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Influence of solute doping on the high-temperature deformation behavior of GaAs

S. Guruswamy, R. S. Rai, K. T. Faber, and J. P. Hirth
The Ohio State University, Columbus, Ohio 43210

J. E. Clemans
AT&T Engineering Research Center, Princeton, New Jersey 08544

S. McGuigan and R. N. Thomas
Westinghouse Research and Development Center, Pittsburgh, Pennsylvania 15235

W. Mitchel
Air Force Wright Aeronautical Laboratories, Dayton, Ohio 45433

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The role of isovalent dopants in the high-temperature deformation of GaAs has been studied in the temperature range 500–1150 °C. Additions of In, Sb, and B increase the critical resolved shear stress for deformation at a given strain rate and result in lowering the dislocation density of as-grown liquid-encapsulated Czochralski GaAs crystals. Phosphorus, because of its minor influence on the lattice strain, shows little enhancement of the yield stress. These results are consistent with a solute hardening model, in which the solute atom surrounded tetrahedrally by four Ga or As atoms comprise the hardening cluster. Codoping with In and Si hardens GaAs, but codoping with Si is less effective than the isovalent solutes In, Sb, and B, and produces softening at high temperatures. The effect of solutes on both dislocation nucleation and multiplication are reviewed here.

I. INTRODUCTION

Control of the dislocation density and distribution in single crystals of GaAs and related compounds during crystal growth and subsequent device fabrication is important in achieving improved performance, reliability, and yield of optoelectronic devices. Thermal stresses produced during growth seem to be responsible for the generation of dislocations during liquid encapsulated Czochralski (LEC) growth in GaAs and other III-V compounds when the thermal stress imposed on the crystal exceeds the critical resolved shear stress (CRSS). The reduction of thermal stresses during growth and the enhancement of crystal strength by doping result in crystals with reduced dislocation density. The drastic reduction in dislocation density in GaAs containing small amounts of dopants such as In suggests that the dopants are related to a large increase in high-temperature strength.

On the basis of the fact that the In—As and Ga—As bond lengths remain relatively invariant with In concentration in the (Ga,In)As system, Ehrenreich and Hirth suggested that tetrahedral InAs clusters act analogously to solute atoms in metals in hardening the GaAs system. With the assumption that bond lengths remain similarly constant in other systems, other isovalent solutes can be evaluated for strengthening of compound semiconductor matrices in terms of variations in lattice parameters.

With strain fields associated with the solute clusters, several possibilities exist for hardening of the crystals as follows: (i) pinning of gliding dislocations by the Orowan–Friedel–Fleischer process as explicitly derived in Ref. 10; (ii) formation of either core or Cottrell atmospheres and hardening associated with the drag of these atmospheres (as reviewed in Ref. 12, with either of these mechanisms, one would expect to observe serrated flow, the Portevin–LeChatelier effect, and, above a critical temperature, breakaway of the dislocations); (iii) pinning of climbing dislocations by core or Cottrell atmospheres with solute drag associated with dislocation motion.

There are other possible effects of isovalent solute additions, including influences on defect concentrations and mobilities, influences on core reconstructions, and weak effects on electronic states at dislocations. None of these effects, however, would scale directly with the size of the solutes.

In this study, experimentally obtained CRSS data on GaAs crystals with different dopants are analyzed to help clarify the mechanism of strengthening and dislocation density reduction. GaAs single crystals containing different combinations of the dopants (In,B), B, P, Sb, and (In,Sn) were investigated in the temperature range 500–1150 °C. Critical resolved shear stress measurements were made on single crystals tested in compression in [123] axial orientations.

II. EXPERIMENTAL PROCEDURE

A. Material preparation

Table I summarizes the different materials used in this investigation and the relevant material characteristics such as composition, average dislocationetch pit density, resistivity, and mobility. All the crystals except crystal A were grown by the LEC process. Crystal A was grown by the vertical gradient freeze process. A description of this process for the growth of semi-insulating GaAs single crystal is given in Ref. 13. The crystal orientations were determined by the Laue x-ray back reflection technique. Compression test specimens were cut in appropriate orientations with a diamond wire saw. The specimen faces were mechanically pol-

ished through a sequence ending with 0.3-μm alumina powder followed by chemical polishing in a 1% bromine-methanol solution. The specimen faces were parallel and orthogonal to within 0.5°. The final specimen dimensions were 2.75×2.75×5.5 mm or 5×5×10 mm. The [123] specimen, oriented for operation of a single slip system, had lateral faces parallel to (111) or (541) planes.

