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THE PREPARATION OF Ga-rich $Ga_xIn_{1-x}Sb$ ALLOY CRYSTALS

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Radially homogeneous bulk single crystals of $Ga_xIn_{1-x}Sb$ have been grown by the Czochralski technique in the range $0.9 < x < 1$. High seed rotation rate and appropriate shaping of the crystal boule are essential for the suppression of interface breakdown phenomena. Electron microprobe analyses of the first to freeze ends of the crystal necks produced by Czochralski pulling reveal effective distribution coefficients close to the corresponding equilibrium distribution coefficients. The etch pit density on (111)A faces of Czochralski pulled $Ga_xIn_{1-x}Sb$ crystals is $\lesssim 10^4 cm^{-2}$. Their electrical properties are similar to those of zone leveled $Ga_xIn_{1-x}Sb$ crystals.

Key words: Czochralski pulling, Zone leveling,
III-V compounds.

Introduction

In view of the present interest in extending the range of optoelectronic devices from the near infrared towards longer wavelength alloys of the group III antimonides deserve particular attention. Their higher yield strength, lower melting temperatures and smaller decomposition pressures facilitate thermal processing as compared to the group III arsenides and phosphides. Both laser diodes and detectors suitable for optical communication at wavelength near 1.3 μm have been made from $Al_xGa_{1-x}Sb$ and $Al_xGa_{1-x}As_ySb_{1-y}$ epitaxial structures on GaSb substrates (1-3). However, the range of solid solutions in the $Al_xGa_{1-x}As_ySb_{1-y}$ system that lattice match GaSb is restricted by a miscibility gap and there exists a lattice mismatch of 0.65% at the AlSb/GaSb pseudobinary. The present study is motivated by the apparent need for new substrate materials that expand the range of available lattice constants and energy gaps.

The $Ga_xIn_{1-x}Sb$ alloy system encompasses a continuous regime of lattice constants a_0 and band gaps E_g which are 6.0959A $\leqslant a_0 \leqslant$ 6.4794Å and 0.172 eV $\leqslant E_g \leqslant$ 0.726 eV (5) at room temperature. Normal freezing (6), solution growth methods (7-10), and zone leveling (11,12) have been used to grow $Ga_xIn_{1-x}Sb$ single crystals. However, very small growth rates are required with these techniques because of the wide solidus-liquidus separation at the GaSb/InSb pseudobinary and because of the related interface breakdown phenomena due to constitutional supercooling (12). In this paper we report the growth of $Ga_xIn_{1-x}Sb$ alloy crystals by the Czochralski method that allows better control of the kinetic limitations.

Experimental Results

The $Ga_xIn_{1-x}Sb$ alloys were synthesized from 6N's pure Ga and Sb and were subjected to Czochralski pulling in a flowing 85% N_2 + 15% H_2 atmosphere. For comparison and for the preparation of seeds we prepared also several $Ga_xIn_{1-x}Sb$ crystals by zone leveling applying four alternating passes at a rate of 3-7 mm/day. The ratio of the zone length to the length of the ingot was typically 1:10 and the temperature gradient at the solid/liquid interface was 280°C/cm. Figure 1 shows a crystal of $Ga_{0.88}In_{0.12}Sb$ obtained by zone leveling without seeding. As observed in the randomly nucleated growth of other III-V alloys the growth axis aligns close to the $<12\bar{3}>$

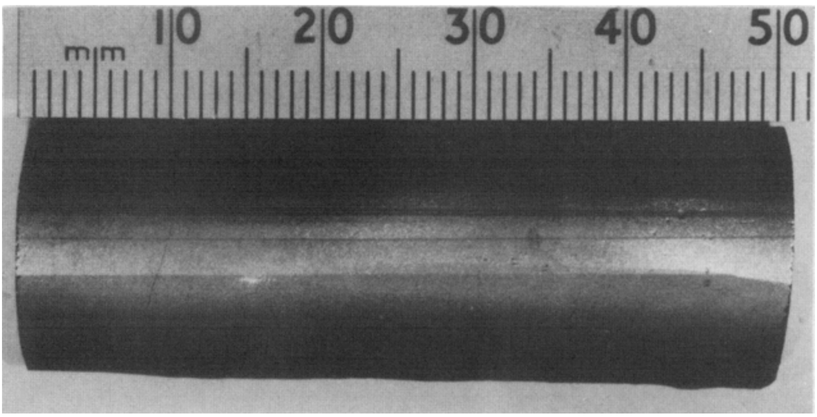

Fig. 1. Zone leveled crystal of nominally updoped p-type $Ga_{0.88}In_{0.12}Sb$. $N_A - N_D = 1.4 \times 10^{17} cm^{-3}$, $\mu_h = 472 cm^2V^{-1}s^{-1}$ at room temperature.

