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LIQUID-PHASE EPITAXY OF In(As, Sb) ON GaSb SUBSTRATES USING ANTIMONY-RICH MELTS

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NOTATION

Δa	Lattice mismatch with $\Delta a = a_L - a_S/a_S \times 10^6$ ppm, where a_S is the lattice parameter of the substrate and a_L is the relaxed lattice parameter of the epitaxial material.
$\Delta a^{R.T.}$	Lattice mismatch existing at room temperature.
k_{Ga} and k_{Sb}	Segregation coefficients of gallium and antimony, respectively.

INTRODUCTION

The solid solution In(As, Sb) is an important material for opto-electronic devices operating at mid-infrared wavelengths (3–5 μm). High-performance diodes in $InAs_{0.84}Sb_{0.16}$ grown on InAs substrates by liquid-phase epitaxy (LPE) using a multilayer step grading technique[1] have been fabricated, but show narrow-band response when backside-illuminated owing to absorption in the graded layers[2]. To simplify the growth procedure and to provide broader response it is preferable to grow a lattice-matched ternary directly onto a binary substrate of larger band gap. Gallium antimonide is a suitable substrate for In(As, Sb) as its band gap E_g is 0.73 eV at 77 K and its lattice constant matches that of $InAs_{0.91}Sb_{0.09}$ at room temperature (E_g for $InAs_{0.91}Sb_{0.09}$ is 0.33 eV at 77 K).

Attempts to grow the ternary on GaSb from In-rich melts result in rapid dissolution of the substrate followed by polycrystalline regrowth if conventional LPE conditions are used, i.e. small supercooling of the melt or two-phase solution growth. The only method which has successfully prevented substrate erosion relies on the production of a state of extreme supersaturation at the melt–substrate interface[3]. This technique involves maintaining a large temperature difference ($\geqslant 20°C$) between the melt and substrate prior to their contact and results in rapid initial growth. As many semiconductor devices require thin (submicron) epitaxial layers, fast growth rates are undesirable and an alternative method of controlling erosion of GaSb substrates by In–As–Sb melts is needed.

The phase diagram of the In–As–Sb system[4] indicates that the lattice-matched solid $InAs_{0.91}Sb_{0.09}$ might be growth from either indium-rich or antimony-rich solutions at similar temperatures. As previous workers[5] have suggested that antimony from the GaSb substrate is preferentially dissolved by In-rich melts, epitaxy during this work was carried out using Sb-rich melts in order to reduce the severity of substrate dissolution.

EXPERIMENTAL WORK

Melt compositions used in our experiments were close to points A, B, and C marked in Fig. 1. The calculated iso (solid concentration) line indicates the melt compositions which are in equilibrium with the lattice matched ternary $InAs_{0.91}Sb_{0.09}$.

Crystal growth was carried out in a high-purity graphite boat of the horizontal sliding-carriage type in an atmosphere of Pd/Ag-diffused hydrogen. The (100) GaSb substrates were Siton polished and given a final etch in HF(aq.) : HNO_3(aq.) : HCl(aq.), in the proportions 2 : 1 : 50 by volume, prior to their introduction into the LPE apparatus. The melt was prepared by placing the appropriate amounts of 99.9999% In, Sb, and polycrystalline InAs into the graphite boat. The liquidus temperature of each new melt was determined to within $\pm 1°C$ and growth was initiated by imposing a supercooling of 3°C on the melt before moving it over the substrate.

Initial experiments (close to point A in Fig. 1) gave rise to sharp substrate-layer interfaces but when assessed by multiple beam X-ray diffraction the layers were found to have large positive mismatches ($\Delta a \sim$ 3000 ppm) at room temperature. Electron microprobe analysis confirmed that the layers were deficient with respect to arsenic. Increasing the proportion of arsenic in the melt, while retaining a constant atomic fraction of indium X^l_{In}, reduced the degree of mismatch but produced uneven substrate-layer interfaces and, in some cases, polycrystalline regrowth. Experimental results indicated that the proportion of antimony in the melt was no longer sufficient to prevent substrate erosion and so further work was carried out using melts with lower values of X^l_{In}, i.e. compositions close to points B and C in Fig. 1.

