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High-temperature hardness of $Ga_{1-x}In_xAs$

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Substantial solid-solution strengthening of GaAs by In acting as $InAs_4$ units has recently been predicted for an intermediate-temperature plateau region. This strengthening could account, in part, for the reduction of dislocation density in GaAs single crystals grown from the melt. Hardness measurements at high temperatures up to 900 °C have been carried out on (100) GaAs, $Ga_{0.9975}In_{0.0025}As$, and $Ga_{0.99}In_{0.01}As$ wafers, all of which contain small amounts of boron. Results show a significant strengthening effect in In-doped GaAs. A nominally temperature-independent flow-stress region is observed for all three alloys. The In-doped GaAs shows a higher plateau stress level with increasing In content. The results are consistent with the solid-solution strengthening model. The magnitude of the solid-solution hardening is sufficient to explain the reduction in dislocation density with In addition.

INTRODUCTION

Doping of GaAs with In in single crystals grown by the Czochralski process has been known to reduce the dislocation density from 10^3–10^4 cm/cm^3 to $< 10^2$ cm/cm^3.[1] There is a consensus that the generation of dislocations in GaAs and other III-V compounds occurs when the thermal stress imposed on the crystal during growth exceeds the critical resolved shear stress (CRSS) of the crystal. While the minimization of thermal gradients and hence the stresses during growth are achieved by the control of process parameters such as the B_2O_3 encapsulant height, cone angle, diameter control, and ambient pressure, enhancing the inherent strength (CRSS) of the crystal is achieved by addition of isovalent dopants as well as other group-IV and -VI elements. Of these, the isovalent In and the group-IV element Si have been found to be the most effective.[2] However, In doping is desirable because of the minimal influence on the electrical behavior of the GaAs. The mechanism of dislocation density reduction at such low concentration levels of the dopant is yet to be resolved unequivocally. The drastic reduction in dislocation density suggests a very large increase in the strength with In doping. Thermal stress calculations suggest that the maximum stress experienced by the crystal is several times that of the extrapolated CRSS of an undoped GaAs crystal.[3] It has been suggested[4] that hardening akin to solid-solution hardening occurs in GaInAs with an $InAs_4$ tetrahedral cluster being the solute unit that causes strengthening. Extended x-ray-absorption fine-structure (EXAFS) studies by Mikelson and Boyce[5] show that in the Ga-In-As system, the overall lattice parameter varies linearly with In concentration in accordance with Vegard's law, while the Ga-As and In-As bond lengths are essentially the same as in the corresponding pure crystals. The interpretation of these results[4] is that each In atom together with its four nearest As neighbors acts as a center of strain analogous to a solute atom in a metal. Such a unit would cause a local tetrahedral strain field corresponding to a volume dilatation, $\delta V/V$, of about 21%. This large strain field should result in substantial solid-solution strengthening in an intermediate-temperature plateau region. When the dislocations are pinned strongly by these strain centers, the increase in strength for an alloy containing 5×10^{19} atoms/cm^3 of In is estimated to be about 120%.

Generally compounds such as GaAs have strong temperature dependences for flow at low temperatures, corresponding to a rate-controlling mechanism related to the intrinsic lattice resistance or Peierls' barrier. An athermal, plateau region appears at intermediate temperatures corresponding to extrinsic effects such as solid solution hardening, while at high temperatures other creep-type mechanisms would be applicable. The low-temperature process consists of dislocation motion controlled by nucleation and lateral propagation of double kinks. With an increase in temperature, the nucleation and motion of double kinks occur much more easily and the flow stress drops sharply (Fig. 1). Misfit strain centers promote double-kink nucleation while impeding the subsequent lateral propagation of the two kink segments.[6] The solute addition at low concentration levels could result in either hardening or softening depending on

