Observation of self-organized superlattice in AlGaInAsSb pentanary alloys

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An unexpected self-organized superlattice structure has been observed in the AlGaInAsSb pentanary alloys grown by metalorganic vapor-phase epitaxy. The samples were studied by transmission electron microscopy, double-crystal x-ray diffraction, and secondary ion mass spectrometry measurements. The modulation strength and period of the self-organized superlattice are correlated to the alloy composition. © 2003 American Institute of Physics. [DOI: 10.1063/1.1581979]

The AlGaInAsSb pentanary alloy, with the lattice constant ranges from 6.479 to 5.653 Å and the direct band-gap energy ranges from 1.8 to 0.17 eV, is a potential material system for the future midinfrared devices. During the growth of the AlGaInAsSb alloys by metalorganic vapor-phase epitaxy (MOVPE), we observed the unexpected spontaneous formation of a superlattice structure in this alloy. This self-organized superlattice structure shows compositional modulation with high periodicity. The formation of this self-organized superlattice is reproducible and the superlattice structure is spatially extended over the whole sample.

A III–V mixed alloy semiconductor was usually considered as a uniformed material that had its individual compositional elements distributed randomly. Molecular-beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD) are the two major methods used in producing high-quality III–V epilayers. Both methods grow the epilayer by randomly dispatching molecules onto the surface of the substrate. It is natural to believe that the epilayer grown by these methods shall have its compositional atoms randomly mixed. However, in some cases, the III–V mixed alloys grown by epitaxy exhibit an ordered structure. The well-known CuPt ordered structure in GaInP is the most noted example.\textsuperscript{1} A similar ordered structure has been observed in almost every ternary III–V mixed alloys.\textsuperscript{2–4} The CuPt ordered structure could be considered as a superlattice with the period of two monolayers along the [111] direction. It is believed that surface kinetics play important roles in the formation of the CuPt ordered structure.\textsuperscript{5} On the other hand, an ordered structure along the [001] growth direction was reported in II–VI mixed alloy ZnFeSe epilayers.\textsuperscript{6} Following that, a self-organized superlattice structure with a longer period was reported on ZnSeTe alloys.\textsuperscript{7} The formation mechanism for this self-organized superlattice structure has been explained by the surface step-flow model.\textsuperscript{8,9} It is generally believed that epilayers shall not have an ordered structure with a very long period. If the period of the ordered structure is longer than the surface atom diffusion length, the surface kinetic models will have difficulties in explaining its formation mechanism. However, reports have been given for the observation of self-organized superlattice structure in InAsSb and GaAsSb mixed alloys,\textsuperscript{10,11} with the thickness of the superlattice platelet extended up to 50 nm. Instead of the surface kinetics, the authors refer to the coherent phase separation\textsuperscript{12} as the mechanism for the formation of their self-organized superlattice. In this letter, we report the observation of a self-organized superlattice in AlGaInAsSb pentanary alloys grown by MOVPE.

The samples we studied were grown on a (100)-oriented Fe-doped InP substrate. The wafer supplier specified the substrate to be in the exact (100) direction. We analyzed the substrate surface steps by atomic force microscopy and conclude them to be 0.1° off the exact (100) plane. This is within the uncertainty of the specification of the supplier. The growth temperature and pressure are 650 °C and 100 Torr, respectively. Trimethylgallium, trimethylindium, trimethylaluminium, trimethylantimony, arsine, and phosphine are used as the Ga, In, Al, Sb, As, and P sources, respectively. Before the epilayer is grown, a 0.5 μm undoped InP buffer layer was grown. After the growth of the pentanary alloys, another 0.5 μm clapping layer of InP was grown to protect the Al-content pentanary epilayer.

Beside the pentanary alloy under study, the two boundary quaternary systems: AlInAsSb and GaInAsSb, have also been grown by the same reactor with the same growth temperature and pressure. Details of the growth condition and characterization for these quaternary alloys have been published elsewhere.\textsuperscript{13,14} It is important to note that no naturally formed ordered structure could be found in these quaternary alloys. The phenomenon of the self-organized superlattice only appears in the pentanary system.

The average solid composition of the samples is determined by JEOI (JXA-8800M) electron-probe microanalysis. The uncertainty of the measured composition is within 1% compared to the standard of calibration.

Figure 1(a) shows the double-crystal x-ray rocking curve for sample A12 with composition \(Al_{0.12}Ga_{0.44}In_{0.44}As_{0.85}Sb_{0.15}\). Two peaks appear in the spectrum. One corresponds to the InP substrate and the other one corresponds to the average lattice constant of the epilayer.

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This is a quite normal x-ray diffraction (XRD) spectrum for mixed alloy epilayer. It represents a randomly mixed alloy with its average lattice constant close to the lattice constant of the InP substrate. For samples with low Al content, no phase separation or any self-organized structure can be observed in the epilayer.

However, Fig. 1(b) is the XRD spectrum for another sample, A20, with composition $\text{Al}_{0.20}\text{Ga}_{0.36}\text{In}_{0.44}\text{As}_{0.85}\text{Sb}_{0.15}$. As shown in Fig. 1(b), beside the two peaks stand for the substrate and the epilayer, four small satellites show up, denoted as S. The four satellites are equally separated by an almost a constant distance. These satellites are very similar to the satellites observed in the XRD spectrum for epilayers grown with a man-made superlattice structure. The satellites are constructed by diffraction from the period of the superlattice. The period of the superlattice can be estimated by the distance between satellites. The period estimated for this sample is 11.3 nm. The high-angle and low-angle satellites have a different intensity. This is due to the interference from nonperfect periodicity, or it is due to the interference from the strain modulation and the chemical modulation.\(^7\) We must emphasize that the growth condition for this sample, A20, is nearly the same as that of the previous sample, A12.

