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Dislocation Loops And Precipitates Associated With Excess Arsenic in GaAs

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Dislocation loops and precipitates in an arsenic-rich GaAs crystal have been studied by transmission electron microscopy to investigate their formation mechanism and establish their relationship to point defects. The precipitates are identified to be a hexagonal arsenic phase having a simple orientation relationship with the GaAs matrix. Detailed analyses of the loops indicate that they are composed of two separate defects lying on (111) planes: a faulted loop and a perfect loop. It is proposed that the loops are formed by condensation of excess arsenic interstitials followed by clustering of excess Ga vacancies and subsequent generation and movement of Shockley partial dislocation(s). The faulted loop is interpreted as an hcp arrangement of arsenic atoms. This model supports the hypothesis that arsenic interstitials and Ga vacancies coexist in GaAs at high temperatures although arsenic interstitials initiate the formation of arsenic-related dislocation loops. Implications concerning the formation process of the EL2 deep level defect are also discussed.

I. INTRODUCTION

It is generally accepted that dislocations adversely affect the performance of GaAs-based devices.¹ Substantial research effort has consequently been devoted to the study of dislocations in GaAs. Condensation of native point defects due to nonstoichiometry has been proposed to be an important mechanism of dislocation generation. In a study of GaAs crystals grown by the Horizontal Bridgman (HB) technique, Brice² has shown that the dislocation density increases with arsenic pressure over the melt during growth. Furthermore, Parsey³ et al discovered that in HB crystals a minimum dislocation density was obtained at an optimum arsenic source temperature which gives an exact stoichiometry. Lagowski et al⁴ suggested that this mechanism is dominant when the crystal is grown at low thermal stresses. This was later supported by Elliot et al,⁵ who studied dislocation generation during Liquid Encapsulated Czochralski growth.

The formation mechanisms and types of point defects responsible for the loops are not yet clearly known. Brice² attributed his results to the condensation of Ga vacancies (V_{Ga}) based upon X-ray data. From the observed relationship between the Fermi energy and the dislocation density, Lagowski et al⁴ and Aoyama et al⁶ also proposed that Ga vacancies are mainly involved in the formation of dislocation loops. In contrast, Gilling et al⁷ studied effects of doping elements (S and Si) on the dislocation density and claimed that arsenic interstitials (As_i) play a dominant role. In terms of concentration, several studies showed that the arsenic interstitials are dominant in arsenic-rich materials by measuring the lattice parameter by X-ray methods.^{8;9} Thermodynamic calculations of point defect concentrations give conflicting results; some predict dominance by Ga vacancies¹⁰ and some by arsenic interstitials.^{11;12} As to the condensation mechanism, it has been assumed without clear evidence that the condensation follows a typical sequence in which the responsible point defects form Frank type dislocation loops.⁴⁻⁷

In this work, dislocation loops formed as a result of an excess arsenic concentration have

been studied using transmission electron microscopy (TEM). Arsenic-rich GaAs crystals are of particular interest because semi-insulating GaAs crystals are grown from an arsenic-rich melt and contain excess arsenic atoms. Investigation of the formation mechanism of the dislocation loops at an atomic scale is reported. A model is presented that shows which types of point defects are involved in this formation. Precipitates observed with the loops are also characterized. Based upon the results, possible processes of arsenic antisite defect (As_{Ga}) formation by point defect interactions are discussed.

II. EXPERIMENTAL

The GaAs crystal studied in this work was grown by the Horizontal Gradient Freeze technique, with high arsenic concentration. In this technique, the optimum arsenic source temperature to grow a stoichiometric compound is known to be $617 \pm 1^\circ\text{C}$.⁵ Therefore, the source temperature was maintained at 630°C to grow the arsenic-rich crystal. TEM samples of various orientations were prepared either by chemical thinning (chlorine in methanol) or ion milling. No difference was observed between samples prepared by these different techniques. A Siemens Elmiskop 102 TEM and a JEOL JEM 200CX TEM with an ultrahigh resolution pole piece were used for observation. The image simulation was performed using the CEMPAS program developed by R. Kilaas.¹³

III. RESULTS AND DISCUSSION

A high density of dislocation loops was observed on the $\{111\}$ GaAs planes, often associated with small (~ 10 nm) precipitates. Figure 1a shows a typical example of such loops and precipitates and Fig. 1b shows the corresponding selected area diffraction pattern (SADP). To identify the nature of the precipitates, images and diffraction patterns from the same area were recorded under different conditions, i.e. different sample orientations ($\mathbf{B}$) and different diffracting vectors ($\mathbf{g}$). Figure 2 shows the observed bright field TEM images and their corresponding SADP's.

