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Stoichiometric defects in semi-insulating GaAs

NuoFu Chen*, Hongjia He, Yutian Wang, Lanying Lin

Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, People's Republic of China

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Abstract

The influences of arsenic interstitials and dislocations on the lattice parameters of undoped semi-insulating (SI) GaAs single crystals were analyzed. It was shown that the dislocations in such crystals serve as effective gettering sites for arsenic interstitials due to the deformation energy of dislocations. The average excess arsenic in GaAs epilayers grown by molecular-beam epitaxy (MBE) at low temperatures (LT) is about 1%, and the lattice parameters of these epilayers are larger than those of liquid-encapsulated Czochralski-grown (LEC) SI-GaAs by about 0.1%. The atomic ratio, $[As]/([Ga] + [As])$, in SI-GaAs grown by low-pressure (LP) LEC is the nearest to the strict stoichiometry compared with those grown by high-pressure (HP) LEC and vertical gradient freeze (VGF). After multiple wafer annealing (MWA), the crystals grown by HPLEC become closer to be strictly stoichiometric.

1. Introduction

The stability and uniformity in semi-insulating (SI) GaAs single crystals have close correlation with the stoichiometry in the crystals. Generally speaking, any structural defects in SI-GaAs may deviate the crystal from strict stoichiometry. The non-stoichiometry in SI-GaAs will deteriorate the related devices fabricated on GaAs [1–3]. Microdefects, including point defects and dislocations, and microprecipitates in SI-GaAs have been studied in detail [4–10]. However, the relationship between stoichiometry and the microdefects and microprecipitates was scarcely dealt with.

The stoichiometry in GaAs is deteriorated seriously by the dislocations and precipitates attached to the dislocations [1–3]. Molten KOH etching [4] is very sensitive for revealing the emergences of dislocations on the surfaces of GaAs single-crystal wafers. However, precipitates cannot be revealed by molten KOH method. It is considered that Abrahams–Buiocchi (AB) etchant [5] can be used for revealing both dislocations and precipitates in GaAs single crystals. But it is difficult to identify the etch pit patterns of dislocations and precipitates revealed by AB etching. Ultrasonic (US) AB [6] and US Doniach–Šunjić (DS) [7] methods are quite reliable for revealing both dislocations and precipitates in GaAs single crystals with low resistivity. The dislocations and precipitates in SI-GaAs can be revealed clearly with the newly improved USAB [11]. It has been detected

* Corresponding author.

by transmission electron microscope (TEM) equipped with energy dispersive X-ray spectrometer (EDS) that the precipitates attached to the dislocations in undoped SI-GaAs are arsenic depositions [12, 13]. However, it is very difficult to find a precipitate in LEC SI-GaAs with TEM.

In this paper the stoichiometrical defects in SI-GaAs grown by molecular-beam epitaxy (MBE) at low temperatures (LT) and liquid-encapsulated Czochralski (LEC) will be investigated. First, the theoretical basis is introduced in Section 2. The stoichiometrical defects in LT-MBE GaAs and LEC SI-GaAs are analyzed in Sections 3 and 4, respectively. Finally, Section 5 draws the conclusions.

2. Theoretical basis

The dislocations cause changes in the lattice parameters, since the lattice parameters over and below the dislocation line are contracted and stretched, respectively, the effect of dislocations on the average lattice parameter of the crystal is negligible. Due to the deformation energy of dislocations, the excess arsenic atoms are attracted to the dislocations and form precipitates there. In effect, such dislocations may serve as effective gettering sites for arsenic interstitials. Regions around these dislocation-dense regions are clear, representing essentially interstitial-free SI-GaAs. The amount of As atoms in an etch-pit-dense region, measured by scanning electron microscope (SEM) equipped with EDS [11], is approximately 1% larger than that in the adjacent clear region, and the amount of As in the etch-pit-free region is about the average of the amounts in the former two regions. Such results identify that the dislocations serve as effective gettering sites for arsenic interstitials.

The lattice dilation in SI-GaAs is principally caused by arsenic interstitial couples (i.e., two As atoms share the site of one As) [14]. The overall effect with respect to lattice dilation is, therefore, decrease in lattice parameter with increase in dislocation density.

