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INFLUENCE OF THE IMPURITY ON MORPHOLOGY OF GaSb EPILAYER GROWN ON GaSb(001) PATTERNED SUBSTRATE BY LIQUID PHASE EPITAXY

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Abstract

Tellurium (Te) impurity was revealed to have a significant effect on morphology of GaSb epilayer grown on GaSb (001) circular patterned substrates by liquid phase epitaxy. This was clarified by comparing GaSb epilayers with or without Te doping under identical growth conditions. After addition of Te, it was found that (311)B facet appeared instead of (111)B while (111)A was kept. The cross-sectional (110) plane of Te doped GaSb epilayer after stain etching in a permanganate etchant revealed that two boundaries separating differently doped upper and lateral parts of epilayer existed, moreover, some Te impurity striations were found in the lateral part of epilayer while no one was found in upper part. The time-development of growth morphology of Te doped GaSb epilayer was studied. It was found that (311)B facet appeared initially and formed dominantly after 3 hours' growth and the epilayer in initial state was concave.

Keywords: epitaxial growth, impurity, liquid phase epitaxy, selective epitaxy, tellurium, gallium antimonide. .

1. Introduction

In recent years, the growth of epilayers with pyramidal structure has attracted much attention because of their promising potential applications [**?**]. For example, CAMPBELL et al. found that pyramidal texturing of the substrate surface gave rise to a significant degree of light trapping within the substrate [1]. Based on the pyramidal textured structure, silicon solar cell was obtained with a high efficiency[2, 3]. Furthermore, a new silicon light emitting diode (LED) with the pyramidal textured structure has an efficiency of 1%, which is about 100 times higher than previous silicon LED [4]. WILLIAMS et al. found that the square based pyramidal structures have the desired geometry for the formation of a corner cube mirror upper reflector and for novel microcavity device applications by regrowth [6]. Compared with vapor phase epitaxy, liquid phase epitaxy (LPE) has the advantage of offering higher crystal quality, as well as greater selectivity in selective area epitaxy. No spurious nucleation is observed on the masking layer. GaSb has been considered a promising material for detectors, thermo-photo-voltaic cells, etc. in the

near infrared region [7]. In our previous investigation, a hollow truncated pyramidal structured GaSb epilayer was grown on a GaSb (001) patterned substrate [8]. The pyramidal epilayer can be employed to fabricate thermo-photo voltaic cell and light trapping is expected to be realized between these pyramidal epilayers. As an important *n*-type dopant for GaSb semiconductor, the influence of Te impurity on morphology of GaSb epilayer was investigated in the current study.

2. Experimental Method

A GaSb (001) patterned substrate with circular open window diameter of 600 μm was employed in the study. *Fig. 1* shows its schematic illustrations. In order to fabricate the patterned substrate, first a 0.2 μm thick amorphous SiN_x film was deposited on GaSb (001) substrates by plasma-assisted chemical vapor deposition (PCVD) using SiH_4 and N_2 gases. The circular open windows in the SiN_x film were formed by the combination of standard photolithography and reactive ion etching (RIE) using CF_4 and O_2 gases.

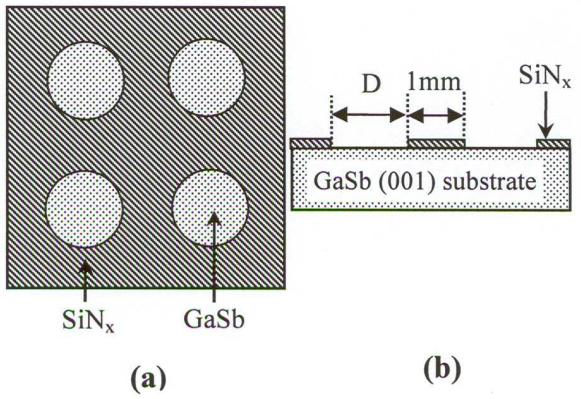

Fig. 1. Schematic illustrations of GaSb (001) circular patterned substrates with D value of 600 μm. Top view (a) and cross-sectional view (b).

