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SILICON AND INDIUM DOPING OF GaAs: MEASUREMENTS OF THE EFFECT OF DOPING
ON MECHANICAL BEHAVIOR AND RELATION WITH DISLOCATION FORMATION

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Abstract

The effect of indium and silicon doping on dislocation formation in GaAs single crystals has been studied experimentally using dynamic compression tests and indentation rosettes. By direct measurements of the critical resolved shear stress (CRSS) in temperature range from 400 to 1100°C using dynamic compression tests, we found that the critical resolved shear stress of GaAs:In is twice that of undoped GaAs. More recent measurements show that the critical resolved shear stress of silicon-doped crystals is lower than that of undoped GaAs. Well-defined indentation rosettes were obtained at high temperatures from a Vickers indenter using small loads. Analysis of such rosettes confirm that the mechanical behavior of the GaAs crystals is not drastically affected by the presence of dopants. Reduction of dislocation densities in doped crystals is attributed to modifications introduced by the dopant in the equilibrium concentration of native defects at the melting point (particularly gallium and arsenic vacancies).

1. Introduction

It is well established that dislocation-free crystals of GaAs can be obtained if high concentrations of suitable dopants are added to the melt [see e.g. 1,2]. In particular, indium is used for the growth of dislocation free, semi-insulating crystals, while silicon doping leads to dislocation free n-type crystals. Controlling the stoichiometry of the GaAs melt also reduces dislocation densities but it is less effective than doping especially for large diameter crystals. It has been suggested that dislocations in GaAs originate from crystallographic glide induced by excessive thermal stress associated with crystal growth [3]. The crystallographic glide model implies that the CRSS of doped crystals increases compared to that of undoped crystals. Applying the thermoelastic stress model [3] to their results for growth of dislocation-free In-doped GaAs, S. McGuigan et al. [4] estimated that the CRSS of this material at temperatures close to the melting point had to exceed that of undoped GaAs by as much as a factor of 28 for dislocations to be eliminated. At the time these results could not be compared to experimental data on the mechanical properties of GaAs demonstrating the need for direct measurements at high temperatures of the CRSS of undoped and doped GaAs crystals. The objective of this paper is to review our results on the mechanical properties, in particular the CRSS, obtained on undoped, indium-doped and silicon-doped crystals from dynamic compression tests and to compare these results with data obtained from indentation rosettes. The consequences of our experimental results regarding dislocation formation and multiplication will be discussed.

2. Experiments

The experimental technique used for the compression tests has been described previously [5]. All crystals used in this study were Liquid Encapsulated Czochralski (LEC) grown in a low thermal gradient environment ($\approx 6^\circ\text{C}/\text{cm}$), fully encapsulated in B_2O_3 . All crystals were grown under identical conditions in order to minimize differences in native defect concentration, stoichiometry and residual stress that might influence the deformation behavior. For both indium and silicon doping, there is no real progressive decrease of dislocation density as the concentration of dopant is increased. An abrupt decrease of dislocation density is observed for an indium concentration of $1\text{--}2 \times 10^{19}/\text{cm}^3$. For silicon-doped crystals, this transition occurs at a net donor concentration of about $8 \times 10^{17}/\text{cm}^3$ which corresponds to $[\text{Si}] = 2 \times 10^{18}/\text{cm}^3$ (figure 1). The indium-doped sample was chosen above that transition, at $2.9 \times 10^{19}/\text{cm}^3$, and the two silicon-doped samples were chosen to correspond to values below and above this apparent critical value, at $[\text{Si}] = 1.5 \times 10^{18}$ and $3 \times 10^{18}/\text{cm}^3$. The characteristics of the samples are summarized in Table 1.

Statistical analysis of the experimental data obtained from a large number of samples have shown that the values obtained for the lower yield point (or CRSS) are reproducible within ± 12 percent [5]. However, in order to reassess our measurements and to increase our data base on the mechanical properties of the samples, well-defined indentation rosettes were generated at high temperatures with a Vickers indenter using small loads of 0.5, 1, and 1.5 g. These loads were chosen to correspond to the range of loads necessary to generate slip during the compression tests. A schematic of the set-up is shown on figure 2. The indenter itself was

machined to standard Vickers shape from a high purity sapphire rod 2 mm in diameter and mounted on a molybdenum rod. The motion of the indenter into the furnace cavity was electronically controlled so that a constant impact rate of 4 mm/hour was achieved which corresponds to the nominal strain rate of 10^{-4} /s used in the compression tests. To prevent oxidation of the surface of the sample, the furnace cavity was constantly flushed by a flow of Argon gas (4 liters/minute). This set-up allows indentation at up to 700°C. It is now being modified for indentation at higher temperatures. The samples, about 20x20x3 mm³ in size, laid flat on an oxygen-free boron nitride block, their lower and upper surfaces being parallel and polished. A chromel-alumel thermocouple, located under the sample in the boron nitride block was used to monitor the temperature of the sample during the indentation. The indents were performed on (111) B faces which can be etched reproducibly and in a controlled manner with HF:H₂O₂:H₂O (1:1:2).

