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**Effect of substrate orientation on the growth rate, surface morphology and silicon
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ABSTRACT

The growth and dopant incorporation during metal-organic vapor phase epitaxy (MOVPE) strongly depends on the orientation of the starting substrates. MOVPE of Si-doped GaSb layers on (100), (111)B and (111)A substrates were used to investigate the effect of orientation on the growth rate, the surface morphology and the silicon incorporation. Orientation dependence of growth rates was studied as a function of temperature and V/III ratio. As the V/III ratio increases, the growth rate on the (111)B oriented substrate decreases, whereas that on the (111)A oriented substrate increases. The surface morphology on different substrates was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Flat-top hexagonal hillocks were observed on (111)B surface, and the growth was by step-flow on these facets. A surface kinetic growth model has been proposed to describe the growth features observed on (111)B surfaces. Finally, the orientation dependence of silicon incorporation was studied by secondary ion mass spectrometry (SIMS) and Hall measurements. It was found that the silicon incorporation rate was four times higher on (100) oriented surface than on (111)B oriented substrate. Although no conduction type switch was found on (111)B oriented substrate, throughout the Si doping range studied, a Ga slightly rich growth condition might be one of the factors accounting for the discrepancy between theoretical prediction and experimental results.

Keywords: metal-organic vapor phase epitaxy, GaSb, substrate orientation, silicon amphoteric doping

I. INTRODUCTION

The effect of substrate orientation on the III-V epitaxial growth process has received tremendous attention for many years. Understanding of defect formation and dopant incorporation on different orientations is crucial to grow device quality epilayers for use in commercial applications. Among them, the silicon amphoteric doping phenomenon has been exploited extensively, primarily on GaAs by MBE¹⁻⁵, in which silicon behaves as a p-type dopant on GaAs (h11)A substrates, and as an n-type dopant on (100) and (h11)B substrates ($h \leq 3$). For (511) and higher index planes, the polarity of A-face and B-face no longer matters, and the final conduction type depends on the growth conditions. Many theories have been proposed⁶⁻⁸, however, none of them can interpret all the experimental observations. The physics of site preferential silicon occupation is still a matter of debate. To the best of our knowledge, very little work has been done investigating the epitaxial growth and Si doping behavior in GaSb of different orientations.

In this paper, we present a detailed study of the effect of substrate orientation on the growth rate, surface morphology and Si incorporation behavior on GaSb grown by MOVPE. Orientation dependence of growth rate was studied as a function of temperature and V/III (TMSb/TMGa) ratio. Morphology of epitaxial layers grown on (100), (111)B and (111)A substrates was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Three distinct growth features on (111)B substrates were observed. Evidence of layer-by-layer step flow growth was identified using AFM. A surface kinetic growth model has been proposed to explain the growth features observed on the (111)B surface. Finally, silicon incorporation in GaSb was studied by secondary ion mass spectrometry (SIMS) and Hall measurements.

II. EXPERIMENTAL CONDITIONS

GaSb epitaxial layers were grown by low pressure MOVPE in a horizontal quartz reactor with an RF-heated graphite susceptor. The organo-metallic sources were trimethylgallium (TMGa) kept at -7°C and trimethylantimony (TMSb) at 4°C . Experiments were performed under a total hydrogen flow of 5 standard liter per minute (slm), with V/III ratios in the range from 0.8 to 6, at temperatures in the range from 550 to 620°C . Unintentionally doped, p-type (100), (111)B and (111)A oriented GaSb substrates were used in this study. The dopant source was silane diluted to 102 ppm in H_2 , with flow rate varying from 30 sccm to 4800 sccm. In order to perform electrical characterization by Hall measurements, (100), (111)B and (111)A semi-insulating (SI) GaAs substrates were mounted side by side with corresponding GaSb substrates on the susceptor. Before loading into the reactor, GaSb substrates were given an initial degrease followed by a two-minute soak in HCl and 30-second etch in 1% Br-methanol. Samples were then rinsed with 2-isopropanol and blown dry with N_2 . It is recommended to avoid using de-ionized water for rinse purpose, since it often leads to hazy surface on GaSb substrates after cleaning.

