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December 1986

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Prepared for the U.S. Department of Energy
under Contract DE-AC03-76SF00098

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Critical resolved shear stress measurements for silicon-doped GaAs single crystals

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The critical resolved shear stress of GaAs single crystals doped with silicon was directly measured using dynamical compression tests at high temperatures. At the melting point the critical resolved shear stress is 0.032 and 0.027 Kg/mm^2 fo crystals doped with $1.5x10^{18}$ and $3x10^{18}$ cm^{-3} silicon, respectively. These values are lower than that for undoped GaAs. This reinforces our earlier conclusion that solid solution hardening and the reduction of crystallographic glide is not the only mechanism by which dopants reduce the formation of dislocations during the growth of single crystals from the melt.

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We recently reported studies of the dynamic compression behavior of undoped and In-doped, liquid encapsulated Czochralski (LEC) grown GaAs at elevated temperatures[1]. We found that at the melting point the critical resolved shear stress (CRSS) for In-doped GaAs (2.9×10^{19} cm^{-3}) was only twice that of undoped material. Further, at low temperatures the activation energy for the motion of dislocations was not affected by the indium doping. As mentioned therein, these results have significant implications regarding the mechanism for dislocation formation during single crystal growth (heavily indium doped GaAs single crystals may be grown free of dislocations). It appears that the incorporation of In into the GaAs lattice does not manifest itself via a solution hardening mechanism as has been proposed,[2] and does not significantly reduce the extent of glide strain that might arise from thermoelastic stress at temperatures near the melting point.

Other dopants, silicon in particular, also have been found to significantly reduce dislocation density during single crystal growth.[3-6] The effect of these dopants likewise has been rationalized as a solution hardening phenomena.[3] However, Swaminathan and Copley[7] have examined the temperature and orientation dependence of the plastic deformation of single crystal, Si-doped GaAs, and extrapolation of their data to the melting point yields a CRSS of .042 Kg/mm^2, which is nearly the same as the CRSS of .041 Kg/mm^2 found for undoped material, suggesting that there is no solution hardening taking place.[1] Such behavior is very inconsistent with the currently accepted model for dislocation formation during single crystal growth, i.e., the thermoelastic stress model proposed by Jordan and others.[8,9]

The silicon concentration ([Si]=4.5x10^{18} cm^{-3}*) used in the study by Swaminathan and Copley is sufficient to reduce dislocation densities below those found for undoped GaAs provided that thermal gradients during growth are sufficiently low.[6,10] However, their material was grown by the horizontal Bridgman method and contained ≃ 10^5 dislocations/cm^2. It is important then to determine the effects of silicon dopant concentration and LEC growth on the critical resolved shear stress. In this letter we report on direct measurements of the critical resolved shear stress for Si-doped, LEC grown GaAs as functions of both temperature and composition, using dynamic compression testing.

The experimental technique used for the compression tests is the same as that described previously.[1] The crystals were grown in a low thermal gradient environment (6°C/cm axial gradient), fully encapsulated in B_2O_3 using the low pressure LEC process.[6] 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. The crystals were grown on the <100> axis 1200 grams charges presynthesized using the standard physical vapor transport technique.[11] Dopants were added to the gallium prior to synthesis. The crystals were cooled at ≃1°C/min after solidification. Figure 1 shows the effect of the carrier concentration in Si-doped crystals on the dislocation density. An abrupt decrease of dislocation density is observed when the free carrier concentration

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* This value for Si concentration was determined using the electrical parameters published by Swaminathan and Copley and tables of compensation ratio versus mobility and free-carrier concentration published by Walukiewicz, et al.[12] This assumes that the dominant shallow level impurities are Si_{Ga} and Si_{As}.

concentration is increased beyond about $5x10^{17}$ cm^{-3}. Reproducible growth of crystals with an etch pit density of less than 100 cm^{-2} is obtained for carrier concentration > $8x10^{17}$ cm^{-3} (which corresponds to [Si] ≃ $2x10^{18}$ cm^{-3}). The concentrations of silicon of $1.5x10^{18}$ cm^{-3} and $3x10^{18}$ cm^{-3} used in this study were chosen to correspond to values below and above this apparent critical value. The dopant concentration and etch pit densities at the top of the ingots used are shown in Table I. The samples for these deformation studies were rectangular prisms with square bases cut from regions near the top of the ingots. They were 8 mm in length with cross sectional areas of 8.5 mm^2. The length to width ratio was kept greater than 2.0.[1]

