One Alternative Process to Vapor Pressure Control for the Bulk Crystal Growth of GaAs

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〈Abstract〉 In this work, aiming at improvement of growth processes for the bulk GaAs single crystals, efforts have been made first to investigate thermodynamic properties of the Ga and As system and second to suggest that bulk GaAs crystals could be grown in principle with the single temperature zone only by determining the excess arsenic charge as a function of growth conditions. During crystal growth, this will be evaporized inside the growth chamber to induce the required inner pressure, instead of arsenic vapor pressure in the double temperature zone method, so as to be in equilibrium with the dissociation pressure from GaAs melt. For the practical applicability of this method, growth experiments have been prepared and carried out for doped and undoped GaAs crystals with the newly built Bridgman system which was designed according to this principle. To compare the results to those of the double temperature zone method, the same numbers of GaAs crystals have been grown with both processes and all of them were characterized in single crystallinity, lattice defects and electrical properties. Especially, the relationship between growth conditions and crystal quality was discussed from the viewpoint of growth peculiarities with this method.

Introduction

Until recently, two major technologies of Bridgman and Czochralski have been used for the bulk growth of GaAs crystals. Especially for IC applications of GaAs substrates, the needs for large diameter crystals are increasing so that crystal growth technology of 6 inch diameter GaAs is currently being developed. As the diameter becomes larger, it is more important to maintain the equilibrium arsenic pressure in the growth chamber to suppress the arsenic dissociation from GaAs melt during crystal growth even in the Czochralski process[1]. From the viewpoint of phase equilibrium, the Ga and As system is a uni-variant system such that once a growth parameter like temperature is determined, other ones like composition and equilibrium pressure ought to be dependent upon this. Furthermore, GaAs crystals can not be grown in the open system due to high volatility of the arsenic element[2]. It is, therefore, important to control growth parameters on the basis of intrinsic

thermodynamic properties. By doing so, desirable thermochemical equilibria for melt stoichiometry can be maintained during crystal growth[3], thus enabling large crystals like 6 inch diameter GaAs to be grown in uniform quality.

Theoretical Background

Regular solution model is applied for the calculation of arsenic partial pressures in equilibrium with GaAs melt, as Vieland[4] did for the first time in the Ga and As system. In view of non-ideal properties of GaAs solution, activity coefficient of arsenic element can be defined under the regular solution model. To obtain the excess free energy of GaAs solution upon mixing of Ga and As, Brebrick's model of cubic function of composition was adapted[5]. In consideration of the asymmetrical properties of reported experimental data of GaAs liquidus line, linear temperature approximation method[6] for binary compounds was chosen in our work, instead of the regular solution model[7,8,9,10]. With this, constants such as heat of fusion, entropy and melting point were referred to Lichter · Sommelet's experimental data[11]. As a result, liquidus line could be derived after average heat of formation at m.p. was determined.

If thermochemical data of the solid arsenic were referred to Herrick · Feber's result[12] and those of As_2 and As_4 were to Rau's[13], vapor pressures of As_4 and As_2 vapor species in equilibrium with the solid arsenic could be obtained. Thus, partial pressures of $As_2(g)$ and $As_4(g)$ over the pure liquid arsenic were determined by solving simultaneous equations. Thus, P_{As2} and P_{As4} can be calculated by substituting P^o_{As4} and P^o_{As2} along the liquidus line. In Table 1, partial pressures of arsenic vapors in equilbrium with GaAs melt at each liquidus temperature are listed.

Since arsenic dissociation pressure is calculated as 1.042 atm for stoichiometric GaAs at the melting point, it is necessary to suppress this by arsenic partial pressures

