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NONDESTRUCTIVE MEASUREMENTS OF STOICHIOMETRY IN UNDOPED SEMI-INSULATING GALLIUM ARSENIDE BY X-RAY BOND METHOD

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The influences of microdefects and dislocations on the lattice parameters of undoped semi-insulating GaAs single crystals were analyzed, and a novel nondestructive method for measuring stoichiometry in undoped semi-insulating GaAs was established in this letter. The comparison of this method with coulometric titration indicates that the method of nondestructive measurements is indeed convenient and reliable.

There is a great need for semi-insulating (Si) GaAs single crystals in integrated circuit (IC) fabrication because of its high electron mobility, high saturation velocity, high working temperature, and low noise. However, variations in threshold voltages of field effect transistors (FETS) fabricated from ion-implanted, Si-GaAs wafers grown by the liquid-encapsulated Czochralski (LEC) technique makes it difficult to realize large scale GaAs ICs. These variations in device response are caused by microstructural non-uniformities in the Si-GaAs substrate.

Non-uniformities in Si-GaAs wafers are associated with both dislocations [1, 2], and micro-defects [3, 4]. It is also found that the activation efficiency and uniformity of carrier concentration profiles in Si-implanted layers are affected by the stoichiometry in LEC Si-GaAs substrate [5]. Many methods [6-9] exist for studying and characterizing dislocations in GaAs. However, stoichiometric defects can only be measured directly by coulometric titration method [10]. Because this technique is based upon a destructive electrochemical measurement, the coulometric titration is inconvenient as a conventional method for studying such defects.

Our recent studies [11] about the effects of point defects on the lattice parameters of undoped Si-GaAs

reveal that the dilation in lattice parameters of undoped Si-GaAs is principally caused by arsenic interstitial couples (i.e., dimeric arsenic in one site of arsenic atom). Empirically, it was determined that the relationship between excess arsenic and the lattice parameters in dislocation-free Si-GaAs is given by:

$$\frac{\Delta a}{a} = 0.3777 \frac{N_c}{N_0} \quad (1)$$

where $\Delta a = a - a_0$ is the difference between the measured and standard lattice parameters of undoped Si-GaAs, N_0 and N_c are the respective densities of GaAs (#Total Ga and As atoms/cm³) and arsenic interstitial couples (#Excess As atoms/cm³). This correlation is in accordance with the experimental results that the lattice parameters of undoped Si-GaAs are directly proportional to the amount of excess arsenic atoms found by Terashima et al. [12].

The effects of dislocations on the lattice parameters sketched in Fig. 1. Because 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 As interstitials. Regions around these dislocations represent essentially, interstitial-free Si-GaAs. The overall effect in regards to lattice dilation is therefore, a decrease in lattice parameter with an increase in dislocation density. This effect has indeed been observed as shown in Fig. 2. It can be seen in Fig. 2 that the lattice parameter remains invariant for dislocation etch pit densities both below $3 \times 10^4 \text{ cm}^{-2}$ and above $3 \times 10^5 \text{ cm}^{-2}$. Between these two regions, there is a significant decrease in lattice parameter from approximately 5.6539 to 5.6532 angstroms with increasing dislocation etch pit density. It indicates that below a certain threshold level of dislocation density ($3 \times 10^4 \text{ cm}^{-2}$ in this experiment) the deformation energy is not powerful enough to attract As interstitials around dislocations, when dislocation density exceed this threshold it begin to attract As interstitials

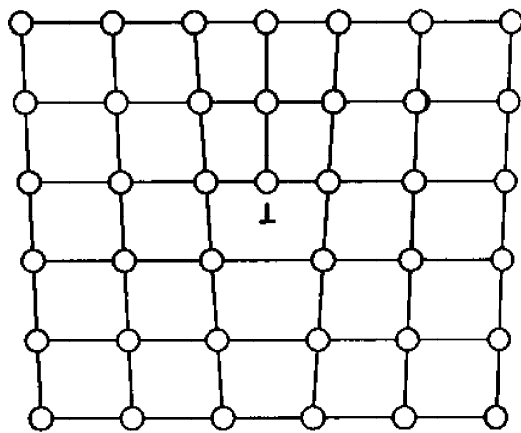


Fig. 1 Sketch of the effects of a dislocation on the lattice parameters of single crystal.

significantly, and after the dislocation density reaches another threshold ($3 \times 10^5 \text{ cm}^{-2}$ in this experiment) all of the As interstitials around dislocations are attracted to them and precipitate there. The dislocation density shown in this figure was measured by etch pit density revealed by molten KOH etching [7] and the lattice parameters were calculated by Bond's method [13] utilizing SLX-1A X-ray double crystal diffractometer (Rigaku, Japan), with Cu $K\alpha$, radiation and (004) reflection. The precision in lattice parameter determined by our measurements is estimated to be better than 1 part per million (ppm).

