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Study on fundamental defects and their effect on GaAs device properties (*)

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Résumé. — L'état de notre compréhension des relations entre les paramètres du matériau et de la tension seuil du transistor GaAs à effet de champ est présenté brièvement sous l'angle des réactions entre défauts ponctuels. L'accent est d'abord mis sur les dislocations dans GaAs semi-isolant (LEC) et sur leur rapport avec la dispersion des tensions seuil. On discute ensuite des défauts ponctuels associés à ces dislocations, auxquels on attribue la dispersion des tensions seuil. On montre qu'un recuit haute température produit une augmentation de la concentration d'EL2 et une homogénéisation des caractéristiques des dispositifs, même en présence de dislocations. Un modèle possible de défauts au voisinage des dislocations, basé sur des interstitiels d'arsenic, et une évolution de ces défauts, en cours de croissance et de cycles de recuit est proposé.

Abstract. — Our understanding of the causal relationship between material parameters and GaAs FET threshold voltage is briefly presented from the viewpoint of point defect reactions. Primarily, dislocations in LEC-grown GaAs are focused on in light of threshold voltage scattering, and point defects associated with dislocations attributable to threshold voltage scattering are discussed. High temperature post-growth annealing results in the increase in [EL2], which provides homogenization of device characteristics, even when the crystal contains dislocations. A possible defect model around dislocations and evolution of such defects in crystal growth and annealing cycles are proposed, where As-interstitial is mainly considered.

1. Introduction.

Since the first GaAs integrated circuit (IC) was reported in 1974 [1], GaAs IC technology has progressed remarkably because of performances which show potential. Strong demand for a good IC device yield has accelerated the study on the characterization of semi-insulating GaAs crystals used as a substrate for direct ion-implantation. The liquid encapsulated Czochralski (LEC) crystal growth technique has eventually been established to produce undoped and/or slightly Cr doped, stable semi-insulating crystals having a large size suitable for device processing.

With regard to this, the most important requirement for the IC substrate is uniformity of the threshold voltage \(V_{\text{th}}\) for metal-semiconductor field-effect transistors (MESFETs) over the whole area of the substrate, which are usually fabricated by direct Si ion implantation into the semi-insulating substrate. One of the major issues facing the application of LEC-GaAs to IC technology is the large random fluctuation or scattering of \(V_{\text{th}}\) over the substrate.

While many reports concerning the origin of \(V_{\text{th}}\) scattering on the substrate have appeared elsewhere, the notable results may be summarized as follows; (i) dislocations [2, 3], (ii) residual C concentration [4], (iii) local EL2 concentration [5], and (iv) local lattice strain caused by the deviation from stoichiometry [6]. A contrary result has also been reported, in that no dislocation effect on \(V_{\text{th}}\) scattering was demonstrated [7]. Most of all studies on characterization of the crystal have predominantly met the nature and origin of crystallographic and electronic defects contributing to semi-insulating behavior. The main defect of current interest is a deep level native defect EL2, while the origin has...
not been definitely recognized yet. In considering these factors, it is worth noting that there should be a tight correlation between $V_{th}$, dislocations and native defect EL2.

This paper describes first a retrospective of our achievement in coming to understand the dislocation effect on $V_{th}$, and it discusses the causal relationship between the native defect EL2 and the activation mechanism for the implant in light of the competition between Ga and As sites for implanted Si. A plausible defect model for the $V_{th}$ fluctuation or scattering around dislocations will be presented, and a mechanism by which the post-growth annealing results in homogenizing the $V_{th}$ fluctuation also will be discussed.