Table 1. Calculated partial pressures of dissociation from GaAs melt along the liquidus line (T : liquidus temp., γ_{As} : activity coefficient of arsenic in GaAs melt, P_{As2}, P_{As4} : partial pressure of each vapor species over GaAs melt)

x_{As}	T (K)	γ_{As}	P_{As2} (atm)	P_{As4} (atm)	P_{tot} (atm)
0.10	1243.48	0.1025	8.820 E-5	8.130 E-7	8.880 E-5
0.20	1364.75	0.1725	2.852 E-3	1.040 E-4	2.957 E-3
0.30	1447.33	0.2751	2.990 E-2	3.960 E-3	3.400 E-2
0.40	1493.95	0.4030	0.159	6.248 E-2	0.221
0.45	1508.95	0.4733	0.298	0.192	0.490
0.50	1513.005	0.5435	0.530	0.511	1.042
0.55	1509.00	0.6122	0.746	1.200	1.948
0.60	1497.03	0.6779	1.010	2.514	3.524
0.70	1448.50	0.7956	1.375	8.232	9.606
0.80	1361.84	0.8918	1.192	18.98	20.17
0.90	1214.28	0.9640	0.468	25.80	29.27

during crystal growth. For the single temperature zone method to be applicable to the bulk growth of GaAs, excess arsenic charge should be determined for the inner pressure to be exerted, so that it can be in equilibrium with the dissociation pressure during crystal growth. This was calculated on the basis of the simultaneous relationship between thermodynamic properties of arsenic element and its chemical reaction, as indicated in equation(1) and (2).

$$n^{As_4}_{tot.} = \frac{0.644(V_h - V_m)}{RT_h} + \frac{V_t}{R}\left[a + \frac{b}{\Delta T}\ln\left(\frac{T_h}{T_e}\right)\right] \quad \text{---(1)}$$

$$n^{As_2}_{tot.} = \frac{0.395(V_h - V_m)}{RT_h} + \frac{V_t}{R}\left[a' + \frac{b'}{\Delta T}\ln\left(\frac{T_h}{T_e}\right)\right] \quad \text{---(2)}$$

V_h : volume of growth chamber at the temperature T_h
V_m : melt volume of GaAs
R : gas constant
$\Delta T = T_h - T_e$ [T_e : the coldest temperature in the growth chamber]
a = -2.4×10^{-3} , b = 4.267 [constants for $As_2(g)$]
a' = 2.4×10^{-3} , b' = -3.23 [constants for $As_2(g)$]

Crystal Growth Experiments

Among various types of growing systems, the horizontal Bridgman type furnace was chosen for the growth system of this work, in consideration of experimental accessibility to fabrication and operation. The furnace system was designed and fabricated according to the principle of the single temperature zone method. The whole system is schematically depicted in Fig. 1.

Into this system, presynthesized poly-GaAs of 6N grade purity and excess arsenic charge, dopants in case of doping, a seed crystal of <111> orientation were charged after cleaning. Etchant was the solution of (H_2SO_4 : H_2O_2 : H_2O = 3 : 1 : 1). Residual particles were removed with DI(deionized) water and then baked under vacuum. Quartzwares such as boat and ampoule were treated with the solution of (HF : HNO_3 : H_2O = 1 : 10 : 10) in the same manner. Especially, quartz boat was sandblasted and etched with *aqua regia* solution. In the baking process, inner vacuum was adjusted in the range of 10^{-6} torr and then residual impurities were removed as a final step. Gas torch was used for sealing of ampoule with precaution not to evaporate the excess arsenic charge.

As it was calculated that effect of 1 ℃ variation in the single temperature zone method is equivalent to that of 28.5 ℃ in the double zone method, the temperature profile difference between the initial and final position during the growth run was controlled within ± 70 ℃ at the coldest temperature, as shown in Fig. 2.

To compare growth results of this process to those of the double temperature zone method, the same numbers of GaAs crystals were grown with both processes

and characterized from the viewpoint of single crystallinity, lattice defects level and electrical properties.