In Fig.1, the spacing of Moiré fringes on the precipitates is measured to be about 2.5nm. Since this spacing is represented by a vector connecting the GaAs $2\bar{2}0$ spot and the nearby A spot, it may be concluded that the A spot is from the precipitates. This is further supported by the observation that the direction of the vector is perpendicular to the Moiré fringe direction. Similar results are obtained under different diffraction conditions, as shown in Fig.2. More importantly, Fig. 2 shows that the precipitate spots form a hexagonal array in every (111) SADP, although only one or two of the spots are visible in each diffraction pattern due to the diffraction condition. Since the diffraction pattern composed of the A spots corresponds to an [001] pattern of hexagonal arsenic phase, the small precipitates are identified as hexagonal arsenic with their basal plane parallel to a GaAs (111) plane. The orientation relationship observed between the GaAs matrix and hexagonal arsenic phase, $(\bar{2}02)_{\text{GaAs}}||(\bar{1}20)_{\text{As}}$ and $[111]_{\text{GaAs}}||[001]_{\text{As}}$, is the same as that previously reported in studies of as-grown indium-doped LEC GaAs¹⁴ and thermally-oxidized GaAs.¹⁵

The (111) SADP's also show that the diffraction spots B from the loop represent an interplanar spacing of 0.35nm and comprise a hexagonal pattern. This indicates that the loop contains a stacking fault which is confirmed by the high resolution images. It is believed that the extra spots marked C are due to the two-dimensional nature of the defects involved.

Figure 3a shows a high resolution image of an edge-on dislocation loop similar to that in Fig.1. Figure 3b is a magnified image of the boxed area 1 in Fig.3a, with a Burgers circuit drawn around the loop. Detailed analysis of the Burgers circuit reveals that the loop is composed of two separate defects, one faulted loop with $1/6\langle 112 \rangle$ type Burgers vector and one perfect loop with $1/2\langle 110 \rangle$ type Burgers vector associated with an extra {111} plane.

It is also observed that the deformation vector associated with the entire defect, enclosing both loops, is $1/3\langle 111 \rangle$ and the GaAs lattice between the two loops has been sheared by two

times $1/6\langle 112 \rangle$ with respect to the surrounding lattice, on the $\{111\}$ plane parallel to the loops. This suggests that the unfaulting of an interstitial-type Frank loop may have occurred during formation of the defect, through the dislocation reaction $1/3[111] + 1/6[11\bar{2}] + 1/6[\bar{1}2\bar{1}] = 1/2[110]$, leading to the formation of the perfect loop.¹⁶ Considering the arsenic-rich nature of the crystal, it may be concluded that the interstitial loop was initiated by arsenic interstitials.

It is believed that the formation of the other component, the faulted loop, is also related to nonstoichiometry. The crystal was grown under very low thermomechanical stresses and therefore formation of faulted loops would be very unlikely without being associated with nonstoichiometry. Since the sample contains an excess of arsenic, it is proposed that the faulted loop represents an hcp arrangement of arsenic atoms only ('hcp' arsenic), which can be created by clustering of Ga vacancies followed by movements of Shockley dislocations to form a stacking fault.

Figures 4a, 4b, 4d and 4e show the arrangement of arsenic atoms on (a) $\{111\}$ and (d) $\{001\}$ planes of GaAs and (b) $\{001\}$ and (e) $\{110\}$ planes of hexagonal arsenic (the stable isomorph of elemental arsenic). Figures 4c and 4f show the positions of arsenic atoms on the 'hcp' arsenic planes corresponding to (a) and (d), respectively. By comparing these atomic arrangements, it is found that the 'hcp' arsenic has an intermediate structure between the GaAs structure and that of hexagonal arsenic. It is therefore suspected that the 'hcp' structure may appear as a metastable phase of elemental arsenic in GaAs and as a consequence a local cluster of Ga vacancies, i.e. a loose agglomerate of arsenic atoms in GaAs, may transform into the 'hcp' arsenic structure. Formation of a vacancy-type Frank loop is known as a typical procedure for the condensation of excess vacancies in the fcc materials. However, the generation of interstitials of one component (arsenic, in this case) is required for the excess vacancies of the other component (gallium) to form a Frank loop in the zincblende structure (GaAs). Therefore, if the arsenic interstitial is very unstable at the temperature of condensation, this procedure may be energetically less favorable

than formation of 'hcp' arsenic.

An image simulation study was performed to verify the assignment of the observed faulted loop as 'hcp' arsenic. In the image simulation process, theoretical images are calculated based upon a given atomic model and compared with the observed images. A result of such a simulation is shown in Fig.5, where a calculated image of the 'hcp' arsenic is compared with an experimental image of the faulted region, magnified from box 2 in Fig.3. The theoretical image is inserted on the left of the picture. A sample thickness of 10nm and a defocus value of -60nm was used in the calculation. The calculated image matches the observed image well, supporting the proposed interpretation. However, the theoretical images of a faulted loop calculated with and without Ga atoms showed only minimal differences in contrast. Therefore the possibility of a faulted region filled with Ga atoms cannot be totally excluded. Nevertheless, as discussed before, the formation of stacking faults not associated with nonstoichiometry is very unlikely due to the history of the crystal used for this study.

