor deposition on GaAs.

Keywords: Gallium antimonide; Epitaxy of thin films; Optical properties; Electrical measurements

1. Introduction

GaSb and the related family of ternary compounds GaAsSb, GaAlSb and GaInSb are of special interest for optical device applications working in the wavelength range of 1.55 μm or longer [1]. At 2 K, the bandgap energy of bulk GaSb is 810 meV [2], while the three-dimensional bandgap of InGaAs at low temperature lattice-matched to InP is 812 meV [3]. The radiative efficiency is also very high and, for a long time, the continuous wave (CW) laser action of current-injected GaSb/AlSb multi quantum well (MQW) diodes has been reported [4]. However, the potential development of antimonide-based devices has been stopped by the technical difficulty encountered in solving two major problems. One problem is to control the residual (p-type) doping level; the other problem is depositing large areas of high quality, epitaxial material [5–9]. This is particularly true in the case of GaSb/GaAs.

The heteroepitaxial growth of GaSb on GaAs substrates has been attempted many times [5,7–11]. However, because of the very strong lattice mismatch (about 8%) which separates the two material systems, the experimental situation is very difficult. In fact, it is very close to the situation encountered in the case of SiC/Si, where there also exists a very large difference (23%) between the Si–Si and Si–C bond lengths [12]. In both cases, a large number of defects are generated at the lower interface and, even if most of them relax as a function of the film thickness, a large density remains present in the bulk of the sample. As a consequence, all attempts to deposit heteroepitaxial layers of GaSb on GaAs (similar to SiC on Si)—even if a low level of residual doping could be achieved—always result in a lower quality material as compared with the material homoepitaxially deposited on GaSb [5,8]. Basically, the same thing happens in the case of 3C–SiC deposited on Si with respect to 3C–SiC deposited on 6H–SiC [13].

In this work, we show that the heteroepitaxial growth of thick, high quality GaSb buffer layers can be achieved on 2 in GaAs substrates without noticeable residual strain. This is because, provided the GaAs surface has been stabilized under an arsine flux, the lower interface is abrupt and the 8 per cent lattice mismatch relaxes in the first few monolayers. As a consequence, there is no evidence of dislocations

*Corresponding author.

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propagating in the bulk of the GaSb material, and the photoluminescence signal ranks as well as (or even better than) the signal obtained with comparative homoepitaxial samples. The X-ray spectra are as narrow as those collected for the GaAs substrate and the electrical properties are very satisfactory.

2. Experimental details

2.1. Epitaxial growth conditions

All epitaxial material investigated in this work has been grown in a metal-organic chemical vapor deposition (MOCVD) prototype reactor (Semco Engineering, Montpellier) using TMG (tri-methyl-gallium) and TMSb (tri-methyl-antimony) precursors. The organo-metallic sources were respectively kept at 0 °C and −10 °C. The reactor design follows the path previously described by Mason and Walker [7,9], and uses a horizontal silica cell operating at 700 torr with two separate lines to introduce the group III and group V elements into the cell through a calibrated mixing orifice.

Most substrates were 2 in semi-insulating (SI) ⟨100⟩ GaAs. They were deposited on a 2 in Mo disc recessed into the top of a rectangular graphite susceptor heated by r.f. induction. To compare heteroepitaxial and homoepitaxial material, Te-doped ⟨100⟩ GaSb substrates were also used.

All the GaSb layers investigated in this work were deposited under a hydrogen flow of 14 l min^{-1} at 600 °C, using a V/III ratio of 1.5 and a TMG partial pressure of 0.5×10^{-4} atm. The resulting growth rate was 2.6 $\mu m\, h^{-1}$.

2.2. Electrical and optical measurements

Hall measurements were carried out in the temperature range 80–300 K, using conventional (mesa-etched) Van der Pauw structures. The optical spectra were obtained at pumped liquid helium temperature (2 K) to achieve a minimum line width. Experimental values of the order of 0.3–0.4 meV have been reported in the literature for high quality homoepitaxial samples grown by liquid phase epitaxy (LPE) [2,14]. Up to now, these data remain unmatched and, to the best of our knowledge, no similar results could be found for material grown by MOCVD or molecular beam epitaxy (MBE) [5,6,8].

