Control and characterization of ordering in GaInP

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$Ga_{0.51}In_{0.49}P$ layers have been grown by organometallic vapor phase epitaxy on GaAs substrates with [110]-oriented grooves on the surface that have an important effect on the formation of Cu-Pt ordered structures during growth. In this work, the groove shape is demonstrated to be critically important. For the optimum groove shape, single domains of the $(\bar{1}11)$ and $(1\bar{1}1)$ variants of the Cu-Pt ordered structure are formed on the two sides of the groove. Shallow grooves produce large domains on each side of the groove containing small domains of the other variant. For deep grooves, only a single variant is formed on each side of the groove, but the domains are small. For substrates with deep grooves on a GaAs substrate misoriented by 9°, every groove contains large regions of highly ordered and completely disordered material separated by a few micrometers. This allows a direct determination of the effect of ordering on the band gap of the material using cathodoluminescence spectroscopy, allowing the first direct demonstration that ordering reduces the energy band gap of a III/V alloy.

The phenomenon of atomic-scale ordering has been observed in a wide variety of III/V semiconductor alloys.[1] The mechanism of formation of ordered structures is an interesting and important fundamental question that promises to extend our knowledge of the surface processes occurring during vapor phase epitaxial growth. Ordering also has important practical implications, since it is believed[2,3] to result in a smaller band gap than for the disordered alloy. Thus, ordering must be avoided for short wavelength lasers.[4]

The experimental investigation of the effect of ordering on the energy band gap has been based on indirect evidence. The effect is inferred from the dependence of photoluminescence (PL) emission[3] and electroreflectance spectra[5] on growth conditions.[3] The problem with this approach is that the band-gap measurements are macroscopic; they measure a relatively large area of the sample containing many domains as well as the disordered matrix. This often gives rise to extremely complex spectra that cannot be easily interpreted. The low temperature PL spectra of partially ordered GaInP typically consists of several peaks.[6,7] Special techniques have been used in an attempt to determine which peaks originate from the disordered matrix and which from the ordered regions. In this letter we report the results of direct, spatially resolved measurements of the cathodoluminescence (CL) from adjacent ordered and disordered regions.

Ordering is generally accepted to be driven mainly by a reduction of the microscopic strain energy of the crystal.[1,8] However, the detailed configuration of the atoms on the surface determines the ordered structure formed during epitaxial growth.[9] Kinetic factors are also important, since the growth rate is a key factor in determining the degree of order produced during epitaxial growth.[10] Our earlier studies[11] demonstrated that patterning of the surface with [110]-oriented grooves can be used to control the sizes and shapes of the ordered domains. In this letter, we explore the effects of groove shape on ordering. For a particular combination of substrate misorientation and groove shape, large (>1 μm^2 cross section and several mm long) adjacent regions of ordered and disordered material are produced. Distinctly different CL spectra are observed from these regions, with the CL peak occurring at lower energies in the ordered material. Thus, we present the first *direct* evidence that in $Ga_{0.5}In_{0.5}P$ ordering produces a shrinkage of the band gap by more than 100 meV.

The GaInP layers were grown on GaAs substrates in a horizontal reactor using trimethylgallium, trimethylindium, and phosphine. The temperature and input V/III ratio were 670 °C and 160, respectively, and the growth rate was approximately 2 μm/h. For some experiments grooves were photolithographically produced in the surface by wet etching.[11] The 10 μm wide grooves running along the [110] direction were obtained by etching the patterned surface in a 4 wt % bromine in methanol solution for 4 min. This produces a U-shaped etching profile in the [110] direction.[12] In addition, various substrate misorientations (always in the $[\bar{1}10]$ direction) were used to control the relative step densities on the two sides of the groove in a further effort to control the ordering process during growth. After removing the photoresist, the substrates were thoroughly degreased and then etched for different times in either a 1.5 wt % bromine in methanol solution or by H_2SO_4 followed by an A etch (H_2SO_4:H_2O_2:H_2O in a ratio of 4:1:1), resulting in grooves with various shapes and with depths ranging from 0.2 to 1.5 μm.

The layers were characterized using PL, CL, and transmission electron microscopy (TEM). The PL (10 K) was excited with the 488 nm line of an Ar^+ laser. The spatially resolved, low-temperature (5 K) CL measurements were performed in a modified JEOL JSM840 scanning electron microscope under high resolution CL imaging conditions. The unique technique of wavelength imaging, which involves measurement of a complete CL spectrum at every image pixel while the focused excitation electron beam is digitally scanned over the surface is de-

