Compositional modulation in $Al_xGa_{1-x}As$ epilayers grown by molecular beam epitaxy on the (111) facets of grooves in a nonplanar substrate

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We report the first observation of a lateral junction formed in an alloy due to an abrupt transition from segregated to random AlGaAs alloy compositions. $Al_{0.25}Ga_{0.75}As$ epilayers were grown by molecular beam epitaxy on $[01\bar{1}]$ oriented grooves in a nonplanar (100) GaAs substrate. A quasi-periodic modulation of the aluminum concentration occurs spontaneously in material grown on the (111) facets of the groove, with a period of 50–70 Å along the [111] direction. The compositional modulation is associated with a reduction of the band gap by 130 meV, with respect to the random alloy. While segregation of the AlGaAs alloy has been seen previously, this is the first observation of segregation of AlGaAs grown on a (111) surface. The compositional modulation terminates abruptly at the boundaries of the (111) facet, forming abrupt lateral junctions in the AlGaAs layers grown on a groove.

The ability to tailor the band gap of a compound semiconductor crystal in one dimension with precision of a single monolayer has led to the development of a variety of devices whose existence would not otherwise be possible. The extension of this control to the lateral dimensions is a pressing issue, because it would greatly increase the scope of crystal growth as a tool for solid-state device design and fabrication. Growth on a patterned substrate is a technique which has been demonstrated to yield some lateral control of the crystalline properties. This technique is being used to produce low threshold quantum well lasers in a single growth step, and it has been proposed for use in the fabrication of quantum wires.[1] Recently, a lateral variation in the composition of $Al_xGa_{1-x}As$ grown over oriented grooves in a GaAs substrate has been observed.[2–5]

In this letter, we report the first observation of a lateral junction in an alloy due to an abrupt change from segregated to random AlGaAs alloy compositions.[3] Transmission electron microscopy (TEM) and cathodoluminescence scanning electron microscopy (CL) of growth over a $[01\bar{1}]$ oriented groove show an abrupt transition in the composition of AlGaAs epilayers at the interface between material grown on the (111) facets and adjacent facets. The band gap in the segregated alloy is reduced by 130 meV relative to the random alloy.

Epitaxial growth on the grooves produces well-defined facets (see Fig. 1). Cathodoluminescence scanning electron microscopy[6] reveals a correlation between the facet orientation and the composition of AlGaAs epilayers grown on the grooves. Growth of the sample and details of the CL measurements have been described elsewhere.[2] Figure 2 shows spectrally resolved cathodoluminescence images taken of the cross section of a groove at two different wavelengths. Luminescence at 6700 Å [Fig. 2(a)] emanates from the unpatterned areas of the sample (facet *e*; see Fig. 1), the top edge of the groove (facet *c*), and the bottom of the groove (facet *a*). Luminescence at 7000 Å [Fig. 2(b)] occurs exclusively on the sides of the groove (facet *b*). Emission peaks in the corresponding luminescence spectra occur at 6670 Å (bottom of the groove and unpatterned region) and at 7160 Å (side of the groove). This corresponds to a 130 meV reduction in the band gap of material grown on the side of the groove relative to material on the bottom of the groove. The spatial resolution of CL, which is on the order of a micron in GaAs, is insufficient to determine the length scale on which the compositional transition takes place. In order to determine this, transmission electron microscopy was performed on a cross section of a groove.

The sample was prepared for cross-sectional transmission electron microscopy using the standard techniques of mechanical thinning and argon ion milling. The sample was cooled with liquid nitrogen during the final thinning. Dark field imaging of the sample was done with a Philips EM430 transmission electron microscope, using the (200) diffracted beam to reveal variations in the AlGaAs composition.[7] We observe a quasi-periodic modulation in the composition of AlGaAs grown on the side of the groove (Fig. 3). The modulation occurs in the (111) facets of the groove, forming layers with alternately high and low Al concentration. Within the limits of experimental error, the modulation occurs along the [111] direction. The layers are not perfectly straight, nor is the modulation perfectly periodic. The period of the compositional modulation, though variable, is typically in the range 50–70 Å. On the bottom of the groove [(811) orientation] and the top of the groove [(411) orientation] the AlGaAs composition is observed to be uniform. At the

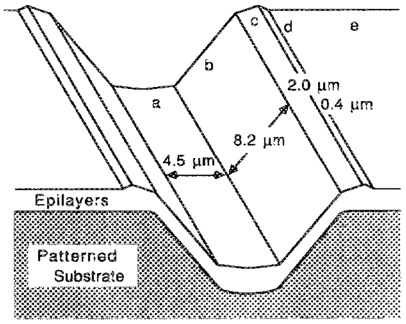

FIG. 1. Diagram of the AlGaAs epilayers grown by molecular beam epitaxy on a nonplanar substrate. Growth in the groove takes place on well-defined facets, which are labeled on the diagram, together with their dimensions.

