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On the absence of decoration As precipitates at dislocations in Te-doped GaAs

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Abstract. This paper is aimed at explaining the absence of As precipitates decorating dislocations in Te-doped GaAs which are found instead when other dopants are used. By transmission electron microscopy it is seen that dislocations in Te-doped GaAs are always tangled and surrounded by clouds of extrinsic loops but are not decorated with any As precipitate. Diluted Sirtl-like etching used with light (DSL etching), micro-Raman and EBIC (electron-beam-induced-current) results support the conclusion that the regions containing the loop clusters around dislocations are enriched in the $Te_{As}V_{Ga}$ acceptor complex that has formed due to the diffusion of Te towards the dislocation. The formation of $Te_{As}V_{Ga}$ causes an undersaturation of Ga vacancies and hence the production of a supersaturation of Ga interstitials. The latter is the driving force for the formation of the observed extrinsic loops and dislocation tangling through climb. Such processes, however, consume As interstitials which are thus no longer available for the formation of decoration As precipitates. The peculiar characteristic of Te of forming acceptor complexes like $Te_{As}V_{Ga}$ is discussed with reference to the group IV dopants.

1. Introduction

There is a large body of experimental evidence that As precipitation on dislocations occurs in all bulk GaAs crystals whatever the dopant impurity, as well as in semi-insulating ingots. Among other papers, see for instance Buhrig *et al* (1994), Cullis *et al* (1980), Fornari *et al* (1989), Frigeri *et al* (1993), Gleichmann *et al* (1989), Lee *et al* (1989a), Lodge *et al* (1985), Oda *et al* (1992), Schlossmacher *et al* (1992), Stirland (1990), Weyher *et al* (1998), Wurzinger *et al* (1991). Te-doped GaAs, however, is the exception to this very general rule, since, to the authors' knowledge, no As precipitate decorating dislocations was ever reported for it. The probability of formation of the decorating As precipitates is very high in bulk GaAs due to the supersaturation of As interstitials (As_i) that are easily incorporated into the GaAs lattice because of the high As pressure usually applied during bulk growth. The As precipitates decorating a dislocation then form by diffusion of As_i along the dislocation that has gettered them, until they locally reach a threshold density for precipitation. Decoration As precipitates have also been found in semi-insulating LEC (liquid-encapsulated Czochralski) GaAs crystals grown under special 'Ga-rich' conditions with an arsenic atomic fraction of 0.492, i.e. lower than the one usually employed (Frigeri *et al* 1993). It should be noticed that besides heterogeneous nucleation at dislocations, in GaAs crystals subjected to annealing

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to homogenize the electrical properties, As interstitials can also precipitate homogeneously everywhere in the matrix, producing so-called matrix precipitates (Lee *et al* 1989b, Weyher 1995). Both matrix and decoration precipitates are made of either pure As or As oxide(s), sometimes also in combination with voids as shown recently (Weyher *et al* 1998).

As to Te-doped GaAs, matrix prismatic loops (Hutchinson and Dobson 1975), matrix faulted defects (Laister and Jenkins 1971) and clusters of large extrinsic faulted Frank loops around grown-in dislocations (Chu *et al* 1981) have been observed but no decoration As precipitate has ever been reported, as stated above, although the crystals were grown under standard As-rich conditions. No explanation for such a result was ever given. The present contribution is aimed at explaining the absence of decoration As precipitates in as-grown Te-doped GaAs.

2. Experimental procedure

The (100)-oriented GaAs crystals were grown by the vertical Bridgman method and doped with Te to an average free-electron density n of 1.5×10^{18} cm^{-3}. They were analysed by means of TEM (transmission electron microscopy), DSL etching (diluted Sirtl-like etching used with light), EBIC (electron-beam-induced-current) and micro-Raman measurements. TEM was used in the bright-field mode on plan-view specimens prepared by back-surface ion beam thinning of DSL-etched samples. DSL etching was carried out by using a 1:1 aqueous solution of HF–CrO_3 (ratio 1:5). DSL produces the oxidative dissolution of the sample whereby a GaAs molecule is dissolved by absorbing six holes (Kelly *et al* 1985, Weyher and van de Ven 1986, Frigeri and Weyher 1990). The holes are those generated by the light used during etching and their density depends on the density of acceptor-like impurities. As the etching rate increases with the hole density, optical microscopy images of DSL-etched n-type GaAs are maps of the distribution of the net free-electron density n and of the compensation ratio, in particular around defects. EBIC and micro-Raman measurements were used to get a quantitative evaluation of the inhomogeneous distribution of n at the defect atmospheres. For EBIC this was achieved, with a micron-scale spatial resolution, by the local measurement of the depletion width associated with an Au Schottky diode deposited on the GaAs surface (Frigeri 1987, Frigeri and Weyher 1989). The determination of n by micro-Raman spectroscopy was done by measuring the ratio between the intensity of the longitudinal optical (LO) phonon mode peak and that of the L_--mode peak (Pollack 1991). The presence of the transverse optical (TO) mode in the micro-Raman spectrum gives instead information on the lattice disorder (Pollack 1991).

