

Invited

Nonstoichiometric Defects in GaAs

Jacek Lagowski and Harry C. Gatos

Massachusetts Institute of Technology

Cambridge, Massachusetts 02139

Defects in as grown GaAs crystals and their evolution during subsequent device processing depends critically on the stoichiometry of the growth melt. Native point defects, whose formation is enhanced by deviations from melt stoichiometry towards arsenic-rich conditions are beneficial to GaAs technology, since they are responsible for the compensation mechanisms of semi-insulating undoped GaAs. Detrimental effects of nonstoichiometry originate in the high dislocation densities which affect reliability and yield of GaAs IC's. In this paper we discuss the current views and state of understanding nonstoichiometric defects, especially the antisite (and EL2!) and dislocations.

I INTRODUCTION

It is now well established that the reproducible growth of high quality SI GaAs requires stringent control of the crystal growth parameters and especially of the melt stoichiometry and of the thermal gradients in the solidifying ingot. The major role of melt composition was demonstrated in 1981-82 when the research groups of Rockwell International¹⁾ and Westinghouse R&D Laboratories²⁾ found that growth from melts slightly rich in arsenic yield SI GaAs crystals which have high electron mobilities, and are highly stable with respect to thermal annealing used in IC processing. These results had an immediate impact on GaAs IC technology. The beneficial effect of arsenic-rich growth conditions was clearly linked to an increase in the concentration of the native defect EL2. For the very first time in the semiconductor history a fundamental technological advantage was attained not by the elimination of native defects, but by the increase of their concentration.

In parallel, also in 1981-82, the MIT group demonstrated the crucial role of melt stoichiometry in minimizing the dislocation density³⁾. Furthermore, in the light of the effect of melt stoichiometry and donor impurities on the EL2 concentration they proposed the antisite defect model of creation of the midgap level EL2⁴⁾.

Table 1. MIDGAP LEVELS IN GaAs GROWN BY DIFFERENT METHODS

Growth Method	Concentration cm^{-3}	Dominant Level	Additional Levels	Major Factor	
				Upon Solidification	Post-Solidification
HB	1 to 5×10^{16}	EL2	-- ELO(1)	arsenic pressure above the melt	slow cooling low thermal gradients
CZ LEC	0.3 to 2×10^{16}	EL2	ELO(2) EL2 and/or others(3)	[As]/[Ga] in the melt	fast cooling, thermal gradients
VPE & MOVPE	0.1 to 5×10^{14}	EL2		[As]/[Ga] ratio in gas phase	low temperature
LPE	undetectable			Ga-rich conditions	low temperature
MBE	undetectable			very low growth temp.	very low temp.

(1) heavily 0-doped crystals
(2) small diameter crystals
(3) other midgap levels in large diameter crystals

The understanding of the formation and nature of native defects in GaAs is intimately related to two stages of crystal growth⁵⁾; (a) solidification phenomena, which take place at the solid-liquid interface during the crystal growth and (b) post-solidification phenomena which take place in the solidified material during subsequent cooling. The evolution of EL2 during GaAs growth involves both solidification and post-solidification phenomena. The various midgap levels (Table 1) in GaAs grown by different methods originate from differences in the characteristics of solidification and/or post-solidification processes.

II SOLIDIFICATION-RELATED PHENOMENA

Solidification-related effects on native defects are determined by the following major

factors:⁵⁾ (a) elevated temperature necessary for crystal growth; it promotes atomic disorder which is metastably retained in the crystals. (b) a finite existence region in which the Ga/As atom ratio in the solid can be different than one (deviation from stoichiometry). (c) dynamic effects; i.e., pronounced variations in the microscopic growth rate which lead to the incorporation of defects at the growth interface.