2. Retrospective of the dislocation proximity effect on $V_{th}$.

Conventional LEC-grown, either undoped or Cr-doped, semi-insulating crystals exhibit a so-called « W » shape variation of dislocation density. This ranges from a low $10^4$ to more than $5 \times 10^5$ cm$^{-2}$ across a round wafer. Many material properties and parameters have been investigated to date, and they are collectively related to this dislocation density variation, as summarized in figure 1. Electrical resistivity varies opposite to the « W » shape on the order of $10^7 \Omega$ cm [8]. An X-ray quasi-forbidden reflection experiment [9] showed a « W » shape of intensity reflected from the As lattice plane. This result strongly suggests that the higher the dislocation density, the higher the concentration of As interstitials or Ga vacancies. Leakage current $I_{L}$ intensity distributes an inverse « W », i.e., « M » shape [10]. The measure of $I_{L}$ is believed to be closely correlated to deep vacant traps [11]. The concentration of the neutral deep donor defect EL2 measured by infrared absorption exhibits a « W » shape across a wafer [12]. Photoluminescence peaks relating to semi-insulating behavior show either « W » or « M » [13]. Variations of all these material parameters are consistently correlated to each other, reflecting the dislocation density variation. Such variations in either a positive or a negative way are quite consistent with each other, when a semi-insulating mechanism is considered. When Si ions are directly implanted and annealed into this substrate, electrical properties of the Si-implanted layer and subsequent device characteristics, namely FET threshold voltage, also exhibit either « W » or « M » shaped variation [14].

The dislocations are, however, localized by forming a cellular network of a few hundred $\mu$m and often lineages consisting of dislocations, as shown in figure 2. On this wafer, FETs with a 1 $\mu$m gate length were fabricated at intervals of 200 $\mu$m followed by Si ion implantation and subsequent SiN cap annealing at 800 °C for 15 min. The sample was etched with molten KOH so as to reveal dislocation pits, after measuring $V_{th}$ for each FET. Figure 3 shows a micrograph of an etched feature, where the FET channel position (channel) can be recognized as indicated. The $V_{th}$ value and the distance $x$ between the corresponding FET gate position and its nearest neighbor dislocation pit are also inserted. One can easily deduce that dislocations affect a $V_{th}$ value, depending on the distance $x$.

The proximity effect of dislocations on $V_{th}$ was then carefully examined on the regions close to lineage and dislocation network boundaries [3]. Variations $V_{th}$ measured around lineages and on

Fig. 1. — Variations of several material parameters in LEC-grown, semi-insulating GaAs collectively correlated with dislocation density variation, and resultant variations in Si-implanted layer.
Fig. 2. — A microscopic observation of dislocation distributions on an LEC-grown, (100) GaAs substrate. On the central part, a dislocated cellular structure is obvious, and on the middle part lineage boundaries as a dislocation pit array exist.

Fig. 3. — Enlarged feature of the KOH-etched surface with FET metallization.

dislocation network area are shown in figure 4(a) and (b), respectively. We noticed that the shorter the distance $x$, the lower the $V_{th}$ at a distance of less than approximately 50 $\mu$m, while $V_{th}$ for FETs located far from approximately 50 $\mu$m apart is almost constant, independent from the distance $x$. Open circles in (a) and (b) correspond to FETs located on intra-lineages and inside cellular networks. Remember that regions beside lineages and inside the networks are essentially dislocation-free. This aspect is well recognized by X-ray topography.

Fig. 4. — Dislocation proximity effects on $V_{th}$ observed around lineages (a) and cellular networks (b). Open circles correspond to the regions essentially dislocation-free.
and chemical etching. We can readily understand that dislocation-free crystals exhibit quite a uniform distribution of \( V_{th} \). This was confirmed later with In-doped, dislocation-free GaAs substrates [15].

It has been well recognized that the native defect EL2 concentration increases by \( 4 \sim 5 \times 10^{15} \text{ cm}^{-3} \) at lineage and network boundaries [12]. A very suggestive relation between \( V_{th} \) and the local EL2 concentration was reported by Dobrilla et al. [5], indicating that \( 1.6 \times 10^{15} \text{ cm}^{-3} \) of EL2 provides a \( V_{th} \) shift of roughly 100 mV. This experimental relationship can qualitatively explain the \( V_{th} \) shift around dislocations shown in figure 4. EL2 is, however, a deep donor and does not directly influence a \( V_{th} \) value, although its nature as a point defect must influence the activation of implanted Si ions, as will be discussed in section 4.