B. Compression testing

The compression testing was done on an Instron™ 1322 servohydraulic universal testing machine. The experimental setup has been described elsewhere. Tests were performed at temperatures of 500, 700, 900, 1000, and 1150 °C at strain rates of 1×10⁻⁵, 1×10⁻⁴, and 1×10⁻³ s⁻¹ in UHP argon. For tests at temperatures of 700 °C and above the specimen was immersed in B₂O₃ liquid. The compression rams used were made of high-purity alumina, and a special fixture made of alumina was used for alignment and positioning of the specimen. The elongation was measured on alumina rams by means of an extensometer and was corrected for fixture compliance, measured at temperature, in converting data to strain. The results are presented as yield strength calculated at the yield point or, if present, the lower yield point, and converted to critical resolved shear stresses.

III. RESULTS AND DISCUSSION

A. Summary of work on undoped and B- and In-doped crystals

Extensive earlier work was performed on materials E and C in Table I, the undoped and In-doped crystals containing large amounts of boron that were not deliberately added as a dopant. As shown in Fig. 1, the undoped, low boron crystals, A, have similar dependencies of yield stress as a function of temperature, but lower work hardening rates, so the trends in behavior are expected to be similar to E and C.

Compression tests on [123] crystals for crystals E and C revealed six-stage behavior (A, I, II, III, IV, V) at 900 °C and four-stage behavior above and below 900 °C, with the stage III mechanism switching above and below that temperature. Transmission electron microscopy together with analogous work on Si, Ge, InSb, and InP (reviewed in Ref. 16), indicated that the microyield stage A, the yield stress at the start of stage I, and stage I were glide-controlled processes. Stage II was controlled by dislocation intersection and jog drag. Stage III at the lower temperature represents recovery associated with thermal assistance of jog drag by vacancy motion, and at the higher temperatures by climb of extended jogs in hexagonal dislocation networks that form as recovered substructures (stage V at 900 °C). Stage IV is associated with changes in mesh size of the network dislocations as extrinsic dislocations are absorbed in the boundaries. For both stages II and IV, the role of In is deduced to be to provide a friction stress, via the size effect discussed earlier, resisting the motion of dislocation segments bowing out between jogs.

For observations of stage A and stage I, the behavior in the low-temperature region 500–700 °C is consistent with dislocation motion by double-kink motion with the solute hardening retarding the motion of kinks along the dislocation line. Above 700 °C the solute hardening directly provides a friction force resisting dislocation glide motion. To further test this interpretation, the yield stress was determined as a function of strain rate for undoped crystals A. As shown in Fig. 2, there was a strong temperature dependence of the yield stress at 500–700 °C, consistent with a small acti-

![FIG. 1. Variation of CRSS as a function of temperature at a strain rate of 10⁻⁴ s⁻¹ for undoped crystal A (open squares), boron containing crystal E (open circles), and (In,B) containing crystal C (asterisk).](image-url)
tion area and the double-kink model, but a weak temperature dependence at higher temperatures, in accordance with a larger activation energy and the model for bowout between pinning points.

B. Isovalent dopants

The solute hardening analysis indicates that the yield strength should scale with the size effect of the appropriate tetrahedral cluster. Yield strengths for the present study are listed in Table II. The pinning force for the size effect is proportional to the relative volume change, $\delta v/v$, associated with the hypothetical insertion of a solute tetrahedron into the matrix. With the assumption that solute bond lengths are invariant with composition, as for the (Ga,In)As case, the volume change is related to the difference in lattice parameters $\Delta a$ of GaAs and InAs, for example, by $(\delta v/v) = [(a + \Delta a) - a]/a$.

Values for $\delta v/v$ so calculated are listed in Table III for several isovalent dopants. Also listed is the change in flow stress $\Delta \sigma$ produced by the change in concentration $\Delta c$ (in units of atom fraction on the anion or cation site). The results for P, Sb, and B are obtained by comparison with crystal A, while that for In is obtained by comparison with crystal E, which has the same boron content.

The qualitative trends in the data are expected, with $\Delta \sigma/\Delta c$ monotonically increasing with $\delta v/v$. One cannot test the data for the expected quantitative form $\Delta \sigma(c) \propto \delta v/v$ at a fixed concentration because the flow stress-concentration relation is usually not linear for dilute solutes and only data for one value of $c$ were obtained. Very dilute solutes often produce strengthening of the form

$$\Delta \sigma = Ae^{1/2}.$$  \hspace{1cm} (1)

If this behavior is followed, the constant $A$ should be proportional to $\delta v/v$. Values of $A$ are also listed in Table III and scale in the expected manner except for the case of Sb at 1100 °C.