3. Results

3.1. Compression tests

The experimental curves obtained as load on the sample versus time, were transformed into resolved shear stress versus percentage glide strain. The experimental values for the lower yield stress (or CRSS) versus inverse temperature are shown in figure 3(a) and 3(b) for undoped and indium-doped crystals and for undoped and silicon-doped crystals, respectively. The values obtained from constant loading experiments performed at low temperatures by Swaminathan and al. [6], (which have been used as reference data in the theoretical work mentioned previously [3,4]) are shown for comparison. Differences between these data and our results

have been discussed in [7]. The straight lines obtained by least-squares fit were used to determine the values of the CRSS at the melting point. These values are summarized in Table II.

At low temperatures ($T < 390^{\circ}\text{C}$), the CRSS of GaAs:In is less than that of undoped GaAs, while at higher temperatures it is greater. At the melting point, the CRSS of GaAs:In ($[\text{In}] = 2.9 \times 10^{19}/\text{cm}^3$) is only twice that of undoped GaAs. The opposite behavior is observed for GaAs:Si. At low temperatures, GaAs:Si is much more resistant to deformation. However, at elevated temperatures the CRSS of GaAs:Si is significantly lower than that of undoped GaAs and more surprisingly decreases with increasing concentration of Si.

3.2. Indentation

A typical indent (or rosette) on a $\langle 111 \rangle$ face revealed by chemical etching is shown in figure 4. This indent was obtained on an undoped sample at 500°C under a load of 0.5 grams applied for 2 seconds. This photograph shows that, under small loads, very well-defined rosettes can be obtained without cracks or slip lines to interfere with the motion of the dislocation loops generated by the indenter. The rosette displays a six-fold symmetry but does not exhibit the expected strong asymmetry between dislocations gliding on the internal apex of the tetrahedron formed by $\{111\}$ surfaces and those gliding on the external apex of the tetrahedron also formed by the $\{111\}$ surfaces [8]. It is significant that differences in velocities of the corresponding α and β dislocations could not be clearly revealed. We have performed similar indentations on (100) wafers of the same crystals, following the same experimental procedure, and observed different lengths of the rosettes' arms corresponding to α

and β dislocations. We have no explanation for these differences at the present time.

The method proposed by Hu [9] was first used to determine the CRSS of the samples and the results pointed to CRSS values equivalent to those obtained from our compression tests. However, for undoped samples numerous interactions between the dislocation loops created during the indentation and the dislocations present in the material prior to indentation are the source for excessively high scattering in the measurements, and it was found that the method could not provide reliable results. Therefore measurements of the indent size (i.e. average diameter) were chosen as a characteristic measurement of the material's hardness.

Vickers hardness values are obtained from the ratio of the load applied to the contact area which is: $VHN = 0.22 \times P/d^2$, where VHN is the Vickers hardness, P is the load and d is the indent size. However, increases in hardness values with decreasing indentation loads and indentation depth are often observed [10]. In addition, the relation between hardness and CRSS (or lower yield stress) is unknown for semiconductors. Therefore we use the ratio of hardness between the undoped (VHN_u) and indium-doped samples (VHN_{In}): $VHN_{In}/VHN_u = (d_u/d_{In})^2$, which is representative of the relative hardness of the samples.

Indentations were performed on undoped and indium-doped GaAs at 500 and 700°C. The results, indent size versus load, are shown in figure 5. At a given temperature, the size of the indents increases proportionally to the applied load. The ratio of hardness obtained for each load and temperature are summarized in Table III and compared to the ratio of the

CRSS obtained by compression. VHN_{In}/VHN_u is about 2.9 at 500°C and 3.2 at 700°C. These ratios are about two times the ratio of the CRSS obtained by compression tests at the same temperatures. As mentioned before, no precise relationships are known between CRSS and hardness and a more in-depth comparison of the data cannot be done. However, we can conclude that the indentation results confirm the results obtained from compression tests. GaAs:In is only two to three times more resistant to deformation than undoped GaAs.

4. Discussion

Both Si and In exhibit the same effects on dislocation density reduction except that one order of magnitude more In than Si is required to yield dislocation-free crystals (minimum $[In]=1-2 \times 10^{19} \text{cm}^{-3}$ versus minimum $[Si]=2 \times 10^{18} \text{cm}^{-3}$) [11]. Further, the behavior of axial dislocation and complex defects formed during single crystal growth is precisely the same in both In- and Si-doped, dislocation-free crystals [12]. Our results show clearly, as stated previously [5,7], that the effect of dopants on dislocation density reduction during crystal growth does not occur solely through a reduction of the crystallographic glide imposed by thermoelastic stress. It strongly suggests that once temperature gradients have been reduced to a value below which the thermoelastic stress is no longer dominant, a different mechanism, involving precipitation of native defects, must be operative. The subsequent distribution of any dislocations created must reflect the prevailing stress distribution within the ingot. This conclusion was also reached by Jordan et al. [13] who recently showed theoretically that for standard Czochralski growth conditions involving thermal gradients

exceeding $50^{\circ}\text{C}/\text{cm}$, it is not possible to grow dislocation-free crystals. They also showed that a dislocation density as low as $2000\text{--}4000/\text{cm}^2$ can in principle be achieved by using extremely low thermal gradients ($<10^{\circ}\text{C}/\text{cm}$) or a combination of moderate thermal gradients ($\approx 40^{\circ}\text{C}/\text{cm}$) and small amounts of impurity hardening. However, these authors used, as measure of hardening levels, values of CRSS slightly exceeding our experimentally measured values (0.1 to 0.3 kg/mm^{-2} compared to the experimental value of 0.08 kg/mm^{-2}). This difference is significant in that it shows that the main crystal growth technique in use today for production of GaAs, the LEC technique, has operating requirements that might prevent growth of dislocation-free undoped materials even if growth with shallow thermal gradients at the crystal/encapsulant interface is achieved.