A more negative \( V_{th} \) shift around dislocations was confirmed by measuring sheet carrier concentration using the van der Pauw method by means of small Hall chips (40 \( \times \) 40 \( \mu \text{m}^2 \)) fabricated at intervals of 400 \( \mu \text{m} \) [16]. Sheet carrier concentration \( N_s \) is inversely proportional to \( V_{th} \), to the first approximation, as expressed by the following equation.

\[
V_{th} = V_{bi} - \frac{q}{2\varepsilon} N d^2 \alpha \propto N_s d ,
\]

where \( V_{bi} \) is built-in Schottky barrier height, \( q \) is electric charge, \( \varepsilon \) is dielectric constant, \( N \) is carrier density in the Si implanted n type layer, and \( d \) is layer thickness.

The measured \( N_s \) value was plotted against the distance from the nearest neighbor dislocation pit to the center of the Hall chip, as shown in figure 5a. The closer the distance, the higher the \( N_s \) at a distance less than approximately 50 \( \mu \text{m} \), while \( N_s \) is almost constant far approximately 50 \( \mu \text{m} \) away from a dislocation. This tendency is quite consistent with the \( V_{th} \) variation shown in figure 4, when equation (1) is considered. Since Si is amphoteric in the GaAs host lattice, Si on Ga site (Si\(_{Ga}\)) becomes donor, while Si on As site (Si\(_{As}\)) becomes acceptor.

Therefore, the measured \( N_s \) corresponds to the net \( (\text{Si}_{Ga} - \text{Si}_{As}) \) concentration, when the concentration of other residual impurities \( [N_D - N_A] \) is neglected. This leads to the conclusion that either the concentration of the Ga site to be replaced by Si is higher or the concentration of the As site to be replaced by Si is lower around dislocations than it is approximately 50 \( \mu \text{m} \) away from the dislocations.

Since it is well established that S replaces the As site preferentially and becomes donor in GaAs, it can be anticipated that the dislocation proximity effect in the S implanted layer must be opposite to that in the Si implanted layer, because high \( N_s \) around dislocations in Si implanted layer is caused by the competition between a decrease in Si\(_{As}\) acceptor and an increase in Si\(_{Ga}\) donor. Figure 5b shows the result plotted in the same manner for the S implanted layer annealed with a SiN cap. The dose was \( 10 \times 10^{12} \text{ cm}^{-2} \), which resulted in an average \( N_s \) comparable to that in the Si implanted layer. The shorter the distance, the lower the \( N_s \), which is opposite to the result for the Si implanted layer shown in (a). This tendency proves that the As-site concentration around dislocations is lower than that far from dislocations, suggesting that the concentration of As vacancy (\( V_{As} \)) being Si\(_{As}\) acceptor is low around dislocations.

3. Microscopic defect distribution around a dislocation.

To investigate microscopically local variations of defects or deep levels around dislocations, scanning DLTS experiments were performed. The experimental setup and details have already been reported elsewhere [18]. Figure 6 presents preliminary results on distributions of dominant electron and hole traps (ET and HT, respectively) across a dislocation network cell boundary. The sample was Se-doped, \( n \)-type GaAs grown by LEC pulling. The mean carrier concentration was \( 4 \times 10^{16} \text{ cm}^{-3} \). The upper picture is an EBIC image, showing part of the cellular dislocation network wall. Dark spots in bright areas correspond to dislocations. The lower figure demonstrates distributions of three typical levels, 0.83 eV(ET), 0.45 eV(HT) and 0.40 eV(HT), obtained from the current DLTS mode along A to A' across a dislocated network wall shown on the EBIC image. Each average concentration was referred to that measured by a conventional capacitance DLTS.