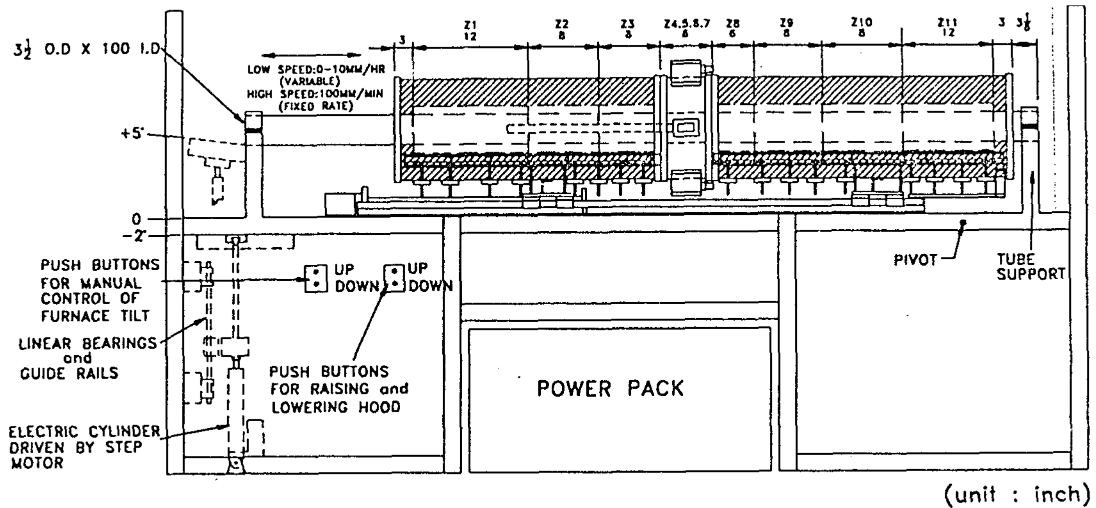

Fig. 1. Schematic diagram of the single temperature zone system

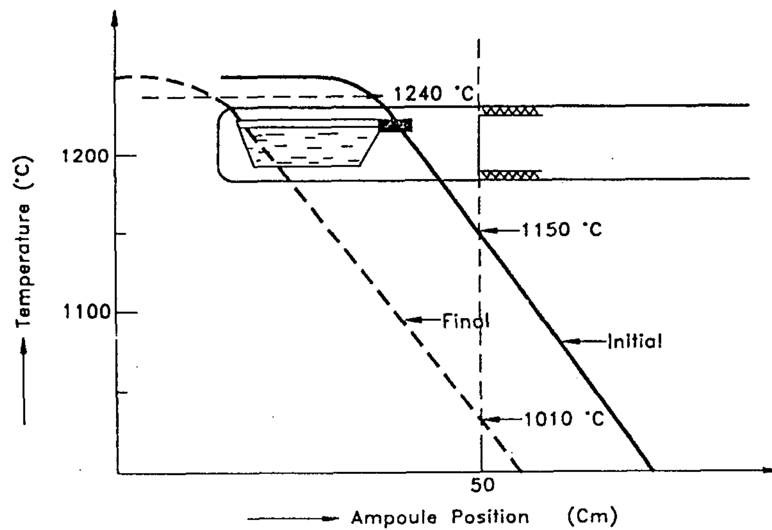

Fig. 2. Relationship between temperature profile and ampoule position before and after the growth run with the single temperature zone method

Results and Discussion

From the viewpoint of single crystallinity, all of crystals were twinned when they were grown without excess arsenic charge. Among various mechanisms of twin

generation during crystal growth of GaAs, the Ga-rich melt state seemed to be the main cause for this[14], because considerable arsenic dissociation should occur from GaAs melt without it. On the other hand, with the proper determination of excess arsenic charge, single crystals were successfully grown in this single temperature zone method(1-T) for not only undoped and but also doped crystals with Si and Zn. In comparison of the double temperature zone method(2-T), grown crystals with this method exhibit slightly higher yield in single crystalinity.

Sliced wafers were characterized on the (111) Ga face after etching with image analyzer system by mapping. For undoped crystals, EPD(etch pit densities) were in the range of 2×10^4 cm^{-2}, and for Zn-doped crsystals $\sim1\times10^4$ cm^{-2}, for Si-doped crystals $\sim5\times10^3$ cm^{-2}. At solidified fraction(g) of 0.1, they become by one order of magnitude higher than at the seed and then drastically decreasing after that of 0.3, as shown in Fig. 3. This shows that thermal shock can cause dislocation generation during and after seeding and that dislocations not parallel with growth axes will be finally extended to the free surface[15,16,17]. As a whole, lattice defects of grown crystals with both single and double zone methods show the similar tendency of EPD along the crystal length, irrespective of doping element.