To obtain information about the in-depth stress and homogeneity of our materials, we collected both photoluminescence (PL) and transmission spectra. In the first case (PL), we used a low power (5 mW) He–Ne laser focused to a diameter of about 350 μm. This gave an excitation power density of about 5 W cm^{-2}. It is typical of most spectra collected for high quality GaSb material [2,4,7]. In the second case (transmission), a broad spectrum from a tungsten–halogen lamp was shone on the sample. The transmitted light was then focused on the entrance slit of the spectrometer. In both cases, we used a 0.75 m HRS2 grating spectrometer from Jobin-Yvon ISA. The detector was a Ge photodiode from Applied Detector Corp., cooled to liquid nitrogen temperature. Conventional lock-in detection techniques were used.

3. Results and discussion

A constant problem when using GaAs substrates is that it is necessary simultaneously to prevent surface erosion and to optimize the transition region. To this end, we investigated two different approaches. In the first case, the substrate was kept under TMSb, up to 680 °C, and then annealed for 5 min before starting the growth. The idea was to initiate a very thin and very defective transition layer similar to the so-called carbonization layer used in the case of SiC/Si [12]. In the second case, the same temperature ramp was used but the surface was kept under a flow with 1% AsH_3 in H_2. In both cases, as soon as the temperature was lowered to 600 °C, the growth started.

Fig. 1 displays a comparison of transmission spectra collected at 2 K on two nominally identical samples grown using the two different procedures. Except for slight differences in thickness (3.5 and 3.0 μm respectively), which can be found from the series of interference fringes resolved at low energy, the most striking feature comes from the difference in line shapes. In the first case (annealing under arsine), a clear excitonic feature is resolved at 810 meV. This is the well-known signature of the $n = 1$ free-exciton state which has been resolved for a long time for bulk GaSb samples [2]. Nothing similar appears in the second case. The band edge is broad and characteristic of strained material. This means that ramping the temperature under arsine and then initiating the growth results in a more abrupt interface region (i.e. a better quality free-standing layer with almost no strain incorporated into the material). In this case, the overall quality was as good as for bulk GaSb, and a satisfactory luminescence intensity could be found. In the second case (annealing under TMSb), there is much more initial coupling between the GaAs wafer and the GaSb epilayer. As a consequence, one has to accommodate a larger strain. Of course, it does vary from about 8% at the bottom of the transition layer (lower interface) to about 0% after a few hundred nanometers, but this generates a large number of dislocations. Depending on whether they propagate deeply into the epitaxial layer or not, one should find

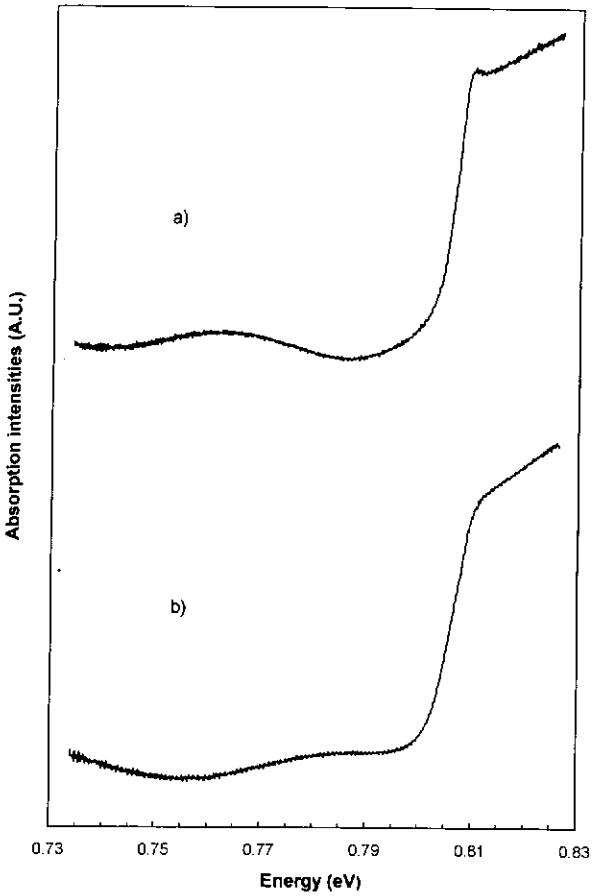

Fig. 1. Comparison of absorption spectra collected at 2 K in the case of two nominally identical layers of GaSb deposited on GaAs substrates. Only the switching sequence between the substrate passivation and the epitaxial layer deposition was changed: (a) 1% arsine in hydrogen; GaSb/AsH_3/GaAs, $e = 3.5$ μm; (b) TMSb; GaSb/TMSb/GaAs, $e = 3$ μm.

more or less luminescence. In the particular case of the sample 3 μm thick in Fig. 1(b), no PL intensity could be found.