Typical stress-strain curves for heavily Si-doped material ([Si]=$3x10^{18}$ cm^{-3}) tested at various temperatures are shown in Figure 2. These curves were obtained by transforming the sample load as a function of time into resolved shear stress versus percentage glide strain. As discussed previously,[1] the lower yield point of the stress-strain curves was chosen as a valid estimate of the CRSS for slip.[13-15] The experimental values for the lower yield stress versus inverse temperature are shown in Figure 3. Values for undoped GaAs[1] are included for reference, as are data from Swaminathan and Copley.[7] The straight lines obtained by least-squares fit were used to determine $E/(m+2)$[1,16] and the values of the CRSS at the melting point of GaAs. These values are summarized in Table II. The values for the lower yield point (or CRSS) are reproducible within ±12%.[1]

Swaminathan and Copley obtained their data from constant loading experiments and their measurements of yield stresses are taken at the point of departure from linearity (elastic behavior). Thus, at high stress levels one expects lower values of their yield stress compared to the present data. At high temperatures, however, where the stress-strain curves are relatively flat

for either technique, one expects more similar results. Thus the extrapolations to the melting point give quite consistent CRSS values.

The theory of yielding[16] gives for the lower yield stress the following relation:

$$\tau_{ly} = C\,\dot{\varepsilon}^{(m+2)^{-1}}\,\exp[E/(m+2)kT]$$

where C is a function of the strain rate $\dot{\varepsilon}$, m is a kinetic factor characterizing the dependence of the dislocation velocity on stress, and E is the activation energy for the motion of dislocations. For the present case of Si in GaAs no value for m has been determined and, thus, no insight into the effects of Si on dislocation velocity in GaAs may be deduced. However it should be noted that Te, also an n-type dopant for GaAs, has been found to reduce dislocation velocity.[17-21]

Clearly, Si-doping affects the CRSS of GaAs. At low temperatures Si-doped material is much more resistant to deformation. However, at elevated temperatures the CRSS of Si-doped crystals is significantly lower, and more surprisingly decreases with increasing concentration of Si. This result reinforces our earlier conclusion that the effect of dopants on dislocation density reduction during single 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 below a value wherein thermoelastic stress is no longer a dominant process, a different mechanism must be operative. However, the subsequent distribution of any dislocations created must reflect the prevailing stress distribution within the ingot. The transition temperature at which CRSS (undoped) equals CRSS (GaAs:Si) is 900°C for [Si] = 1.5×10^{18} cm^{-3} and 1033°C for

[Si]=3x10^{18} cm^{-3}. Thus if one assumes that some type of a strengthening mechanism is operable, then the dislocations observed in undoped and lightly Si doped GaAs must be formed at temperatures below 1033°C.

Brice and King,[22] and Parsey, et al.[23] have shown that for the case of small geometries in the horizontal Bridgman growth of GaAs there is a close relationship between melt stoichiometry and dislocation density in the crystal grown from that melt. Lagowski et al.[24] have shown, using the same experimental arrangement as Parsey, et al., a correlation between dislocation density and Fermi level when melt stoichiometry is held constant. They found, in agreement with Mil'vidskii et al.[14] and with deKoch et al.[25] that with p-type doping (Zn) dislocation density increases while with n-type (Si) doping dislocation density decreases. Parsey et al.[26] 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 stoichiometric composition but are still quite high (≈10^{18} cm^{-3}). As indicated by the above results, dislocation formation is closely related to these concentrations of point defects. Dislocation motion and multiplication occurs through glide or climb by nucleation and growth of jogs which must depend on the presence of point defects. High thermal stresses will activate crystallographic glide creating the well-known four-fold symmetry pattern on (100) wafers, cut from crystals grown in the <100> direction. Reducing thermal stresses (crystals grown fully encapsulated or with afterheaters or crystals grown by Bridgman-type techniques), reduces the driving force for dislocation multiplication. However, for large diameter undoped GaAs, the average density of dislocations decreases to values in the range 1,000-5,000 cm^{-2}, but not to zero even for material grown at stoichiometry.

