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TEM Study of the Effect of Growth Interruption in MBE of InGaP/GaAs Superlattices

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The influence of growth interruption during the MBE growth of (100) $In_{0.5}Ga_{0.5}P$/GaAs superlattices is investigated by cross-sectional TEM. A roughening of the growth front is observed during an interruption after the exchange of the group-V molecular beams. The roughening of growth front occurs due to a spontaneous change in the growth orientation of the superlattice from [100] to ⟨311⟩ directions. This change in growth orientation is characterized by an initial formation of V-shaped grooves with {311} facets on the GaAs growth front which eventually lead to the formation of regions of {311} superlattice structures. The direction of V-shaped grooves is along the [01$\bar{1}$] axis, which is parallel to the surface dangling bonds of the group V atoms in the unreconstructed (100) plane. The most critical stage for the spontaneous change of the growth orientation is the interruption after the growth of a GaAs layer with the P_2 flux.

Key words: InGaP/GaAs superlattices, MBE, TEM, growth orientation

INTRODUCTION

Lattice matched $In_{0.5}Ga_{0.5}P$/GaAs quantum well heterostructures have attracted significant interest for applications in visible light sources and 2-dimensional electron gas (2-DEG) transistors.[1] High quality InGaP/GaAs superlattices have been grown recently by gas source molecular beam epitaxy (GSMBE).[2] These investigations have shown that a "growth interruption" scheme is an important requirement for the growth of structures with flat and compositionally abrupt interfaces. In order to grow the alternating arsenide and phosphide layers it is necessary to switch the group-V molecular beams at each heterointerface, that is, an exchange from As_2 to P_2 molecular beam at the GaAs growth front and P_2 to As_2 molecular beam at the InGaP growth front. It is possible to have two different growth interruptions. The first interruption is done before the exchange of the group-V molecular beam and the second interruption is done after the exchange of the group-V molecular beam. During the first interruption each growth front is exposed to its own group-V atmosphere; that is the GaAs growth front is exposed to the As_2 atmosphere and the InGaP growth front is exposed to the P_2 atmosphere. During the second interruption each growth front is exposed to the other group-V element atmosphere; that is the GaAs growth front is exposed to the P_2 atmosphere and InGaP growth front is exposed to the As_2 atmosphere. In this paper the duration of the first growth interruption is denoted by t_1 and that during the second growth interruption is denoted by t_2.

Earlier studies on the growth of InGaP/GaAs by GSMBE[2,3] have examined the influence of t_1 and t_2 on the gas-source MBE of InGaP/GaAs superlattices grown on (100) GaAs substrate, based on reflection high energy electron diffraction (RHEED) patterns obtained in-situ during the growth/interruption and from post-growth double crystal x-ray diffraction (DCXR) pattern. It was observed that with increasing t_1 (t_2 fixed), the satellite peaks became sharper and more well defined, indicating that the interfaces were flat and atomically abrupt. With increasing t_2 (t_1 fixed), on the other hand, the satellite peaks from DCXR became broader indicating roughening of the interfaces. Noticeable changes in the RHEED patterns occurred after the switching of the group V molecular beams, with the half-order diffraction streaks becoming weaker and more diffuse. With further increase in growth pause, the RHEED patterns became increasingly spotty, indicating the formation of a rough interface.

The observations mentioned above form the primary basis for the present study. The observed effects of growth pause after the switching of the group V molecular beams indicate significant changes in the growth front of the superlattice. In this paper we report a TEM study performed to investigate the influence of growth interruption on the microstructural evolution of these superlattices. The results of this study show that a spontaneous change in the growth orientation from [100] to [311] direction occurs depending on the flux conditions and the growth pause duration. This change is characterized by the formation of well defined {311} planes in the GaAs growth front.