Level 0.83 eV corresponds to the well-known electron trap EL2. The scanning DLTS signal across A-A' shows that the EL2 concentration at a dislocated boundary is higher by 10 to 30% than inside the cell boundary. This feature is quite consistent with the results of the infrared absorption experiment. On the other hand, the 0.40 eV hole trap
concentration level is found to be lower in the dislocated boundary by more than 10%. The origin of the 0.40 eV hole trap is not clear yet, but this trap is the dominant point defect under Ga-rich conditions, as denoted by the « A » center [19]. Therefore, distributions of EL2 and the 0.40 eV level strongly suggest that regions close to dislocations of approximately 50 μm are in As-rich, compared with regions far from dislocations.

More recently, clear evidence of local segregation of EL2 around a dislocation has been demonstrated by Ogawa [20]. He succeeded in observing simultaneously an infrared absorption image and infrared light scattering image along dislocation lines. The former gives neutral EL2 and the latter shows the existence of fine precipitates as scattering center. Figure 7 shows a series of observed result with an experimental setup. The sample is In doped, partially dislocated, semi-insulating GaAs. By moving down a 1.15 μm focused laser beam, bright spots which are scattering centers decorated on dislocation lines go down along dislocation lines, while absorbed pipes belonging to dislocation lines do not move. From these figures, it can be emphasized that neutral EL2 concentration increases around dislocations to some degree, and simultaneously scattering centers exist along dislocation lines. The origin of the scattering centers are not identified yet, but As-rich fine precipitates have been recognized to exist on dislocations [21, 22]. This feature is very significant when considering a defect model around dislocations.

4. Defect model around dislocations.

Based on the experimental results described above, we have eventually reached a defect model around dislocations [23]. It seems to be the most likely explanation for the defects around dislocations, as illustrated in figure 8, which can qualitatively explain the $V_{th}$ shift or the fluctuation of $V_{th}$ due to dislocations. The model basically includes an increase in As-interstitials ($As_i$) toward dislocation(s), considering the following experimental facts:

(i) Semi-insulating GaAs is As-rich to some degree from the stoichiometric composition,
(ii) As-rich fine precipitates or aggregates exist on dislocation lines,
(iii) EL2 concentration is higher around dislocations than it is far from them,
(iv) EL2 concentration increases with excess As fraction in crystals. Although the nature of EL2 has not been definitely identified as yet, there are numerous findings suggesting that EL2 is an $As_{Ga}$ antisite defect associated with $V_{Ga}$ [24] and/or $As_i$ [25], or As aggregates [26]. The increase in $As_i$ must provide fine As-precipitates on dislocation lines, when $As_i$ supersaturates to some degree.
Since the crystal composition of semi-insulating GaAs is As-rich to some degree, excess As$_i$ may react with residual $V_{As}$, resulting in neutral As$_{As}$, producing As$_{Ga}$ antisite:

$$\text{As}_i + V_{As} = \text{As}_{As}$$

and/or

$$\text{As}_i + V_{Ga} = \text{As}_{Ga}.$$  

Consequently, these likely reactions result in a decrease in $[V_{As}]$ and an increase in antisite [EL2] around dislocations. From another point of view, the mechanism often referred to for the EL2 evolution is expressed by the following mass action [27]:

$$\text{As}_{As} + V_{Ga} = \text{As}_{Ga}^+ \text{(EL2)} + V_{As}^+ + 4e^-$$  

$$K = [\text{As}_{Ga}(\text{EL2})]/[V_{As}]/[V_{Ga}] \cdot n^4.$$  

The increase in [EL2] results in the decrease in the ratio of $[V_{As}]/[V_{Ga}]$, according to the thermodynamic mass action law. Then, it can be emphasized that $[V_{As}]$ decreases around dislocations. This hypothesis is quite consistent with the low activation for implanted S ions around dislocations, as was demonstrated in figure 5b, which implies that the concentration of As site to be replaced by S is lower than that far from dislocations. The sDLTS shown in figure 6 supports this hypothesis.