Deep Level EL2

The finite existence region is the dominant factor accounting for the increase of the EL2 concentration during growth from arsenic-rich melts. The results of the MIT group⁴⁾ (see Fig. 1) on Horizontal Bridgman (HB) growth of GaAs with the melt stoichiometry varied by changing the temperature of the arsenic source, T_{As} , have shown that the concentration of EL2 increases with increasing partial As pressure over the melt (i.e., with increasing arsenic atom fraction in the melt). Similar EL2 behavior was also observed in LEC-grown GaAs¹⁾. In Fig. 2 we have summarized the literature data on EL2 as a function of [As]/[Ga] ratio in the gas phase for VPE- and MOVPE-grown layers (o, Δ , I, & \square) after Ref. 6, 7, 8, & 9, respectively. Vapor phase growth takes place at about 700°C in contrast to melt growth at 1238°C. Thus, the epitaxial layers exhibit EL2 concentration 2 to 3 orders of magnitude lower than HB crystals. Nevertheless, an increase of EL2 concentration with increasing [As]/[Ga] ratio is evident in Fig. 2. Extrapolation of the VPE results of Fig. 2 to Ga-rich growth conditions representative of LPE growth (at a similar temperature range) leads to very low EL2 concentration consistent with experimental findings. Undetectable concentration of EL2 in MBE layers is a direct consequence of the very low growth temperatures at which the existence region vanishes. The dependence of EL2 concentration on [As]/[Ga] ratio in the melt is consistent with the assignment of EL2 to the arsenic antisite As_{Ga} , and it explains the stoichiometry induced n- to p-type transition encountered during LEC growth of undoped GaAs^{1,2)}.

Dislocations

The MIT group has also demonstrated the relationship between stoichiometry and density of dislocations³⁾. As shown in Fig. 3, the dislocation

density in HB GaAs crystals responds to the changes in melt composition in a way which is very similar to the behavior of nonstoichiometry, δ , shown in Fig. 4 and defined as the difference between the concentration of arsenic and gallium atoms (Ref. 10-11).

Stoichiometry-Controlled Inhomogeneities

The first indication of the effects of stoichiometry on the properties of GaAs on a micro-scale was provided by the analysis of the carrier concentration variations in melt-grown crystals (Ref. 12). In elemental semiconductors electrical inhomogeneities are caused by variations of the growth velocity. In GaAs, however, carrier inhomogeneities can develop even when impurities are distributed homogeneously throughout the crystal. Experimental results illustrating such behavior are shown in Figs. 5 and 6. It is seen in Fig. 5 that the total concentration of impurities [Ge] remains constant, whereas the concentration of free electrons exhibits dramatic fluctuations. This effect, which cannot be explained in terms of standard segregation kinetics, stems from stoichiometry-induced amphoteric behavior, i.e., impurity incorporation into Ga or on As sites, which leads to donor or acceptor behavior, respectively. Indeed we have proven that effects similar to those of Fig. 5 are produced by intentional stoichiometry changes during crystal growth, as shown in Fig. 6

III POST-SOLIDIFICATION PROCESSES

Post-solidification processes are related to two major factors²⁾: (a) supersaturation of the crystals with vacancies during cooling which migrate, recombine, interact, form complexes, coalesce into dislocations, and participate in dislocation climb. (b) excessive thermal stresses in the cooling crystal which generate dislocations and point defects with an inhomogeneous distribution dictated by the stress field.

For melt-grown GaAs the post-solidification defect interactions (factor a) can be identified and distinguished from processes taking place during solidification because they depend on the Fermi energy. At the melting point temperature, 1238°C, the Fermi level in GaAs is fixed at its intrinsic value and it cannot be changed by intentional doping at a level below 10^{18} cm^{-3} .

However, at lower temperatures experienced by the crystal during cooling, the intrinsic carrier concentration, n_i , decreases significantly, and moderate doping can be sufficient to vary the Fermi energy and thus change the charge state of the defects and their tendency to coalesce and migrate. The Fermi energy control of the EL2 concentration was demonstrated by the MIT group in 1981⁴⁾. In 1984 the same group¹³⁾ demonstrated the Fermi energy control of the coalescence of vacancy into dislocation loops. Both sets of results are summarized in Fig. 7 together with the corresponding Fermi energy change at a temperature of about 1100 K, which is believed to be a critical temperature in defect interactions.