EXPERIMENTAL

The superlattices were grown on (100) GaAs substrates by gas source MBE at substrate tempera-

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tures ranging from 530 to 600 °C. Details of the growth conditions are described elsewhere.[3] Each sample consisted of a $In_{0.5}Ga_{0.5}P$ buffer layer (1 μm in thickness) closely lattice-matched to GaAs, followed by a 20-period MQW of $In_{0.5}Ga_{0.5}P$ (approximately 240Å in thickness) and GaAs (approximately 95Å in thickness), capped off with a InGaP layer (0.25 μm in thickness). For the substrate temperature used, a (2 × 1) RHEED reconstruction pattern was observed during the growth of both the GaAs and InGaP layers. At each interface of the superlattice the growth was interrupted for t_1 = 6 sec, by closing the group-III shutters. This was followed by the exchange of the group-V molecular beams and an interruption of fixed duration (t_2) after which growth was resumed by opening the appropriate group-III shutters. The length of interruption after the exchange of the molecular beams was varied systematically among samples, ranging from t_2 = 6 sec to 60 sec.

For the TEM observation, samples with ⟨011⟩ cross-sections were prepared by ion thinning at low temperature. The samples were examined using a JEM-2000 EX electron microscope equipped with an ultra-high resolution objective lens pole piece and operated at 200 kV. For all the samples the two mutually orthogonal cross-sections, [011] and [0$\bar{1}$1], were examined. The [011] and the [0$\bar{1}$1] axes of the samples in the growth temperature study were identified from the RHEED patterns of the GaAs surface.[5]

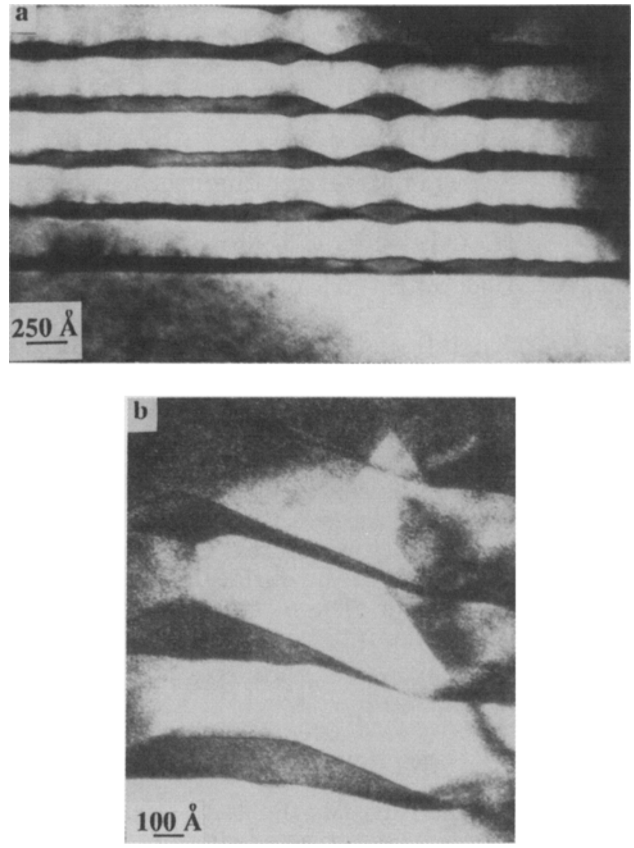

Fig. 1 — [0$\bar{1}$1] cross-sectional 200 dark-field micrograph of the superlattice grown at 530 °C showing (a) the formation of irregularities and V-shaped facets on the InGaP-on-GaAs interfaces (b) top region of the superlattice where (311)-GaAs planes are well developed and the growth of InGaP layer along the ⟨311⟩ direction.

