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# GaAs/GaSb strained-layer heterostructures deposited by metalorganic vapor phase epitaxy

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The growth of strained GaSb/GaAs quantum wells has been attempted for the first time (7% lattice mismatch), with the antimonide layers being constrained to take on the GaAs lattice parameter in the interface plane. The critical thickness for pseudomorphic growth of the strained layer was about 15 Å, with further growth resulting in islands of GaSb crystallites over the wafer surface. Photoluminescence spectra and photoconductivity from both single and double wells showed a strong signal at approximately 1.3 eV, identified as a Γ point transition. This was not consistent with band structure calculations for a GaSb/GaAs well, suggesting an error in the estimation of the band offsets and/or As incorporation in the strained layer.

GaSb has a band gap of 1.6 $\mu$m making it potentially suitable for use in fiberoptic devices. Lasers and photoconductive detectors have already been fabricated from GaSb/$GaAs_{1-x}Sb_x$ by molecular beam epitaxy (MBE).[1] Adjustments can be made to the operating wavelength of such devices by several means, for example, by altering the width of the active layer, changing its composition, or straining the layer to change its band structure. In this letter we consider a particularly extreme case of the latter situation. The growth of GaAs/GaSb heterostructures was attempted in which the GaSb was constrained to take on the GaAs lattice parameter in the plane of the interface (7% mismatch). The accompanying tetragonal distortion increases the lattice parameter perpendicular to the interface. A radical change in the GaSb band structure results[2-5] and the experimental data will be discussed in the light of band diagram calculations.

Growth of these structures was by metalorganic vapor phase epitaxy (MOVPE) at atmospheric pressure and 600 °C from TMGa, TMSb, and $AsH_3$ starting materials. (100) GaAs substrates, cut 2° off towards ⟨110⟩, were used. Prior to fabricating strained-layer structures, the deposition of the constituent bulk materials was optimized and these conditions were then used for strained-layer growth. The growth conditions and characteristics of the bulk MOVPE GaSb have been reported in detail elsewhere.[6,7] Characterization was by transmission electron microscopy (TEM), photoconductivity (PC), and photoluminescence (PL) experiments.

Despite the large lattice mismatch, it appeared that thin strained single quantum wells (SQWs) of GaSb could be deposited in GaAs. Under the conditions used for bulk growth, 15 Å was the limiting thickness for pseudomorphic growth. Increasing the growth time (beyond about 1 s) did not yield a thicker strained layer but resulted in a 15 Å strained layer interspersed with islands of elastically relaxed GaSb. For example, Fig. 1(a) shows a cross-sectional TEM micrograph of sample 243, a SQW with 10 s GaSb growth time (see Table I). A region of strained GaSb and an example of island growth can be seen (left). The microcrystallites (which form the islands) are about 300 Å thick and are associated with misfit dislocations. Figure 1(b) shows a plan view of sample 269 (2 s GaSb growth) with islands of GaSb about 180 nm in diameter distributed over the surface. At higher magnification, moiré fringes can be seen on the islands and the separation of these (27 Å when imaging in the 220 dark field mode) corresponds closely to that expected for unstrained GaSb on GaAs.

PC measurements were made at 4 K on a series of SQWs fabricated using different GaSb growth times. These all showed a strong onset for the signal at about 1.3 eV and a weaker one starting at about 1.0 eV [Fig. 2(b)]. Both of these are well below the GaAs band gap of 1.52 eV and considerably above the unstrained GaSb band gap of 0.81 eV. A very strong peak was also seen in the PL spectrum at an

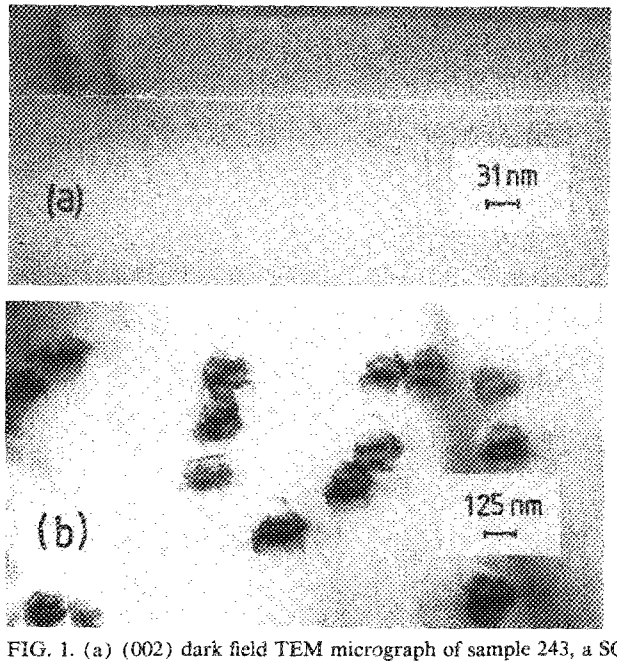


FIG. 1. (a) (002) dark field TEM micrograph of sample 243, a SQW of GaSb in GaAs (10 s GaSb growth). The area of island growth (left) is about 300 Å thick and the strained layer 15 Å thick. (b) Plan-view (002) bright field micrograph of sample 269, a SQW with 2 s GaSb growth time. Islands of elastically relaxed GaSb ~180 $\mu$m across can be seen.