A conventional LPE system was employed in the study. After charging the source materials of six-nine pure Ga in grade, non-doped polycrystalline GaSb and Te powder for Te doped GaSb epilayer, the solution was heated to 700°C and held at the temperature for 3 hours to make the solution homogeneous. Subsequently, the solution was cooled down to 550°C and kept in contact with an undoped GaSb source substrate for 1h to saturate the solution. Epitaxial growth was conducted with a supercooling of 1°C by decreasing the temperature from 549°C at a cooling rate of 10°C /h. The residual solution on the epilayer's surface was removed by immersing samples in a dilute HCl solution. The resultant epilayers were analysed

by a scanning electron microscope (SEM) facility. All the SEM images appearing in this article were taken under secondary electron mode. The cross-section of Te doped GaSb epilayer was analysed after stain etching in a permanganate etchant.

3. Results and Discussion

3.1. Influence of the Doping Concentration on the Morphology of GaSb Epilayer

In order to analyse the effect of the doping concentration on morphology of the GaSb epilayer, undoped GaSb and Te doped GaSb epilayers were grown on GaSb (001) patterned substrate under identical growth conditions. Corresponding SEM images of the resulting epilayers are given in *Fig. 2 (a)* nominally undoped GaSb, and Te doped GaSb epilayers with Te concentration in the starting solution of: *(b)* 0.012 mol%, *(c)* 0.053 mol%, and *(d)* 0.12 mol%, respectively. The non-doped GaSb epilayer appears a hollow truncated pyramidal structure with mirror-like top (001) and side {111} facets. In our previous work [8], the side {111} facets had been identified as two kinds of facets, namely, (111)A and (111)B. Te doped GaSb epilayers are not simple pyramidal structures, but complicated polyhedron structures. The Te doped GaSb epilayers shown in *Fig. 2(b)* and *(c)* appear as a hollow truncated polyhedron structure with top (001) facet and irregular side faces. And the epilayer shown in *Fig. 2(d)* is a regular polyhedron structure with regular side faces and without a top (001) facet. Obviously, the morphology of undoped GaSb epilayer was affected greatly as a result of the addition of Te impurity.

In order to clarify the structure of Te doped epilayers, the epilayer shown in *Fig. 2 (d)* was dealt with as follows. First, the GaSb:Te sample was cleaved to reveal the (110) cross-sectional plane, and then the cross-section was lapped down up to line W as drawn in *Fig. 2 (d)*, subsequently polished with an abrasive of 0.05 μm particles. In order to reveal Te impurity distribution on the (110) cross-sectional plane, a permanganate etchant ($KMnO_4$ (0.05M):HF:CH_3COOH = 1:1:1, vol. ratio) was employed to etch the sample for 5 minutes at room temperature since the etchant is very sensitive to the Te concentration in the crystal [9, 10]. The resulting SEM image is shown in *Fig. 3 (a)*, in which the angles between the side facets and (001) the face is about 25.2°, thus the two side facets are identified as (311)B facets. Moreover, the other two side facets are identified as (111)A facets according to their inverse triangular etching pattern shown in the inset of *Fig. 3(a)*, which is a surface feature of the (111)A facet [8]. Furthermore, it is found that (111)A facet appears in each epilayer in *Figs. 2(a)-(d)*. With the increasing of Te concentration in the starting solution, the irregular face that appears in *Fig. 2 (b)* and *(c)* becomes a regular face, the (311)B facet. In addition, growth in the central seed area of the substrate is enhanced so that the hollow structure was not obtained for the Te doped epilayer in *Fig. 2 (d)*, as evidenced by the cross-sectional image in *Fig. 3 (a)*.