RESULTS

Although samples grown at different substrate temperatures were examined by TEM, in this paper we present our observations on the samples grown at 530 and 600 °C. The combined influence of the substrate temperature and growth interruption is reported elsewhere.[6] Examination of the [0$\bar{1}$1] cross-sectional (200) dark-field images of the samples grown with different t_2 with the substrate temperature at 530 °C revealed that an increase in t_2 resulted in an increased roughening of the interfaces. Fig. 1 shows the image of the sample grown with t_2 = 60 sec. In this image the GaAs and InGaP layers appear as dark and bright bands, respectively. It is seen that during the initial stages of growth, corresponding to the first periods of the superlattice, irregularities in the growth front are present. These appear as ripples at the interfaces and occur more frequently on the InGaP-on-GaAs interface than on the GaAs-on-InGaP interface. On continued growth, the irregularities gradually evolve into well defined V-shaped grooves on the InGaP-on-GaAs interfaces. An examination by high resolution transmission electron microscopy HRTEM showed that the facets were atomically well defined and were {311} type. In Fig. 1(a) it is also observed that the initial formation of the V-shaped facets on the GaAs growth front has very little effect on the subsequent growth of the InGaP layer and that it continues along the ⟨100⟩ orientation. However, Fig. 1(b) shows that in the topmost regions of the superlattice where the {311}-GaAs planes were well developed, the growth of the InGaP layer was observed to occur along the ⟨311⟩ orientation and not along the ⟨100⟩ orientation. Thus, in these regions there is a spontaneous change in the growth orientation of the superlattice from the ⟨100⟩ orientation to the ⟨311⟩ orientation. It is also interesting to note in Fig. 1(a) that the V-shaped grooves occur at almost identical locations of the GaAs growth front despite the observed recovery of the smooth (100) growth plane during the growth of InGaP layers. An examination of the [011] cross-section did not reveal the features seen in Fig. 1. Thus the formation of the V-shaped facets and the subsequent change in the growth orientation occurs only along the [0$\bar{1}$1] axis, which is parallel to the surface dangling bonds of the As atoms in the unreconstructed (100)-GaAs plane.[5]

In order to examine which interruption after the exchange of the Group-V molecular beams was responsible for the change in the growth orientation, another study was conducted, in which the interruption length t_2 at the GaAs and InGaP growth fronts for the first two periods of the superlattice were different. At the GaAs growth front t_1 = 1 sec, and t_2 = 1 sec and at the InGaP growth front t_1 =

1 sec and t_2 = 60 sec. For the subsequent periods of the superlattice t_1 = 1 sec and t_2 = 60 sec at both the GaAs and InGaP growth fronts. Figure 2 is the $(0\bar{1}1)$ cross-sectional 200 dark-field image showing the first few periods of the sample grown at 600 °C. It is seen that in the first two periods of the superlattice the interfaces are flat, whereas in the subsequent periods irregularities are seen on the InGaP-on-GaAs interface. These features appear similar to those seen in Fig. 1(a). The interruption in the first two periods differs from that in the subsequent periods only in terms of the length of interruption at the GaAs growth front under P_2 flux, with the latter region having the longer duration. Hence, it is clear that P_2-on-GaAs interruption is responsible for the formation of the irregularities on the GaAs growth front. Examination of the top region of the sample revealed features identical to those observed in Fig. 1(b). Again, these features were observed only on the $(0\bar{1}1)$ cross-sections. Thus the results of this study confirmed the observations described in the previous paragraph. However, it must be mentioned that the results of a study on the temperature dependence of the above observations[6] has led us to believe that the substrate temperature of the sample in Fig. 1 must have been higher than 530 °C.

DISCUSSION

The results of these studies reveal an hitherto unobserved effect of the role of growth interruption on roughening of the growth front during MBE. It is observed that for certain combinations of interruption lengths and group-V fluxes, the growth orientation change from the [100] to ⟨311⟩ orientation. The spontaneous nature of this process implies that the formation of (311) facets on (100) GaAs growth front is favored energetically to the continued growth of GaAs along ⟨100⟩ orientation. These results lead to two important questions concerning the influence of growth interruption on the MBE of InGaP/GaAs superlattices. The first question relates to the role that P_2-on-GaAs interruption plays in the formation of the growth front irregularities which in turn lead to the formation of the {311} facets. The second question concerns why a change from [100] to ⟨311⟩ is favored in preference to the other directions.

In order to explain the observed effect of P_2-on-GaAs interruption we invoke an argument that under normal MBE growth conditions the (100)-GaAs growth front is metastable with respect to the energetically more stable (311)-GaAs, as illustrated in Fig. 3(a). The driving force for the change in growth orientation from ⟨100⟩ to ⟨311⟩ is the reduction in the surface free energy associated with the formation of (311)-GaAs facets. The feasibility of a transformation from the (100)-GaAs to (311)-GaAs is dictated by the magnitude of the activation barrier that has to be overcome for the formation of stable (311) facets. Under normal MBE growth conditions the activation barrier is prohibitively large so that the transformation is not feasible. During the P_2-on-GaAs interruption the magnitude of the activation barrier is reduced, as illustrated in Fig. 3(b), thereby enabling the nucleation of stable (311) facets on the parent (100)-GaAs growth front. The role of P_2 on GaAs is analogous to that of a catalyst which promotes a chemical reaction by reducing its activation barrier.