Using our optimized growth procedure, we grew several layers with different thicknesses, and investigated the electrical properties. They varied slightly from run to run but, every time, ranked very well. Our best results were obtained on a rather thin film (about 2.5 μm thick) and corresponded to the following values:

$p_{300\,K} = 1.1 \times 10^{16}$ cm^{-3} $\quad \mu_{300\,K} = 910$ cm^2 V^{-1} s^{-1}

$p_{77\,K} = 3.5 \times 10^{15}$ cm^{-3} $\quad \mu_{77\,K} = 5500$ cm^2 V^{-1} s^{-1}

Because these experimental data compared well with the most recent literature (see, for instance, Refs. [9–11] for a review of the heteroepitaxial deposition of GaSb/GaAs using both MOCVD and MBE growth techniques), we attempted to deposit a thick GaSb buffer layer on a full size 2 in wafer. After deposition, the wafer was cleaved and 45 different pieces were

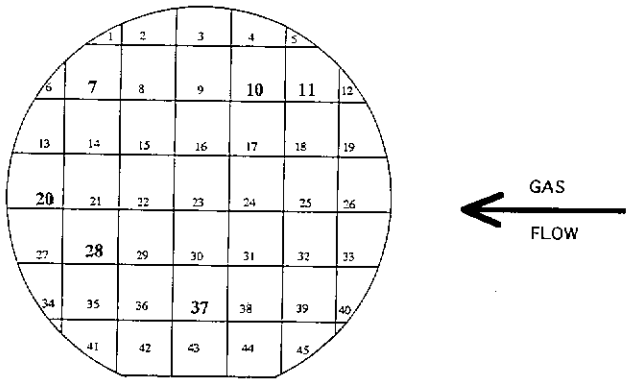

Fig. 2. Schematic cleavage map of the 2 in heteroepitaxial GaSb/GaAs sample investigated in this work (see text).

obtained. For convenience, they have been schematically drawn in Fig. 2.

For pieces 7 and 11, X-ray spectra have been obtained. Using the Cu 1.54 Å line as incident radiation and collecting standard {400} reflections, we could simultaneously probe the GaAs substrate and the GaSb epilayer. A typical example is shown in Fig. 3. Two points should be noticed. First, there is a large difference in the diffracted intensities (factor of 20), which originates from the two different cubic systems. This indicates a large ratio of the epitaxial thickness with respect to the X-ray absorption length. Secondly, the very small change in line width (if any) which appears between the two diffracted spectra indicates very similar crystalline qualities. Remember that essentially two mechanisms contribute to the experimental broadening of the X-ray data. One mechanism is the flucutation of the lattice constant, as induced by local (residual) strain. The second mechanism is imperfect two-dimensional growth. Resulting in stacking faults at the coalescence of two neighboring islands, this broadening reduces the coherence length and, of course, spreads the full width at half-maximum (FWHM) of the X-ray spectra. Our experimental results establish that there is almost no significant difference in the FWHM between the GaAs substrate and the GaSb epilayer.

For pieces 10, 20 and 37, transmission measurements have been carried out. They all display sharp $n = 1$ excitonic features at 810 meV (see Fig. 4) and, except for small changes in the interference patterns, no specific dependence on the relative position of the sample on the 2 in wafer could be found. Such a satisfactory homogeneity of the optical response indicates good in-plane homogeneity of the crystalline quality.

Returning to the interference patterns, we computed 8.7, 10.2 and 8.8 μm for the thicknesses of the layers deposited on samples 10, 20 and 37 respectively. From the results collected for pieces 10 and 37, we deduce a satisfactory lateral uniformity. This is no longer true

