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Invited

X-Ray Diffraction Analysis of Stoichiometry of GaAs Crystals

Isao Fujimoto

Broadcasting Science Research Laboratories of NHK

1-10-11 Kinuta, Setagaya-ku, Tokyo 157, Japan

Nonstoichiometry of GaAs was detected in an accuracy of $c_{Ga}-c_{As}=3\times10^{-5}$ by measuring the X-ray intensities of quasi-forbidden reflections. Impurity doping and exhaustion of As by heat treatment were clearly observed. Fairly large deviations ($\sim10^{-4}$) with higher atomic concentrations in As lattice plane were found for liquid-encapsulated Czochralski(LEC) grown crystals compared with horizontal Bridgman(HB) grown ones, and their distribution were observed to have a close correlation with EPD. Nonstoichiometry of epitaxial layers(LPE and MBE) was found to depend on the growth conditions such as the species of the substrate and ratio of beam flux.

§1. Introduction

In contrast to Si, nonstoichiometry is a crucial problem in compound semiconductors such as GaAs. A high concentration of native defects associated with nonstoichiometry have a large influence on the electrical, optical and mechanical properties of GaAs; change of carrier concentration due to heat treatment under various As pressure,[1] effect of As pressure on the perfection of crystals grown by a horizontal Bridgman method,[2] thermal conversion during heat treatment and insulator-semiconductor interface problems. The low reliability and yield of GaAs devices compared with Si are due mainly to these unstable composition of compound semiconductors. Therefore, the characterisation of nonstoichiometry is important and various methods have been used to detect it; lattice parameter measurement,coulometric titration, ion beam scattering, photoluminescence measurement and other approaches. Each method, however, has some shortcomings and the detail of nonstoichiometry has not been clarified yet. In the present work,a new method[3] is presented by which a deviation from stoichiometry can be detected with an accuracy as high as $c_{Ga}-c_{As}\sim3\times10^{-5}$. Capabilities of the method is demonstrated by some applications.

§ 2.Principle of the measurement

Theprinciple is rather simple: The intensities of X-rays diffracted by a crystal are specified by the structure factor F which reflects the configuration of the constituent atoms as follows:

$$F=\sum_j (f_j+f'_j+f''_j)\exp(-M_j)\exp(2\pi i\mathbf{h}\cdot\mathbf{r}_j) \qquad (1)$$

where f_j is the atomic scattering factor of a j-th atom, f'_j and f''_j are the anomalous dispersion correction, $\exp(-M_j)$ is Debye-Waller factor and $\mathbf{r}_j$ is the atomic coordinate. There are some weak reflections in which X-rays scattered from Ga and As atoms are in opposite phases. For example, the hkl reflections with h+k+l=4n+2(n=0,±1,±2,---) arise from the small difference in scattering factors between Ga and As:

$$F=4\left\{(f+f'+if'')_{Ga}\exp(-M_{Ga})-(f+f'+if'')_{As}\exp(-M_{As})\right\} \qquad (2)$$

Equation (2) is the ideal formula assuming that Ga and As sites are fully occupied by the respective atom. In real crystals, nonstoichiometry is expected; there exist native defects such as vacancies, interstitials and their complexes which make the probability of finding a Ga and As atom at the respective site differ from unity. Since atomic scattering power increase with the number of electrons of the atom, vacancies and/or substitutional impurities with the atomic number much smaller than the host atoms diminish the scattering power of the net plane, whereas interstitials and/or impurities with larger atomic numbers increase it(it should be noted that the effect of antisite is small). Then, eq.(2) should be modified as

$$F=4\left\{c_{Ga}(f+f'+f'')_{Ga}\exp(-M_{Ga}) - c_{As}(f+f'+f'')_{As}\exp(-M_{As})\right\} \qquad (3)$$