The thickness of the epitaxial film was determined by measuring the weight change, as well as by the interference pattern from infrared reflectance. Optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to characterize the surface morphology. The carrier concentration and mobility of Si-doped GaSb epilayers grown on SI-GaAs substrates were measured using standard Van Der Pauw technique. To determine Si incorporation rate on different crystallographic orientations, secondary ion mass spectroscopy (SIMS) measurements were performed on selected samples, using a 14.5 keV Cs^+ beam as the primary sputter source.

III. RESULTS AND DISCUSSIONS

A. Growth Rate

In the first set of experiments, the effect of temperature on the growth rate has been studied, with temperature varied from 550 to 620 °C, and V/III ratio fixed at 1.24. Unlike GaAs growth, the growth rate of GaSb on all orientations studied followed the Arrhenius behavior, showing a strong temperature dependence (Fig.1). For GaSb grown on (111)B surface, the activation energy was 0.84 eV, while the growth rate was 2.1 $\mu\text{m/hr}$ at 600 °C. The relative growth rates on the low index surfaces were in the order of (111)A > (100) > (111)B under Sb-rich condition. Similar results were previously reported on GaAs study ⁹.

A series of experiments was then carried out to investigate the effect of V/III ratio on the growth rate and its orientation dependence. Four sets of growths were performed at 600 °C under V/III ratios of 0.8, 0.96, 1.24 and 1.6. Table listed the growth rates calculated from weight measurement. It was clear that under the Sb-rich conditions when V/III ratio was 1.6, there was very little GaSb growth on (111)B substrates, which was only 10%-15% of those on other orientations. FTIR spectra confirmed the results obtained from weight change measurements. This finding was in agreement with the early work conducted by Kamon on GaAs ⁹, in which, growth suppression was reported on (111)B GaAs substrates under As rich condition (V/III = 88).

For growth on (111)B substrates, good morphology was obtained when V/III ratio was close to unity but slightly Ga-rich (V/III = 0.96). However, under this condition, a lower growth rate on (111)A substrates was observed, compared to those on (111)B and (100) orientations.

Under highly Ga-rich conditions ($V/III = 0.8$), Ga droplets/clusters dominated over the surface on all substrates studied, and hence the growth rate monitoring was no longer meaningful.

It appears that the orientation dependence on growth rate is also affected by V/III ratio. Such phenomenon was overlooked in many early studies conducted on III-V systems. The interesting finding can be explained by the fact that the GaSb (111)B surface is terminated by rows of Sb atoms with a single dangling bond on each site. The outermost Sb atoms can capture either Sb or Ga atoms. Under Sb rich condition, the probability of Sb-Ga bond formation on GaSb (111)B is statistically low, due to heavy competition from incoming Sb atoms. Most of the expected Ga sites are not available for incoming Ga atoms. The growth front is retarded, until such blocking effect is eliminated when Sb atoms are desorbed from the Sb-Sb ad-molecule. The reverse is true for the growth enhancement on (111)A planes under Sb rich condition.

B. Surface Morphology

Fig. 2 shows typical growth features occurring on different orientations after grown at 600 °C for 40 min. The surface morphology of GaSb grown on GaSb (100) substrate is mirror-like over a relatively wide range ($V/III = 0.96 \sim 1.6$, temp = 550~ 620 °C). The only defects seen are a few rectangular shaped hillocks [Fig. 2 (a)]. Under Ga rich growth condition, GaSb grown on (111)A substrates reveals a large number of triangular hillocks covering almost the entire surface [Fig. 2(b)]. As the V/III ratio increases, the formation of such hillocks tends to reduce. Near the edge of the sample, the number of hillocks is lowered dramatically due to the effect of polishing-induced beveling. The edges of each triangular hillock are parallel to $[\bar{1}\bar{1}0]$, $[\bar{1}01]$ and $[01\bar{1}]$ directions clockwise.