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TABLE I. Summary of the structures studied and their PL peak energies.

| Run No. | Structure | GaSb growth time (s) | GaAs barrier width (Å) | PL peak energies (eV) | |
|---|---|---|---|---|---|
| 334 | SQW | 1 | ··· | 1.398 | |
| 269 | SQW | 2 | ··· | 1.292 | |
| 242 | SQW | 5 | ··· | 1.318 | |
| 243 | SQW | 10 | ··· | 1.289 | |
| 250 | SQW | 20 | ··· | 1.284 | |
| 251 | SQW | 30 | ··· | 1.307 | |
| 252 | SQW | 60 | ··· | 1.389 | |
| 253 | SQW | 120 | ··· | 1.417 | |
| 351 | DQW | 2 | 25 | 1.263 | 0.972 |
| 352 | DQW | 2 | 50 | 1.283 | 0.990 |
| 353 | DQW | 2 | 100 | 1.256 | 1.007 |
| 354 | DQW | 2 | 200 | 1.280 | 0.933 |

energy corresponding to the strong PC onset around 1.3 eV [Fig. 2(a)]. The peak energy varied by $\pm$ 50 meV from sample to sample, showing some correlation with GaSb growth time (see Table I). The intensity of this luminescence was several times greater than that seen from the bulk GaAs. None of the SQWs showed PL corresponding to the weak PC onset at 1.0 eV. However, in a series of double quantum wells (DQWs) with 2 s GaSb growth, the PL also showed a weak, broad signal at about 1.0 eV ( $\pm$ 80 meV sample to sample variation). Otherwise, these structures showed qualitatively the same PL and PC features as the SQWs (see Table I).

In the antimonide layer, the strain is compressive in the (100) plane and tensional in the [100] direction. The resulting change in the band structure can be calculated using deformation potential theory.[3–5] Qualitatively, lattice mismatch induced strain affects the direct gap of a III-V semiconductor in the following way: the conduction band $\Gamma_c$ moves up in energy relative to the valence band $\Gamma_v$, and the latter splits as the degeneracy of the $m_j = 3/2$ and $m_j = 1/2$ levels is lifted. Calculations for GaSb under 7% strain (after 3 and 4) show the resulting direct gap energies to be $E_g^{3/2} = 1.20$ eV and $E_g^{1/2} = 1.55$ eV, respectively.

The indirect energy gaps also change under strain. In particular, the hydrostatic pressure causes the $X$ minima in the GaSb conduction band ($X_c$) to fall slightly in energy, with the measured pressure coefficient being $-1.5$ meV/kbar.[2] They are then split by the [100] uniaxial compression component of the stress; the [100] valley is raised and the [010] and [001] valleys are lowered in energy. The drop in energy of these two valleys is given by

$$X_c = -1/3[\Xi_u(C_{11} + C_{12})E/C_{11}],$$

where $C_{11}$ and $C_{12}$ are elastic constants, $E$ is the strain, and $\Xi_u$ is the appropriate deformation potential. Calculations using the pressure coefficient data from Ref. 2 and an estimated value of 8.5 eV for $\Xi_u$ indicate that, under 7% strain, the smallest GaSb energy gap is indirect at the $X$ point. [The $L$ conduction-band minima $L_c$ rise in energy with hydrostatic stress, with the pressure coefficient being 5 meV/kbar.[2] This puts $L_c$ between $X_c$ and $\Gamma_c$ in energy.]

The GaAs/GaSb band offsets have been estimated using the model-solid theory of Van de Walle and Martin,[5] which includes the influence of strain. It predicts that most of the offset occurs in the valence bands. From the above calculations, the band diagram for a single layer of GaSb in GaAs was constructed. Figures 3(a) and 3(b) show the direct gap and indirect gap band structure, respectively. The principal features are that the GaSb forms a hole well and an electron barrier at the $\Gamma$ point with the lowest conduction-band minimum $X_c$ located only slightly above $\Gamma_c$ in GaAs. It is important to note that there are uncertainties in several of the parameters used and errors on the band energy positions could easily be 200 meV or more. For example, $\Xi_u$ for GaSb is not well known; the value of 8.5 eV was taken as this is the approximate value in Si and a number of III-V compounds.[8] In addition, the description of the bands as $X$, $L$, and $\Gamma$ may not be a good one for such thin layers and it is possible that the deformation potential approximations break down at such extreme values of lattice distortion.