direction (13). Therefore, twin lamellae nucleated at the (111) twinning plane are maintained over the entire length of the crystal. Crosstwinning is not observed in this mode of crystal growth. Seed crystals for subsequent crystal growth experiments in the <111> direction were cut perpendicular to the twin lamellae.

Figure 2 shows a $Ga_xIn_{1-x}Sb$ boule pulled from a melt of 50 cm^3 volume containing initially 20% InSb and 80% GaSb using a <111> seed

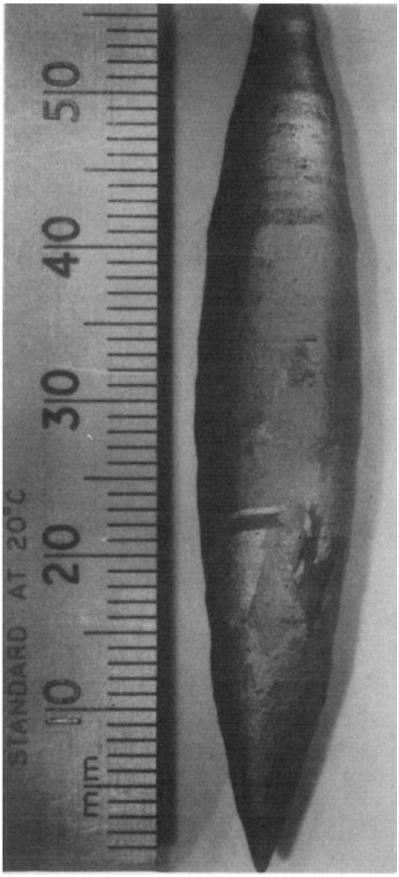

Fig. 2. Czochralski pulled boule of nominally undoped p-type $Ga_xIn_{1-x}Sb$. Initial melt composition $x^l(Ga) = 0.80$, $v_g = 6$ mm/hr, $9.2\times10^{16} \leqslant N_A - N_D \leqslant 9.3\times10^{16} cm^{-3}$, $556 \leqslant \mu_h \leqslant 616 cm^2V^{-1}s^{-1}$ at 298K.

with the (111)B face pointing towards the melt. We observed that high seed rotation rates (100-200 rpm) helped in avoiding dendritic growth and radially homogeneous crystals* were obtained at surprisingly large growth rates (1-6 mm/hr).

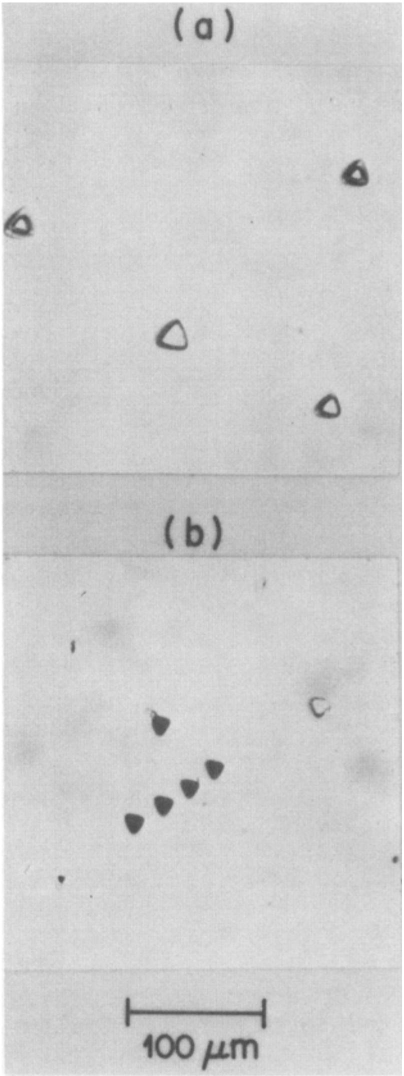

Fig. 3. Etch pits revealed by the 6:6:1 etch on (111)A faces of a) zone leveled and b) Czochralski pulled $Ga_xIn_{1-x}Sb$ crystals.