It appears that growth of GaSb on (111)B planes are more complicated. Similar difficulty was previously reported while growing GaAs on (111)B substrates^{9, 10-12}. A common feature on GaSb (111)B is the presence of hexagonal pyramids [Fig. 2 (c)]. It can be seen that those hexagonal hillocks have different sizes and heights, indicating that they should not be artifacts formed during sample preparation etching. Fig. 2(c), (d), and (e) show the morphology of GaSb on (111)B surfaces grown under various V/III ratios from 0.96 to 1.6. As the V/III ratio increases, the average hillock size decreases, but the hillock density increases. It is probably related to the retardation of growth on (111)B surfaces under Sb rich conditions. Bear in mind that those hexagonal defects could not be eliminated under all conditions investigated in this study. However, the morphology was remarkably improved when miscut substrates were used [Fig. 2 (f)]

A more careful observation reveals that there are three distinct types of hexagonal hillocks present on GaSb (111)B substrates. The first type exhibits well-organized spiral growth features with non-flat top surfaces and has six-fold symmetry [Fig. 2 (c)]. The characteristic of the second type is its flat top surface, as shown in Fig. 2(c). Due to its three-fold symmetry, it may sometimes be mistaken as the triangular hillock found on (111)A surfaces. The key difference is that all hillocks on (111)B surfaces have six basal edges, instead of three edges. The third type has a non-flat top with more than one island formed above the hexagonal basal plane, as marked in Fig. 2(c).

Figure 3 (a) shows a top view of typical type I feature by SEM. The hexagonal hillocks are aligned with their basal edges parallel to $\langle 110 \rangle$ directions and their size varying from several microns in length and 2 – 3.3 μm in height. The vertical dimension of such hillock is larger than the average epilayer thickness. This raises an interesting question whether these huge hillocks are

connected with each other at the bottom (Stranski-Krastanov mode), or they are isolated clusters (Volmer –Weber mode). No conclusion can be drawn at this point. Measurements show that the inclined side facets lie at an angle of 14.8° with respect to the (111)B substrate. The six side-facets are not {111} type planes. Instead, they consist of multiple steps. In the case shown in Fig. 3 (a), the resulting nominal side facet has an index close to {221} plane (the angle between {111} and {221} is 15.8°). It is commonly believed that spiral growth mode is related to screw dislocations. Fig. 3 (b) shows a perspective view of type II feature by AFM. The hillocks structure is about 520 nm high with its side facets tilted about 24° with respect to the (111)B substrate. Again, those facets are not {111} planes either. Fig. 4 provides closer views of a spot marked “X” on the top surface shown in Fig. 3. (b). Interestingly enough, AFM images revealed that each large hexagonal hillock shown in Fig. 3 (b) consists of many layers of “micro” hexagonal shaped terraces. Furthermore, the height of each terrace was measured to be about 3.5 to 4 Å, which agrees well with the step height expected for (111) GaSb monolayer ($a / \sqrt{3} \approx 3.52$ Å). The AFM analysis suggests that two dimensional nucleation followed by step flow growth was involved. A surface kinetic growth model has been proposed in Fig. 5, summarizing three distinct growth features observed on (111)B plane. Fig. 5 (a) shows nucleus (edge adatoms) and steps on the growth front. When adatoms land on the vicinity of step edges, they migrate in a short range and re-arrange themselves in such a way that they eventually form a hexagonal terrace with basal edges parallel to $\langle 110 \rangle$ directions. Such geometrical preference is probably related to the requirement to balance extra surface energy and line energy during the growth. It can be easily calculated that, for the same total area, the hexagonal shape has a shorter perimeter compared to the triangular one.

For typical MOVPE growth conditions, fresh adatoms keep landing on the substrate before a full layer-by-layer growth is completed over the whole substrate. Therefore, the hillock density and shape may vary from type I, type II, to type III as shown in Fig. 5 (b), (c), and (d) respectively, depending on the ambient growth conditions at an atomic scale. Use of miscut substrates (see Fig. 2(f)) can reduce the occurrence of these hillocks by enhancing step-flow growth.