3. Results

From TEM observations the grown-in dislocations always appeared arranged in complex tangles or helices surrounded by clouds of large extrinsic faulted Frank loops ($\boldsymbol{b} = (a/3)\langle 111\rangle$) on {111} planes, as well as by tiny loop-like microdefects (figure 1). The loop clouds can be as large as ~5–10 μm. The area around them is depleted of crystal defects over several μm. No decoration As precipitate at the grown-in dislocation was ever detected. Similar TEM results were found by Chu *et al* (1981).

Figure 2 is an image of typical defect structures as revealed by DSL etching. The small hillock produced upon etching by the grown-in dislocation outcrop is surrounded by other microhillocks that are interpreted as being due to the Frank dislocation loops observed by TEM. All microhillocks are located inside a surface depression some μm in size, as confirmed by step profiles taken across the etched features (figure 2(b)). This result is contrary to what

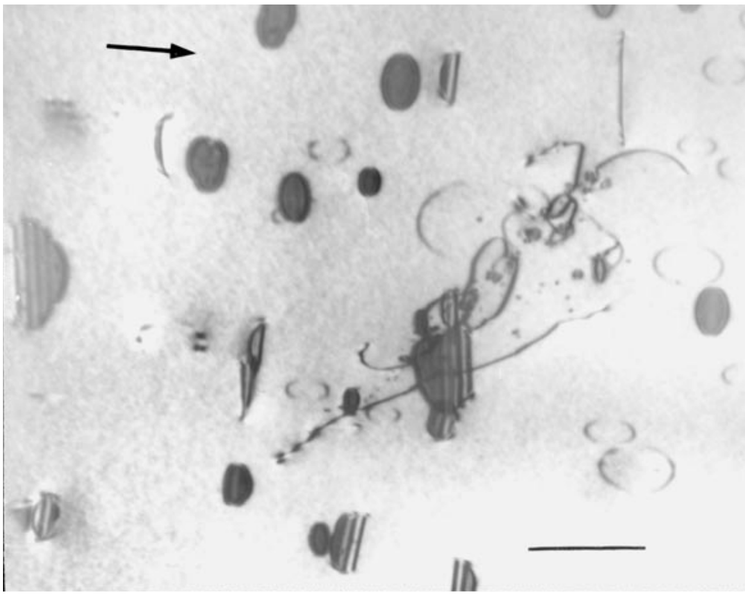

Figure 1. A TEM image of a typical complex defect cluster, i.e. a tangled grown-in dislocation surrounded by extrinsic Frank loops. The whole defect cluster was larger than the field of view of the picture shown here (it was twice as large). The arrow shows $\boldsymbol{g} = [02\bar{2}]$. The bar is 0.5 μm.

is generally observed for As-rich-grown GaAs doped with other dopants, where large hillocks form around the dislocation-related microhillocks (Weyher and van de Ven 1986, Frigeri and Weyher 1989, 1990). The matrix outside this depression is depleted of microhillocks over several μm in agreement with TEM findings. The microhillocks present everywhere in the matrix outside the depleted area are due to isolated loops as confirmed by TEM (Martín *et al* 1996).

Figure 3(a) is the EBIC image of DSL-revealed defect structures similar to those of figures 1 and 2. The etch depressions correspond to areas of EBIC non-radiative dark contrast due to the presence of the dislocation loops, whereas the areas surrounding the depressions exhibit EBIC bright contrast. Figure 3(b) is the plot of n across the defect structure D of figure 3(a) showing a decrease of n in the bright halo which suggests a donor depletion. Reliable measurements of n could not be done in the dark defect cluster due to the presence of the loops in high density that strongly influence the EBIC signal.

Micro-Raman measurements of n inside the etch depressions, but outside the hillocks, showed a clear decrease of n in the depressions with respect to the surrounding area (figure 4). At the hillock sites a strong TO peak always appeared that overlapped with the L_- peak. This indicates that at the hillock sites there is a high degree of crystalline disorder certainly due to the tangled configuration of the dislocation and to the presence of the loops with {111} habit planes in the very close neighbourhood. Other details are given in Martín *et al* (1996).

