

Dislocations in Homoepitaxial Layers on “Dislocation Free” LEC-GaP Substrates

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Dedicated to Prof. Dr. G. Hildebrandt on the occasion of his 60th birthday

Dislocation structures in S- and N-doped homoepitaxial layers on GaP wafers are studied by high voltage electron microscopy. Many dislocations are introduced in the epilayer, even if the substrate is nearly dislocation free. The origins of the dislocations in this case are the microdefects, especially the perfect dislocation loops in the substrate. Dislocation dipoles are induced by dislocation half loops appearing at the epi-substrate interface and are classified into three types, two of which are concerned with the interactions of two dipoles in the epilayer, each interaction yielding a screw dislocation segment. The third type of dipole does not extend into the epilayer so far, but terminates and forms an elongated dislocation loop. The interactions and the terminations of dipoles decrease the density of the induced dislocations in proportion to the distances from the interface. The screw dislocations generated by the dipole interactions relax the torsional lattice distortion of the epilayer caused by dopant materials.

1. Introduction

GaP is a well known LED (light emitting diode) material which provides green and yellow as well as red emissions. Dislocations in the epilayers of a LED act as non-radiative centers and lower its emission efficiency. As the dislocations in the substrate crystals extend into the epilayers, lowering of the dislocation densities in the substrate crystals is desirable. By the liquid encapsulated Czochralski (LEC) method, large GaP single crystals for industrial use are obtained and low dislocation densities can be realized by increasing the amount of doping materials [1, 2]. However lowering the dislocation densities by heavy doping causes an increase of small defects such as stacking faults and dislocation loops, and they act as new origins of dislocations in the epilayers instead of the grown-in dislocations, as was pointed out previously [3, 4]. In our observations, the dislocation density of an LPE (liquid phase epitaxy) layer on a heavily sulfur doped almost dislocation free substrate was higher than that on the substrate containing many dislocations. The mechanism of the dislocation generation in the epilayer from the small defects in

the substrate is not known presently. In this work the nucleation of the dislocations at the epi-substrate interface and the formation of dislocation networks in the LPE layer are studied.

2. Experimental

Specimens were cut from LED wafers for green light supplied by Sumitomo Electric Industries Ltd. The substrate crystals are LEC crystals doped with $3 \times 10^{18} \text{ cm}^{-3}$ of sulfur and are almost dislocation free [5]. The LED wafers have n- and p-type double epilayers grown on the phosphorus side of the (111) substrate wafers by the LPE method. The n-layer ($5 \times 10^{16} \text{ cm}^{-3}$ S-doped) is $30 \mu\text{m}$ thick and is sandwiched by the substrate and a p-layer ($1 \sim 5 \times 10^{17} \text{ cm}^{-3}$ Zn-doped), $8 \mu\text{m}$ thick. Both layers contain nitrogen atoms. The p-layer is removed by thermal aqua regia ($3\text{-HCl} + 1\text{-HNO}_3$) before the specimen preparation.

The RC-etchant ($8\text{-H}_2\text{O} + 4\text{-HF} + 6\text{-HNO}_3 + 10\text{-AgNO}_3$) at 65°C is used to study the etch pit densities (EPD's) of the substrate, and a modified RC-etchant ($8\text{-H}_2\text{O} + 4\text{-HF} + 3\text{-HNO}_3 + 10\text{-AgNO}_3$) at 70°C is used for the examination of the inner epilayers, as the etching speed of normal RC-etchant is too high to observe the thin epilayers near the interface. The successive etching technique [7] is also adopted to distinguish the types of the etch pits.

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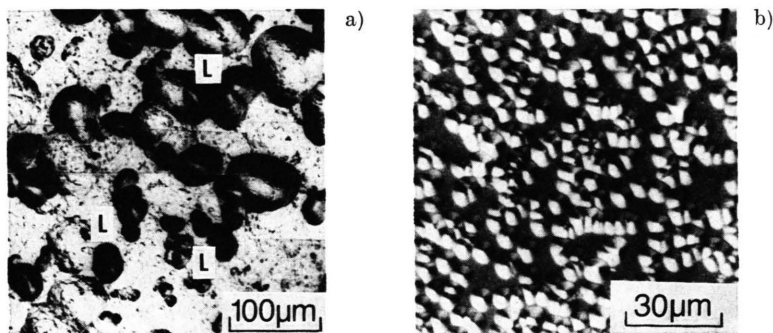


Fig. 1. Etch pit patterns of (a) as-grown LEC-GaP substrate and (b) that of the epilayer. No D-pits are seen in (a), while in (b) only D-pits appear.