The MIT group has proposed that EL2 and dislocations in crystals grown under low thermal stress depend critically on the migration of the gallium vacancy V_{Ga} to a neighboring site As_{As} , which creates the arsenic antisite (see Fig. 6).

Effects of Thermal Stress

Excessive thermal stresses in the solidifying crystal can generate dislocations¹⁴⁾, and point defects and their complexes¹⁵⁾. This additional channel of point defect generation is especially important during LEC growth of large diameter crystals. It leads to the generation of the midgap levels of the EL2 family which are not observed in HB GaAs and in small diameter LEC GaAs crystals grown by non-commercial groups. The spatial distribution of the stress-induced midgap levels follows the critical thermal stress pattern¹⁶⁾. This pattern, however, does not necessarily represent the concentration distribution of just EL2. Thus, relationships between EL2, the stress fields and the dislocation density pattern involves significant ambiguities which have not been realized in the past.

ACKNOWLEDGEMENT

The authors are grateful to the National Aeronautics and Space Administration and to the Office of Naval Research Laboratory for financial support.

REFERENCES

1. D.E. Holmes, R.T. Chen, K.R. Elliott and C.G. Kirkpatrick, Appl. Phys. Lett. 40, 46 (1982).
2. L.B. Ta, H.M. Hobgood, A. Rohatgi and R.N. Thomas, J. Appl. Phys. 53, 5771 (1982).
3. J.M. Parsey, Jr., Y. Nanishi, J. Lagowski, and H.C. Gatos, J. Electrochem. Soc. 128, 936 (1981); 129, 388 (1982).
4. J. Lagowski, H.C. Gatos, J.M. Parsey, K. Wada, M. Kaminska, and W. Walukiewicz, Appl. Phys. Lett. 40, 342 (1982).
5. J. Lagowski and H.C. Gatos, 13th Int. Conf. on Defects in Semiconductors, Coronado, CA, 1984, edited by L.C. Kimerling and J.M. Parsey, Jr., The Metallurgical Soc. of AIME, 1985, p. 73.
6. L. Samuelson, P. Omling, H. Titze and H.G. Grimmeis, J. Cryst. Growth 55, 164 (1981).
7. M.D. Miller, G.H. Olsen and M. Ettenberg, Appl. Phys. Lett. 31, 538, (1977).
8. P.K. Bhattacharya, J.W. Ku, S.J.T. Owen, V. Aebi, C.B. Cooper and R.L. Moon, Appl. Phys. Lett. 36, 304 (1980).
9. Z. Binglin, W. Le, S. Yongfu and C. Qiyu, Acta Physica Sinica 28, 350 (1979).
10. D.T.J. Hurle, J. Phys. Chem. Solids 40, 613 (1979).
11. V.T. Bublik et. al., Sov. Phys. Crystallogr. 17, 218 (1973).
12. L. Jastrzebski et. al., J. Appl. Phys. 51, 2301 (1980).
13. J. Lagowski, H.C. Gatos, T. Aoyama and D.G. Lin, Appl. Phys. Lett. 45, 680 (1984).
14. A.S. Jordan, R. Caruso and A.R. Von Neida, The Bell System Technical Journal 59, 593 (1980).
15. E.R. Weber, H. Ennen, U. Kaufmann, J. Windscheif, J. Schneider and T. Wosinski, J. Appl. Phys. 53, 6140 (1982).
16. D.E. Holms and R.T. Chen, J. Appl. Phys. 55, 3588 (1984).