According to the theory of elasticity, the relative increase in lattice parameter of SI-GaAs caused by

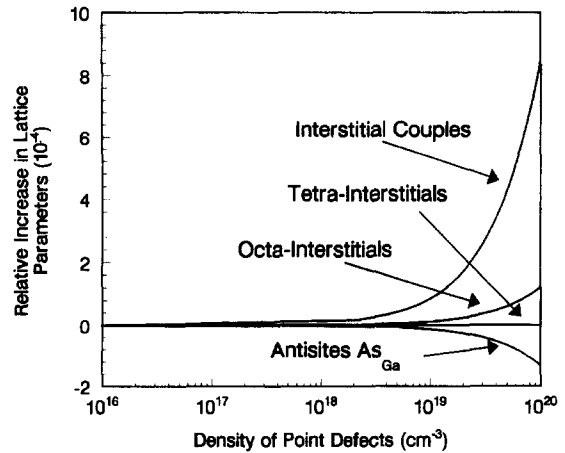


Fig. 1. Relative increase in lattice parameter of GaAs caused by point defects.

arsenic interstitial couples can be calculated [14]:

$$\frac{\Delta a}{a_0} = \mu \frac{d - d_0}{d_0} \frac{[As_{2,i}]}{N_0} = 8.545 \times 10^{-24} [As_{2,i}], \quad (1)$$

where N_0 and $[As_{2,i}]$ are the respective densities of the host atoms and the arsenic interstitial couples in cm^{-3} , $\mu = 1.9057$ is the elastic constant, $d_0 = r_{\text{As}} + r_{\text{Ga}}$, $d = 3^{-1/2} r_{\text{As}} + (d_0^2 - 2r_{\text{As}}^2/3)^{1/2}$, and $r_{\text{As}} = 1.18 \text{ \AA}$, $r_{\text{Ga}} = 1.26 \text{ \AA}$ are the chemical covalent radii of As and Ga, respectively. Compared with arsenic interstitial couples, the effects of other point defects on lattice parameter of GaAs are negligible, as shown in Fig. 1.

3. The stoichiometrical defects in LT-MBE GaAs

In order to study the stoichiometrical defects in LT-MBE GaAs and analyze the lattice parameter dilation, a series of samples were grown in a Riber 32P MBE system. The substrates were (1 0 0) LEC SI-GaAs wafers. The growth cycle consisted of two steps. First, a 200 Å thick conventional MBE GaAs buffer layer was grown at 600°C. Then, the temperature was decreased to 200°C in order to grow a 3 μm thick layer of LT-MBE GaAs. The surface was As-stabilized with an As_4/Ga flux ratio of 2. The growth rate for the epilayers was 1 μm/h.

The strains normal to the surface between the LT-MBE GaAs epilayers and the SI-GaAs substrates were studied utilizing a high-resolution SLX-1A X-ray double crystal diffractometer (Rigaku, Japan), with Cu $K\alpha_1$ radiation and (0 0 4) reflection. A typical X-ray rocking curve for an as-grown LT-MBE GaAs sample is shown in Fig. 2a. The two peaks obtained at different Bragg diffraction angles are shown. The peak at a smaller diffraction angle due to the LT-MBE GaAs epilayer disappeared after the sample was annealed at 600°C for

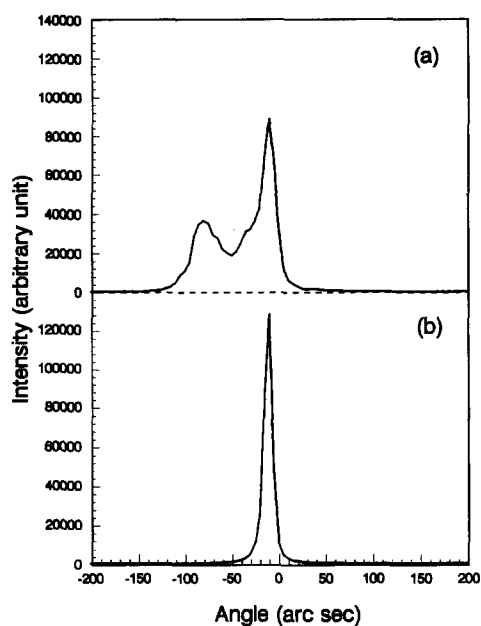


Fig. 2. Typical X-ray rocking curves of (a) as-grown LTMBE GaAs, and (b) after it was annealed at 600°C for 30 min.

30 min in a nitrogen environment, as shown in Fig. 2b. The excess arsenic in these LT-MBE GaAs epilayers were calculated according to Eq. (1), as listed in Table 1. The average excess arsenic in LT-MBE GaAs epilayers is about 1%, and the lattice parameters of these epilayers are larger than those of LEC SI-GaAs substrates by about 0.1%.