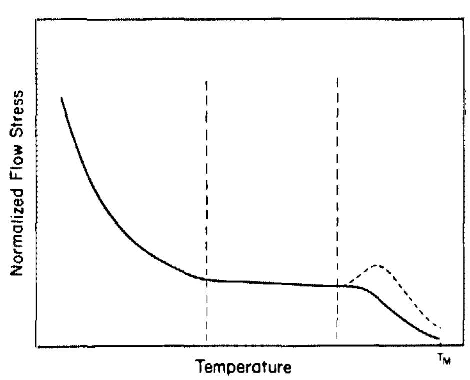

FIG. 1. Schematic normalized flow-stress vs temperature curve for GaAs at a constant strain rate.

the magnitude of these opposing effects. However, the softening effect should be most prominant at the lowest temperatures where the double-kink model is dominant and should be less pronounced as the extrinsic athermal region is approached. Hence, a transition from softening to hardening with increasing temperature below the plateau region would be expected, analogous to observations for bcc metals where the Peierls' mechanism is operative at low temperatures.[7]

In the athermal region beginning at about 700 °C for GaAs, double-kink nucleation no longer controls dislocation motion. In this region, the resistance to dislocation glide derives mainly from the interaction with solutes and other defects such as intersecting dislocations, and the dislocation motion occurs by breaking away from these pins. As in the case of solution-strengthened metals,[8] a nominally temperature-independent flow-stress region would be observed. In actuality, the flow stress is not truly independent in the plateau region but the slope of the flow-stress–temperature plot is significantly less in this region than at lower temperatures.[8] In this plateau region, the thermal component of flow stress is significantly less than the athermal component. The temperature-independent flow-stress level (plateau stress) would increase with increasing solute content. This region is expected to extend to a significant fraction of the melting temperature. Beyond this temperature, the flow stress would be determined by diffusion-controlled deformation processes.

This work concerns the experimental measurement of the flow stress and hardness as a function of temperature and In content. High-temperature hardness testing is used to estimate the influence of indium on CRSS and yield strength and to confirm the existence of the plateau stress. The yield stress level is approximately $\frac{1}{3}$ of the hardness value[9] so the latter indicates expected trends for yield stress.

EXPERIMENTAL WORK

The hardness tester used in this study was designed and fabricated specifically for the testing of GaAs. Loading is applied by dead weights with a counterbalance arrangement to vary the load from 0.1 to 3 N. The indenter is raised and lowered at a constant rate of 3 mm/min by a screw mechanism. The furnace used is a low-heat-capacity Pt–20 at. % Rh resistance wire-wound unit capable of rapid heating and cooling rates and a maximum temperature of 1500 °C. Ultrahigh-purity argon, flowing into the enclosure, is used to cool the upper part of the indenter shaft. Hardness measurements were made from room temperature to 900 °C with a Vickers diamond pyramid indenter.

Testing was performed on (100) surfaces of wafers grown by the Liquid Encapsulated Czochralski (LEC) method at Westinghouse Research and Development Center. Three compositions, undoped GaAs, $Ga_{0.9975}In_{0.0025}As$, and $Ga_{0.99}In_{0.01}As$, all semi-insulating, were studied. The concentration of In atoms in the above three alloys were 0, 5.5×10^{19}, and 2.2×10^{20} atoms/cm^3. The indium content was confirmed by atomic absorption spectroscopy. All three alloys also contained boron at levels of 2×10^{18} atoms/cm^3. Boron contents were determined by spark-source mass spectroscopy analysis at Battelle Columbus Laboratories. All