Here, c_j is an effective atomic concentration in a respective net plane normalised to the ideal crystal, that is, $c_{Ga}=c_{As}=1$ for ideal crystal. For example, c_{Ga} can be given for Ga vacancies as

$$c_{Ga}=[Ga_{Ga}]/\left([Ga_{Ga}]+[V_{Ga}]\right)$$

$$= 1 - v_{Ga} \qquad (4)$$

where $v_{Ga} = [V_{Ga}] / ([Ga_{Ga}] + [V_{Ga}])$

A schematic presentaion of eq.(3) in a complex structure factor diagram is given in Fig. 1. It can readily be seen that a small deviation from unity results in a large variation of diffracted intensities of X-rays. A simple calculation shows that a small deviation of $c_{Ga} - c_{As} = 2.5 \times 10^{-5}$ casuses an intensity variation of 0.1% for MoKα radiation. At present, however, we have not the definite values of F(200) accurate enough for the absolute determination of nonstoichiometry. Therefore, in the present study, nonstoichiometry was measured relatively to a horizontal Bridgman (HB) grown crystal which is considered to have stable quality because of growth under equilibrium conditions.

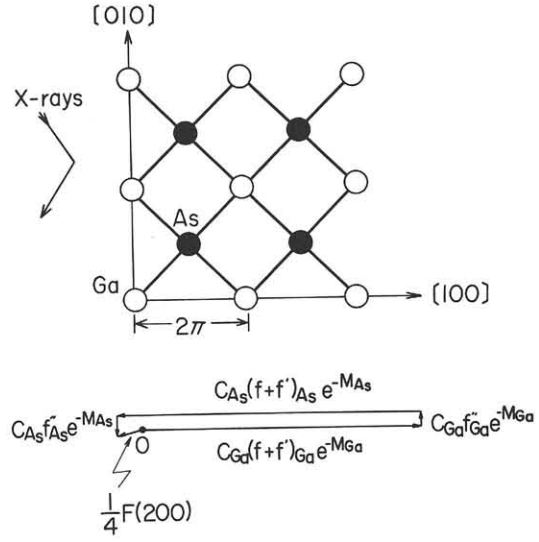


Fig. 1. Schematic presentation of the structure factor of 200 reflection.

Generally, lattice distortion increases the diffracted intensities of X-rays. However, for such a weak reflections as the quasi-forbidden reflections the effect is substantially small,e.g.,the ratios of I(mosaic)/I(perfect) for 200 reflection were calculated to be 1.10, 1.01and 1.03 for CuKα, MoKα andAgKα radiations, respectively, whereas the ratios for 400 reflection were 7.0, 3.9 and 5.5, respectively.[4] This was confirmed experimentally by measuring the change in intensities due to surface damage caused by lapping;I(200) was found to increase only by less than 1.8%, whereas I(400) to increase bymore than 25% for CuKα. Actually, the integrated intensities of 400 reflection from a highly dislocated region(EPD: 1×10^5 cm^{-2}) was observed to be about 4% higher than that from a perfect region. Therefore, the dislocation effect on the intensities of a quasi-forbidden reflection is considered to be negligibly small. The strain effect is still smaller with use of MoKα radiation.

§3. Experimental procedure

MoKα and CuKα radiations from a high power X-ray generator(60 kV 500 mA max.) were monochromatised by Ge 111 reflection. The integrated intensities were measured by rotating the specimen through Bragg position by an angle of 4'-6' of arc. Since for such a weak reflection, the effect of Umweganregung is quite large, the specimen was rotated around the axis vertical to the reflecting plane and set to an Umweganregung-free position. Measurements were made in pairs by rotating the specimen 180° around this axis to make a small correction for a misorientation between the crystal surface and the diffracting plane. The intensities of X-rays incident on specimen were monitored by measuring the scatterd X-rays from a thin mylar film.