4. Discussion

To the authors' knowledge, such a massive formation of complex tangles and large helices at the grown-in dislocations and formation of such clusters of large extrinsic loops, as observed in Te-doped GaAs here and by other authors, have never been detected in GaAs doped with

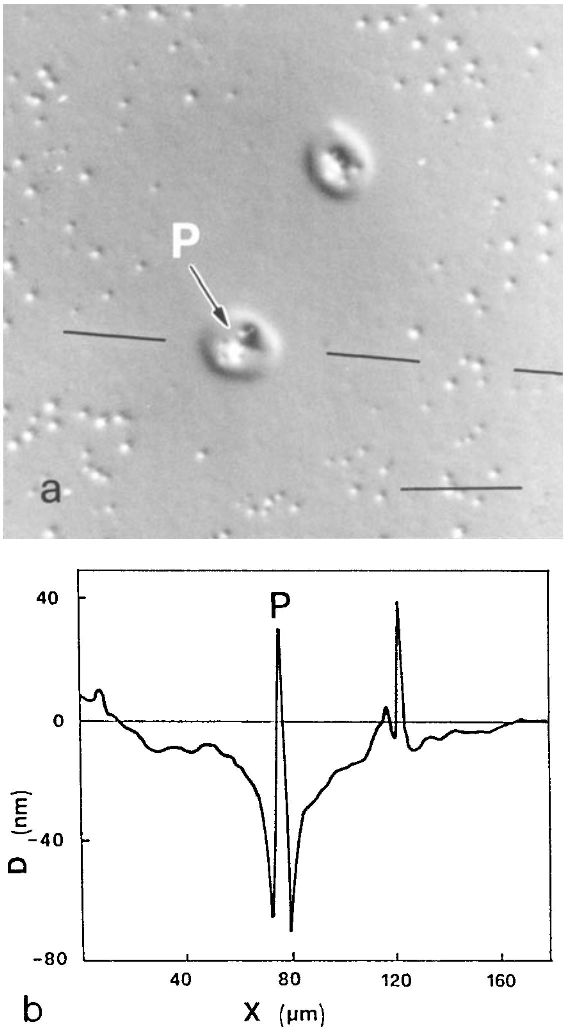

Figure 2. (a) A differential contrast optical microscopy image of two defect clusters as revealed by DSL etching. (b) Step profile along the dashed line across one of the dislocations, whose etch hillock is indicated by P. D is the etch depth. The etch feature consists of a depression surrounding the microhillocks produced by the grown-in dislocation and loops. The bar is 20 μm.

other dopants. Additionally, the DSL etch depressions around dislocations are also uncommon in As-rich GaAs and have never been seen before, as stated above. The latter result, however, helps us to understand the dislocation climb and the formation mechanism of the loops, whose presence can finally be the reason for the absence of the decorating As precipitates, as shown in the following.

The faster etching rate at the etch depressions around the dislocations indicates that in these areas the density of holes available for the etching action is higher than in the matrix. The depletion of the net free-electron density n in the depressions with respect to the less-etched matrix, as measured by micro-Raman spectroscopy, confirms this conclusion. This can be due to either an increase of the density of compensating acceptor-like impurities or a decrease of the donor (Te) density. The EBIC result showing that there is a decrease of n in