Lateral growth is natural anisotropic growth of various crystal faces and sta-

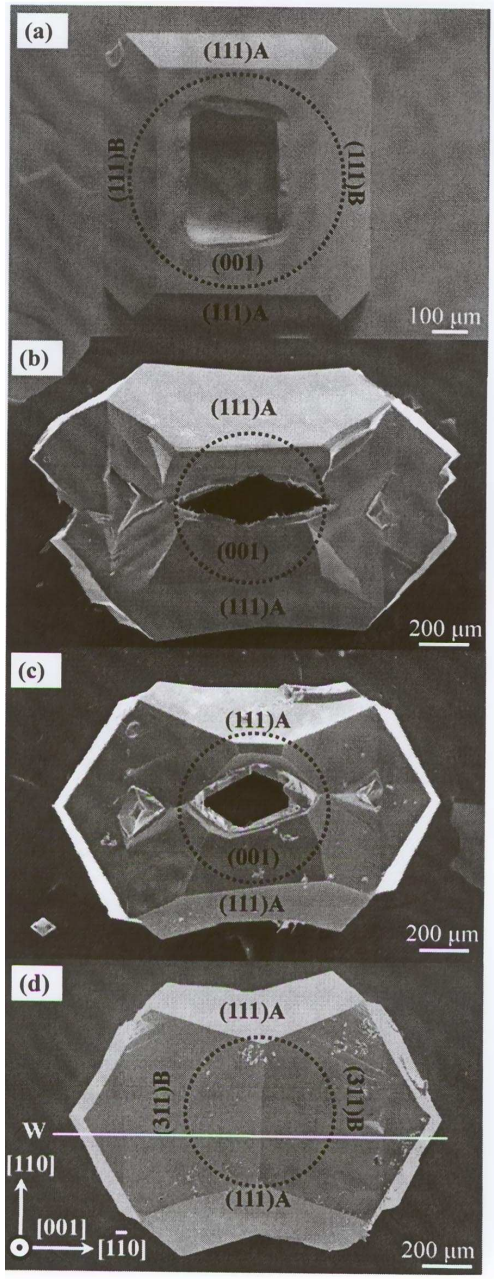

Fig. 2. SEM images of epilayer, (a) nominally undoped GaSb and Te doped GaSb epilayers with Te concentration in starting solution (b) 0.012 mol%, (c) 0.053 mol% and (d) 0.12 mol%, respectively, after 3 hours' growth. Dashed circles represent the edge of the circular open window pattern with diameter of 600 μm.

bility of a crystal face can be reflected by its relative growth rate. The crystal face with the smallest growth rate will be the dominant one. For the undoped GaSb epilayer, the (111)B face has the smallest growth rate and is the most stable one, while after addition of Te impurity (311)B face replaces it. The result clearly indicates that (311)B face becomes more stable than the (111)B face after the addition of Te impurity. It is well known that zinc blende structured III-V compounds exhibit different polarities along the <111> directions. The outermost atomic layer in each face is composed of either group III (for (111)A face) or group V (for (111)B face) atoms which are triply bonded to the lattice. It has been certified that the Te atom enters on a Sb site and form antisite complexes $V_{Ga}Ga_{Sb}Te_{Sb}$ for liquid phase epitaxial GaSb:Te epilayer grown form Ga-rich solution [11, 12]. The outermost atomic layer in (111)B face is composed of Te, Ga and Sb atoms, but the outermost atomic layer in (111)A face is composed of only Ga atom. Thus surface character of the (111)B face is highly affected.

3.2. Striations and Boundaries in GaSb:Te Epilayer

Dashed parts, L and R drawn in *Fig. 3* (a) were enlarged in *Figs. 3 (b)* and *(c)* to be seen more clearly. The most important feature in the two figures is that there are two zigzag boundaries and some curved striations under the zigzag lines. Indeed, the two zigzag boundaries XX' and YY', start from the interface of SiN_x mask layer (X', Y') and propagates into surface of epilayers, X and Y. Corresponding two parts separated by the boundary are called upper part and lateral part, as indicated in these figures. Furthermore, those curved lines appearing in the lateral part are Te striations, as indicated by some white arrows, whereas no striation was found in upper part. On each side of the lateral part in the epilayer, the number of striation was about 34 and they are not distributed uniformly. The interval near X and Y is about 7.3 μm, but the interval near X' and Y' is about 22-25 μm, which is larger than the former. *Fig. 4* shows corresponding schematic illustration of cross-sectional image of GaSb:Te epilayer shown in *Fig. 3 (a)*.