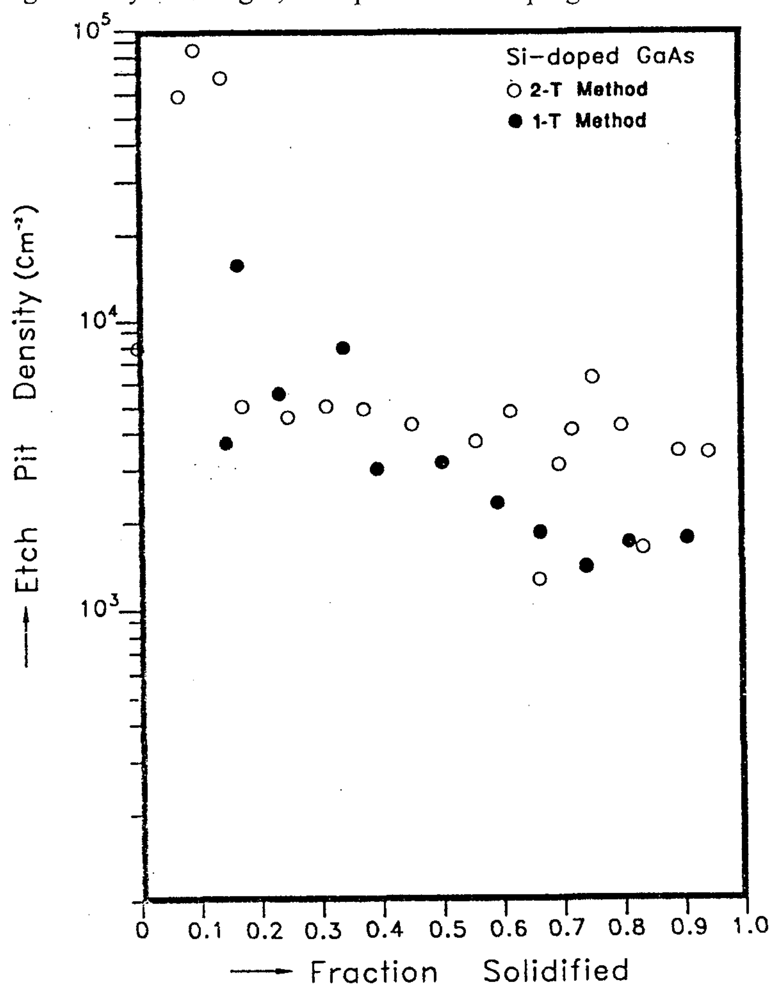

Fig. 3. Variation of EPD along the crystal length for Si-doped GaAs crystals grown with both processes

Carrier concentrations at the seed part are measured as $\sim 1\times10^{16}cm^{-3}$ for undoped GaAs, as indicated in Fig. 4. This is about half those of commonly grown GaAs[18,19,20], thus showing that higher purity crystals could be grown with this method.