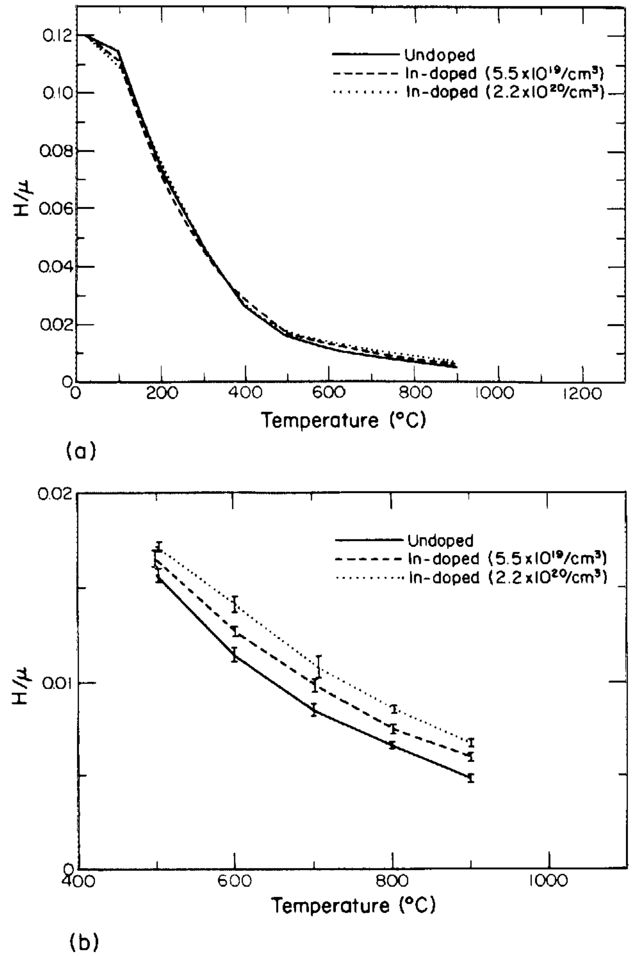

FIG. 2. Normalized hardness vs temperature plot for GaAs, $Ga_{0.9975}In_{0.0025}As$, and $Ga_{0.99}In_{0.01}As$.

hardness data are normalized by the shear modulus to give the residual temperature dependence related to the mechanisms. Data for the Voight average shear modulus were calculated from the anisotropic elastic constants given as a function of temperature by Jordan.[10]

RESULTS AND DISCUSSION

Figure 2 shows the hardness test results for GaAs, $Ga_{0.9975}In_{0.0025}As$, and $Ga_{0.99}In_{0.01}As$ (100) wafers. All data points represent the average of ten hardness readings. The standard deviation for the sets of data is also shown for the high-temperature region [Fig. 2(b)]. Table I also summarizes the hardness values for these three alloys. As indicated in the figure, the hardening effect is significant relative to the scatter. A significant difference in hardness between undoped and In-doped GaAs is seen only above 300 °C. No cracks were observed at indentation corners above 400 °C. This transition from cracking to deformation by slip during indentation has also been observed in GaAs by other workers in the temperature range 300–400 °C.[11,12] However, these hardness studies were confined to temperatures less than 500 °C.

The hardness drops sharply with temperature and flattens out at higher temperatures, indicative of the existence of the plateau stress region. The shape of the curve is very simi-

TABLE I. Hardness data for all three alloys as a function of temperature.

Temperature (°C)	Hardness (GPa)		
	GaAs	$Ga_{0.9975}In_{0.0025}As$	$Ga_{0.99}In_{0.01}As$
25	5.82 ± 0.2	5.82 ± 0.2	5.92 ± 0.22
100	5.52 ± 0.16	5.39 ± 0.15	5.26 ± 0.2
200	3.50 ± 0.3	3.41 ± 0.21	3.65 ± 0.1
300	2.23 ± 0.15	2.13 ± 0.18	2.14 ± 0.25
400	1.20 ± 0.03	1.33 ± 0.04	1.19 ± 0.06
500	0.72 ± 0.02	0.76 ± 0.04	0.79 ± 0.01
600	0.52 ± 0.03	0.58 ± 0.014	0.64 ± 0.013
700	0.38 ± 0.014	0.45 ± 0.015	0.49 ± 0.03
800	0.291 ± 0.01	0.324 ± 0.01	0.38 ± 0.01
900	0.21 ± 0.01	0.26 ± 0.01	0.293 ± 0.01