To study the dislocations in the epilayer induced from the small defects in the substrate, TEM (transmission electron microscope) specimens are made with the electrolytic jet method using a 0.5 wt% NaOH solution, so that the observation area consists partly of epilayer and partly of an area where thin substrate and epilayer are overlapping. Thus the dislocations in the epilayer and their origins in the substrate become observable in the TEM in the same field of vision. The specimen surface is parallel to the epi-substrate interface, i. e. (111). The HVEM, HU-2000, operating at 2,000 kV in the Research Center for Ultra-High Voltage Electron Microscopy of Osaka University is used, by which the three-dimensional structures of the dislocations near the interface within a several microns thick layer can be observed.

D-pits which originate from the dislocation lines and there are a few S-pits, showing the existence of a few small defects in the epilayer. The EPD's of the D-pits are $6 \sim 7 \times 10^6 \text{ cm}^{-2}$, and the densities of the S-pits are at most one order of magnitude lower than those of the D-pits. In Fig. 2 the distributions of EPD's in the radial direction of the substrate and epitaxial wafers are compared. As the as-grown substrate is almost dislocation free except for the periphery of the wafer, dislocations in the epilayer are considered to be introduced by the small defects appearing as S-pits in Figure 1 (a). The D-pit density of the epilayer is one order of magnitude lower than that of the substrate, showing that some dislocations induced by the small defects disappear in the epilayer and that some of the small defects existing at the interface do not induce dislocations in the epilayer.

3. Experimental Results and Discussions

3.1. Etch Pit Observations

Figure 1 (a) is the etch pit pattern of the as-grown S-doped ($5 \times 10^{18} \text{ cm}^{-3}$) LEC-GaP. The distinct pits denoted by "L" change their shapes by successive etchings and are called L-pits, as they originate from large Frank loops $> 10 \mu\text{m}$ in diameter [5]. The background of the pattern becomes irregular by S-pits which have their origins mostly in the small Frank loops of $\sim 0.5 \mu\text{m}$ diameter and partly in the perfect dislocation loops of the same size [5]. The average L- and S-pit densities are about $2 \times 10^4 \text{ cm}^{-2}$ and $5 \times 10^7 \text{ cm}^{-2}$, respectively. Figure 1 (b) shows the etch pit pattern of the n-type LPE layer observed at a place distant from the interface by $12 \mu\text{m}$. As for the as-grown substrate, only L- and S-pits and no D-pits are observed, while the etch pits in the epilayer are mostly

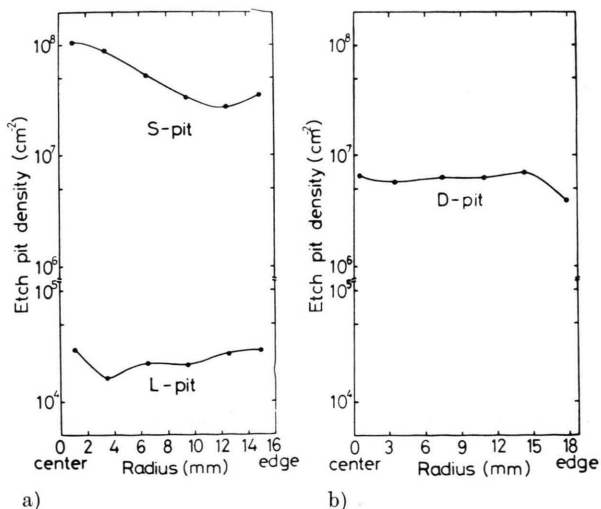


Fig. 2. EPD distributions in the radial direction of (a) as-grown substrate and (b) the epilayer of GaP wafers.