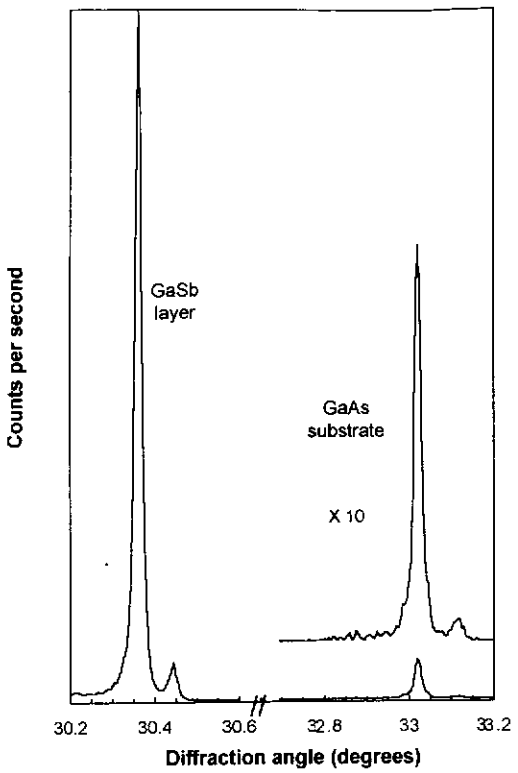

Fig. 3. X-ray diffraction spectra obtained for sample 7. Notice the similar line width of spectra corresponding to the hetero-epitaxial layer (GaSb) and the GaAs substrate.

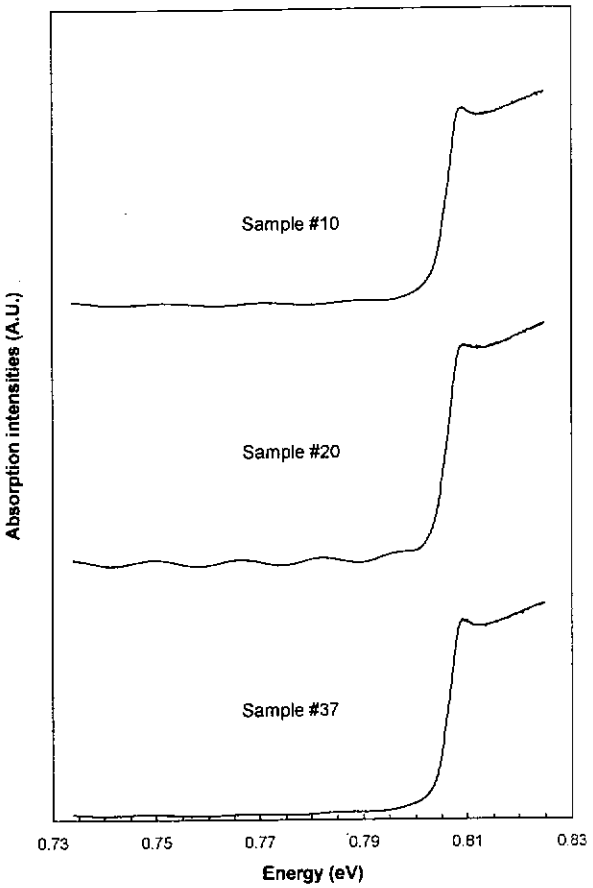

Fig. 4. Comparison of absorption spectra for GaSb/AsH_3/GaAs collected at 2 K for samples 10 ($e = 8.7\ \mu$m), 20 ($e = 10.2\ \mu$m) and 37 ($e = 8.8\ \mu$m).

when looking along the gas flow direction. Indeed, comparing the average thicknesses of samples 10 and 37 with that deduced for sample 20, we find a difference of about 20%. This reveals the existence of a finite (positive) thickness gradient along the gas flow direction, which arises because the temperature was not homogeneous enough and, in fact, slightly increased as the gas flow propagated.

Finally, a quick check of the electrical properties was carried out for sample 28. From this preliminary series of data, we find

$$p_{300\,K} = 1.8 \times 10^{16}\ cm^{-3} \qquad \mu_{300\,K} = 960\ cm^2\ V^{-1}\ s^{-1}$$

$$p_{77\,K} = 5.6 \times 10^{15}\ cm^{-3} \qquad \mu_{77\,K} = 5700\ cm^2\ V^{-1}\ s^{-1}$$

Compared with our (previous) best quality material ($\mu_{77\,K} = 5500\ cm^2\ V^{-1}\ s^{-1}$), this ranks as good or even better. The free carrier concentration appears to be slightly higher than previously found, but the mobility is also (slightly) increased. This suggests a lower compensation ratio. Low temperature experiments are in progress to clarify this point but, already, comparing these results with those previously reported for GaSb deposited on 2 in GaAs substrates [7–9], they rank very highly.