§4. Results

4.1 Impurity effect

First,the effect of impurities on the integrated intensities of quasi-forbidden rerflections as described in §2 were investigatedd. The results are shown in Fig.2. As can be expected, the intensitiy of 200 reflection increases when those impurities like Si and Al, which have smaller atomic number than host atoms, occupy Ga site, whereas it decreases when heavier atoms like In occupy Ga site. The agreement between the measured values and the calculated one is satisfactory, though some deviations are noted for Si. Thus the validity of the present method was verified.

4.2 Evaporation of As by heat treatment

Second, thermal conversion by the heat treatment was investigated. Semi-insulating HB grown crystals were prepared and their surfaces half-coated

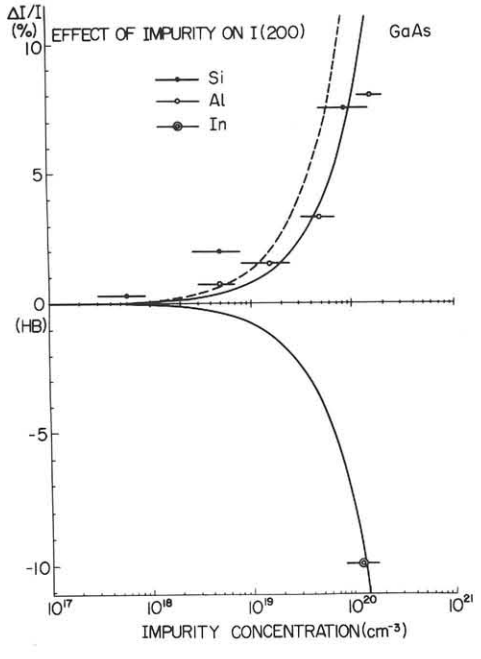
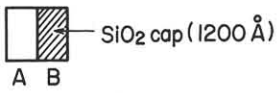


Fig.2. Effect of impurities on I(200). Calculated values for impurities (solid line) and for native defects (dotted line).

by rf-sputtered SiO_2 thin film. Heat treatment was made in N_2 ambient gas at 850°~890°C for 20~50 min. The X-ray intensities of ordinary reflections increased for the uncoated parts because of the lattice distortion around the induced defects, whereas those for quasi-forbidden reflections decreased markedly. It can readily be seen on the basis of formula (3) that a fairly large amount of As is exhausted from the uncoated surfaces. For the (111) Ga surface, no difference was observed in the diffracted intensities of X-rays, indicating that the Ga surface is very stable for heat treatment (Table 1).



	(100) 850°C 50min.		(111) 890°C 20 min.			
hkl	200	400	222	333	$\bar{2}\bar{2}\bar{2}$	$\bar{3}\bar{3}\bar{3}$
I(A) / I(B)	0.78	1.28	1.00	1.00	0.86	1.16
$C_{Ga} - C_{As}$	5×10^{-3}		0		3.5×10^{-3}	

Table 1. Nonstoichiometry of GaAs(HB) caused by heat treatment in N_2 gas.

4.3 LEC(liquid encapsulated Czochralski) crystals

Extensive studies have been made on GaAs IC's. The yield and the stability ,however, are still far behind Si devices due mainly to a high defect densities and to the electrical and optical inhomogeneities in crystal wafers: Resistivities, mobilities,photoluminescence intensities and threshold voltages of FET have shown W-or M-shaped profiles along a wafer diameter which have a close correlation with distribution of dislocation densities(EPD).[5,6] Since the growth condition is not so moderate as in HB method, a high concentration of native defects may still remain at room temperature. From this viewpoint, the undoped semi-insulating LEC crystals were investigated. The result is shown in Fig. 3 ; nonstoichiometry shows W-shaped radial distribution and has a close correlation with EPD. What is more remarkable is that the amount of deviation was fairly large with higher atomic concentration in the As lattice plane compared with HB grown crystals. On the basis of eq.(3), the possible explanations for the observed deviation are

(1) excess Ga vacancies, V_{Ga}

(2)As and/or Ga atoms at interstitial site in the As lattice plane

(3)substitutional impurities at Ga site with small atomic number such as B,C and O.