It would be of interest to analyze critically whether the features observed in Figs. 1 and 2 are in agreement with the suggestion illustrated in Fig. 3(a) and 3(b). An important feature revealed in Fig. 1(b) supports strongly the suggestion illustrated in Fig. 3. A close examination shows that the GaAs layers in the {311} regions of the superlattice are very thin in comparison to the adjacent InGaP layers, thereby indicating its slow growth rate and very stable nature under normal MBE growth conditions. It must be emphasised that according to the suggestion illustrated in Fig. 3(a) the large activation barrier exists only for the nucleation of stable {311} facets. Once this is realized by means of a P_2-on-GaAs interruption, stable growth on {311} facets must occur

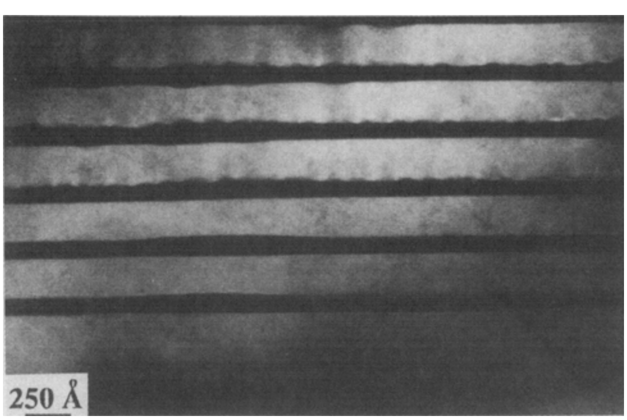

Fig. 2 — $[0\bar{1}1]$ cross-sectional 200 dark-field image of the first few periods of the superlattice grown at 600 °C. Note the formation of irregularities on the InGaP-on-GaAs interfaces in the third and fourth period and their absence in the first and second periods.

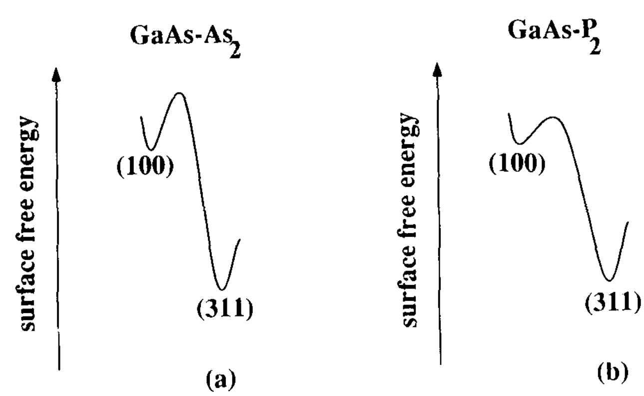

Fig. 3 — Schematic illustration of the relative stabilities of (100)-GaAs and (311)-GaAs showing (a) the metastable (100)-GaAs growth front with respect to a lower energy (311)-GaAs growth front during the As_2-on-GaAs interruption, (b) the stable (311)-GaAs growth front with respect to the (100)-GaAs growth front during the P_2 interruption.

under normal MBE conditions. The features observed in Fig. 1(b) are in agreement with this suggestion, showing stable growth on well developed (311) GaAs planes and accompanied by a corresponding decrease in length of the (100)-GaAs growth front. The need for the formation of stable nuclei which could trigger the continuous emergence of new {311} facets also suggests that the irregularities due to the P_2-on-GaAs, seen in Fig. 2, are either stable {311} facets or precursors that lead to the formation of well developed {311} facets when growth is continued. The features in Fig. 1(a), showing that formation of well developed {311} facets is always preceded by the formation of growth front irregularities lends support to this notion. A careful HRTEM study is however required to verify this speculation.