C. Si Incorporation

Six experiments were carried out to determine orientation dependence of silicon incorporation. The growth temperature was kept at 600 °C and V/III ratio was fixed at 0.96, while silane (102 ppm in H₂) flow rate was varied from 30, 120 to 4800 sccm. Hall measurements have been performed at room temperature on all samples. Fig. 6 shows the plots of carrier concentration and mobility as a function of silane flow rate. It is clear that the carrier concentration rises with the increase of silane flow rate in the low Si-doping region, and then saturates at 10¹⁸ cm⁻³ range. At silane flow of 1920 sccm, the electrically active carrier concentrations are 5.43x10¹⁸ and 1.31x10¹⁸ cm⁻³ on (100) and (111)B substrates, respectively. The relatively higher Hall mobility on the (111)B substrate compared to that on (100) is because of the low doping efficiency on (111)B planes. One might have already noticed that, Si doped GaSb grown on all three orientations investigated are found to be p-type, no matter of Si dosages.

SIMS measurements were performed on Si-doped GaSb on (100) and (111)B substrates, grown at 600 °C, with silane flow of 1920 sccm, and V/III ratio of 0.96. A very high doping

level was achieved due to high Si sticking coefficient. The atomic Si concentration in epilayer was measured to be $6.24 \times 10^{18} \text{cm}^{-3}$ on (100), which was four times of that on (111)B ($1.45 \times 10^{18} \text{cm}^{-3}$). It should be pointed out that there is a pile-up of Si at the interface between GaSb epitaxial layer and GaSb substrate, which is about 1×10^{19} and $3 \times 10^{19} \text{cm}^{-3}$ on (100) and (111)B substrates, respectively. The Si-segregation may suggest a retardation during initial growth, especially on (111)B surface. Such poisoning effect could lead to a large portion of incorporated Si in the form of clusters at the early stage. Furthermore, calculations based on data from Hall measurement and SIMS analysis, indicate that the amount of inactivated Si is about 10% of the total doped concentration in the “bulk” epilayer for both orientations studied.

The Si doping behavior into (100) III-V semiconductor has been well interpreted by the atomic size model ⁶, in which Si atoms tend to occupy the most spacious sites. For example, Si incorporates preferentially as a donor (Si_{Ga}) in GaAs, and as an acceptor (Si_{Sb}) in GaSb. However, this model does not account for the conduction type conversion observed under special growth conditions. The site availability model ⁷ delineates a dynamic picture of the competition among Si, III and V atoms at the growth front. In this model, vacancies, modulated by growth conditions (such as V/III ratio and temperature), play an important role in determining the final doping properties of Si atoms. For the Si doping into (h11) planes, the dangling bond model built upon the surface bonding geometry provides a visual tool to delineate the difference between (111)A vs. (111)B faces, and (100)-like double dangling bond vs. (111)-like single dangling bond ⁸. According to this model, Si prefers to take those sites where the atoms are less tightly bonded, i.e. when Si is doped into GaSb (111)B plane, n-type conduction would be expected. On GaSb (111)B plane, the growth front is characterized by the presence of Sb atoms with three back bonds to the bulk and Ga sites with only one back bond to the bulk. Therefore, Ga atoms

are less tightly bonded to the (111)B bulk compared to the (100) surface. Note that (100) has one double dangling bond to the bulk surface. So, the formation of Ga vacancies (V_{Ga}) is enhanced more on (111)B than on (100) planes. When doping with Si into GaSb (111)B planes, Si atoms are expected to fill the V_{Ga} and behave as donors (Si_{Ga}). However, this is not what we observed in this study.