It should be noted that the X-ray intensities of 200 reflections from HB crystals ,LPE and VPE on HB wafers were at a similar level. If we assume that they have a nearly stoichiometric composition, the observed nonstoichiometry in LEC crystals corresponds to a high concentration of defects, 10^{18}–10^{19} cm^{-3} in total atomic densities. It has been reported by secondary ion mass spectrometry(SIMS) or IR analysis that the contents of B,C and O is usually less than 10^{17} cm^{-3}; therefore our result cannot be attributed to residual impurities alone. The present results indicate that a remarkably high concentration of native defects which have been induced at melting temperature still remains at room temperature. The defect densitiy observed in the present study is much larger than that found so far by electrical and optical measurement of the order of 10^{16} cm^{-3}. This discrepancy, however, may be understoodby assuming that aggregates of point defects act as the electrical and opotical centers observed, though the atomic structure and the electrical and optical properties are yet to be determined.

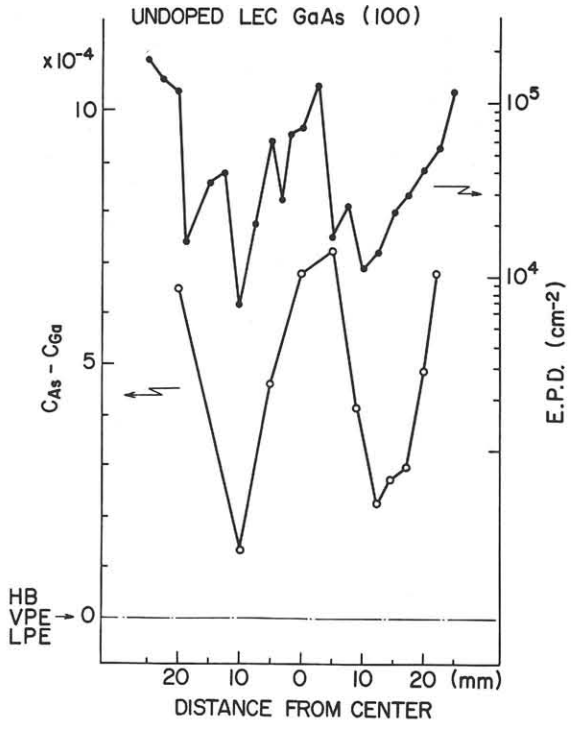


Fig. 3. Profiles of EPD and nonstoichiometry for undoped LEC GaAs (100) wafers.

The observed correlations of nonstoichiometry with dislocation densities could be explained either by dislocation multiplication due to native defects or by the large deviation from stoichiometry around dislocations as a result of Cottrell atomsphere which has been shown recently by variations of electrical and optical properties.

4.4 Epitaxial layers

It has generally been accepted that epitaxially grown crystals show better quality with less amount of defects than bulk crystals. In the present study , the nonstoichiometry of epitaxial layer grown under various conditions was investigated.

4.4.1 LPE(liquid phase epitaxy)

Two types of substrates were prepared;an undoped semi-insulating LEC grown crystal and a Si-doped($1x10^{18}$ cm^{-3}) HB grown one. Undoped epitaxial GaAs layers were grown 50 μm thick on the two substrates simultaneously.The result is shown in Fig. 4. The nonstoichiometry of the epitaxial layer on LEC substrate was found to show similar radial distribution to that of the substrate whereas that on HB substrate does not show recognizable deviation from that of substrate itself. Radial distribution of photoluminescence intensity at room temperature was found to show correlations with that of nonstoichiometry; PL intensity is weak at the position where the deviation from stoichiometry is large. At present detail of the mechanism of this transfer of nonstoichiometry is not clear and left to be solved.