New melts allowed growth of layers with mismatches as low as 500 ppm although substrate erosion became increasingly severe as $\Delta a^{R.T.}$ fell below 1400 ppm. Use of melts with X^l_{In} lower than 0.200 was prevented by the position of the antimony eutectic. The growth rates of epitaxial layers grown from antimony-rich melts were found to be about 1.5 μm/min and the approach towards the lattice matching condition, along with the liquidus temperatures of the melts used in this work, are shown in Fig. 2.

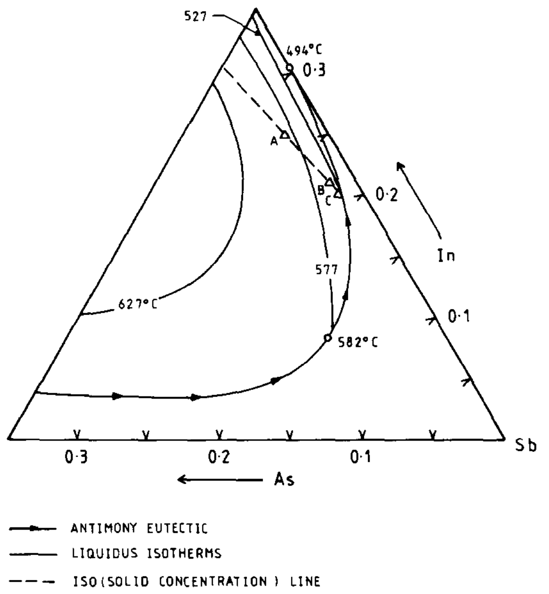

Fig. 1. The antimony corner of the In–As–Sb phase diagram.

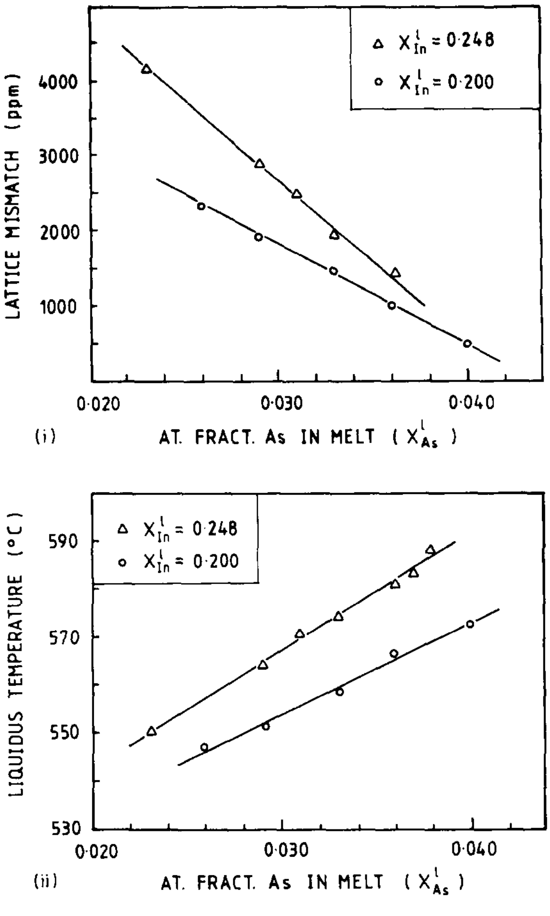

Fig. 2. Dependence of (i) lattice mismatch between In(As, Sb) layers and GaSb substrates, and (ii) liquidus temperature of the melt, on the composition of antimony-rich growth melts.

DISCUSSION

Erosion of GaSb substrates by In–As–Sb melts is suppressed by the use of antimony-rich growth solutions. Successful growth at controllable rates of positively mismatched layers has been demonstrated. As the antimony content of the melt was reduced in order to approach the room temperature lattice-matching condition more closely, erosion of the substrate increased. In order to maximise the atomic fraction of antimony in the melt, the proportion of indium in the melt was reduced to its minimum value of 0.200. Further reduction of X^l_{In} and so growth of the solid solution $InAs_{0.91}Sb_{0.09}$, which would be lattice matched to GaSb at room temperature, was prevented by the position of the antimony eutectic.