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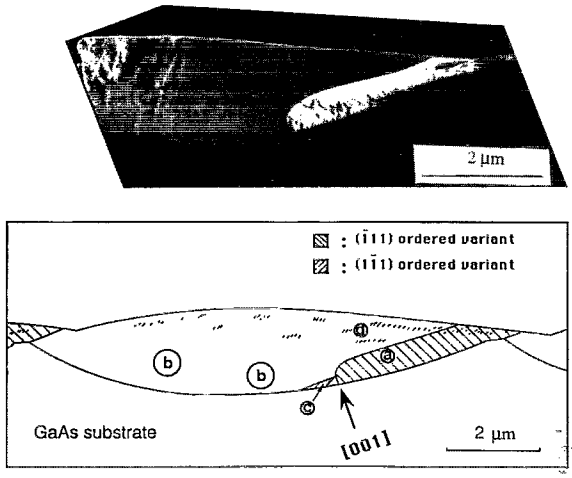

FIG. 1. [110] pole dark field TEM image of $Ga_{0.51}In_{0.49}P$ grown on a (001)-oriented GaAs substrate misoriented by 9° toward the [1̄10] direction. Before growth the substrate was photolithographically patterned and etched to produce [110] grooves on the surface. (a) Dark field image using the 1/2(1̄15) superspot. (b) Schematic diagram of sample showing the ordering observed. The numbers indicate regions where TED patterns were obtained. The TED pattern from region (a) contained only strong 1/2(1̄11) superspots. Region marked (b) contained absolutely no superspots. Region (c) contained only 1/2(11̄1) superspots and region (d) contained weak 1/2(11̄1) superspots.

scribed elsewhere.[13] Transmission electron diffraction (TED) patterns and TEM images were obtained using a JEOL 200CX electron microscope operated at 200 kV.

The etching procedures described above all produced a scallop-shaped surface, viewed from a (110) cross section, with shallow, rounded grooves linked together. These shallow grooves produced the (1̄11) variant in the right-hand side (rsh) of the groove and the (11̄1) variant for the left-hand side (lhs). The line demarcating the two domains is defined by the part of the groove having the exact (100) orientation.

For the shallow grooves produced by etching in H_2SO_4 for 4 min followed by 9 min in an A etch, the ordering was not as well controlled for the shallow grooves as for the groove shapes reported earlier.[11] Dispersed in the large "domains" on each side of the groove were small domains of the other variant.[14] Etching in 1.5 wt % bromine in methanol for 1 min produced deep, steep-sided grooves. This resulted in each side of the groove containing material of only one variant. However, the ordered domains were small, < 300 Å across, with a degree of order much smaller than for other groove shapes.[14]

More interesting are the samples with deep grooves (4 min in Br+methanol) produced on the surface of a substrate misoriented by 9°. A TEM cross section from such a sample is shown in Fig. 1. The figure consists of a dark field image designed to reveal the regions having the (1̄11) variant (a) as well as a schematic diagram to assist in identifying the main features. A large ordered domain was produced in the extreme rhs of the groove. On the lhs, just to the left of the position in the groove oriented exactly (001), a small domain of the (11̄1) variant is formed. The demarcation line between the two domains is observed to be the point where the groove has the exact (001) orientation. Further to the left, the material is completely disordered near the bottom of the groove. This is due to the formation of a (1̄15) facet during growth in the region of the groove having nearly the correct angle to produce this facet after etching. The facet orientation is identified by noting the 16° angle between the (001) plane and the facet. This facet grows considerably more rapidly than the material on the rhs of the groove, which results in the diminution of the size of the (1̄11) domain as growth proceeds, i.e., the position in the groove having exactly the (001) orientation moves steadily to the right during growth. A careful examination of the dark field images clearly reveals traces of the flat, (1̄15)-oriented surface during growth. Inclusion of marker layers unambiguously shows the rapid propagation of the (1̄15) facet during growth.[14]

The 10 K PL spectrum of this sample consists of three peaks at approximately 1.943, 1.884, and 1.842 eV, as seen in Fig. 2(a). This sample presents an opportunity to directly measure the effect of ordering on the band gap of the GaInP. Since the variation in solid composition is small, as discussed below, the change in CL peak energy can be attributed to the effects of ordering. Figure 3 is a color-coded map of the CL peak energy observed for this sample. The sample is tilted at a 45° angle in this figure, so that the CL from both the cleaved cross section and the top surface is observed. The CL emitted from the left side of the groove, in the disordered region, occurs at a high energy of