The only difference is the settings for the precursor flow rates. No sign of modulation for anything appears during the growth.

Figure 1(c) shows XRD for sample A44, with the average composition $\text{Al}_{0.44}\text{Ga}_{0.12}\text{In}_{0.44}\text{As}_{0.85}\text{Sb}_{0.15}$. More obvious satellites show up in this spectrum. The satellites split further with multiple branches. As we marked in Fig. 1(c), they can be organized into three groups with different periods. The periods estimated from the peak distance are 25, 26, and 27 nm for groups a, b, and c. The highly asymmetrical intensity distribution is again due to the interference from different periods or modulations. The x-ray intensity is proportional to the square of the Fourier transform of the electron density. The appearance of multiple satellites indicates a large number of Fourier components are needed to describe the interface. That is, the superlattice structure has a sharp interface.\(^7\)

The correlation between the sample composition and the period of the self-organized superlattice is summarized in Table I. From the samples we studied so far, it appears that more Al content will introduce stronger satellites and a longer superlattice period. We are interested to know what would happen if more than 50% Al is added into the epilayers. However, as we further increase the content of Al, the epilayer surface becomes cracked and the XRD shows phase separation for high Al content sample.

Table I. Summary on the composition and period of the samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition</th>
<th>Period of the superlattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>A12</td>
<td>$\text{Al}<em>{0.12}\text{Ga}</em>{0.44}\text{In}<em>{0.44}\text{As}</em>{0.85}\text{Sb}_{0.15}$</td>
<td>No superlattice structure</td>
</tr>
<tr>
<td>A20</td>
<td>$\text{Al}<em>{0.20}\text{Ga}</em>{0.36}\text{In}<em>{0.44}\text{As}</em>{0.85}\text{Sb}_{0.15}$</td>
<td>11.3 nm</td>
</tr>
<tr>
<td>A44</td>
<td>$\text{Al}<em>{0.44}\text{Ga}</em>{0.12}\text{In}<em>{0.44}\text{As}</em>{0.85}\text{Sb}_{0.15}$</td>
<td>22–27 nm</td>
</tr>
</tbody>
</table>

Figure 2(a) is the transmission electron microscopy (TEM) cross-section image for the sample used in Fig. 1(c),
A44. As expected from XRD, layered structures do appear in the TEM image. The layered structures uniformly extend over the entire sample. The formation of the superlattice begins at the onset for the growth of the pentanary alloy. No intermediate buffer layer is observed. The period of the superlattice can be more precisely estimated from Fig. 2(b). The period we estimated from Fig. 2(a) varied between 22 to 24 nm. This is consistent with the values obtained from DXR within 10%. The difference between the values estimated from the TEM and the XRD may be due to the uncertainty of the TEM magnification.

To further identify the compositional variation of the self-organized superlattice, the samples were measured by secondary ion mass spectrometry (SIMS). Figure 3 shows the SIMS spectra for a sample with and without superlattice structure, samples A12 and A44. For sample A12, the spectrum shows a clear interface between the InP cap layer and AlGaInAsSb pentanary layer. The concentration for each compositional element is a constant along the epilayer depth. However, for sample A44, the spectrum shows that the sample concentration is not uniformly distributed. The sample has a superlattice structure composed by two layers. One layer is rich with Al, In, and As, and the other layer is rich with Sb and Ga. The modulation of individual concentration is large. The peak-to-bottom ratio for the concentration of each element can be as high as 1.6. The actual ratio can be even higher because the bottom value contains high background noise. The period of the superlattice can be estimated by the peak-to-peak distance in the SIMS spectrum.

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![SIMS spectra for samples without and with self-organized superlattice structure.](image)

**FIG. 3.** SIMS spectra for samples without and with self-organized superlattice structure.

<table>
<thead>
<tr>
<th>Growth Temperature (°C)</th>
<th>Layer thickness (nm)</th>
<th>Periodicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>InAsSb</td>
<td>MBE</td>
<td>340–400</td>
</tr>
<tr>
<td>ZnSeTe</td>
<td>MBE</td>
<td>275–350</td>
</tr>
<tr>
<td>AlGaInAsSb</td>
<td>MOCVD</td>
<td>650</td>
</tr>
</tbody>
</table>

The average period estimated from SIMS is 21.5 nm. It is consistent with the values obtained from XRD and TEM.

The only previous report for self-organized superlattice structure in III–V alloys was for InAsSb and GaAsSb alloy.10,11 There are several similarities and differences between their reports and our work, as summarized in Table II. The most significant difference is that our superlattice structure shows a highly periodic structure that made the XRD measurement possible. This makes our superlattice structure more similar to the superlattice structure observed in the ZnSeTe alloy,7 which has almost perfect periodicity. However, the period of our superlattice is much longer than that observed in the ZnSeTe alloy. The surface step-flow model,8,9 which performs well in explaining the formation of the ZnSeTe superlattice structure, will have a problem in explaining the formation of our superlattice structure. The period of our superlattice is similar to the platelet thickness reported for the superlattice structure in the InAsSb alloy. We believe our self-organized superlattice structure and the similar structure observed in the InAsSb alloy shall have the same formation mechanism. It is hopeful that the data provided by this work can shed more light on the issue of self-organized superlattice.