The carrier concentration measured as a sheet carrier concentration in the Si implanted layer is basically determined by the net concentration of $(\text{Si}_{Ga} - \text{Si}_{As})$. The greater negative $V_{th}$ shift is attributable to the higher $(\text{Si}_{Ga} - \text{Si}_{As})$ net concentration around the dislocations. The reaction determining whether Si replaces Ga site or As site is expressed [28] by

$$\text{Si}_{Ga}^+ + V_{As}^+ + 2e^- = \text{Si}_{As}^- + V_{Ga}^- + 2h^+,$$  

\[
\frac{[\text{Si}_{\text{As}}]}{[\text{Si}_{\text{Ga}}]} = K' \left( \frac{[V_{\text{As}}]}{[V_{\text{Ga}}]} \cdot \left( \frac{n_i}{n_i} \right)^4 \right) \tag{6}
\]

where \( n_i \) is intrinsic carrier concentration. Equation (6) implies that the higher the sheet carrier concentration (\([\text{Si}_{\text{Ga}}]/[\text{Si}_{\text{As}}]\) ratio), the higher the \([V_{\text{Ga}}]/[V_{\text{As}}]\) concentration ratio.

Therefore, it is stressed that \( V_{\text{th}} \) scattering or inhomogeneity due to dislocations is attributable to the inhomogeneous distribution of the \([V_{\text{As}}]/[V_{\text{Ga}}]\) ratio associated with an increase in \([\text{As}_{\text{i}}]\). An X-ray quasi-forbidden reflection experiment pronounced a strong As intensity at highly dislocated region [9]. This result gave a conclusion that either \( \text{As}_{\text{i}} \) or \( V_{\text{Ga}} \) concentration is higher at highly dislocated region, that is, very close to dislocations. The model proposed in figure 8 can systematically explain most of the phenomena linked with dislocations.

Anholt and Sigmon [17] analysed the \( V_{\text{th}} \) shift or scattering by means of Monte-Carlo simulation on the basis of our \( V_{\text{th}} \) measurements. They assumed an increase in \([V_{\text{Ga}}]\) around dislocations, based on equations (5) and (6). The calculated results explained very quantitatively our experimentally measured results on the proximity effect.

5. Effect of post-growth annealing on \( V_{\text{th}} \) fluctuation.

Recent interest in crystal technology and also in IC fabrication processes has led to the study of high temperature annealing before ion implantation and the growth of dislocation-free GaAs. Both are aiming to obtain very homogenized electrical properties in crystals. Dislocation-free crystals are successfully grown by doping with isoelectric In, and it has been verified by many groups that the crystals exhibit the most uniform from a device uniformity point of view.

Lengthy high temperature annealing called post-growth annealing results in homogenization of electrical properties in as-grown materials and also of FET threshold voltage. Grant et al. [29] reported in detail, for the first time, the effect of post-growth annealing on improving the electrical uniformity of dislocated materials. The author [30, 31] has independently investigated the effect of the post-growth annealing on \( V_{\text{th}} \) uniformity, and has found it to be quite effective. The post-growth annealing is, in turn, very useful in investigating defect behavior.

Figure 9 is the first evidence of the effect of post-growth annealing on \( V_{\text{th}} \) scattering in the light of the dislocation proximity. The substrate was isothermal-annealed at 800 °C. Both undoped and Cr doped materials exhibited the same tendency [31]. The non-treated substrate shows a clear proximity effect, with a scattering in \( V_{\text{th}} \) as large as \( \pm 200 \text{ mV} \). As the annealing time increases, the scattering becomes smaller, and for the substrate treated for 18 hrs the proximity effect was hardly noticeable. The scattering was less than \( \pm 90 \text{ mV} \), which is less than a half of the non-treated one.

It should be noted here that \( V_{\text{th}} \) values for FETs very close to dislocations do not vary so much, independent of the annealing time, while a negative \( V_{\text{th}} \) shift for FETs far from dislocations is remarkable. The latter is roughly \( 300 \text{ mV} \) toward a normally-on state. It was recognized experimentally that EL2 concentration reaches a thermodynamical equilibrium by annealing, independent of either dislocation density or crystals grown in different ways [32]. Taking into account this fact, a more negative shift of \( V_{\text{th}} \) for FETs far from dislocations is probably related to the increase in [EL2].