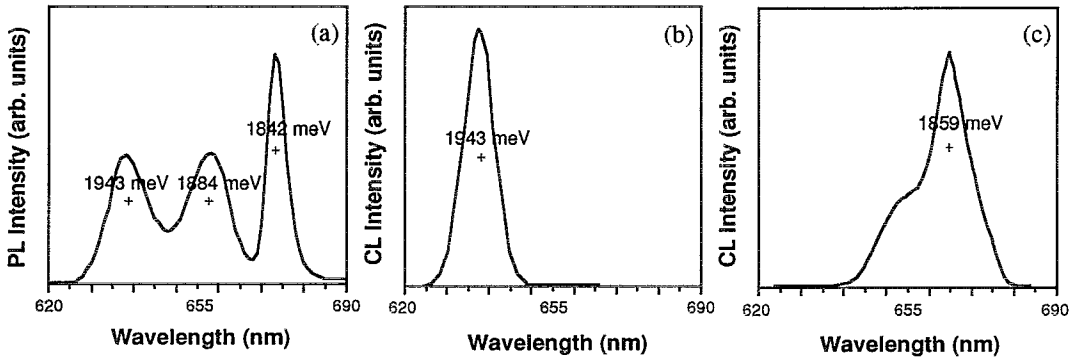

FIG. 2. (a) 10 K photoluminescence spectrum obtained from the top surface of the sample shown in Fig. 1. (b) and (c) spot mode 5 K cathodoluminescence spectra of the top surface. (b) is taken from the disordered region and (c) is taken from the ordered region.

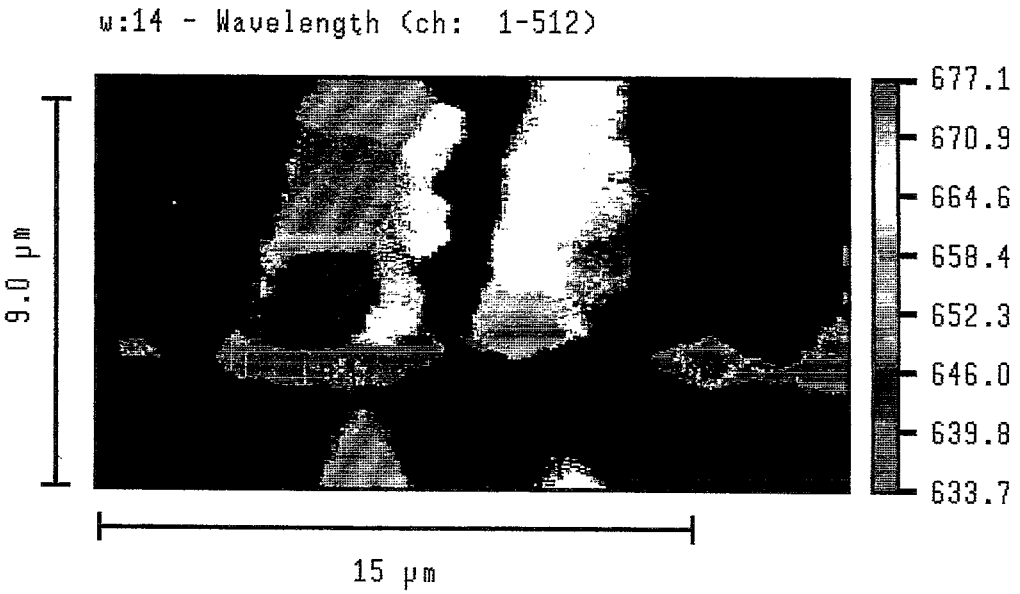

FIG. 3. Cathodoluminescence wavelength image of cleaved surface of the sample shown in Fig. 1. The region having the highest CL peak energy corresponds to the disordered material and the region having the lowest energy to the ordered domain in Fig. 1.

approximately 1.950 eV. The spectrum taken in this region, but from the surface of the sample, occurs at a slightly lower energy. As seen in Fig. 2(b), this peak is similar to the highest energy peak in the PL spectrum [Fig. 2(a)]. On the right side of the groove, within the large $(\bar{1}11)$ domain, the emission occurs at a significantly lower energy of approximately 1.859 eV. This peak, seen in Fig. 2(c), is similar to the lowest energy PL peak. At other locations, a third CL peak is seen with an energy similar to the middle peak in the PL spectrum.

In an effort to determine whether these changes in the PL and CL spectra could be due to compositional variations, the composition was measured at several places on the surface of the sample. In the regions corresponding to the high PL energy, an average of 4 measurement gave a value of x_{Ga} of 0.53. In the regions giving lower energy PL, an average of five measurements gave a composition of $x_{Ga}=0.51$. Since the measurement accuracy is $\pm 2\%$, it is not entirely certain that any change in composition occurs. However, assuming that the compositional difference of 0.02 is valid, this corresponds to an energy shift of only 6 meV, assuming that the layer is coherently strained to lattice match the substrate.[15]

In summary, this study has clarified the importance of groove shape in determining the ordered structure formed during the OMVPE growth of GaInP. A particularly interesting structure was produced using deep grooves etched into a substrate misoriented by 9°. A single, large domain on the Cu-Pt structure was produced adjacent to a large region of disordered material. The PL emission from the sample consists of three peaks, with an energy separation of more than 100 meV. Direct images of the large ordered and disordered regions were recorded by means of CL wavelength imaging. The results indicate that the emission from the ordered region accounts for the lowest energy PL peak, while the highest energy peak comes from the disordered material. Wavelength dispersive x-ray analysis indicates that the shift in energy cannot be due to compositional variations. Thus, this is the first *direct* demonstration of the effect of ordering on the band gap of GaInP.

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