We have also shown [5], in agreement with Sato et al. [14], that indium doping does not reduce dislocation formation by a simple solution hardening as proposed by Ehrenreich et al. [15]. High-resolution electron microscopy results support these findings, in that, at indium concentration sufficient to suppress dislocation formation ($[\text{In}] = 2 \times 10^{19} \text{ cm}^{-3}$), no indium or indium-rich precipitates were found [14].

Dislocation motion and multiplication occurs through glide or climb by nucleation and growth of jogs which must depend on the presence of point defects. Brice and King [17] and Parsey et al. [18] have shown that, for small diameter (20 mm) GaAs crystals grown by the horizontal Bridgman technique, there exists a close relationship between melt stoichiometry and dislocation density. Lagowski et al. [19] have shown, using the same experimental set-up as Parsey et al., a correlation between dislocation

density and Fermi level when melt stiochiometry is held constant. They found in agreement with Mil'vidskii et al. [20] and with deKoch [21] that dislocation density increases with p-type doping (Zn) while with n-type doping (Si) the dislocation density decreases. Parsey et al. [22] also found that doping with Si removed the arsenic pressure dependency of the dislocation density. At high temperatures, undoped GaAs contains large concentrations of intrinsic point defects which reach a minimum at the stiochiometric composition but are still quite high ($\approx 10^{18} \text{ cm}^{-3}$). As indicated by the above results, dislocation formation is closely related to these concentrations of point defects. The results obtained with Si and Zn doping strongly suggest that charged gallium vacancies are the main native defects responsible for dislocation formation and climb in GaAs [19]. However, the Fermi level correlation does not explain the effects of In (isoelectronic) doping nor the dislocation formation mechanism. Through electrical and structural characterization of crystals doped with other isoelectronic, n-type and p-type dopants, we expect to be able to further our understanding of the effects of impurities and native defects on dislocation formation and multiplication in GaAs.

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Table I. Characteristics of the GaAs crystals used for this study.

Crystal	Dopant concentration (cm^{-3})	Average resistivity ($\Omega \text{ cm}$)	Etch pit density (Dislocation density)
undoped	N/A	7×10^6	2000-3000
GaAs:In	2.9×10^9	1.8×10^7	0-100
GaAs:Si(1)	1.5×10^{18}	≈ 0.01	3000-4000
GaAs:Si(2)	3×10^{18}	≈ 0.01	0-100

Table II. Values of the CRSS at the melting temperature of GaAs.

Crystal	τ_{1y} (or CRSS) (g/mm ²)
undoped	41 $\pm$ 5
GaAs:In	82 $\pm$ 10
GaAs:Si (1)	32 $\pm$ 4
GaAs:Si (2)	27 $\pm$ 3

Table III. Ratio of hardness and CRSS measured at 500 and 700°C by indentation and compression, respectively.
(undoped and indium-doped crystals)

Load (g)	Indentation (VHN_{In}/VHN_u)		Compression ($CRSS_{In}/CRSS_u$)	
	500°C	700°C	500°C	700°C
0.5	3.1	3.9	1.2	1.5
1	2.6	3.0		
1.5	2.9	2.8		

Figure captions

- Fig. 1 Etch pit density (EPD) versus free-carrier concentration ($N_D - N_A$) for GaAs:Si.
- Fig. 2 Schematic of the indentation apparatus: (a) thermocouple, (b) sample, (c) indenter, (d) furnace, (e) Argon diffuser, (f) quartz chamber, (g) load, (h) loading cam, and (i) sample contact sensor, timing circuit and indenter lifting mechanism.
- Fig. 3 (a) Experimental values of the lower yield stress (or CRSS) versus inverse temperature for undoped and indium-doped crystals. Results are from compression tests.
- Fig. 3 (b) Experimental values of the lower yield stress (or CRSS) versus inverse temperature for undoped and silicon-doped crystals. Results are from compression tests. Values of ref. 4 are presented for comparison.
- Fig. 4 Photomicrograph of a rosette obtained on an undoped sample at 500°C under a load of 0.5 grams applied for 2 seconds.
- Fig. 5 Plot of indent size versus load applied for undoped (solid line) and In-doped (dashed line) sample at 500°C (full dots) and 700°C (open dots).

XBL 8611-4480

Figure 1.

XBL 874-9643

Figure 2.

Figure 3 (a).

Figure 3 (b).

XBL 8611-4482A

XBB 874-2613

Figure 4.

Figure 5.

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