The arsenic interstitial couples may appear in LT-MBE GaAs. The GaAs grown by MBE requires the interaction of gallium and arsenic species impinging on a heated substrate surface. Either As_4 molecules and Ga atoms, or As_2 molecules and Ga atoms are used as constituent molecular beam species. If the temperature of the substrate surface is not high enough, the arsenic and gallium species impinging on it will not completely interact, and some dimeric arsenic remain as interstitial couples in LT-MBE GaAs. The fact that the arsenic interstitial couples decrease with increasing growth temperature can be interpreted by this model very well. The better interaction of As_2 and Ga than that of As_4 and Ga can also explain the decrease in point defects of LT-MBE GaAs grown with As_2 and Ga species [15].

Look et al. [16] and Liliental-Weber et al. [17] have supposed the existence of dimeric interstitials in GaAs before. The location of the excess arsenic in LT-MBE GaAs has been detected with ion channeling experiments [18]. Because the existence of the arsenic interstitial couples in LT-MBE GaAs is metastable, the rocking curve measurements on annealed samples show that the lattice parameters of the epilayers gradually decrease as the samples were annealed at temperatures higher than 300°C, and finally resume the value of the substrate when

Table 1
Relative increases in lattice parameter and corresponding densities of interstitial couples in LTMBE GaAs

Sample number	Relative increase in lattice parameter (%)	Density of interstitial couples ($\times 10^{20} \text{ cm}^{-3}$)	Growth temperature (°C)
9526	0.001	0.012	300
9510	0.030	0.351	260
9538	0.106	1.240	220
9512	0.108	1.264	200
9524	0.109	1.276	190

the annealing temperature reaches 450°C, as shown in Fig. 2b.

4. The stoichiometrical defects in LEC SI-GaAs

As analyzed above, the main point defects affecting lattice parameters of GaAs are interstitial couples. The density of As_{Ga} related deep centers EL_2 is only about $10^{16}/cm^3$. It will be seen that the density of interstitial couples in SI-GaAs is about $10^{19}/cm^3$. Eq. (1) represents the correlation of the relative increase in lattice parameter with the density of interstitial couples, which is in accordance with the experimental results that the lattice parameter of undoped SI-GaAs is directly proportional to the amount of excess arsenic atoms found by Terashima et al. [19].

Although the formation energy of tetrahedral interstitials is high, dense arsenic tetrahedral interstitials may appear near the melting temperature in melt grown GaAs. When an interstitial arsenic is ionized, it becomes positively charged [20], As_i^{3+} or As_i^+ . The As interstitial will be attracted to one of the nearest matrix arsenic atom's site, when the positively charged As_i^{3+} or As_i^+ deviates from the center of the tetrahedron, or octahedron, due to thermal vibration. Then the two mutually attracted particles will share the same matrix site and form a metastable interstitial couple.

The lattice parameters of GaAs were measured by Bond's X-ray diffraction [21]. The precision in lattice parameter determined by our measurements is estimated to be better than 1 part per million (ppm). The density of excess arsenic atoms in an undoped LEC SI-GaAs wafer can be calculated according to Eq. (1) and the average lattice parameter non-destructively measured with Bond's method in the dislocation-free mid-ring belt of a GaAs wafer.

The non-destructive measurements of stoichiometry (NDMS) in five samples were compared with the results of coulometric titration. Samples 1–3 were adjacent wafers cut from one as-grown undoped SI-GaAs ingot. Sample 3 was annealed at 850°C in a fluid nitrogen atmosphere for 30 min. Sample 1 was first annealed at 1100°C under an arsenic vapor pressure of 1 atm, and then

annealed at 850°C in a fluid nitrogen atmosphere. Sample 4 was cut from an undoped SI-GaAs ingot having had undergone conventional ingot annealing. Sample 5 is an as-grown SI-GaAs wafer. A quarter of each sample was cut off for coulometric titration measurements after their average lattice parameters had been measured. The atomic ratios of $[As]/([Ga] + [As])$ obtained by both the NDMS and coulometric titration methods are shown in Table 2. It can be seen that the results of as-grown wafers obtained by the two different methods agree very well. However, the amounts of As in samples 1 and 4 measured by NDMS technique are larger than those obtained by coulometric titration. This may be due to the dispersion of As thermally decomposed from As precipitates when the samples were annealed at high temperatures. The deviation in lattice parameter within the dislocation-free mid-ring belt is less than $1 \times 10^{-5} \text{ \AA}$, which ensures that the error of stoichiometry, calculated by NDMS technique, is less than 2.34×10^{-6} . The mean error of the two methods is 2.6×10^{-5} , which is less than the average standard deviation of coulometric titration, 6.4×10^{-5} .

Table 3 shows the stoichiometry in a series of SI-GaAs single crystals grown by low-pressure LEC (LPLEC), high-pressure LEC (HPLEC), vertical gradient freeze (VGF) techniques, respectively. From this table, it is clear that the crystals grown by LPLEC are the nearest to the strict stoichiometry compared with those grown by HPLEC and VGF. After multiple wafer annealing (MWA), the stoichiometry in the crystal grown by HPLEC becomes nearer to the value of VGF GaAs.