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.[24] However, the Fermi level correlation does not explain the effects of In (isoelectronic) doping nor the dislocation formation mechanism. Both Si and In exhibit the same effects on dislocation reduction except that an order of magnitude more In than Si is required to give dislocation-free material - $[In]=1\text{-}2\times10^{19}$ cm^{-3} versus $[Si]=2\times10^{18}$ cm^{-3}.[6] Further, the behavior of axial dislocations and complex defects formed during single crystal growth is precisely the same in both In- and Si-doped, dislocation-free material.[27] Indium substitutes for Ga and 94% of all In atoms occupy the Ga sublattice while 6% sit on the As sublattice[28]. Silicon is amphoteric and at a compensation ratio of 0.5, sits about 2/3 on Ga sites and 1/3 on As sites. Thus, both Si and In affect the equilibrium concentration of Ga and As vacancies and related point defects, but in different proportions. Point defects on both sublattices (e.g. $V_{Ga} + V_{As}$) are involved in the dislocation formation and climb processes. The present results suggest that the Fermi energy shifts[24] might be a consequence of defects absorbed or emitted during climb rather than the Fermi level shift being responsible for this behavior. Clearly, further effort is required to completely understand the observed phenomena.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the constant encouragement and support provided by Professor E.E. Haller and thank him for critical reading of the manuscript. They also are pleased to thank Professor E.R. Weber for valuable discussions during this work.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

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TABLE I. Characteristics of the GaAs crystals used for deformation studies.

Ingot #	Dopant (cm^{-3})	EPD* (cm^{-2})
H282	[Si] ≃ $3x10^{18}$	<100
RD1-043	[Si] ≃ $1.5x10^{18}$	3-4000

* EPD: etch pit density

Table II. Measured values for the CRSS of GaAs:Si; $\tau_{ly} = A \exp \frac{B}{kT}$.

Material	A (g/mm^{-2})	B (eV)	τ_{ly} at T = Tm (g/mm^{-2})
GaAs:Si ($3x10^{18}$)	0.15 ± 0.006	0.68 ± 0.03	27 ± 3
GaAs:Si ($1.5x10^{18}$)	0.79 ± 0.04	0.48 ± 0.03	32 ± 4

FIGURE CAPTIONS

Fig 1 Etch pits density (EPD) versus free-carrier concentration (N_D-N_A) for GaAs:Si.

Fig 2 Typical strain-stress curves for GaAs:Si (3×10^{18} cm^{-3}) at various temperatures.

Fig. 3 Experimental values of the lower yield stress vs inverse temperature for undoped[1] and silicon-doped GaAs. Values of ref. 7 are presented for comparison (see text).