It is important to note that in the In(As, Sb)/GaAs system there is a large difference between the thermal expansion coefficients of the substrate and layer. The linear expansion coefficients of GaSb and $InAs_{0.91}Sb_{0.09}$ are 6.9×10^{-6} deg^{-1} and 4.5×10^{-6} deg^{-1}, respectively[6]. This implies that layers which are matched to GaSb at the growth temperature (~ 550°C) are positively mismatched by 1200 ppm at room temperature. Epitaxial layers grown during this work displayed cross-hatching when $\Delta a^{R.T.} \geqslant$ 1400 ppm and the residual strain present in these structures would make them unsuitable for device processing. On the other hand, when $\Delta a^{R.T.} \leqslant 1400$ ppm the lattice mismatch existing at the growth temperature would be close to zero or negative and substrate erosion was found to occur.

The erosion of GaSb substrates by In–As–Sb melts may be explained in terms of the solid–liquid interface relaxation model proposed by Bolkhovityanov[7]. It is well known that thermodynamic solid–liquid equilibrium in multi-component systems requires the equality of pressure, temperature, and chemical potential of every component in each phase considered (Gibbs). It therefore follows that a non-equilibrium system is created every time a hetero-LPE growth is attempted simply because hetero-epitaxy is the growth of one substance upon another. The zeroth law of thermodynamics guarantees that after contact has been made the system will relax in the direction of the final equilibrium state.

If the substrate and intended layer are lattice mismatched at the growth temperature, relaxation is controlled by three criteria which determine whether the system is stable (no erosion) or unstable (erosion of the substrate takes place). These criteria are

(i) the sign of the initial lattice mismatch at the growth temperature;
(ii) the effect of substrate dissolution on the absolute magnitude of the lattice mismatch;
(iii) the effect of substrate dissolution on the solubility of the substrate group *V* component in the adjacent melt.

When the sign of the initial mismatch is negative there is a tendency for the system to be unstable. If the mismatch between the substrate and the solid which is in equilibrium with the melt becomes increasingly negative as the substrate is dissolved into the melt, then the driving force for substrate dissolution is increased. Finally, it has been observed that system stability is diminished when local dissolution of the substrate causes the solubility of the substrate group V component to be increased.

Applying these criteria to the In–As–Sb/GaSb system we can estimate its stability. When the room temperature lattice mismatch is less than +1200 ppm, the mismatch existing at the growth temperature is negative. If a dissolution fluctuation were introduced, a small amount of Ga and Sb would enter solution producing a quaternary melt. As $k_{\mathrm{Ga}} \gg k_{\mathrm{Sb}}$ in this system, the equilibrium solid of the new melt would have a lattice parameter smaller than that of the original In(As, Sb) solid solution, so leading to a decrease in system stability. During substrate dissolution the solubility of Sb (from the substrate) is enhanced and so this also suggests that the In–As–Sb/GaSb system is unstable.

As all three criteria for system instability are fulfilled in the case of In–As–Sb/GaSb we would expect substrate erosion according to Bolkhovityanov's model when $\Delta a^{\mathrm{R.T.}} \leqslant 1200$ ppm.

CONCLUSION

Growth of In(As, Sb) on GaSb substrates at controllable rates was achieved using antimony-rich melts. This was due to the lower solubility of antimony (from the substrate) in Sb-rich rather than In-rich melts. Only layers with $\Delta a^{\mathrm{R.T.}} \geqslant 1200$ ppm were growth without producing erosion of the substrate but these layers displayed cross-hatching owing to high lattice strain. When $\Delta a^{\mathrm{R.T.}} \leqslant 1200$ ppm the lattice mismatch existing at the growth temperature was negative and the system was unstable in accordance with Bolkhovityanov's model. This resulted in erosion of the GaSb substrate by the melt.

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Department of Engineering Science
Oxford University
Parks Road
Oxford
U.K.

J. R. SKELTON[†] and
J. R. KNIGHT

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[†] Now at Plessey Research (Caswell) Limited, Allen Clark Research Centre, Caswell, Towcester, Northants NN12 8EQ, England