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Top edge facet development in asymmetric grooves

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Abstract

The low pressure (20 mbar) organometallic vapour phase epitaxy (LP-OMVPE) of GaAs/GaInP in asymmetric grooves, patterned on $\bar{1}11$ B GaAs substrates, has been examined. One of the characteristic features of this deposition is that facets develop along the top edges where the side wall planes meet the top surface. The origin of small facets at the top edge appears to be due to pre-growth conditions. The development of these facets were found to be related to large relative growth rate differences of the GaAs buffer layer deposition on adjacent planes with different crystallographic orientations.

Keywords: Epitaxy; Etching; Faceting

Crystal growth of compound semiconductors on surfaces other than the commonly used {001}, and related vicinal surfaces, have often been explored. Deposition on surfaces between {001} and {111}A or {111}B – i.e. Group III (Ga) and Group V (As) terminated planes respectively – have attracted particular attention because of their unique properties such as: narrow linewidths and higher intensity photoluminescence spectra on (311)B [1], lower threshold currents on (511)A [2], large ordering domains on (511)B [3,4], quantum box like structures on (311)B [5], exploring the amphoteric character of Si dopant [6] and the highest reported hole mobility attained on (311)A [7].

Growth on pattern surfaces, other than the {001}, has also attracted considerable attention due to the

prospect of depositing novel structures which exhibit low dimensional confinement such as quantum wires [8,9], boxes [10,11] and innovative laser structures [12].

Deposition on non-planar {111}B substrates merits particular attention because advantage may be taken of the slow growing, or in some cases non-growing, nature of this surface in order to explore the pseudo-selective embedded mode of growth for the deposition of the aforementioned nanostructures. One of the inherent anomalies associated with this form of growth is that facets generated along the side walls often dominate and define the resultant crystal habit [13,14]. The primary motivation of this study was to examine fundamental aspects of faceting and in particular address how they originate, develop and under what circumstances they may be suppressed.

The grooves used in this study were made by conventional photolithography and wet chemical etching of stripes etched along the $\bar{1}10$ direction on

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Fig. 1. Schematic of $(\bar{1}\bar{1}0)$ cross sections of the asymmetric grooves used in this study.

$(\bar{1}\bar{1}1)$ B GaAs substrates. The stripe pattern array ranged from 5 to 100 μm wide, etched to a depth of 10 to 14 μm with an intergroove separation distance of 300 μm . The side walls formed had (001) and $(4\bar{4}3)$ A orientation (Fig. 1), thus giving these grooves an asymmetric character.

After preparing these grooves the samples were

then degreased and briefly etched prior to loading into a commercially available low pressure (20 mbar) organometallic vapour phase epitaxial (LP-OMVPE) reactor [15]. The Group V hydride sources consisted of 100% arsine (AsH_3) and phosphine (PH_3), and the Group III organometallic precursors were made up of trimethylalkyls of gallium and indium for the respective binary (GaAs) and ternary (GaInP) depositions. The deposition temperature, growth rate, V/III ratio and total flow rate were: 720°C, 1 to 2 $\mu\text{m/hr}$, 400, and 7 ℓ/min of mainly palladium purified hydrogen carrier gas, respectively. These parameters were fixed and chosen as such in order to produce the stoichiometric lattice matched composition of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ on a (001) GaAs surface. A one to two hour deposition of the ternary structure followed after a 0.2 to 0.4 μm deposition of a GaAs buffer layer. The crystal habits of these non-planar samples were then examined by a scanning electron microscope (SEM).

Fig. 2. SEM $(\bar{1}\bar{1}0)$ cross sections, with 10 μm markers, of GaAs/GaInP deposited in asymmetric grooves which resulted from: an ammonium based oxide removal etchant (a), pre-heat treatment (b), ammonium based oxide removal etchant and only GaAs deposit (c), and 2 μm of only GaInP deposition with respect to the (001) side plane (d).