lar to that observed for metals exhibiting plateau behavior.[8] By virtue of their higher hardness, the alloys containing In are inferred to have a higher plateau stress level. The increase in hardness compared to the undoped material is about 40% at 900 °C for the highly-In-doped alloy. Both the In-associated effects of the softening-hardening transition at low temperatures and the presence of the plateau region are consistent with the model discussed previously of Peierls' control superseded by solid-solution hardening. The interpretation of the solid-solution hardening effect in terms of pinning would require the dislocation configuration to be of a smoothly bowed, line-tension type. This is in accordance with the transmission electron microscope observations of Laister and Jenkins,[13] who found bowed arrays for undoped GaAs after deformation at 800 °C. The plateau behavior for undoped GaAs in Fig. 2 would then be associated with pinning caused by dislocation intersections, residual impurities, jogs, or antisite defects.

Alternatively, another solid-solution hardening effect could be applicable. If dislocation motion occurred by double-kink nucleation and growth, solute hardening would be manifested through a retardation of the growth step of lateral kink propagation, with the kink pinning effect still being proportional to δV. The similar plateau behavior for GaAs with and without In would then be a logical consequence since the same detailed mechanism of dislocation motion would be appropriate for both cases. Deformation of GaAs at the low temperatures of 320 and 400 °C does give straight dislocations[14,15] consistent with a double-kink model and the interpretation of the first stage of deformation in Fig. 1.

We plan to undertake transmission electron microscope studies of the deformed alloys to determine whether the plateau region specimens correspond to bowed or straight dislocations to decide which of the above models is applicable. In the context of the present work, however, either model corresponds to a solid-solution hardening effect of In.

Hardness is approximately equal to three times the lower yield stress.[9] Moreover, the critical resolved shear stress (CRSS) equals the yield stress times the Schmid factor of about 0.5.[16] Thus, the CRSS is approximately equal to $H/6$. The CRSS obtained from hardness data is presented as a function of temperature in Fig. 3. The hardness to flow stress conversion is presented only for temperatures above 400 °C where no cracking at indentation corners is observed and significant plastic flow occurs. For comparison, also shown are CRSS data from compression tests on undoped Bridgman crystals by Swaminathan and Copely[17] and on undoped and In-doped LEC crystals by Tabache,[18] both of which also represent values for the lower yield stress. The greater strength of the present crystals with no In doping may be associated with the presence of boron. Boron, an isoelectronic substitution for gallium, would produce a larger size mismatch, $\delta V/V = 50\%$, than In, but an attendant lower solubility. Hence, it should also be a strong hardener if uniformly distributed in solution, an effect verified experimentally,[1] but could lead to internal stresses and dislocation generation if present in an inhomogeneous distribution or as precipitates.

Extrapolation of data from the present work for the undoped and highly doped cases to the melting point T_m gives