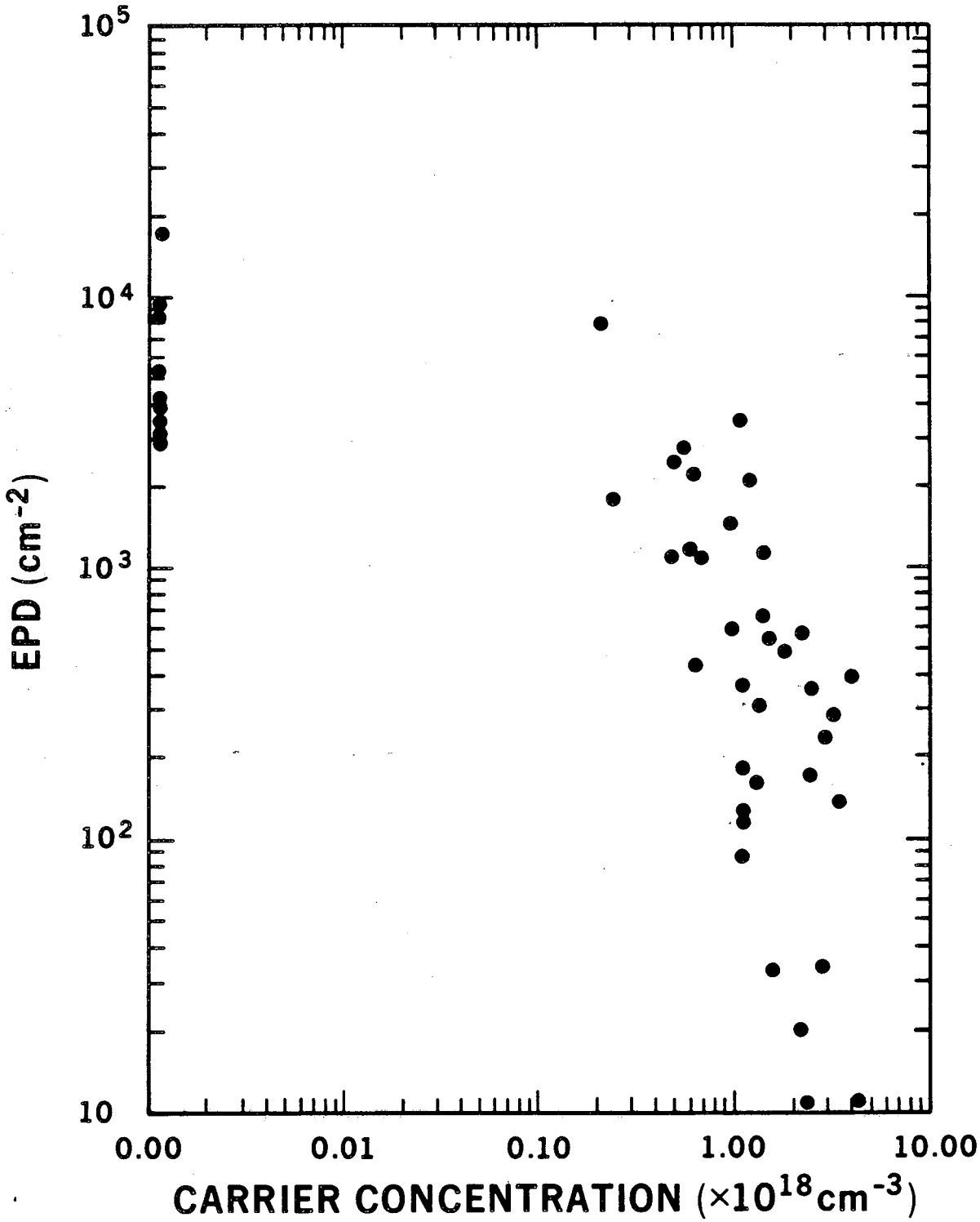

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Figure 1.

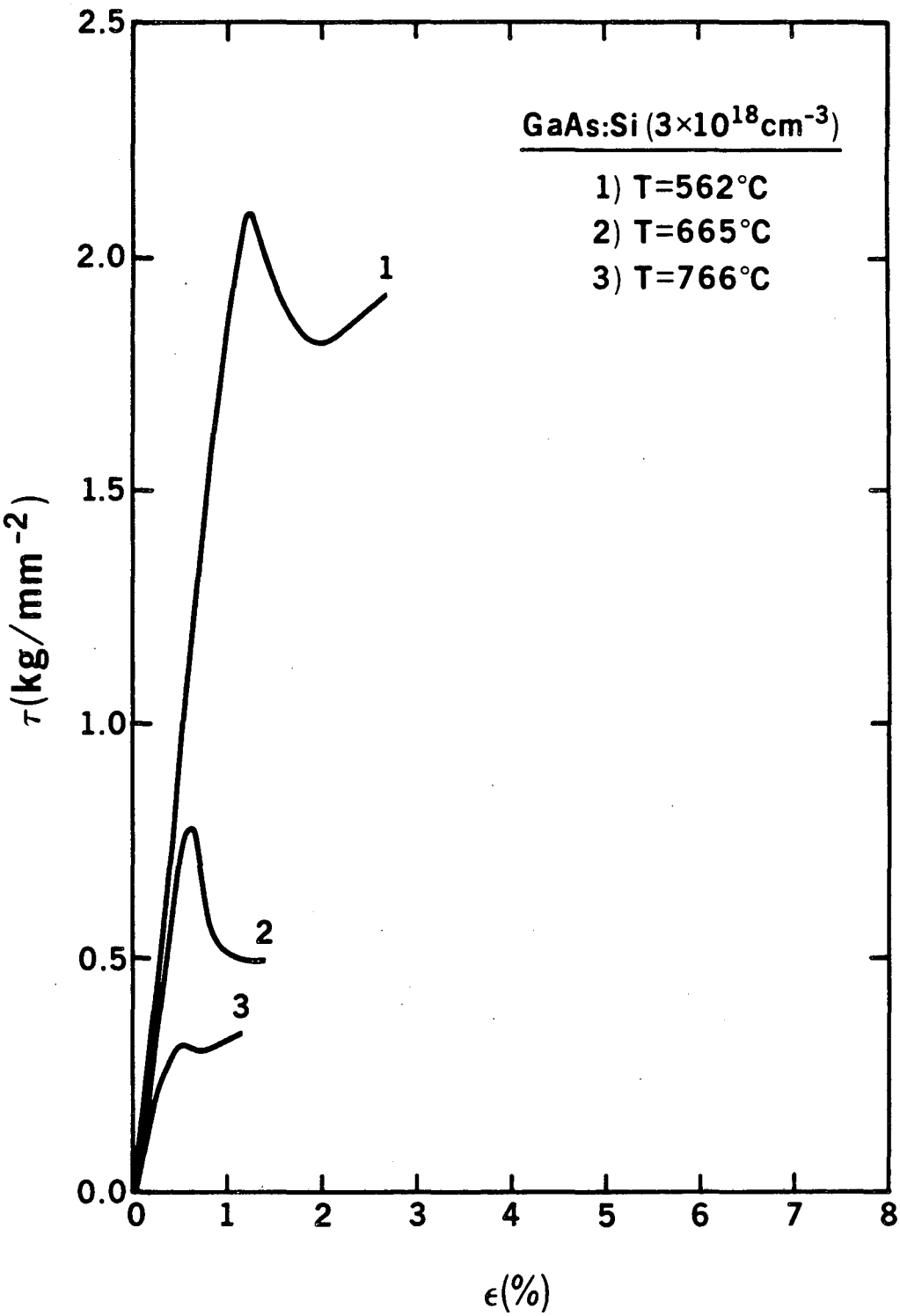

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Figure 2.