The primary feature of both the (001) and ($\bar{4}\bar{4}\bar{3}$)A side walls was that facets were present along the top edges. The origin of these facets appears to depend on the pre-growth conditions such as which type of etchant was used for the substrate cleaning – i.e. removal of the native oxide layer prior to growth, and the reactor heat up to the deposition temperature. In the case of the (001) groove wall two small ($\sim 1 \mu\text{m}$) and adjacent facets ($(\bar{1}\bar{1}2)\text{B}$ and $(\bar{1}\bar{1}3)\text{B}$), not shown for the sake of brevity, had developed as a result of an ammonium based ($2 \text{NH}_4\text{OH}:1 \text{H}_2\text{O}_2:10 \text{H}_2\text{O}$) oxide removal etchant. When this etchant was substituted with a 10% HCL solution these faceting features were no longer present. It was further noticed, however, that in this latter case the reactor heated up, and stabilization to the 720°C growth temperature thermally etched this previously facet free edge into a rounded feature.

The characteristic difference between the facets caused by the ammonium based etchant and the thermally induced edge rounding feature was that the former caused the (001) side wall to develop into a large $(\bar{1}\bar{1}3)\text{B}$ facet (Fig. 2a) from the original $(\bar{1}\bar{1}2)\text{B}$ and $(\bar{1}\bar{1}3)\text{B}$ double facet edge, whereas the latter evolved into a $(\bar{1}\bar{1}5)\text{B}$ facet (Fig. 2b). This result is in contrast with a similar study [13] where only the $(\bar{1}\bar{1}5)\text{B}$ facet was reported after the GaAs growth in an atmospheric pressure reactor.

It is not immediately obvious how the two ($(\bar{1}\bar{1}2)\text{B}$ and $(\bar{1}\bar{1}3)\text{B}$) small ($1 \mu\text{m}$) faceting features, located along the top edge of the (001) side wall, developed into one large (5 to $7 \mu\text{m}$) $(\bar{1}\bar{1}3)\text{B}$ facet (Fig. 2a). The interplay between varying growth rates on adjacent planes, of different crystallographic orientations, may be used in order to elucidate these developments. Top edges may be considered convex surfaces whereby, according to the Borgstrom construction [16], fast growing facets will be consumed by the slower growing facets. In accordance with this experiment this means that the faster growing $(\bar{1}\bar{1}2)\text{B}$ facet develops into, or becomes coplanar with, the $(\bar{1}\bar{1}3)\text{B}$ facet which is slower in growth.

A further extension of the Borgstrom construction [16] helps to elucidate the development of the large $(\bar{1}\bar{1}3)\text{B}$ facet. The relative growth rates of the GaAs buffer layer can be expressed as:

$$R(001)/R(\bar{1}\bar{1}1)\text{B} = 3.6. \quad (1)$$

This high relative growth rate difference results in the rapid development of the (001) side wall into the large $(\bar{1}\bar{1}3)\text{B}$ facet as illustrated in Fig. 2c where only $0.4 \mu\text{m}$, with respect to the (001) planar surface, of GaAs has been deposited.

The $(\bar{1}\bar{1}5)\text{B}$ facet, resultant from the thermally induced edge rounding, is a feature commensurate with the encountered top edge configuration where the $(\bar{1}\bar{1}1)\text{B}$ top surface meets the (001) side wall (Fig. 1). If faceting features are considered to be linear combinations of these primary planes, then the $(15)\text{B}$ facet can be interpreted as a result of the growth rate on the (001) surface being nearly four times greater (expression (1)) than that on the $(\bar{1}\bar{1}1)\text{B}$ plane.

The origin and development of the $(\bar{1}\bar{1}0)$ facet, along the top edge of the ($\bar{4}\bar{4}\bar{3}$)A side wall, appeared to form prior to growth irrespective of the pre-growth treatment. If, for example, the ammonium based etchant was used then this top edge feature was measured to be $2 \mu\text{m}$ prior to growth. After a one hour deposition of GaInP this facet extended to $5 \mu\text{m}$ (Fig. 2a). This facet also originated from a thermally induced edge rounding feature, without the ammonium based etchant, and developed into a $1 \mu\text{m}$ facet after aforementioned hour long deposition (Fig. 2b). An interesting note is that the $(\bar{1}\bar{1}0)$ facet, like its $(\bar{1}\bar{1}5)\text{B}$ counterpart, is also a feature commensurate with the top edge crystallographic configuration (Fig. 1).