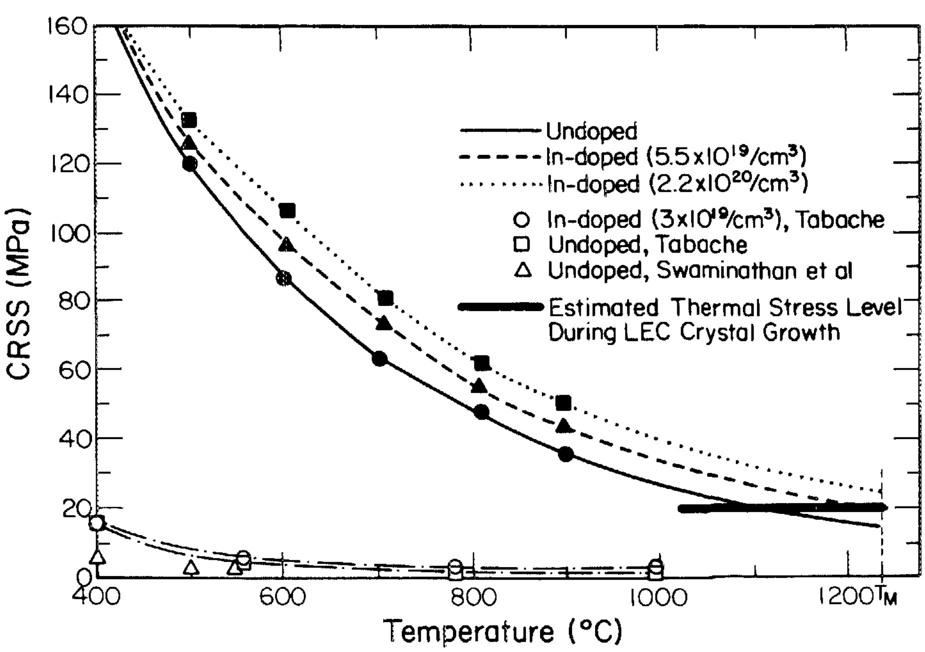

FIG. 3. Critical resolved shear stress estimated from hardness data compared with the compression test data of Swaminathan and Copely (see Ref. 17) on undoped GaAs and of Tabache (see Ref. 18) on undoped and In-doped LEC GaAs.

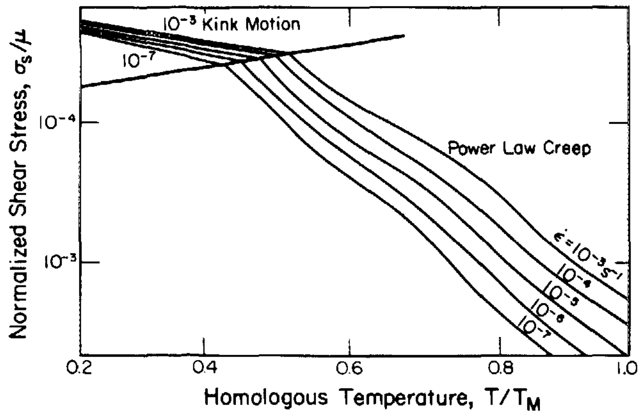

Figure 4. A section of deformation mechanism map of Si which belongs to the same isomechanical group as GaAs (see Ref. 21).

CRSS values of 15 and 23 MPa, respectively. The dislocation content and the resolved shear stress caused by thermal stresses experienced during crystal growth vary across the diameter according to the conventional W form.[3,10] The maximum resolved shear stresses calculated[3,19,20] to arise from thermal stresses at temperatures near T_m during crystal growth are 20 MPa in the central region and rise to 50 MPa at the crystal edges. It must be pointed out here that CRSS values obtained from hardness measurements are upper bound estimates, and the extrapolation to the melting point is made with some reservation because there is most likely an intervening change in the deformation mechanism, as discussed later. However, the present results suggest that crystals highly doped with In and containing B may have sufficient solid-solution hardening to prevent yielding during crystal growth, at least in the center. Further work is needed to resolve the difference between the present results and the compression test results in Fig. 3, in particular with respect to the possible role of boron.

While the above results would suffice to explain the suppression of dislocation formation by means of In additions, the extrapolation of the plateau data to the melting point is questionable, because there is most likely an intervening change in the deformation mechanism. Since GaAs has a structure similar to Si and the deformation map for GaAs is not available at the present time, the Si deformation map[21] is used here as a guideline for this possible transition in mechanism. Figure 4 presents data extracted from the Si map for strain rates of 10^{-3}–10^{-7} s^{-1}. The flow behavior undergoes a transition from flow following the double-kink model to that of a power-law creep model at about $0.5T_m$. For GaAs, the intervention of solid-solution hardening is expected to move the transition to power-law creep to higher homologous temperatures, but, on the basis of all available deformation map data,[21] to still leave a region of power-law creep below the melting point. The cellular dislocation networks present in as-grown GaAs crystals with dislocation densities of the order of 10^3–10^4 cm/cm^3 provide indirect evidence that climb processes are involved in the deformation occurring during crystal growth. As indicated in Fig. 4, the transition to power-law creep at a given strain rate and temperature is less than that for double-kink flow extrapolated to the same conditions. However, even for the power-law creep region, In can have a hardening influence.