The most striking point comes when checking the luminescence intensity collected for our heteroepitaxial material with respect to the homoepitaxial material. The results are shown in Figs. 5(a) and 5(b). First, is the luminescence spectrum collected for piece 20 (hetero-epitaxy) and, secondly, that collected for a control sample (homoepitaxy) grown during the same run. To minimize the effect of growth inhomogeneities, both pieces were positioned as close together as possible on the susceptor. The striking feature in this case is that we find more luminescence intensity for the hetero-epitaxial GaSb/GaAs sample than we find for the homoepitaxial GaSb/GaSb sample. The intensity ratio is only 1.5/1 but is qualitatively opposite to all experimental findings reported up to now (about 1/10 in Ref. [8]).

For the assignment of the PL lines, as usual, both spectra are dominated by strong bound exciton (BE) features. Weak longitudinal optic (LO) phonon replicas, shifted by about 29 meV, appear at lower energies [2,4,7]. In between are small, free to band (conduction band to acceptor) transitions or the A line.

It has already been noticed many times that the relative intensity of BE to A lines is an index of the electrical quality [2,8]. The higher the electrical quality is, the smaller is the A line relative to the BE line. In this respect, our material again ranks very well.

The nature of acceptors involved in the BE lines is unclear. Four lines, referred to as BE1–BE4 in the standard literature, have been identified. All range from 796 to 805 meV [4] but correspond to unidentified defects. The main point is that their relative intensities depend first on the growth technique and, secondly, on the growth conditions. For bulk GaSb grown with excess Sb, one expects from LPE data [2,14] that BE4 at 796 meV will be the most important line. This correlates well with our experimental findings. Using a V/III ratio of 1.5, we resolve the main line at 796 meV in Fig. 5(b).

For the spectrum collected for sample 20 (Fig. 5(a)), we find results qualitatively similar to those reported in Ref. [8]: the overall spectrum looks to be red-shifted. From the energy position of the A and BE–LO lines, we deduce an energy shift of about 3.5 meV. This comes probably from the difference in thermal expansion coefficients between GaSb and GaAs. Returning to the experimental (strained) energy position of the BE line (792.5 meV), we deduce a relaxed line (at 796 meV), which again seems to indicate a BE4 assignment.

Finally, for the experimental line width, in both Figs. 5(a) and 5(b), we notice an FWHM of about 3.0 meV for the main BE lines. This is still very large and, as usual, is much larger than the best value reported for the best epitaxial material [2,14].

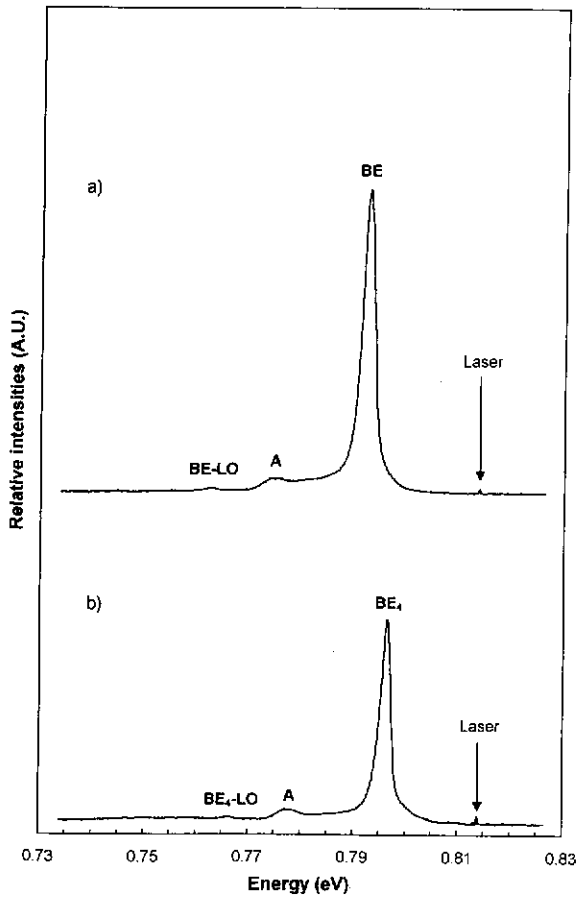

Fig. 5. (a) PL intensity collected at 2 K for sample 20, i.e. heteroepitaxial GaSb/AsH_3/GaAs; (b) homoepitaxial GaSb/AsH_3/GaSb sample grown during the same run (see text).

4. Conclusions

We have shown that high quality buffer layers of GaSb could be grown on 2 in GaAs wafers. The optical, electrical and X-ray data were very satisfactory and, in contrast to all experimental findings reported up to now, the luminescence intensity collected for our heteroepitaxial material was larger than that collected for a control (homoepitaxial) sample deposited during the same run.

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