Consistent with the trends in the experimental $(\Delta \sigma/\Delta c)$ data in Table III, dislocation densities in as-grown crystals are reduced for In, (In,B), and Sb (Refs. 7 and 8) additions at levels equivalent to those listed in Table I. On the other hand, P, which is expected to be a weak strengtheners on the basis of the present work, is less effective in reducing dislocation densities even at levels of $10^{19} - 10^{20}$ cm$^{-3}$.

C. Codoping with In and Si

Referring to Table II, one sees that the yield strength of the (In,Si) codoped material was similar to the (In,B) material at 500 °C. However, at higher temperatures, the yield strengths were much lower than material C or E. Thus, Si appears to lower the yield strength at high temperatures, even though the (In,Si) crystal remains harder than the undoped crystal A at 1100 °C. A similar observation has been made by Bourret, Tabache, and Elliot in the case of Si-doped GaAs crystals with Si contents of $1.5 \times 10^{18}$ and $3 \times 10^{18}$ cm$^{-3}$. They show that there is a crossover of CRSS versus temperature curves for Si-doped and undoped GaAs crystals at high temperatures, with the crossover temperature dependent on Si content. Above this crossover temperature, Si doping lowers the CRSS of undoped GaAs. But both Si-doped and (In,Si)-doped crystals have been found to have low dislocation densities in agreement with our observations of crystal F being harder than crystal A at most temperatures.

Si is an amphoteric dopant acting as a donor or acceptor depending upon whether it occupies a Ga or As site. The distribution between these two sites depends upon stoichiometry (Ga- or As-rich) and temperature. In GaAs grown in a slightly As-rich melt, Si occupies more Ga sites than As sites resulting in n-type behavior, and a concomant strengthening at low temperatures relative to both p-type and undoped GaAs. Should the Si$_{As}$/Si$_{Ga}$ ratio change at high temperatures, consistent with increases in the As/Ga vacancy concentrations, it might be expected that the

<table>
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<th>TABLE II. Yield stress (critical resolved shear stress) values at a strain rate of $10^{-3}$ s$^{-1}$ at different temperatures for the different materials investigated.</th>
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<tr>
<td>A. Undoped (Low B)</td>
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<tr>
<td>B. P doped</td>
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<tr>
<td>C. In doped</td>
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<tr>
<td>D. Sb doped</td>
</tr>
<tr>
<td>E. Undoped (high B)</td>
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<tr>
<td>F. (In,Si) codoped</td>
</tr>
</tbody>
</table>
TABLE III. The change in yield stress (critical resolved shear stress) produced by doping and the size effect $\delta a/\delta_0$.

| Specimen       | $|\delta a/\delta_0|$ | $|\delta /\delta_0|$ | $\Delta /\Delta C (a.Pa./at. \%)$ | A [MPa/(at. \%)]$^{1/2}$ |
|----------------|---------------------|---------------------|----------------------------------|------------------------|
| A. undoped     | 0                   | 0                   | 0                                | 0                      |
| B. P           | 3.6                 | 12                  | 641                              | 136                    |
| C. In          | 7.2                 | 23                  | 796                              | 535                    |
| D. Sb          | 7.8                 | 25.4                | 8110                             | 1852                   |
| E. B           | 15.5                | 40                  | 44200                            | 2102                   |
| F. (In,Si) codoped | 676                | 62                  | 676                              | 0                      |

stress permissible during growth may differ from the presently reported CRSS values. Determination of this stress level below which dislocation nucleation and multiplication could be suppressed requires painstaking static creep experiments at stress levels below the CRSS measured in constant strain rate tests in conjunction with EPD measurements. However, the CRSS measured in constant strain rate tests provide information on the influence of dopants on the strength of the crystals and provides an indication of trends in the allowable stress level during growth.

IV. SUMMARY

The isovalent solutes In, Sb, and B cause increases in the yield strength of GaAs consistent with their role in lowering of dislocation density in as-grown GaAs crystals. The results for these solutes and P, which is a weak hardener, are consonant with a solute hardening model for the strengthening effect. Codoping with In and Si hardens GaAs, but Si is less effective than the isovalent solutes In, Sb, and B and produces softening at high temperatures. A major impediment to dislocation generation is the nucleation process, which, together with dislocation multiplication, would be influenced by the solute hardening effect.

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