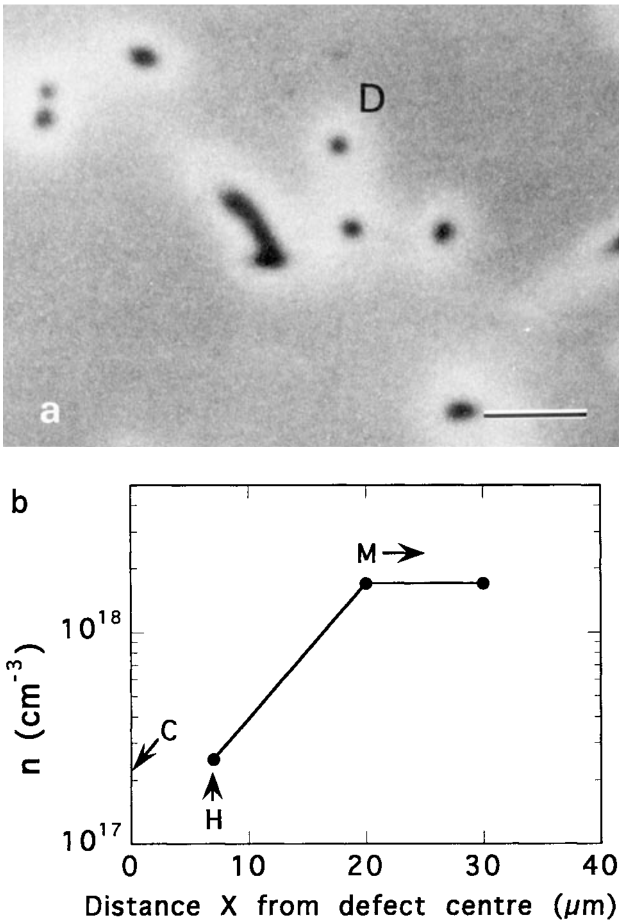

Figure 3. (a) An EBIC image of complex defect clusters similar to those revealed by TEM and DSL (figures 1, 2). (b) Typical plot of n, as determined by EBIC, versus position for the defect cluster D in (a). C = dark-defect-cluster centre, H = bright halo, M = matrix ($X \geqslant 20$ μm). In (a), the bar is 50 μm.

the areas (bright haloes) around the depressions (figure 3) would suggest that in such areas there is a decrease of the density of donors, very probably due to the gettering of Te by the grown-in dislocation. Outdiffusion to the matrix is considered much less probable because dislocations are preferred sinks for impurities. Depletion of donors in the bright haloes was also suggested by Chu *et al* (1981). There is thus an enrichment of Te atoms in the depressions. The increased hole density in the depressions is therefore believed to be due to an increased density of acceptor-like impurities. This does not conflict with the increase of Te donors since the Te atoms themselves can promote the formation of acceptors, namely the $Te_{As}V_{Ga}$ acceptor complex.

According to Hurle (1979a, b, 1995), in fact, in Te-doped GaAs the Te donors are partially compensated with an acceptor density that is directly proportional to the donor density. As such compensation is much more effective when the Te density is greater than (1–2) $\times$ 10^{18} cm^{-3}, it was suggested that such an acceptor contains the Te atom itself and that it can be the $Te_{As}V_{Ga}$ complex (Hurle 1979a, b, 1995). The formation probability of this complex is quite high due

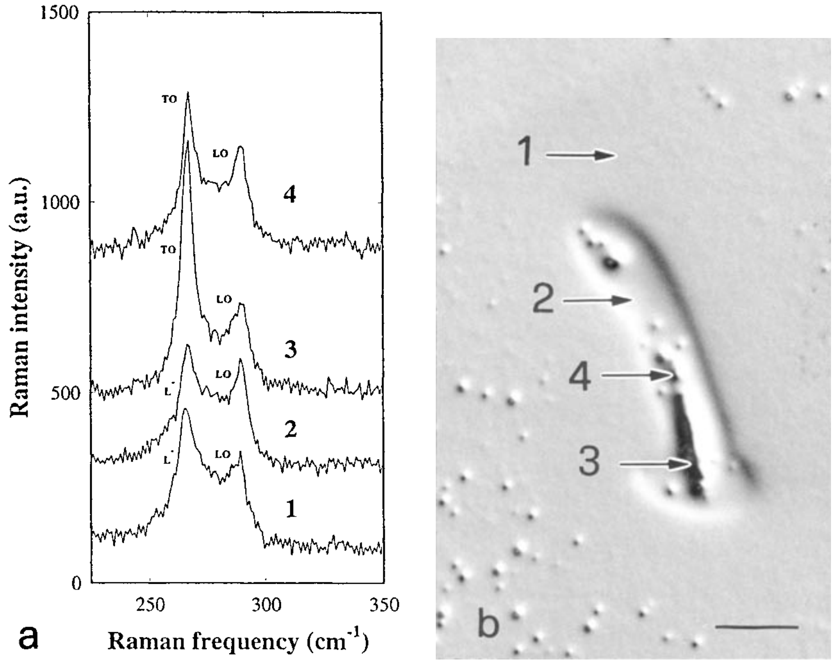

Figure 4. (a) Micro-Raman spectra taken from various areas (1 to 4) of the DSL-revealed defect complex shown in the optical microscopy image in (b), where the magnification bar is 10 μm. In area 2 (depression) there is an increase of the ratio of the LO-peak intensity to the L_--peak intensity with respect to the matrix (area 1) that indicates a carrier depletion. For areas 3 and 4 (microhillocks) the strong TO peak suggests a high degree of crystalline disorder.

to its high binding energy, as the two point defects constituting it are nearest neighbours on lattice sites (Herzog *et al* 1995). The incorporation reaction of Te as a donor in the GaAs lattice is

$$\mathrm{Te} + \mathrm{V_{As}} \rightarrow \mathrm{Te^{+}_{As}} + \mathrm{e^{-}}. \tag{1}$$