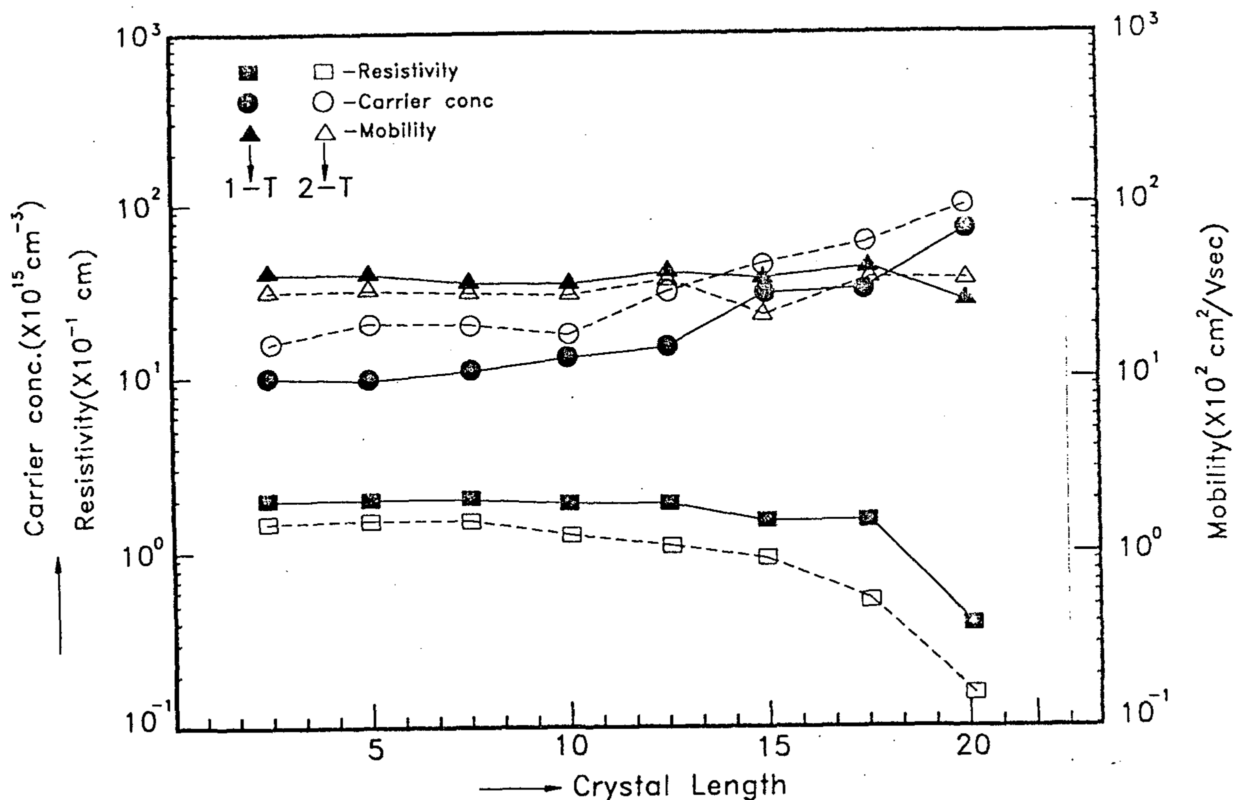

Fig. 4. Comparison of electrical properties with other reported data along the crystal length for GaAs crystals grown with both processes

Summary

In order for the single temperature zone method to be applicable to the crystal growth process for bulk GaAs crystals with such quality as can be competitive with the commercialized double or triple temperature zone method, general equations for the excess arsenic charge have been derived in terms of growth conditions, on the basis of the investigation of thermodynamic properties in the Ga and As system. With this, arsenic partial pressures can be induced in the growth chamber to be in equilibrium with the dissociation pressure from GaAs melt, so that melt stoichiometry can be maintained during crystal growth.

With the newly built Bridgman system according to the design of this principle, single crystals were grown for undoped, Zn-doped and Si-doped GaAs. All of them have been characterized and compared to those of double temperature zone method from the viewpoint of crystallinity, lattice defects and electrical properties. As a result, it is summarized as follows:

1. Arsenic dissociation pressure is calculated as 1.042 atm at the melting point of GaAs with partial pressures of As_2 and As_4 as 0.53 and 0.512 atm, respectively. It varies linearly with melt temperature and exhibits about 7 % increase for GaAs melt at 1260 ℃, compared to that at the melting point for the stoichiometric GaAs .

2. Lattice defects are measured as $\sim 2\times10^4$ cm^{-2} for undoped, $\sim 1\times10^4$ cm^{-2} for Zn-doped and $\sim 5\times10^3$ cm^{-2} for Si-doped GaAs. In comparison of those with the double temperature zone method, no appreciable difference is found. This means that melt stoichiometry could be maintained in the growth chamber at the same level for both processes and that effect of excess arsenic charge in this method is equivalent to vapor presssure control of the double temperature zone method.

3. From the measurement of electrical properties, carrier concentrations are shown as $\sim 1\times10^{16}$ cm^{-3} at the seed part for undoped GaAs, which is less than half those with double temperature zone method. Electron mobility is shown to be ~ 4,000 $cm^2/V\cdot sec$, while resistivity is in the range of ~ 0.2 $\Omega\cdot cm$. This result shows that GaAs crystals of higher purity can be grown with the single temperature zone method as a result of eliminating the colder temperature zone.

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