While the arguments based on the illustrations in Fig. 3 offer an explanation for the formation of (311) facets on GaAs growth front, it is important to examine whether the same arguments could be extended towards an explanation of the observed effects of growth interruption on the InGaP growth front. It is clear from our studies that a growth interruption at the InGaP growth front does not lead to a spontaneous formation of (311)-InGaP facets. Figure 1(a) shows that the As_2-on-InGaP interruption causes a progressive increase in the waviness of the GaAs-on-InGaP interface. The formation of (311)-InGaP planes is not observed until in the top regions of the superlattice, Fig. 1(b), where growth of InGaP along ⟨311⟩ is observed on well developed (311)-GaAs planes. Also, in Fig. 1(b) it is seen that in the regions where the (311) and (100) regions of the superlattice are adjacent to one another, the InGaP layer has more or less the same thickness in both regions and is in contrast to the growth behavior of the GaAs region, where it is seen that the (311) planes are very thin in comparison to the (100) planes. In other words, InGaP is not sensitive the growth orientation. Based on the illustration in Fig. 3, the observed insensitivity to growth orientation may be explained by suggesting that the reduction in the surface free energy associated with the formation of (311)-InGaP is not sufficiently large so as to render the nucleation of this plane preferable to continued growth on (100)-InGaP. In that case, the waviness of the (100)-InGaP observed after the As_2-on-InGaP interruption is not related to the stability of the (100)-InGaP layer. One possible reason could be the desorption of P_2 under an As_2 atmosphere.

We shall next address the question why a change in growth direction from [100] to [311] is favored in preference to other directions. Although the (100) plane is the most common orientation for the epitaxial growth of compound semiconductors, earlier theoretical[7] and experimental[8] studies suggest that other crystallographic planes can become stable growth fronts. Sangster[7] analyzed feasibility of growth of semiconductor compounds on several low index and high index planes and showed that high quality growth was possible on orientations such as the (311) and (511) planes in addition to the low index (100) plane. LEED studies on the (311) surface of GaAs[9] and atomic and electronic structure calculations[10,11] show that the (311) GaAs are stable up to about 600 °C and possess very low surface energies. These observations lend support to the suggestion that the irregularities are small but stable {311} facets which evolve into well defined (311) growth planes as growth proceeds. The observation that these occur only along the $[0\bar{1}1]$ direction indicates that the configuration of the surface chemical bonds along this orientation has an important influence on the formation of the irregularities and are also responsible for the high stability and slow growth rate of the (311) GaAs growth planes. Examination of the atomic arrangements of the four different unreconstructed (311) planes in zinc-blende structures[9] indicate that the facets observed in this study are most likely to be $(311)_{B'}$ type. The subscript B′ refers to As terminated (311)-GaAs surface with two dangling bonds on the surface As atoms and one dangling bond on the Ga atoms belonging to the second layer.

The results of the present study bear significant implications on the current understanding of the role of growth interruption on the MBE of quantum well heterostructures. It is clear that the role of growth interruption in the MBE of InGaP/GaAs superlattices is quite different from what has been observed in previous studies in the MBE of AlGaAs/GaAs superlattices.[12,13] In the InGaP/GaAs system, the roughening of the growth front during interruption after the exchange of the group-V molecular beams is caused by the transition of the growth plane from (100) to the energetically more stable {311} planes. While the studies on AlGaAs/GaAs superlattices[12,13] have shown repeatedly a smoothening of the growth front, the present study shows that this interruption promotes roughening of the GaAs growth front. It is also clear that the roughening process itself is intrinsically different from that observed in the AlGaAs/GaAs system, since it leads eventually to a spontaneous change in the growth orientation from ⟨100⟩ to ⟨311⟩ direction. The simple roughening process observed in the AlGaAs/GaAs system does not necessarily lead to a spontaneous change in the growth orientation, as observed in the earlier studies in this system. Thus, in the AlGaAs system, the roughening of the growth front is caused due to a kinetic factor; insufficient atomic migration results in the formation of a rough growth front. In the InGaP/GaAs system, on the other hand, the roughening of the growth front is caused by an energetic factor; the formation of the energetically more stable {311} facets results in the roughening of the growth front.

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