Table 2
Stoichiometry in SI-GaAs measured by NDMS and coulometric titration methods, respectively

Sample No.	$[As]/([Ga] + [As])$	
	NDMS	Titration
1	0.50012	0.50008
2	0.50016	0.50014
3	0.50013	0.50015
4	0.50014	0.50010
5	0.50017	0.50016

Table 3
Stoichiometry and lattice parameter of different SI-GaAs measured by NDMS

Growth technique	Lattice parameter (Å)	[As]/([Ga] + [As])
LPLEC	5.65348	0.50006
HPLEC	5.65375	0.50012
VGA	5.65363	0.50009
MWA-HPLEC	5.65362	0.50008

5. Conclusions

In summary, it was shown that the dislocations in SI-GaAs single crystals serve as effective gettering sites for arsenic interstitials due to the deformation energy of dislocations. The arsenic interstitial couples take charge of the dilation in lattice parameter of SI-GaAs. The average excess arsenic in LT-MBE GaAs epilayers is about 1%, and the lattice parameters of these epilayers are larger than those of LEC SI-GaAs substrates by about 0.1%. The atomic ratio, $[As]/([Ga] + [As])$, in SI-GaAs grown by LPLEC is the nearest to the strict stoichiometry compared with those grown by HPLEC and VGF. After multiple wafer annealing, the stoichiometry in the crystals grown by HPLEC becomes nearer to the strict stoichiometry.

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References

- [1] S. Miyazawa, T. Honda, Y. Ishii and S. Ishida, *Appl. Phys. Lett.* 44 (1984) 410.
- [2] M. Oyaka, H. Yamamoto, G. Kanno, T. Inoue and D. Oda, *Inst. Phys. Conf. Ser. No. 112* (1990) 311.
- [3] O. Oda, H. Yamamoto, M. Seiwa, G. Kanno, T. Inoue, M. Mori, H. Shimakura and M. Oyaka, *Semicond. Sci. Technol.* 7 (1992) A215.
- [4] J.B. Grabmaier and C.B. Watson, *Phys. Status Solidi* 32 (1969) K13.
- [5] M.S. Abrahams and C.J. Buiocchi, *J. Appl. Phys.* 36 (1965) 2855.
- [6] N.F. Chen, *Chin. J. Semicond.* 13 (1992) 763.
- [7] N.F. Chen, *J. Crystal Growth* 129 (1993) 777.
- [8] D.C. Look, D.C. Walters, M. Mier, C.E. Stutz and S.K. Brierley, *Appl. Phys. Lett.* 60 (1995) 2900.
- [9] M.C. Matragrano, D.G. Ast, G.P. Watson and J.R. Shealy, *J. Appl. Phys.* 79 (1996) 776.
- [10] D. Korytar, *J. Crystal Growth* 126 (1993) 30.
- [11] N.F. Chen, H. He, Y. Wang and L. Lin, *J. Crystal Growth* 167 (1996) 766.
- [12] A.G. Cullis, P.D. Augustus and D.J. Stirland, *J. Appl. Phys.* 51 (1980) 2556.
- [13] B.T. Lee, R. Gronsky and E.D. Bourret, *J. Crystal Growth* 96 (1989) 333.
- [14] N.F. Chen, Y.T. Wang, H.J. He and L.Y. Lin, *Phys. Rev. B* 54 (1996) 8516.
- [15] P.W. Yu, D.C. Reynolds and C.E. Stutz, *Appl. Phys. Lett.* 61 (1992) 1432.
- [16] D.C. Look, J.T. Grant and J.R. Sizelove, *Appl. Phys. Lett.* 61 (1992) 1329.
- [17] Z. Liliental-Weber, A. Ishikawa, M. Tarianchi and M. Tanaka, *Mater. Res. Soc. Symp. Proc.* 208 (1991) 183.
- [18] K.M. Yu, M. Kaminska and Z. Liliental-Weber, *J. Appl. Phys.* 72 (1992) 2850.
- [19] K. Terashima, O. Ohmori, A. Okada, M. Watanabe and T. Nakanisi, in: *Semi-Insulating III-V Materials*, Eds. H. Kukimoto and S. Miyazawa (North-Holland, Amsterdam, 1986) p. 187.
- [20] S.B. Zhang and J.E. Northrup, *Phys. Rev. Lett.* 67 (1991) 2339.
- [21] W.L. Bond, *Acta Cryst.* 13 (1960) 814.