As the ionization reaction for V_{Ga} is

$$\mathrm{V_{Ga}} \Leftrightarrow \mathrm{V^{n-}_{Ga}} + \mathrm{h}^{n+} \tag{2}$$

with $n = 1, 2, 3$, the reaction for formation of the $Te_{As}V_{Ga}$ complex is (Hurle 1979a, b, 1995)

$$\mathrm{Te^{+}_{As}} + \mathrm{V^{q-}_{Ga}} \rightarrow \mathrm{Te_{As}V^{(q-1)-}_{Ga}} + \mathrm{h}^{(q-1)+} \tag{3}$$

with $q = 2, 3$. As the charge state 3− of the Ga vacancy is more abundant than the lower charge states at all doping levels (Tan *et al* 1993), it is very likely that the doubly ionized acceptor $Te_{As}V^{2-}_{Ga}$ prevails over the singly ionized one.

It is thus suggested that the increased density of Te atoms around a dislocation first leads locally to the formation of Te_{As} which then disappears by making $Te_{As}V_{Ga}$ acceptor complexes. The latter ones then compensate the background density of Te_{As} donors, so that the net free-electron density n decreases, thus explaining the high etching rate around dislocations. The probability of formation of the $Te_{As}V_{Ga}$ complex increases by increasing n not only because the density of Te_{As} increases (Hurle 1979a, b, 1995) but also because the density of V^{q-}_{Ga} increases, as shown by Tan *et al* (1993).

The important fact here is that complexing of the Ga vacancies with substitutional Te by reaction (3) leads to an undersaturation of Ga vacancies with the consequent production, by a

Frenkel reaction, of excess Ga interstitials in supersaturation with respect to the equilibrium density. Such Ga_i supersaturation can be the driving force for the formation of As_iGa_i interstitial pairs that can then condense into extrinsic loops upon cooling, i.e.,

$$Ga_i + As_i = Ga_iAs_i \text{ pairs} \rightarrow \text{extrinsic loops.} \tag{4}$$

Due to the expected high density of As_i, typical of bulk-grown GaAs, reaction (4) is very likely. It should be noted that the absence of dislocation loops in the areas surrounding the depressions (EBIC bright haloes) agrees with the decrease of the Te donor density in such areas, in the framework of our model.

The tangled or helical configuration of the grown-in dislocations is an indication that extensive dislocation climb has occurred which can again be accounted for by the Ga_i supersaturation generated due to reaction (3). The excess Ga interstitials closer to the core of the dislocations, in fact, can be absorbed at the core together with As_i and promote their climb. Absorption of interstitial pairs at the dislocation core is a negative climb step $-$CS:

$$As_i + Ga_i \rightarrow -\mathrm{CS} \tag{5}$$

which results in the emission of vacancies into the two sublattices, i.e. $-\mathrm{CS} \rightarrow V_{As}+V_{Ga}$. Both types of vacancy so produced can then feed reactions (1) and (3), so that an undersaturation of V_{Ga} is maintained and the formation of the extrinsic loops as well as dislocation climb can continue. Due to the extensive formation of complex tangles and large helices affecting almost all grown-in dislocations, a large consumption of both types of interstitial is expected to occur in association with the dislocation climb process.

The reason for the absence of decoration As precipitates in Te-doped GaAs is thus straightforward. As a consequence of reactions (4) and (5), i.e. formation of extrinsic loops and dislocation climb, a depletion of As interstitials in the close surroundings of the dislocations occurs, with the result that their diffusion to the dislocation and subsequent precipitation do not take place simply because they are missing. It should be noted that a depletion of Ga vacancies also takes place due to reaction (3) which further tends to decrease the probability of As precipitate formation as the latter ones are also partially made of voids according to some recent results (Weyher *et al* 1998). From the discussion above, the primary reason for the depletion of As interstitials is the formation of the $Te_{As}V_{Ga}$ acceptor complex and associated V_{Ga} undersaturation, which seem to be characteristic features of Te-doped GaAs not present for GaAs doped with other n-type dopants. The key to understanding this difference lies in the role played by the Ga vacancies, as they behave differently depending on whether the dopant is Te, of group VI, or other dopant impurities, of group IV. With group IV dopants, in fact, the role of V_{Ga} is that of accommodating the dopant atoms thus creating donors. In contrast, the group VI Te atoms become donors by occupying V_{As} sites and the main destination of V_{Ga} is to combine with Te_{As} to form the acceptor $Te_{As}V_{Ga}$ complexes, rather than donors, which causes their strong undersaturation close to dislocations.

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