The development of these originally small top edge facets into larger facets is induced by concentration gradients along the edges [14,17]. The lateral extension of the edge facets diminishes the supply of gas phase species and lowers the growth rate on the neighbouring $(\bar{1}\bar{1}1)\text{B}$ plane. The disparity between the high deposition rate on the side walls and the low growth rate on the reference $(\bar{1}\bar{1}1)\text{B}$ top surface induces a locally well pronounced lateral concentration gradient. This lateral profile serves as the driving force responsible for the extension of the top edge features.

The morphological reason for the development of these top edge facets is that they confine the resulting crystal habit with stable, minimum energy surfaces. The $(\bar{1}\bar{1}0)$ facet, developing along the top edge of the ($\bar{4}\bar{4}\bar{3}$)A side wall, belongs to a set of planes, with a “zig-zag” bonding arrangement, commonly

Fig. 3. Schematic of $(\bar{1}\bar{1}0)$ cross section of the $(\bar{1}\bar{1}3)B$ (a) and $(\bar{1}\bar{1}5)B$ (b) facets. The dangling bond configuration per step is highlighted by a dashed box, and the possible dimer bond formation is indicated by a bold face arrow.

referred to as the “cleavage” planes for zincblende crystal structures and they are by definition low energy surfaces.

The dangling bond configuration for the $(\bar{1}\bar{1}3)B$ is depicted in Fig. 3a. This surface can be regarded to be built up from a single $(\bar{1}\bar{1}1)B$ like step with steps formed by two rows of atoms having an (001) orientation. If surface reconstruction were to occur, by the formation of dimer bonds along directions orthogonal to the step (Fig. 3a), then this would imply a reduction of two, out of the original three, dangling bonds.

The $(\bar{1}\bar{1}5)B$ surface would undergo a similar dangling bond reduction (Fig. 3b). This surface is comprised of a single $(\bar{1}\bar{1}1)B$ like step with a (001) terrace comprised of three rows of atoms. If complete reconstruction were to occur then this would entail that the five dangling bonds originally present on such a (001) terrace would be reduced to a single surface bond. This minimization by dimer formation is obstructed by a relatively large gain in surface energy due to an increase in bond strain [18]. If reconstruction were to occur on the $(\bar{1}\bar{1}5)B$ surface

then, because of the strain consideration, it is believed that two, out of the possible five dangling bonds, would dimerize thus leaving three surface bonds (Fig. 3b).

So far the origin and development of top edge facets have been addressed. Attention must now be focused on how these $(\bar{h}hk)B_{k>h}$ facets can be suppressed.

Crystal growth of compound semiconductors is dependent not only on surface orientation but also on the process parameters – e.g. supersaturation and temperature – as well as the material system to be deposited. The deposition on non-planar surfaces of different binaries may exhibit a completely different relative growth rate relation as, for example, the homoepitaxy of GaAs [19],

$$R\{001\} > R\{110\} \geq R\{111\}A > R\{111\}B, \quad (2)$$

as juxtaposed to heteroepitaxy, on non-planar surfaces, of other Ga related binaries such as GaN, [20]

$$R\{111\}B > R\{001\} > \{111\}A, \quad (3)$$

illustrates. It is therefore not surprising that the deposition of the ternary GaInP alloy, with respect to the process parameters set forth in this study, would also relay a different growth rate relation [19,21] as expressed by:

$$R\{111\}A > R\{110\} > R\{100\} > R\{111\}B. \quad (4)$$

The relative growth rate difference between the (001) side wall and the $(\bar{1}\bar{1}1)B$ reference top surface, with respect to the parameters set forth in this experiment, for this ternary alloy, is:

$$R(001)/R(\bar{1}\bar{1}1)B = 1.3, \quad (5)$$

which is significantly lower than the 3.6 value obtained for the GaAs deposition (expression (1)). The consequence of this is that by depositing the ternary, without the binary layer, then the (001) side wall orientation, along the top edge, is maintained as depicted in Fig. 2d.