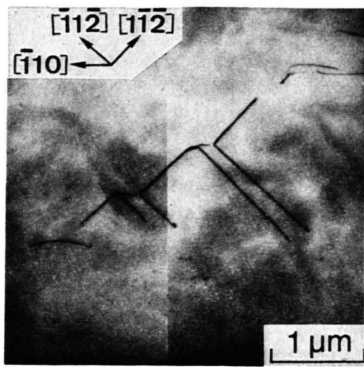


Fig. 3. TEM image of a dislocation network formed by successive dipole reactions in the n-type epilayer, looked from $[111]$ direction. The directions shown in the figure are projections onto the (111) plane and show the growth directions of the dislocation lines. The upper direction in the figure is towards the epilayer surface. $g = [220]$.

3.2. HVEM Observations

Figure 3 shows a typical dislocation network in the n-type epilayer. The straight dislocations extending along the $\langle 112 \rangle$ or $\langle 110 \rangle$ directions are dislocation dipoles constructing networks. Two types of dipole interactions are observed as shown in Fig. 4 (a) and (b), that is in (a) the lower terminating edges of the two dislocation dipoles are lying parallel to $\langle 110 \rangle$ (hereafter called Type A) and in (b) parallel to $\langle 211 \rangle$ (Type B). In the epilayer few intrinsic type stacking faults are observed, which are the origin of the S-pits in Figure 1 (b). Figure 5 shows a dark field image of a stacking fault obtained with $g = [02\bar{2}]$. As the diffraction vector points to the dark fringe, the stacking fault is of the intrinsic type according to the criterion given by Gevers et al. [8]. Figure 6 (a) and (b) show A and B type dipole reactions ob-

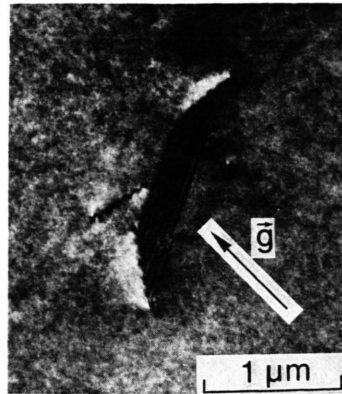


Fig. 5. A dark field image of an intrinsic type stacking fault in the epilayer. $g = [02\bar{2}]$.

served in the area where substrate and epilayer are overlapping. The dislocation loops in the substrate are indicated by arrows. It is clearly seen that the dipoles are induced by the half loops appearing at the interface and extend into the epilayer. The dipoles are composed of a pair of 60° dislocations with Burgers vectors of opposite senses and lying on the $\{110\}$ plane inclined to the interface and extending along the $\langle 1\bar{1}2 \rangle$ or $\langle 1\bar{1}0 \rangle$ direction. Figure 7 shows another type of dipole in the epilayer; in this case however, the dipole does not interact with other dipoles and ends as an elongated loop (Type C). Such nonreactive dislocation dipoles were observed by Petroff et al. [9], and the existence of dislocation dipoles in the epilayer was also found by the etch pit method by Werkhoven et al. [3].

Detailed observations by the HVEM revealed the following:

(1) Dislocation loops existing in the substrate and giving rise to dislocation dipoles in the epilayer

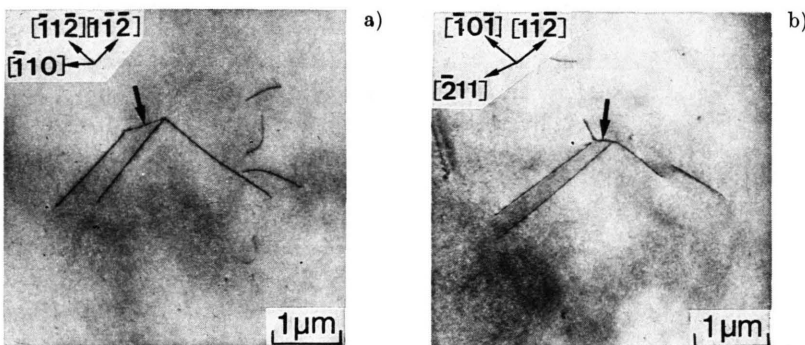


Fig. 4. Reactions of the dislocation dipoles in the epilayer, looked from $[111]$ direction. (a) Type A and (b) Type B. Directions in the figure are projections onto the (111) plane. The arrows indicate the screw dislocation segments generated by the reactions. $g = [02\bar{2}]$.