It is known that the main feature of the epitaxial lateral overgrowth (ELO) technique is a difference in properties of the upper and side faces of the ELO layer. ZYTKIEWICZ et al. found that differently doped parts of Te doped GaAs layer were separated by two boundaries and the upper part of epilayer showed increased CL intensity [13]. NISHINAGA et al. also observed the similar result for N-doped GaP ELO layer [14]. In our case, the boundaries are resulted because of the different growth mechanisms of the upper part and the lateral part.

Since all the striations appearing in lateral part are resulted at the solid-liquid interfaces during the growth and are curved, the lateral growth front is atomically rough. In this case there are no nucleation problems and particles can be added singly in a statistically random manner. On the other hand, the upper part with growth in front of (311)B facet grows by two-dimensional nucleation or propagation of steps supplied by substrate dislocations. Consequently, different incorpora-

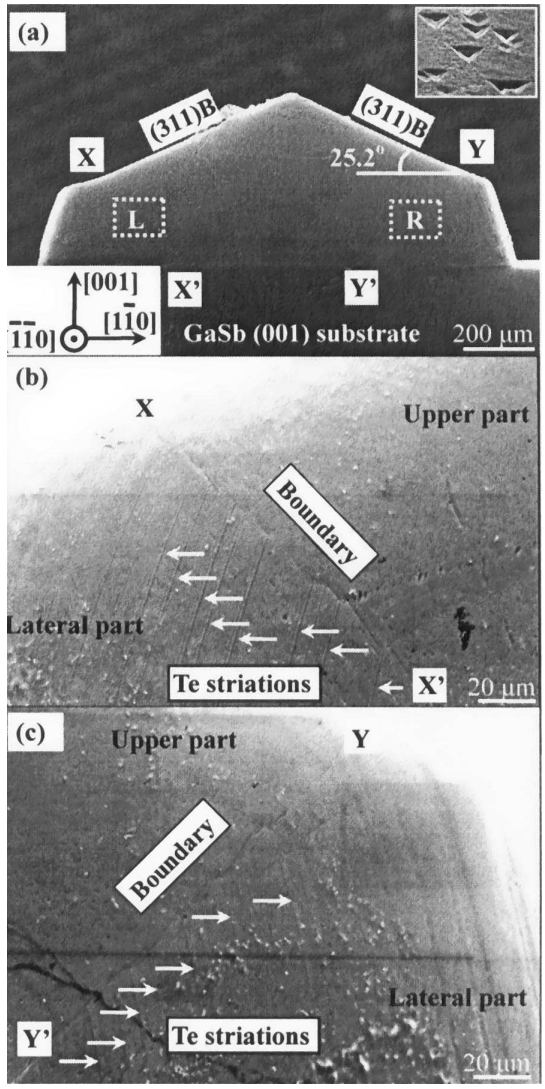

Fig. 3. (a) Cross-sectional image of Te doped GaSb epilayer along line W drawn in *Fig. 2(d)* after stain etching. The inlet image is an etching pattern on another facet after etching in chemical solution ($HCl:HNO_3:H_2O$=1:1:1, vol. ratio) for 3 min. at room temperature. (b) Enlarged image of dashed part L drawn in (a). Note that the epilayer is divided by a boundary (XX') into lateral and upper parts. Moreover, some Te striations are found only in the lateral part as indicated by some white arrows. (c) Enlarged image of dashed part R is drawn in (a).