Figure 10 shows changes in the EL2 distribution and concentration in In doped, partially dislocated crystals, as a function of isochronal annealing temperature. The annealing time was fixed at 5 hrs. In the as-grown sample (a), inhomogeneity of the EL2 concentration was clearly observed around dislocations existing at the central part and the periphery of the crystal. The EL2 concentration around the dislocations increased by approximately \( 4 \times 10^{15} \text{ cm}^{-3} \) more than the background concentration in a dislocation-free area of \( 9 \times 10^{15} \text{ cm}^{-3} \). As the
annealing temperature increased, inhomogeneity of EL2 concentration disappeared gradually, and it disappeared completely at 1000 °C. Inhomogeneity associated with dislocations still exists weakly in 800 °C-annealed crystal. Even if the annealing time becomes longer, uniformity improvement is suspicious. This was verified by measuring $V_{th}$ uniformity for the crystal annealed for 18 hrs, as was already shown in figure 9 and will be demonstrated in section 7.

By increasing the annealing temperature, it was found that background EL2 concentration, i.e., EL2 concentration at dislocation-free area, increased from about $9 \times 10^{15}$ up to $1.6 \times 10^{16} \text{ cm}^{-3}$, while EL2 concentration around dislocations did not increase so much even after annealing cycles. This increase in background EL2 concentrationCovered up the concentration of EL2 originally existing around dislocations. This hypothesis seems to be closely consistent with a large $V_{th}$ shift in essentially dislocation-free area, when compared with a small $V_{th}$ shift toward a negative $V_{th}$ value close to dislocations, as was shown in figure 9.

From equations (4) and (5), we obtain the following correlation:

$$[\text{As}_{\text{Ga}}(\text{EL2})] = A \cdot \frac{[\text{Si}_{\text{Ga}}]}{[\text{Si}_{\text{As}}]} \cdot n_i^4.$$  (7)

Then, we compare the increase in EL2 concentration caused by annealing with sheet carrier concentration for each annealed, dislocation-free crystal followed by Si implantation, as shown in figure 11 [33]. As is seen in the figure, there is a close correlation between sheet carrier concentration and EL2 concentration. This means that the higher the EL2 concentration, the lower the $V_{th}$ because of the increase is net carrier concentration when considering equation (1). It can be emphasized, therefore, that the increase in [EL2] results in the decrease in $[V_{As}]$, allowing for the increase in $N_s$ because of the decrease in SiAs acceptors.


We carefully observed the annealed sample by chemical etching, and compared it with the non-
treated one. A noticeable appearance was observed, for the first time, on the annealed sample by etching with an AB etchant. Figure 12 shows etched features for (a) as-grown and (b) 800 °C for 20 hrs annealed samples. In (b), a roughly etched feature appeared in an essentially dislocation-free area inside dislocated cell boundaries, as indicated by the arrow. This means that agglomeration of point defects or probably precipitation of very fine clusters occurs during the annealing cycle. The feature shown in figure 12(b) is the first proof of defect agglomeration caused by annealing in essentially dislocation-free regions. The other significant change after annealing is that the etched feature at the dislocation lines becomes stronger than that for the non-treated ones. This strongly suggests that precipitation of As-related insulators was enhanced by the annealing.

To confirm the agglomeration of defects or precipitates, infrared light scattering tomography was carried out. In figure 13, (a) is a scattered light intensity variation on line A-A' for the non-treated sample. Cellular network boundaries exhibit strong scattered intensity caused by precipitates decorated on dislocation lines. While the annealed sample shows much stronger scattered intensity at the dislocated boundaries, as shown in (b). This coincides fairly well with the etched feature at the dislocation lines shown in figure 12(b). Moreover, we should take note of background intensity. It can be seen that background intensity in essentially dislocation-free areas inside networks is stronger for the annealed sample than that for the non-treated one. This phenomenon is probably evidence of fine agglomerates within the dislocation-free areas.