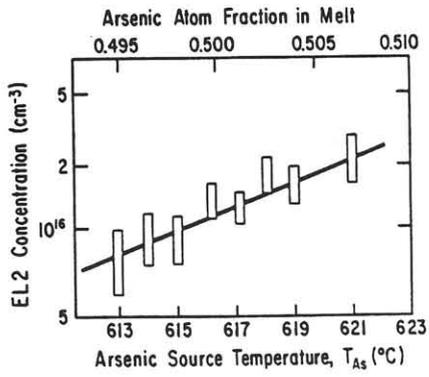


Fig. 1

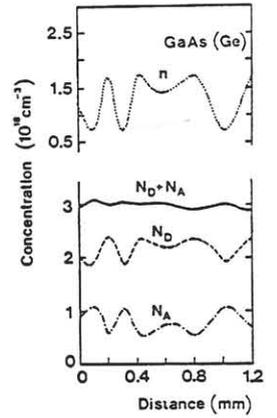


Fig. 5

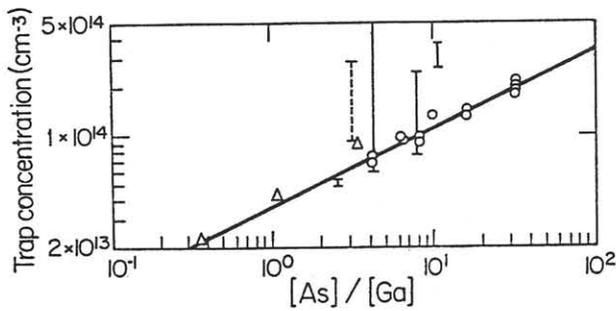


Fig. 2

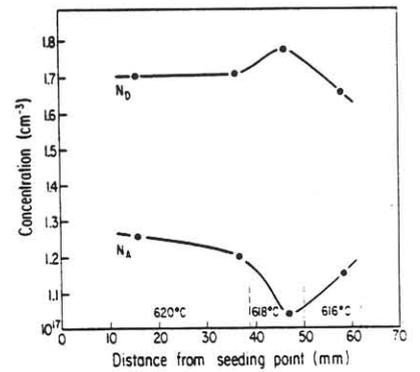


Fig. 6

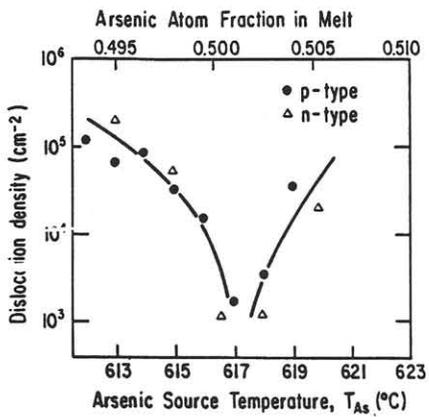


Fig. 3

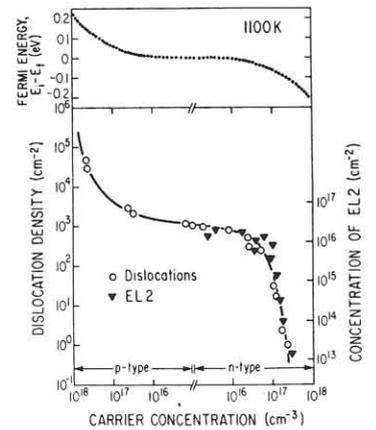


Fig. 7

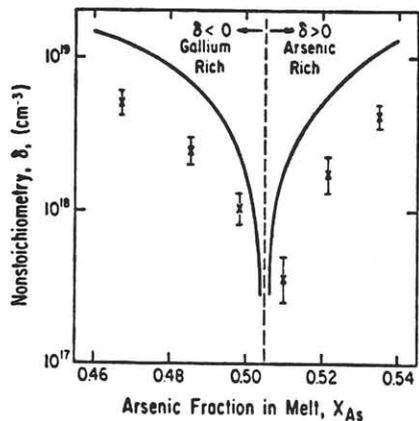


Fig. 4.

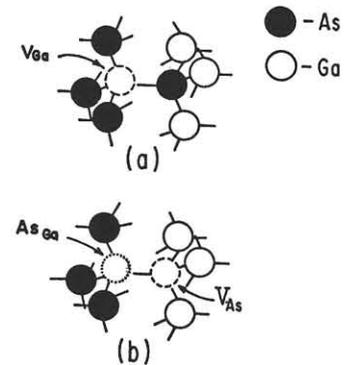


Fig. 8