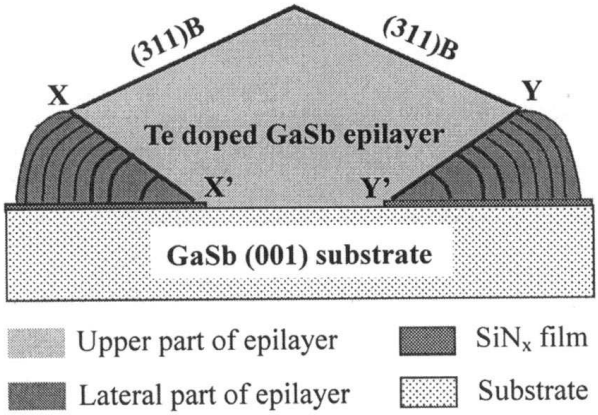

Fig. 4. Schematic illustration of cross-sectional view shown in *Fig. 3(a)*

tion rates of impurity on these faces could be expected. On the rough lateral growth front the impurity distribution coefficient should be the equilibrium one, but on the upper singular face the kinetics should govern the impurity incorporation process with the distribution coefficient being dependent on the vertical growth rate. As a result of the different incorporation rates of impurity, some Te striations occur in the lateral part but none were found in the upper part. It is well known that impurity striations are due to variations of non-equilibrium distribution coefficients which are caused by temperature fluctuations near the solid-liquid interface, as proved by Witt et al. [15]. These Te striations are equally likely to appear in both the lateral part and the upper part. However, these Te striations appear only in the lateral part. It is a direct evidence to highly support that there are different mechanisms of incorporation of Te in each region.

3.3. Time Development of Growth Morphology of Te Doped GaSb Epilayer

The time development of growth morphology of Te doped GaSb epilayer is studied in order to investigate the formation process of the (311)B facet. Two Te doped GaSb epilayers were grown for 30 minutes and 1 hour, respectively. Both of the epilayers and the Te doped GaSb epilayer presented in *Fig. 2 (d)* have identical growth conditions and nominally the same Te concentration of the starting solution of 0.12 mol%. Corresponding SEM images are shown in *Figs. 5 (a)* and *(b)*. It is found that the (311)B facet appears initially (see *Fig. 5(a)*), and then develops gradually (see *Fig. 5(b)*) and becomes dominant after 3 hours' growth (see *Fig. 2 (d)*). During the growth the boundary between the upper part and the lateral part can be observed in different periods on the surface of epilayer. In addition, the lateral growth front along $1\bar{1}0$ growth direction appears as a zigzag line, which

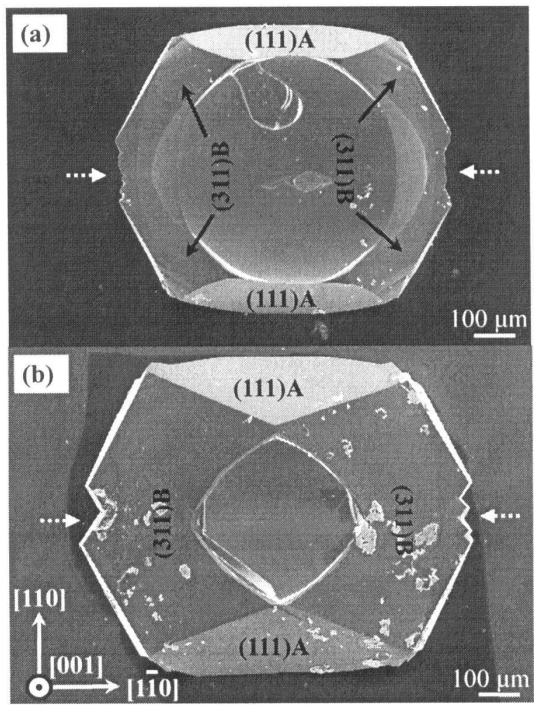

Fig. 5. SEM images of Te doped GaSb epilayers with Te concentration 0.12 mol% in starting solution (a) after 30 minutes' growth and (b) after 1 hour growth. The two images have the same scale given in (b). Note the lateral growth front profile indicated by the dashed white arrows.

contains many small growth fronts. And these growth fronts coalesce with additional growth, as indicated by the white dashed arrows.

Cross-sectional ($1\bar{1}0$) plane view of the epilayer shown in *Fig. 5(b)* after stain etching, using the same conditions as described in section 3.1, is given in *Fig. 6 (a)*. It is found that two downward facets appear under two (111)A facets and they are identified as (311)B facets according to the angle drawn in the figure. Note that the growth front along [110] direction is different from that along $1\bar{1}0$ growth direction, a rough face as shown in *Fig. 3(a)*. Indeed, the growth front in this direction is initially faceted and there is no striation found in the lateral part along the [110] direction. The result agrees well with the discussion presented in section 3.2. A corresponding cross-sectional schematic illustration is drawn in *Fig. 6 (b)*.