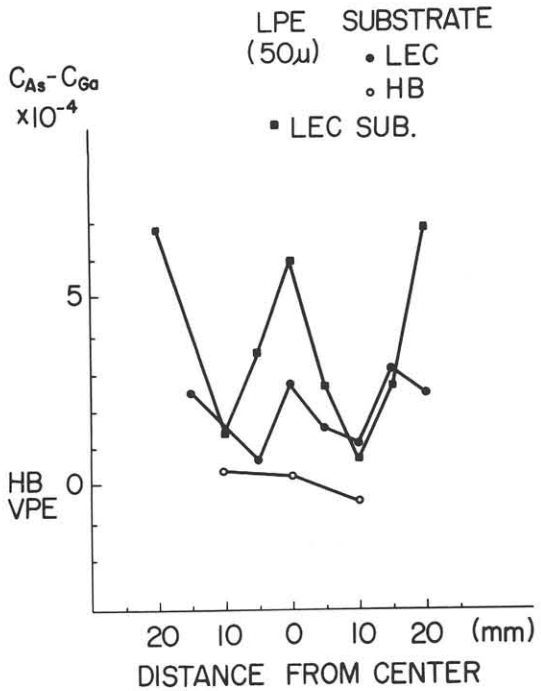


Fig. 4. Profiles of nonstoichiometry of LPE layers on HB and LEC substrate.(▪) represents the profile of LEC substrate.

4.4.2 MBE(molecular beam epitaxy)

Extensive studies have shown[7] that the characteristics of MBE grown GaAs layer varies with the flux ratio $\gamma = J_{As_4}/J_{Ga}$. Therefore, the present method was applied to the characterisation of nonstoichiometry of epitaxial layer(4μm thick) grown under various γ(0.5< γ<5.6). Photoluminescence intensity at room temperature was also measured. The results are shown in Fig.5a,b. For higher γ case (γ> 2.8), the atomic concentration of As lattice plane is higher than that of Ga plane, and the PL intensity is weak. For 1<γ<2, the nonstoichiometry come close to that of HB crystals, and PL intensity was found to show maximum. For Ga rich condition (γ<0.7), however, the concentration of As lattice plane was also found

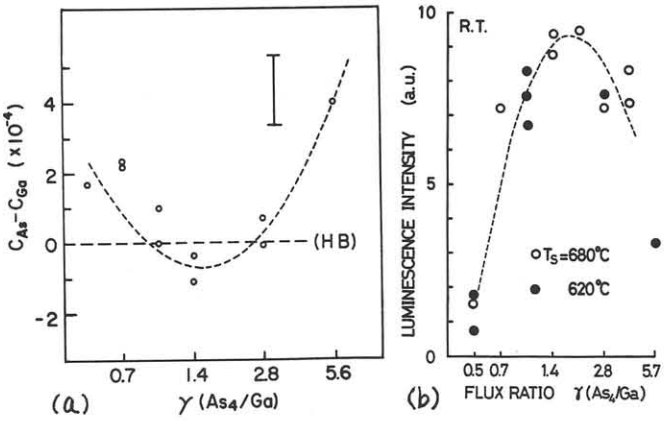


Fig. 5 Variations of nonstoichiometry(a) and PL intensity(b) with flux ratio γ.

to rise, and correspondingly PL intensity decreases. A plausible explanation for this unexpected behaviour will be given by a detailed study.

§5. Conclusion

The nonstoichimetry of GaAs was directly measured by a new X-ray diffraction method, though some problems are yet to be solved; exploitation of the method for its absolute determination, identification of species of defects and the improvement of accuracy. Further refined measurements with higher accuracy will provide us with an important knowledge on GaAs such as conversion of surface layers caused by ion implantation or by deposition of insulating films.

We can also apply the present method to other kinds of crystals such as InSb,ZnSe,CdTe,AlP and BN. Although its application to GaP and InP is difficult as can be seen from the principle of the present method, ternary and quaternary compounds like InGaAs, InGaAsP,CdHgTe,---,etc. with appropriate composition ratio can be investigated.

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