In summary, the top edge faceting features present after the growth of GaAs/GaInP in asymmetric grooves, patterned on $(\bar{1}\bar{1}1)B$ substrates, have been examined. Although the $(\bar{1}\bar{1}0)$ facet occurred under every circumstance the $(\bar{1}\bar{1}3)B$ or $(\bar{1}\bar{1}5)B$ facets, present along the top edge of the (001) side wall, formed and developed as a consequence of both

pre-growth conditions and the interplay of the large difference in the binary growth rates on adjacent planes of different crystallographic orientations. The $(\bar{h}hk)B_{k>h}$ faceting features can be suppressed by substituting the buffer layer with the ternary GaInP alloy. This unique surface structuring of asymmetric grooves opens up novel possibilities for the low dimensional quantum confinement of nanoscale arrays.

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References

- [1] A. Valster, C.T.H.F. Liedenbaum, M.N. Finke, A.L.G. Se-verens, M.J.B. Boermans, D.E.W. Vandenhoude and C.W.T. Bulle-Lieuwma, *J. Cryst. Growth* 107 (1991) 403.
- [2] I.W. Tao, C. Schwartz and W.I. Wang, *J. Vac. Sci. Technol. B* 10 (1992) 838.
- [3] L.C. Su, S.T. Pu, G.B. Stringfellow, J. Christen, H. Selber and D. Bimberg, *J. Electron. Mater.* 23 (1994) 125.
- [4] S.R. Kurtz, J.M. Olson, D.J. Arent, M.H. Bode and K.A. Bertness, *J. Appl. Phys.* 75 (1994) 5110.
- [5] R. Nötzel, J. Temmyo, H. Kamada, T. Furuta and T. Tamamura, *Appl. Phys. Lett.* 65 (1994) 457.
- [6] S.S. Bose, B. Lee, M.H. Kim and G.E. Stillman and W.I. Wang, *J. Appl. Phys.* 63 (1988) 743.
- [7] M. Henini, P.J. Rodgers, P.A. Crump, B.L. Gallagher and G. Hill, *J. Cryst. Growth* 150 (1995) 451.
- [8] Y. Nomura, Y. Morishita, S. Goto and Y. Katayama, *J. Electron. Mater.* 23 (1994) 97.
- [9] T. Fukui, S. Ando and Y.K. Fukai, *Appl. Phys. Lett.* 57 (1990) 1209.
- [10] T. Fukui, S. Ando, T. Honda and T. Toriyama, *Surf. Sci.* 267 (1992) 236.
- [11] Y. Sugiyama, Y. Sakuma, S. Muto and N. Yokoyama, *Appl. Phys. Lett.* 67 (1995) 256.
- [12] S. Ando, N. Kobayashi and H. Ando, *J. Cryst. Growth* 145 (1994) 302.
- [13] K. Yamaguchi and K. Okamoto, *J. Cryst. Growth* 94 (1989) 203.
- [14] K.M. Dzurko, S.G. Hummel, E.P. Menu and P.D. Dapkus, *J. Electron. Mater.* 19 (1990) 1367.
- [15] P.R. Hageman, M.H.J.M. de Croon, J.N.H. Reek and L.J. Giling, *J. Cryst. Growth* 116 (1992) 169.
- [16] H. Buckley, *Crystal Growth* (Wiley, New York, 1951) p. 125.
- [17] M.J. Anders, M.M.G. Bongers, P.L. Bastos and L.J. Giling, *J. Cryst. Growth*, accepted for publication.
- [18] D.J. Chadi, *Phys. Rev. B* 29 (1984) 785.
- [19] B. Elsner, R. Westphalen, K. Heime and P. Balk, *J. Cryst. Growth* 124 (1992) 326.
- [20] M. Nagahara, S. Miyoshi, H. Yaguchi, K. Onabe, Y. Shiraki and R. Ito, *J. Cryst. Growth* 145 (1994) 197.
- [21] M.M.G. Bongers, P.L. Bastos and L.J. Giling, *J. Cryst. Growth* 145 (1994) 981.