One point we want to emphasize is that, a Ga-slightly-rich condition was selected during the study, to meet the requirement for reasonable growth rate and acceptable film properties (morphology and mobility). We speculate that the little extra Ga flow may have just offset the weak Ga bonding on the (111)B surface, and therefore pinned the hole-dominated conduction mechanism. Under typical growth window for GaSb, there is always a deficiency of Sb at the growth front. This antimony deficiency creates Sb vacancies and antisite defects (Ga_{Sb}), and therefore, increases the chance for Si atoms to land on Sb sites. Note that both Ga_{Sb} and Si_{Sb} act as acceptors. Such problem does not exist for GaAs since it has a much larger process window $V/III = 5 \sim 100$). Furthermore, lacking of SI-GaSb substrates, all the electrical data in this study are from Hall measurements of heteroepitaxial layers grown on SI-GaAs substrates. This system has 7.8% of lattice mismatch, adding another factor of complexity for Si amphoteric doping study in GaSb.

IV. CONCLUSIONS

The orientation dependence of Si-doped GaSb grown by MOVPE has been studied using (100), (111)B and (111)A substrates. It was found that the GaSb growth rate strongly depends on the crystallographic orientation, besides growth temperature and V/III ratio. As the V/III ratio

risers, the growth rate on the (111)B oriented substrate decreases, whereas that on the (111)A oriented substrate increases.

The growth of GaSb on (111)A and (111)B surfaces are more difficult than that on (100). It appears that slightly Ga-rich condition gives better morphology and reasonable growth rate on (111)B oriented substrate, while Sb-rich condition is needed for (111)A. On (111)A substrate, triangular hillocks are the dominant defects observed, while on (111)B plane, three distinct types of hexagonal hillocks have been identified. They are non-flat top hexagonal structure with spiral growth features (Type I), flat top structure with lateral growth features (Type II), and non-flat top hexagonal structure with multiple islands (Type III). For all types, the basal edges of each hillock are preferentially aligned along $\langle 110 \rangle$ directions. A closer look reveals that the top surface of type II feature consists of many levels of small hexagonal shaped terraces, with each step height in monolayer range, indicating a step flow growth involved. A surface kinetic growth model has been proposed to describe the growth features observed on the (111)B surface.

Finally, it has been found that the silicon incorporation rate was four times higher on (100) oriented surface than on (111)B. All Si-doped layers grown on (111)B substrates still exhibited p-type conductivity, contrast to our prediction. A Ga slightly rich growth condition might be one of the factors accounting for the discrepancy.

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Figure Captions

FIG. 1. Semilog plot of growth rate as a function of reciprocal growth temperature $1000/T$, on (100), (111)B and (111)A substrates. The V/III ratio was fixed at 1.24.

FIG. 2. Surface morphology of GaSb epilayers grown at 600 °C for 40 min on various orientations. (a) GaSb (100) substrate; (b) GaSb (111)A substrate; (c, d, e, f) GaSb (111)B substrates. (X 200)

FIG. 3. (a) A top view of Type I feature by SEM, showing a non-flat top hexagonal hillock with spiral growth. The edge of the base is aligned preferentially along $\langle 110 \rangle$ directions. (b) A perspective view of Type II feature by AFM, showing the flat top hexagonal structure. Scan size 30 x 30 μm .

FIG. 4. Surface plot AFM image showing the detail of the region marked X in Fig. 3(b). Scan size 10 x 10 μm . (b) Surface plot AFM image showing a closer view of the region marked Y in Fig. 4(a). Scan size 2 x 2 μm . (c) Cross-section along the line indicated in Fig. 4(b).

FIG. 5. Surface kinetic growth model shows multi-levels of hexagonal shaped terraces (a) perspective view, (b), (c) and (d) two-dimensional views of Type I, Type II and Type III features, respectively.

FIG. 6. Carrier concentration and mobility as a function of SiH_4 flux rate ($T_g = 600$ °C, $V/\text{III} = 0.96$).

Table Caption

Table 1. Effect of V/III ratio on growth rate on different orientations (by weight measurement).

Growth temperature was kept at 600 °C.

FIG

(b)

(a)

(f)

(g)

(h)

G

perspective view

FIG. 5

FIG. 6

Table

V/III ratio		Growth Rate (($\mu\text{m/hr}$))	
0.96	(100)	(I 1)A	(I 1)B
	3.365	3.001	3.287
	24	3.121	109
6	3.098	3.721	0.434