Fig. 12. — AB-etched features for (a) as-grown and (b) annealed at 800 °C for 30 hrs. The arrow indicates a rough etched feature probably caused by fine agglomerates.

Fig. 13. — Line scannings of infrared light scattering intensity from (a) as-grown and (b) annealed samples.
precipitates resulting from an agglomeration of defects being scattering centers.

It is very interesting to puzzle out a probable correlation between EL2, scattering center and the implant activation, and to deduce the evolution of EL2. The phenomena resulting from the post-growth annealing are summarized as follows:

(i) Shift of $V_{th}$ to a more negative value at distances far from dislocations,
(ii) increase in infrared light scattering intensity at both dislocations and background,
(iii) increase in EL2 concentration and uniform distribution of EL2,
(iv) high activation of implanted Si,
(v) no remarkable change in dislocation density.

Taking these facts into account, a mechanism for the uniformity improvement of as-grown, dislocated crystals by the post-growth annealing can be explained, as shown schematically in figure 14, based on the model described in figure 8.

When the crystal was annealed at an elevated temperature, namely more than 800 °C, the EL2 concentration increases to a certain degree in an essentially dislocation-free region, i.e., inside cellular networks and lineages. If EL2 is assumed to be originated from excess As$_i$, the reason why background EL2 concentration becomes comparable to the highest EL2 concentration at dislocations is resulted from the increase in As$_i$ concentration in essentially dislocation-free regions. This model is likely given the fact that high activation for the implanted Si for the annealed substrate was observed experimentally, because As vacancies in the region far from dislocations may decrease by the evolution of EL2 or As$_i$. Defect evolution will be discussed in section 8.

7. Homogeneity evaluation of annealed crystals by $V_{th}$.

A comparison of the threshold voltage uniformity for (a) as-grown, dislocated substrate, (b) post-growth annealed, dislocated substrate, and (c) In doped, perfectly dislocation-free substrate is shown in figure 15. FETs were fabricated by a SAINT process reported elsewhere [28]. The standard deviation $\sigma V_{th}$, the measure of the uniformity, for (a), (b) and (c) were approximately 80 mV, 70 mV and 20 mV, respectively. For the as-grown crystal, $V_{th}$ variation exhibits essentially a « W » shape across a wafer which reflects the « W » shaped dislocation density variation. On the other hand, the annealed substrate shows great uniformity compared with that of the as-grown one, but extra points exist. These extra low $V_{th}$ values were not necessarily corresponding to dislocations. Referring to the defect model indicated in figure 8, they are probably

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corresponding to areas locally segregated with high EL2 concentration, which was not recovered sufficiently by the post-growth annealing, as was discussed in section 5. When these extra points are deleted, the standard deviation was estimated to be as small as 40 mV, roughly one half of the as-grown one, but the uniformity is still poorer than that of the dislocation-free one. The dislocation-free substrate exhibits very high uniformity.

Optimization for the post-growth annealing conditions must provide the uniformity comparable to the dislocation-free one. For that purpose, deep considerations on defect behaviors around dislocations caused by the post-growth annealing should be performed [34].


Here, we discuss the evolution of As-related defects during crystal growth and/or post-growth annealing cycles from the basis of the classical understandings of GaAs-As pseudo-binary phase diagram as illustrated in figure 16 [35]. Although several phase diagrams for the existence region of GaAs, where the GaAs solid-solution region is retrograde in both Ga-rich and As-rich sides, have been reported [36], a simplified diagram [37] was assumed here for simplicity. The solid-solution region to be swelled out toward an As-rich side, to some extent, from the stoichiometric composition (Ga/As = 50.00).