With the faulted loops in the observed images identified as 'hcp' arsenic, a simple formation mechanism of the loops is proposed and illustrated in Fig.6. Since this crystal was grown in an arsenic-rich environment, a high concentration of arsenic interstitials and Ga vacancies exists at the growth temperature, which tends to agglomerate during cooling of the crystal. As the critical temperature is reached, excess arsenic interstitials become unstable and begin formation of interstitial-type Frank loops, generating extra Ga vacancies, Fig.6a. These vacancies trigger condensation of extra Ga vacancies in the matrix leading to Fig.6b, in which the defect is composed of an interstitial type Frank loop and a Ga vacancy cluster. At this point, there is a strong driving force for the generation and movement of Shockley partial dislocation(s), which will lower the energy of the interstitial loop by unfauling it and, as well, lower the energy of the Ga vacancy cluster by transforming it into 'hcp' arsenic. The resulting structure, Fig.6d, consists

of an 'hcp' arsenic plate and a perfect loop, the same structure as that observed experimentally.

High resolution images of a slightly different composite loop are shown in Fig.7. This defect consists of a perfect loop and a monolayer faulted loop. It is believed that this loop was formed by the same mechanism except that in this case the {111} layers between two loops were subjected to movement of only one Shockley partial dislocation because only one or two layers of Ga vacancies were formed after the arsenic interstitials condensed.

It must be stressed that the proposed model is self-consistent in that it shows the arsenic interstitials initiate the loop formation process and therefore are less stable than Ga vacancies at the condensation temperature. This was an assumption in describing the observed faulted loops as the 'hcp' arsenic. It is also emphasized that the present model shows that both arsenic interstitials and Ga vacancies are involved in the process. This in fact can explain inconsistent results previously reported on the point defects responsible for the loop formation.⁴⁻⁷ Since two defects are involved, loop formation may be affected by the behavior of any one component.

Finally, these results give direct insight into the formation process of arsenic antisite defects in GaAs by point defect interactions, which is significant in its relation to the formation of the deep level defect EL2. Two processes have been proposed, $As_{As} + V_{Ga} = As_{Ga} + V_{As}$,¹⁷ and $As_i + V_{Ga} = As_{Ga}$.^{18;19} Our study supports the latter mechanism by showing that arsenic interstitials and Ga vacancies coexist at high temperature.

IV. CONCLUSION

A TEM study was performed to investigate the formation of dislocation loops and precipitates in GaAs due to an excess arsenic concentration. The results reveal that the precipitates are hexagonal arsenic with a clear orientation relationship with the matrix. The loops consist of two separate defects; one, a loop associated with stacking fault and the other, a perfect dislocation loop associated with an extra {111} plane. It is proposed that the loop is formed by dual

condensation of both excess arsenic interstitials and Ga vacancies, followed by generation and movement of Shockley partial dislocation(s). In this model, the faulted loop is actually composed of only arsenic atoms. The proposed model shows that arsenic interstitials and Ga vacancies coexist at the condensation temperature, although it is arsenic interstitials that initiate the formation of arsenic-related dislocation loops in GaAs. This result suggests that the formation of the arsenic antisites by point defect interaction may follow a previously proposed process, $As_i + V_{Ga} = As_{Ga}$.

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FIGURE CAPTIONS

Fig.1 (a) Bright field and (b) selected area diffraction pattern of precipitates and a dislocation loop. Precipitate spots are marked A and loop spots are marked B. Sample orientation is $(111)_{\text{GaAs}}$.

Fig.2 Results of a tilting experiment reveal that the precipitates are hexagonal arsenics. Sample orientation (**B**) and diffracting vector (**g**) are changed as indicated.

Fig.3 High resolution images of a typical edge-on loop. (a) low magnification image showing the entire defect and (b) magnified image of box 1 in (a) showing the loop is composed of two separate defects.

Fig.5 Positions of arsenic atoms on the atomic planes of different structures. (a) $\{111\}_{\text{GaAs}}$, (b) $\{001\}_{\text{As}}$, (d) $\{110\}_{\text{GaAs}}$ and (e) $\{110\}_{\text{As}}$. (c) and (f) describe the 'hcp' arsenic planes matching to (a) and (d), respectively. The numbers in (a),(b) and (c) denote the heights of atoms in z direction. Numbers in (d), (e) and (f) are the y coordinates of corresponding atoms.

Fig.5 Result of the image simulation shows that the calculated image of the 'hcp' arsenic layer fits very well with observed image of the faulted loop. Inserted at left middle is the calculated image.

Fig.6 Proposed formation mechanism of the loop in GaAs due to extra concentration of arsenic. (a),(b) Excess arsenic interstitials condense emitting Ga vacancies. (b) The emitted Ga vacancies along with vacancies from the matrix form a cluster. (b),(c) Shockley partial dislocations are generated and move. (d) The final state of the defect is same as one observed.

Fig.7 High resolution images of another composite loop showing same characteristics as Fig.3 except that the stacking fault is monolayer.

XBB 871-70

Figure 1

Figure 2

XBB 877-5917-B

Figure 3

XBL 8711-4977

Figure 4

XBB 877-5916

Figure 5

XBL 8711-4978

Figure 6

XBB 877-5919A

Figure 7

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