* Homogeneous within the error limits of electron microprobe analysis scans of cross-sections of the crystal boules, i.e., within ±1% of the nominal composition.

Note that interface breakdown must be suppressed with respect to both the vertical and the horizontal components of the growth of the crystal, i.e., the shoulder angle after the necking section of the crystal boule must be kept below a critical value to avoid dendritic growth parallel to the surface of the melt. In view of the steep slope of the solidus and the flat slope of the liquidus (14,15) for Ga-rich melt compositions the gradation in the composition in the first to freeze part of the crystal boule is small (see Fig. 5a). Therefore, seeding of Ga-rich $Ga_xIn_{1-x}Sb$ melts is possible starting with pure GaSb seeds. Proceeding in small steps of 5-10% in a series of successive Czochralski pulling experiments the In-concentration in the melt may be increased up to 40% InSb. For higher In concentrations progressively smaller steps must be taken to avoid cracking of the crystal neck due to the misfit strain. In addition, the growth rate must be decreased below 0.5 mm/hr. making the growth of $Ga_xIn_{1-x}Sb$ crystals by the Czochralski method impractical for liquidus compositions $0.1 < x^l(Ga) < 0.5$.

A 20 sec etch in aqua regia is suitable for distinguishing the polar (111)A and (111)B faces that appear dull and shiny, respectively. Both the HNO_3:H_2O:HCl = 6:6:1 etchant and a modified AB etch (16) reveal etch pits on the (111)A faces of $Ga_xIn_{1-x}Sb$ crystals. Figures 3a and 3b show etch pits on the (111)A faces of zone leveled and Czochralski pulled $Ga_xIn_{1-x}Sb$ crystals, respectively. The etch pit density is typically $10^3 - 10^4 cm^{-2}$ for zone leveled crystals and is $\approx 10^4 cm^{-2}$ on Czochralski grown material. The electrical properties of $Ga_xIn_{1-x}Sb$ crystals grown by the Czochralski technique are similar to those of zone leveled crystals and agree with the reported data of Refs. 6, 10, and 12.

In order to derive the effective distribution coefficients k_e as a function of the liquidus composition the first to freeze ends of Czochralski pulled boules were checked by electron microprobe analyses. Figure 4 shows a plot k_e(Ga) vs. x^l(Ga) indicating that the solid/liquid interface is close to equilibrium. Note that for a given liquidus composition our values of x^s(Ga) are actually slightly larger than the corresponding solidus data of Ref. 14. This indicates that the solidus data presented in Ref. 14 may not represent equilibrium and thermodynamic interpretations of these data (15) must be considered with caution.