In the region of power-law creep, the dislocation velocity and hence the flow-stress level would depend on the lattice interdiffusion coefficient or diffusivity. In this regime, the dislocation velocity for a given applied stress is given by[21]

$$v \approx D_v \sigma_n \Omega / bkT.$$

Here D_v is the bulk diffusivity, σ_n is the local normal stress that produces a climb force on the dislocation, k is Boltzmann's constant, and Ω is the atomic volume. Because σ_n is proportional to the flow stress σ_s and the average dislocation velocity is proportional to the strain rate $\dot\epsilon$, the latter is given by[21]

$$\dot\epsilon \approx (AD_v \mu b / kT)(\sigma_s/\mu)^3,$$

where μ is the shear modulus, A is a dimensionless constant, and b is the length of the Burgers vector. For a binary compound, D_v is replaced by $D_{\text{eff}} = D_{\text{Ga}} D_{\text{As}} / D_{\text{Ga}} + D_{\text{As}}$.[21] Thus, the stress for a given strain rate would be controlled in the GaAs lattice by the slower of the diffusing species, which is arsenic. The influence of solute elements on the diffusion in the arsenic sublattice would thus be an important factor in determining the effect of solute elements on the deformation behavior. The trapping of arsenic vacancies because of elastic interactions or electronic interactions with In solute centers would be a possible factor that could reduce D_{eff} and hence provide a hardening effect in the power-law creep regime.

At high temperatures, where solute atoms are mobile, resistance to dislocation motion also comes from the drag of a solute atmosphere by the dislocation. The force-velocity relationship for this Cottrell drag has been treated in detail.[22] For a given dislocation velocity v, the drag stress increment caused by the solute atmosphere varies as the square of the strength of solute-dislocation interaction δV and inversely as the effective diffusivity. The solute-drag stress versus temperature curve would exhibit a maximum and if present, would be superposed on the strength versus temperature plot as shown by the dotted line in Fig. 1. Because of very low diffusivities in the GaAs lattice, the solute-drag effect is expected at quite high temperatures.

All of the preceding discussion has been in terms of quasi-steady-state flow corresponding to deformation at and subsequent to the lower yield point. An additional hardening-type influence of In could be manifested if the deformation during crystal growth occurred mainly in the transition region reflected by the microyield stress, the upper yield point, and deformation between the upper and the lower yield points. A retarding effect of In on dislocation motion during multiplication would tend both to increase the upper yield point and to prolong the strain range between the upper and lower yield points.[23,24] The microyield stress, at which dislocation motion begins, would also be increased by such a retarding effect.

Thus while the plateau stress data extrapolated from 900 °C indicate sufficient hardening to suppress flow on the basis of estimated thermal stresses, other hardening or softening effects associated with different deformation mechanisms above 900 °C could be present. Such mechanisms are expected on the basis of theory. We are presently extending the deformation work to temperatures above 900 °C where conventional indentation methods are inapplicable.

SUMMARY

High-temperature hardness tests at up to 900 °C of undoped and In-doped GaAs showed an appreciable strengthening effect of In in GaAs. The existence of an athermal, plateau stress region is indicated for the three alloys. The GaAs containing In shows a higher plateau stress level compared to GaAs with no In. Calculations suggest that the hardening produced by indium may be sufficient to exceed the thermal stress experienced by the crystal during growth. However, studies at higher temperatures are needed to resolve the possibility of a change in the deformation mechanism near the melting point. Strengthening at higher temperatures with In additions is consistent with a solution hardening model for dislocation density reduction in In-doped GaAs.

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