The effect of the large strain in the GaSb layer is to transform a narrow, direct gap material into a larger, indirect gap material. Because the valence-band offsets in Sb/As systems are also large, the GaSb acts as an electron barrier. It is thus emulating the properties of AlAs. This opens up a variety of possibilities for the fabrication of superlattices and tunneling structures made without Al in the system, thus

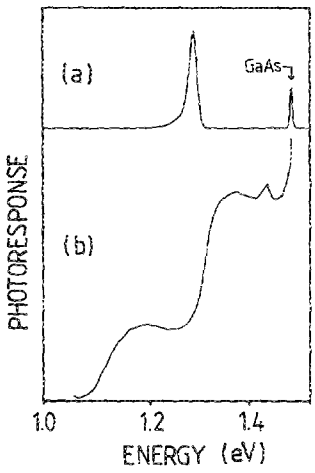


FIG. 2. (a) Photoconductivity at 4 K of sample 269, a SQW of GaSb (15 Å) in GaAs. (b) PL spectrum at 4 K of sample 269.

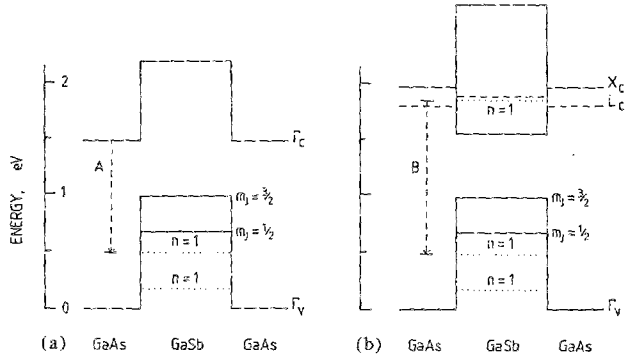


FIG. 3. (a) Direct gap band structure ($\Gamma$ point), (b) indirect gap band structure ($X_c$ and $L_c$) for a GaAs/GaSb quantum well. Dotted lines indicate subbands.

avoiding many growth problems associated with this hydrophilic element.

Considering the PL and PC results of Fig. 2 in conjunction with the band diagram in Fig. 3, it seems highly unlikely that the photoresponse at 1.3 and 1.0 eV is due to the direct transitions in GaSb, $E_g^{3/2}$ and $E_g^{1/2}$. On first inspection it appears that a transition indirect in $k$ space from the GaSb $X_c \rightarrow \Gamma_v$ ($m_j = 3/2$) would be the most likely assignment for the high-energy (1.3 eV) peak [Fig. 3(b), transition $B$]. However, pressure-dependent PL revealed a high pressure coefficient for this transition ($\sim 10$ meV/kbar)[9] implying that it occurs at the $\Gamma$ point, i.e., that it is transition $A$ in Fig. 3, resulting from penetration of the electron wave function in the GaAs conduction band into the thin GaSb barriers. However, the calculated energy of transition $A$ is only $\sim 0.75$ eV, well below the measured value of 1.3 eV. Therefore, the band diagram in Fig. 3 does not accurately represent our structures. While some error may arise in the band offsets, it is also possible that As has been incorporated into the GaSb, significantly changing the band structure. It has previously been reported that attempts to grow highly strained InAs/GaAs quantum wells resulted in diffusion of some Ga into the InAs giving InGaAs/GaAs structures.[10] The effect of a similar phenomenon occurring in GaSb/GaAs would be to increase the type II spatially indirect gap (GaAs $\Gamma_c \rightarrow$GaSb $\Gamma_v$) and also the $k$-space indirect gap. If the discrepancy between calculation and experiment were entirely due to As uniformly distributed throughout the strained layer, the As content of this layer could be as high as 50%. However, there may be a gradation from GaAs to GaSb altering the quantum well shape and reducing the amount of As needed to produce the increased energy of transition $A$. Variation in both the thickness and the precise composition of the strained layer might also account for the slightly varying PL peak energies. No explanation has yet been found for the weaker 1.0 eV signal seen more strongly in the DQWs. However, it may be a defect or impurity related transition.

In summary, attempts to grow GaSb quantum wells in GaAs under the conditions used for bulk growth resulted in a strained layer of 15 Å before the onset of dislocations. After this, islands of three-dimensional crystals formed preferentially at dislocation sites. Calculations showed that under 7% strain the GaSb direct gap increases to 1.2 eV and the light and heavy hole valence bands are split by about 0.35 eV. As most of the band offset between GaSb and GaAs occurs in the valence bands, GaSb forms an electron barrier in GaAs at the $\Gamma$ point. The $X_c$ minima fall slightly in energy as a result of the hydrostatic pressure and have a large splitting caused by the uniaxial component of the stress. The band gap becomes indirect at the $X$ point (0.5 eV). PL and PC both showed a strong signal at $\approx 1.3$ eV, which was shown to be a $\Gamma$ point transition. This must therefore be indirect in real space, from the GaAs conduction band to the GaSb valence band. The calculated energy of this transition for a GaSb/GaAs well does not coincide with the observed energy. However, some combination of an error in the band offsets and/or As incorporation into the GaSb could account for the discrepancy. Further experimental evidence is needed to elucidate the exact composition of the strained layer.

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