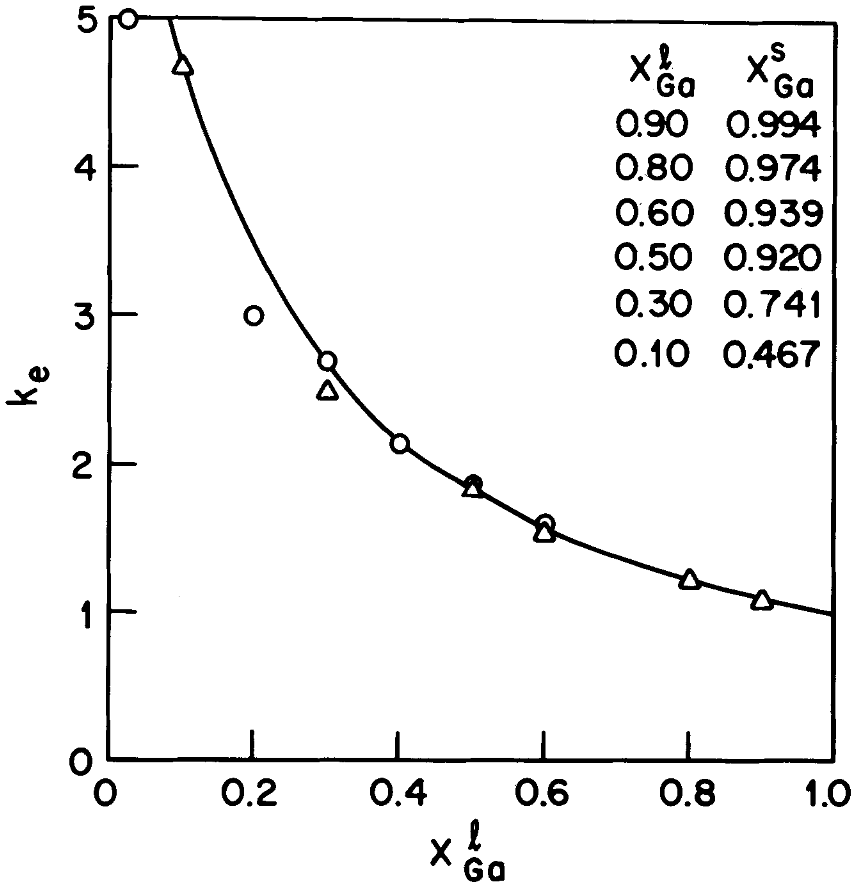

Fig. 4. Effective distribution coefficient k_e (Ga) vs liquidus composition x^l(Ga). Czochralski pulling 0.1 mm/hr $\leqslant v_g \leqslant$ 6 mm/hr; 0 equilibrium distribution coefficient k_0(Ga) taken from the phase diagram Ref. 14;— k_0(Ga) derived from Ref. 15.

Figure 5a shows normal freezing curves calculated with the set of distribution coefficients representing Czochralski pulling. G refers to the solidified weight fraction and the number written as a parameter on the families of curves in Figs. 5a and 5b indicate the initial melt composition x^l(Ga). Figure 5b shows the calculated strain gradient $(1/a_0) \times (da_0/dG)$ in the solidified boule as a function of G. For x^l(Ga) > 0.5 a substantial fraction of the melt can be solidified keeping the misfit strain < 1% which is a necessary condition for avoiding cracking and excessive generation of defects. Therefore, Czochralski pulling is a suitable means of preparing

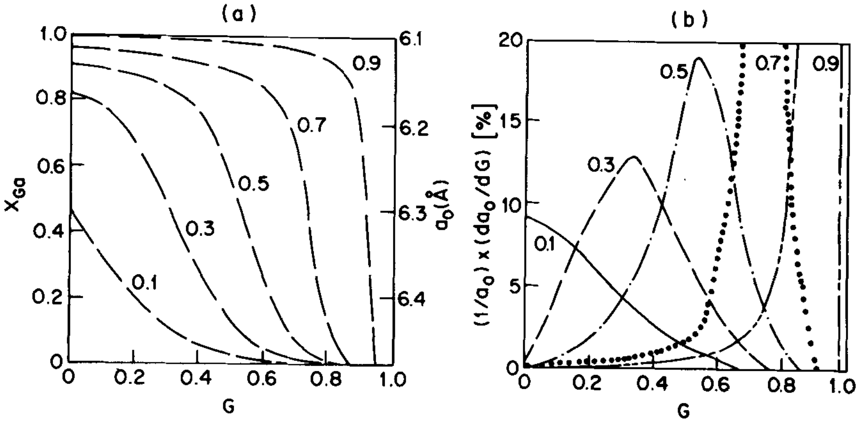

Fig. 5. a) Atom fraction of Ga on the cation lattice of $Ga_xIn_{1-x}Sb$ produced by normal freezing vs. solidified weight fraction G.
b) Strain gradient $(1/a_0) \times (da_0/dG)$ vs. G.

$Ga_xIn_{1-x}Sb$ crystals for solidus compositions $x^s > 0.9$. This range suffices for the preparation of lattice matched epilayers of $Al_xGa_{1-x}Sb$ over the entire range of direct energy gaps that is of primary interest in the context of optical communications. Note that in the later stages of Czochralski pulling the change in the gradation of composition accelerates leading often to a loss of single crystallinity. In case of the crystal shown in Fig. 2 this happened at the position measured 23 mm upwards from the bottom tip of the boule.

Summary

Radially homogeneous bulk single crystals of $Ga_xIn_{1-x}Sb$ have been grown by the Czochralski technique in the range $0.9 < x < 1$. High seed rotation rate and appropriate shaping of the crystal boule are essential for the suppression of interface breakdown phenomena. Electron microprobe analyses of the first to freeze ends of the crystal necks produced by Czochralski pulling reveal effective distribution coefficients close to the corresponding equilibrium distribution coefficients. The etch pit density on (111)A faces of Czochralski pulled $Ga_xIn_{1-x}Sb$ crystals is $\lesssim 10^{-4} cm^{-2}$.

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