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interface between these facets and the (111) facet, we observe an abrupt lateral transition from uniform to compositionally modulated AlGaAs (Fig. 4).

The period of the modulation is not correlated with the period of rotation of the substrate. A simple calculation shows that approximately 3–5 Å of AlGaAs were deposited in the time required for one rotation of the sample holder.

Transmission electron microscopy was done on another growth to verify the existence of compositional modulation on the sides of the groove. The growth was done under the same conditions, and the results confirm the observations presented in this letter. Compositional modulation was observed to occur only on the (111) facets in the groove, along the [111] direction. The modulation was associated with a reduction in the band gap observed by CL.

Previous work has shown that compositional modulation due to alloy ordering is associated with a reduction in the effective band gap of the material.[8–11] Thus, the TEM data are consistent with the CL data, which show that the peak in the luminescence spectrum of the sidewall is shifted to lower energy by 130 meV relative to the corresponding peak in the spectrum of the bottom of the groove. A first-order calculation, based on a simple Kronig–Penney model of the potential, indicates that the amplitude of the modulation is quite large, with a minimum Al concentration near zero.

In order to verify that the compositional modulation observed by TEM is responsible for the facet dependence of the CL emission, zinc was diffused into the sample. Zinc diffusion is known to disorder GaAs/AlGaAs superlattices by facilitating the intermixing of Ga and Al atoms within the column III sublattice. The sample was sealed in an evacuated quartz ampoule with $ZnAs_2$ as the diffusion source, and placed in a 650 °C furnace for 1 h. The diffusion conditions were chosen to completely disorder the compositional modulation. After the diffusion, CL spectra taken at 77 K showed that the emission peak occurred at 6920 Å throughout the sample, indicating that the composition of the AlGaAs epitaxial layers was uniform. Thus, the compositional modulation is responsible for the differences in the spectra from the various facets. Furthermore, the average aluminum concentration of the AlGaAs grown on the (111) facet is about the same as the aluminum concentration of uniform $Al_{0.25}Ga_{0.75}As$ grown on the (100) areas of the sample.

FIG. 2. Spectrally resolved cathodoluminescence micrographs of a cross section of a groove in the surface. The micrographs represents spatially resolved luminescence at (a) 6700 Å, and (b) 7000 Å. Note that at 7000 Å, only the sides of the groove luminesce, whereas at 6700 Å, the other facets luminesce and the sides of the groove are dark.

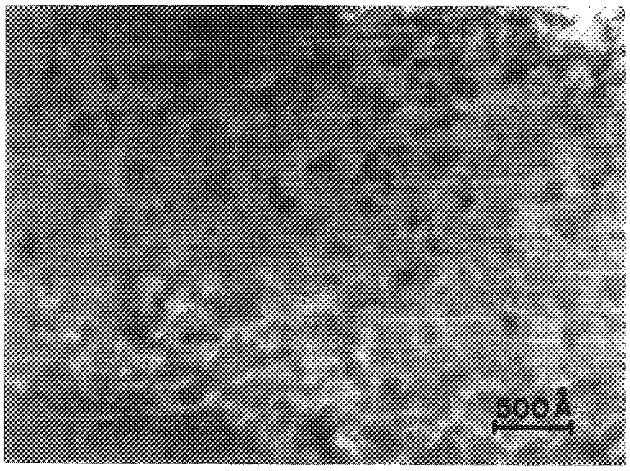

FIG. 3. Dark field transmission electron micrograph of a cross section of the side of the groove, using the (200) reflection. The quasi-periodic contrast corresponds to a compositional modulation of the AlGaAs grown on the (111) facet of the groove. The segregation of Al and Ga occurs spontaneously during the growth, forming layers of alternating Al concentration along the [111] direction. The period in this area is about 70 Å.