When the crystal with a hatched composition is pulled, the crystal just solidified is thought to include point defects on the order of $10^{18}$-$10^{19}$ cm$^{-3}$. They must condense, followed by successive cooling, and dislocation loops are created. Dislocations are generated from loops and move by gliding and/or climbing caused by thermal stresses due to successive cooling. Dislocation motions may emit As$_i$ at jogs [38], and dislocations may be decorated with As$_i$. Excess As$_i$ may cluster as the crystal is cooled down. Thus agglomerated As$_i$ possibly provide a pinning effect for dislocation movements. In successive cooling, the crystal goes down through the solvus line below 810 °C. At passing the solvus temperature, As solid-solution (As$_{ss}$) of the pseudo-binary end member appears (precipitation) in GaAs matrix to form a eutectic mixture of GaAs and As$_{ss}$, even though the amount of As$_{ss}$ is very small.

Since As$_{ss}$ solid-solution is As dissolved with GaAs, it is likely that As$_{ss}$ distributes as a form of As$_i$-agglomerates. Below the solvus temperature, for example, at room temperature, the amount of As$_{ss}$ obeys the lever rule. Therefore, why the EL2 concentration varies from crystal to crystal and/or from seed end to tail end of the ingot is probably depending on crystal stoichiometry and cooling conditions. When the cooling rate is relatively high, the precipitation may be frozen in to room temperature, but only dislocations in the crystal act as a nucleation center for precipitates. Precipitation of excess As$_i$ occurs preferentially on dislocations, which results in the enhancement of As$_i$ around dislocations as was shown in figure 8, and fine precipitates appear on them because of the limitation of supersaturation. When the As$_{ss}$ as a part of eutectic component is intrepidly assumed to be the origin of EL2, the EL2 evolution temperature of approximately 1 050 K analytically predicted by Lagowski et al. [27] coincides fairly well with the precipitation of As$_{ss}$ at less than 810 °C.

When the as-grown crystal is heated and held around the solvus line (at 800 °C in our experiment of post-growth annealing), the crystal is length aged. During this aging, As$_{ss}$ is precipitated as a part of the eutectic components. The appearance of a rough etched feature observed in an essentially dislocation-free area inside dislocation networks shown in figure 12(b) is probably due to As$_{ss}$ or As$_i$ precipitations. This hypothesis seems to be most likely in connection with the increase in background scattered intensity, i.e., in dislocation-free region. The increase in EL2 is also connected with this hypothesis.

Therefore, it is worth to conclude that the origin of EL2 is probably the evolution of As$_{ss}$ (As$_i$) distributed coincidently in the GaAs matrix. Precipitation of As$_{ss}$ (As$_i$) provides the decrease in residual As vacancies by replacing each other, allowing for the decrease in Si$_i$ acceptor concentration. And, high activation for implanted amphoteric Si and a great negative $V_{th}$ shift around dislocations are resulted, because Si preferentially occupies Ga vacancies and net carrier concentration (Si$_{Ga}$ – Si$_{As}$) increases. The defect model of Anholt and Sigmun [17], where $V_{Ga}$ concentration is enhanced around dislocations, is opposite to the hypothesis described above, but it must be complementary to our model.

Fig. 16. — A simplified pseudo-binary phase diagram for explaining the evolution of defects in semi-insulating GaAs.

Our present achievement in understanding the behavior of defects in LEC-grown, semi-insulating GaAs crystals was retrospected in light of the proximity effect of dislocations on FET threshold voltage. From the basis of overall phenomena observed around dislocations, a possible mechanism for the shift of threshold voltage was discussed, where As-interstitials are attributable to an inhomogeneity of FET device characteristics. The defect model around dislocations can explain qualitatively not only the $V_{th}$ scattering due to dislocations, but also the enhancement of EL2 concentration and As precipitates on dislocations.

Although the post-growth annealing provides the improvement of $V_{th}$ uniformity, it is still inferior to that of dislocation-free materials. Thus, further studies on defect behavior should be considered for the generation mechanism during crystal growth cycles, as well as its origin. Insight into the mechanism by which EL2 increases seems to be necessary to understand the effect of the annealing and the evolution mechanism of EL2.

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