The arsenic interstitial couples are decomposed at high temperatures. Some of them near very dense dislocations or dislocation walls precipitate, and the other in dislocation-free regions recover as the temperature goes down due to the lack of nucleation centers. It agrees with that the precipitates revealed by Abrahams and Buiocchi (AB) etching [6] are always along dislocation lines, and transmission electron microscope (TEM) observations identify that most of the precipitates are arsenic [14, 15]. Fig. 3 shows the distribution profile of lattice parameters of a (001) undoped Si-GaAs wafer along (110) direction. The distribution profile shows a M-shape, which is reciprocal with the W-shape distribution profile of dislocations. The amounts of As atoms in an etch-pit-dense region and an adjacent etch-pit-free region were measured by scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometer (EDS). The results of EDS show that the amount of As in the etch-pit-dense region is approximately 1% larger than that in etch-pit-free region. Such results indicate, once more, that the dislocation serve as effective gettering sites for As

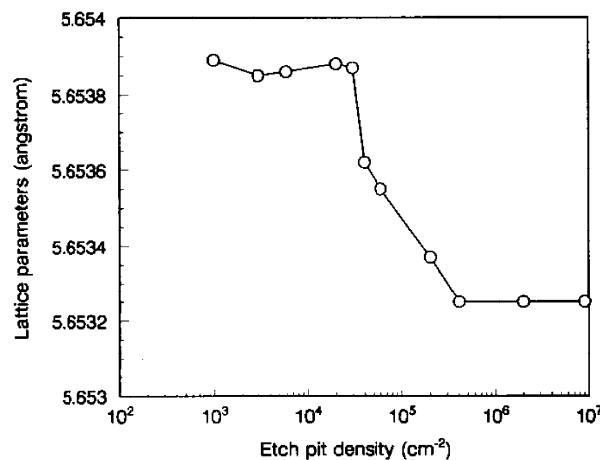


Fig. 2 The correlation of lattice parameters with dislocation densities.

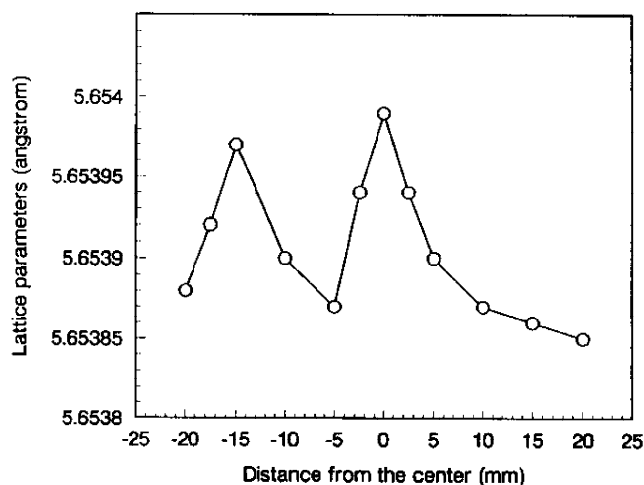


Fig. 3 The distribution profile of lattice parameters of a (001) GaAs wafer along (110) direction.

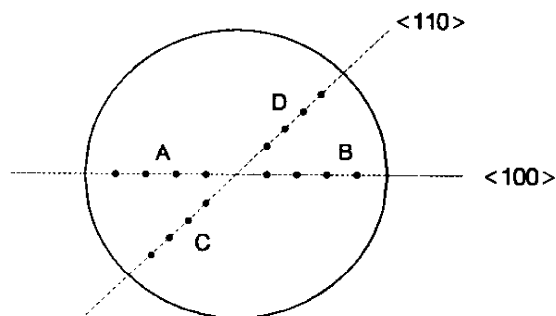


Fig. 4 Stoichiometrical measurement regions A, B, C, and D on a (001) Si-GaAs wafer.

interstitials, and the dilation in lattice parameters is principally caused by the arsenic interstitial couples. Herefrom, we are provided an access to the nondestructive measurements of stoichiometry (NDMS) in undoped Si-GaAs single crystals.

Suppose the excess arsenic atoms distribute uniformly in the undoped Si-GaAs wafers and there are no arsenic precipitates in dislocation-free regions. Then most of the excess arsenic atoms in the dislocation-free belt near the mid-ring of the wafer are in the form of interstitial couples. Therefore, The density of excess arsenic atoms in an undoped Si-GaAs wafer can be calculated according to the lattice parameter and Eq. (1). The average lattice parameter used in Eq. (1) can be measured with Bond method in the dislocation-free mid-ring belt, along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions, on a (001) Si-GaAs wafer, as shown in Fig. 4. Five samples were measured with NDMS and

coulometric titration methods, subsequently. Samples 1, 2 and 3 were adjacent wafers cut from one as-grown undoped Si-GaAs ingot. Sample 3 was annealed at 850°C in 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 fluid nitrogen atmosphere. Sample 4 was cut from an undoped Si-GaAs ingot having 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 $[\text{As}]/[\text{GaAs}]$ obtained by both the NDMS and coulometric titration methods are shown in Table 1. 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 at high temperatures. The deviation in lattice parameter within the dislocation-free mid-ring belt is less than 1×10^{-5} angstrom which ensures 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} .

In summary, the influences of As interstitials and dislocations on the lattice parameters of undoped Si-GaAs single crystals were analyzed.

Table 1 Stoichiometry in Si-GaAs measured by NDMS and coulometric titration methods, respectively.

| Sample | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 | Method |
|--------|---------|---------|---------|---------|---------|-----------|
| [As]/ | 0.50012 | 0.50016 | 0.50013 | 0.50014 | 0.50017 | NDMS |
| [GaAs] | 0.50008 | 0.50014 | 0.50015 | 0.50010 | 0.50016 | Titration |

It was shown that dislocations in such crystals serve as effective gettering sites for As interstitials when etch pit density exceed $3 \times 10^4 \text{ cm}^{-1}$ due to the deformation energy of dislocations. The lattice parameter of these dislocated regions remain relatively constant due to the counterbalance between lattice compression and dilation around the dislocation. Regions away from dislocations show a linear dependence of lattice parameter with As interstitial concentration. Measurements of the lattice parameter in these latter regions by the nondestructive measurement of stoichiometry technique (NDMS) can be used to determine As interstitial concentrations.

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