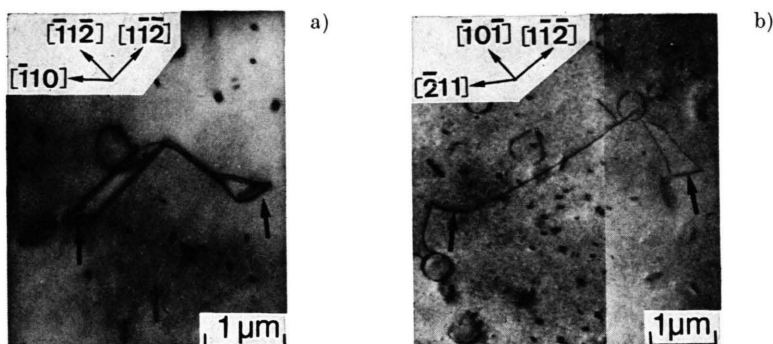


Fig. 6. Dipoles originating from the dislocation loops in the substrate which are indicated by arrows. (a) Type A reaction and (b) Type B reaction. Directions in the figure are projections onto the (111) plane. $g = [20\bar{2}]$.

are edge dislocation loops of the vacancy type lying on $\{110\}$, the Burgers vector being $\mathbf{b} = a/2\langle 110 \rangle$, i. e. they are prismatic loops. Such perfect loops are scarcely observed in the as-grown crystals [5].

(2) Three types (A, B, C) of dislocation dipoles originate from the half loops at the interface, and their Burgers vectors are the same as that of the half loops, that is $\mathbf{b} = a/2\langle 110 \rangle$.

(3) The half loops related to Type A and B lie on the $\{110\}$ planes which are perpendicular to the interface, i. e. (111).

(4) In Type C the half loops and the elongated loops lie on the same $\{110\}$ planes inclined to the interface by 35.5° .

(5) By the dipole reaction of Type A or B a screw dislocation is formed as indicated by arrows in Fig. 4 and either of the reacting dipoles stops its extension.

The dipole reactions of Types A and B are schematically shown in Fig. 8 (a) and (b). Thompson's tetrahedra are drawn in the upper part of

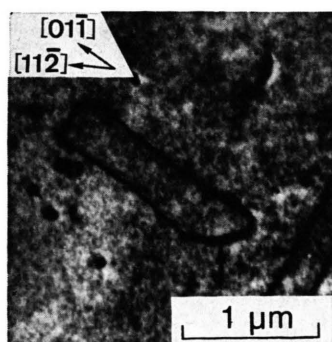


Fig. 7. A dislocation dipole which does not interact with other dipoles but closes in the epilayer (Type C). The dislocation half loop in the substrate is indicated by an arrow. $g = [02\bar{2}]$.

Fig. 8, in which thick solid lines on the $\{111\}$ planes correspond to the dislocation lines shown in the lower part of the figure. It is seen that a possible dipole reaction occurs with a combination of dislocations along $\langle 211 \rangle - \langle 211 \rangle$ or $\langle 110 \rangle - \langle 211 \rangle$, in the slip planes and consequently a screw dislocation is produced. The appearance of such screw dislocations suggests the existence of some torsional distortions in the growth plane of the dipoles. The screw dislocations play the same role as the misfit dislocations, and the torsional lattice mismatch between the epilayer and the substrate is relaxed. The screw type misfit dislocation was first observed by Kishino in the homoepitaxy of GaP, in which torsional lattice mismatch existed at the interface [10]. In the present case the slight lattice mismatch was relaxed by screw dislocation segments produced by the dipole reactions instead of long screw dislocations. However, the torsional distortion cannot be relaxed by a reaction of Type C dipole [5], as their Burgers vectors are perpendicular to their growth plane, and so reactions of Type C dipoles are not observed.