An important feature in *Fig. 5* is that the epilayers are concave, as evidenced in *Fig. 6 (a)*. The growth mode on the inner part of the epilayer, corresponding to the dashed part drawn in *Fig. 6 (a)*, is schematically drawn in *Fig. 6 (c)*. Since

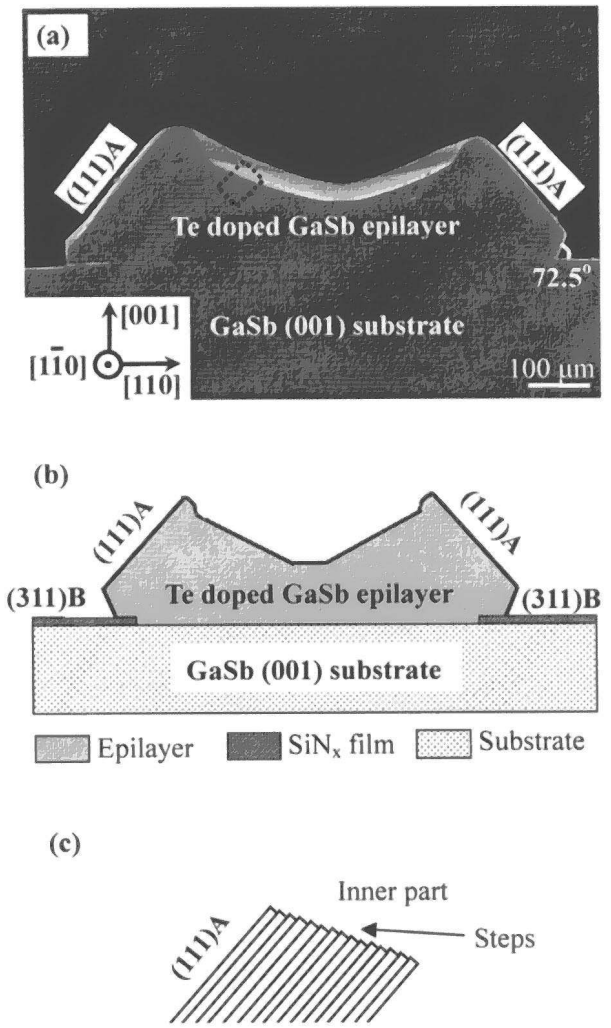

Fig. 6. Cross-sectional view (a) of Te doped GaSb epilayer shown in Fig. 5(b) after stain etching and (b) corresponding cross-sectional schematic illustration. (c) Illustration of growth mode on inner part of epilayer, corresponding to dashed part drawn in (a).

(111)A and (311)B faces develop as the side facets of Te doped GaSb epilayer, the two faces are relative stable compared with the other crystal faces. During the development of the (111)A facet (or (311)B facet) many steps and kinks are not supplied for growth on inner part of epilayer until the (111)A facet (or upper (311)B facet) on the other side is formed. The growth style is similar to the epitaxial growth overgrowth (ELO) on misoriented substrate [16]. Thus the kinetics still governs the impurity incorporation process with the distribution coefficient being dependent on the vertical growth rate.

4. Summary

Influence of Te impurity on GaSb epilayer grown on GaSb (001) circular patterned substrate by LPE was investigated. It was found that with the increasing of Te concentration in the starting solution, first the irregular side face appeared and then it became a regular side face, (311)B facet. In addition, growth in the central seed area of the substrate is enhanced so that hollow structure was not obtained for Te heavy doped epilayer. The cross-sectional (110) plane view of epilayer after stain etching in a permanganate etchant revealed that two boundaries separating the upper and lateral parts of epilayer existed. Furthermore, some Te striations were found only in the lateral part of epilayer, but no one was found in the upper part, what proves that there are different growth mechanisms on the upper and the lateral part. The time-development of Te doped GaSb morphology indicates that (311)B facet appears in initial state and two downward (311)B facets appear under two (111)A facets.

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