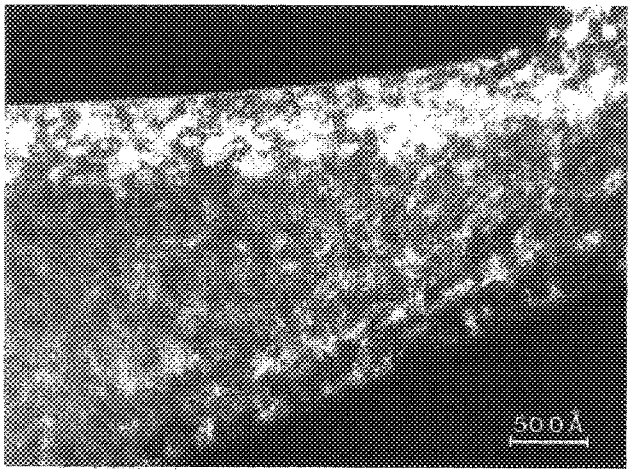

FIG. 4. Dark field transmission electron micrograph of a cross section of the groove, showing the interface between material grown on the side of the groove and on the bottom of the groove. The left half of the micrograph shows material grown on the bottom of the groove. The right half, in which compositional modulation is seen along the [111] direction, shows material grown on the side of the groove. The compositional modulation is observed to terminate abruptly at the border between facets.

In III-V materials other than AlGaAs, ordering has been observed in the form of monolayer superlattices in the [111] direction, sometimes accompanied by compositional modulation along the [100] growth direction.[8,11,12] Bellon *et al.* show that the compositional modulation occurred exactly along the [100] direction, even though the growth direction was tilted by 6°.[12]

Segregation in $Al_xGa_{1-x}As$ is surprising because of the unique properties of this alloy. The sizes and electronegativities of Al and Ga are nearly identical, and the bulk phase diagrams indicate that AlAs and GaAs should be fully miscible under normal growth conditions.[13] Nevertheless, long-range ordering of the $Al_xGa_{1-x}As$ alloy has been observed. To the knowledge of the authors, compositional modulation of AlGaAs grown by conventional MBE has only been seen in the [110] and [100] directions.[14,15] In both cases, the modulation is observed to occur along the growth direction. Our observation of compositional modulation occurring spontaneously in growth on a (111) surface appears to be new for the $Al_xGa_{1-x}As$ alloy.

The compositional modulation which we observe bears some similarity to results of migration-enhanced epitaxy on vicinal (100) GaAs substrates.[16] There are several significant differences between these results and ours. First, the direction of growth is different. Second, in our work the molecular beams were on continuously, whereas migration-enhanced epitaxy on (100) vicinal substrates requires sophisticated shuttering of the beams. Finally, the junctions formed between compositionally modulated material and uniform material are lateral to the growth plane in our work, whereas they occur in the growth plane in the case of migration-enhanced epitaxy. Still, there may be a connection between the mechanisms responsible for alloy segregation in the two experiments. This possibility is under investigation.

Our observation of an abrupt lateral junction in a semiconductor alloy grown by MBE is new and potentially useful, since it is associated with a corresponding change in the band gap. Such an abrupt compositional change could be used to simulate a lateral heterojunction, providing a way to use the orientation-dependent properties of crystal growth to yield three-dimensional control of the electronic states in a crystal.

In conclusion, we have used transmission electron microscopy and cathodoluminescence scanning electron microscopy to study AlGaAs epilayers grown on a nonplanar substrate. AlGaAs grown on the (111) facets of the grooves in a (100) GaAs substrate exhibits quasi-periodic compositional modulation along the [111] direction, with a period of 50–70 Å, and an associated 130 meV reduction of the effective band gap. This has not been seen previously in the $Al_xGa_{1-x}As$ alloy. At the interfaces between material grown on the side of the groove and the two adjacent facets, we observe abrupt termination of the compositional modulation. These interfaces represent a novel type of junction in epitaxial growth of semiconductors, unique because they are abrupt and lateral to the plane of growth. Since the compositional modulation is associated with a change in the effective band gap, this junction could find application as a way to simulate a lateral heterojunction.

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