Nitrogen atoms in the epilayer are located at the substitutional sites of phosphorus atoms. As the covalent length of nitrogen is shorter than that of phosphorus, the lattice constant of the epilayer is considered to be somewhat smaller than that of the substrate. (Kishino obtained $1 \times 10^{-4} \text{ \AA}$ for the difference in lattice constants [10].) Therefore, the epilayer suffers a two dimensional tensile stress near the interface. As the dislocation loops and the induced dipoles are of the vacancy type, the dipoles tend to form a loop rather than to extend into the epilayer under the tensile stress, as seen in Figure 7. The dipoles concerning Types A and B might also form a loop in the epilayer, but most of them would react with other dipoles before the loop formation.

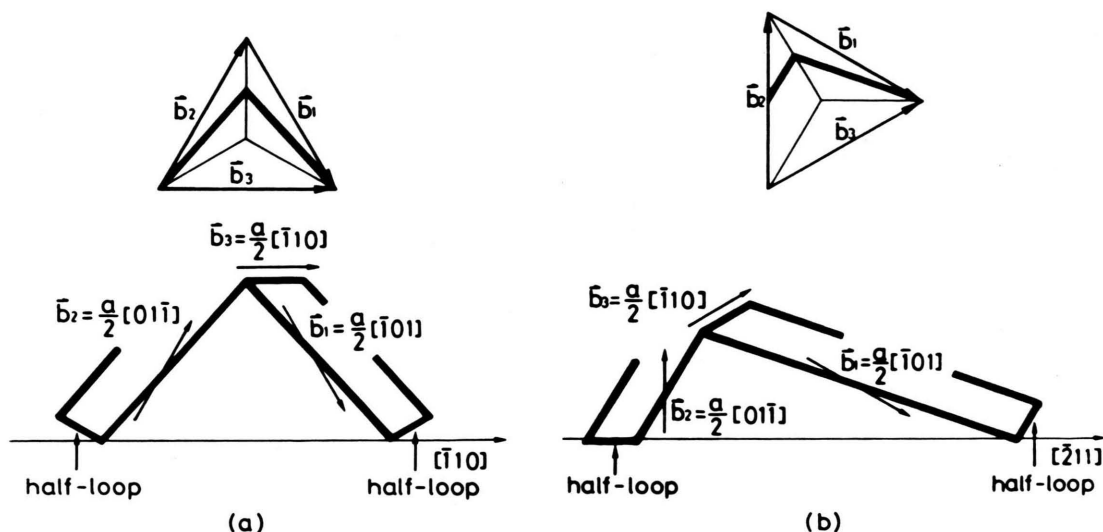


Fig. 8. Schematic diagrams of reactions (a) Type A and (b) Type B. The Burgers vectors of the dipoles are the same as those of the half loops from which they are induced. The Thompson tetrahedra show that the dipole reactions produce screw dislocations.

Therefore, it is considered that the torsional lattice distortion is relaxed by the screw dislocations created by interactions of Type A and B dipoles, and that the tensile distortions due to the lattice mismatch prevent the extension of Type C dipoles.

The termination of dislocation dipoles in an epilayer has also been found for vapor phase epitaxy (VPE) of GaP by Stringfellow et al. [11]. The present study reveals that there exist three types of termination of dislocation dipoles. As the dipole reactions decrease the total number of the related dislocations and the reactions proceed successively as seen in Fig. 3, the EPD of an epilayer reduces in proportion to its thickness. Considering the small defects in the as-grown substrate as the origin of the dislocations in the epilayer, the difference of almost one order of magnitude between the densities of S-pits of the substrate and D-pits of the epilayer in

Fig. 1 could be attributed to such dipole reactions. As for the dislocation loops in the substrate it is quite possible that they are transformed from Frank loops existing in the as-grown state by the unfaulting reaction caused by the thermal shock and the heat treatment for the LPE growth. The formation of perfect loops by the unfaulting reaction in GaP crystals is reported elsewhere [5].

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