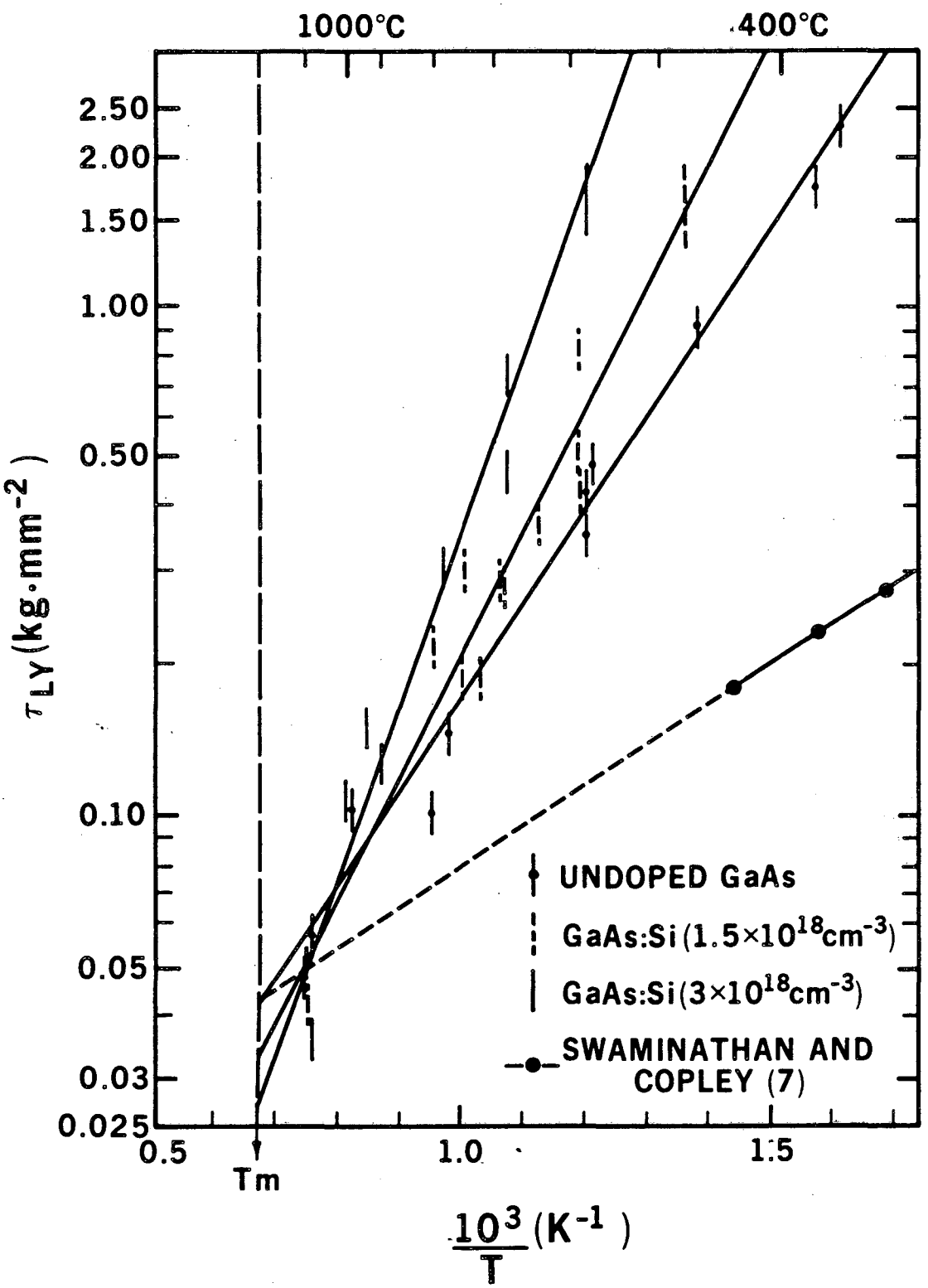

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Figure 3.

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