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Compositional Nun-Uniformity of Selectively Grown $Ga_xIn_{1-x}P$ from High Resolution Double-Crystal X-Ray Measurement

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In this work, selective epitaxial growth (SEG) of GaInP on a GaAs substrate patterned with silicon nitride film is performed by low-pressure metalorganic chemical vapor deposition. The group III sources employed are the combinations of triethylgallium and ethyldimethylindium, triethylgallium and trimethylindium, and trimethylgallium and trimethylindium. High-resolution double-crystal X-ray diffraction is used for the measurement of the compositional variation in the SEG area. Different combinations of group III sources lead to different extents of GaP and InP incorporation rates due to the decomposition and diffusion characteristics of the precursors.

1. INTRODUCTION

Selective epitaxial growth (SEG) of III-V compounds has received much attention recently as a promising technique for monolithic integration of electronic, optoelectronic, and quantum devices. Several attempts have been made for selective growth of GaAs[1), InP[2)], GaInAs[3)] and GaInP[4)] on substrates patterned with SiO_2, SiN_X or other insulators, using metalorganic chemical vapor deposition (MOCVD) process. In MOCVD processes, where reaction occur under highly nonequilibrium condition, high resisitivity polycrystalline GaAs can be deposited on the insulating films. Ridge growth is observed near the edge of the selectively grown area. In SEG of ternary alloys, not only the thickness but also the composition varies. This variation is believed to be caused by the migration of reactant species on the masking film or the lateral diffusion of undepleted reactant species above the masking film to the selectively grown area[5)].

2. EXPERIMENTAL

The reactor used in our experiment is a horizontal quartz tube containing a rotating graphite susceptor heated by RF induction. The metalorganic sources are held in temperature controlled baths. TMI is kept at 10°C with the vapor pressure of 0.75 Torr. EDMI is kept at 10C with the vapor pressure of 0.4 Torr. TEG is kept at 15°C with the vapor pressure of 4 Torr. TMG is kept at -12°C with the vapor pressure of 35.08 Torr. The hydride sources are 100% AsH_3 and PH_3. The growth pressure is kept at 40 Torr with a total flow rate of 10 l/min. The growth temperatures range from 625°C to 675°C, and the V / III ratios are 100, 150 and 200. The High-resolution double-crystal X-ray diffraction (HRXRD) measurement which is used for the solid composition is the (400) reflection rocking curve with the X-ray spot size of 250 μm X 250 μm. The SiN_X film, prepared by plasma enhanced chemical vapor deposition (PECVD), is used as the masking material with thickness of about 100 nm to 150 nm. Patterns for SEG is defined by conventional photolithographic method. The patterns are circles with a diameter of 500 μm. Reactive ion etching (RIE) is used for removing the SiN_X film and residual photoresist.

3. RESULTS AND DISCUSSIONS

For SEG of GaInP using TEG+EDMI, the surface morphology of the masking SiN_X films for samples grown at 625°C and 650°C with a V / III ratio of 100 shows the existence of Ga-related particles. The diameters of these polycrystalline GaInP grown at 625°C and 650°C for 1h are about 7 to 8 μm and 3.5 to 4.5 μm, respectively. The density of polycrystalline GaInP on SiN_X film is higher at 625°C. The featureless surface of samples grown at 675°C with a V / III of 150 indicate the complete selectivity. The complete selectivity can be attributed to two reasons. One is that there is enough kinetic energy for the migration of adsorbed Ga and In reactants to the open area, and the other is that the desorption of group III related organic byproducts on the SiN_X film is enhanced at this temperature. There is a further mechanism affecting the geometry of the deposit. Different crystallographic orientations lead to different growth rates because of surface-catalytic reaction of the semiconductor. This can result in different migration lengths of reactants on different oriented planes. Usually, the geometry of the deposit is bounded by slow growth planes. Deposition on such planes can be prevented as long as the migration length on these planes exceeds the dimensions of these surfaces. Otherwise, overgrowth on the masking film will occur. The clean edges in our experiment indicate that the overgrowth on SiN_X film is suppressed at 675°C.

Figure 1 shows the rocking curves of samples grown under the near-lattice-matched ([TEG] / [EDMI] = 4.9) and the Ga-rich ([TEG] / [EDMI] = 6) conditions. Under the Ga-rich condition, although the crystallization is poor, the In composition in the SEG area is still found to be increased. The shift of the curve from SEG substrate toward the low angle side is beyond the deviation of composition uniformity, and is attributed to the In enrichment in the SEG area.

Samples grown using TEG+TMI under the conditions of T = 625°C, V / III=150, and [TEG] / [TMI] = 1.25 show the even-spread GaInP polycrystals on the masking SiN_X film and poor surface morphology in the SEG area. The GaInP polycrystals for 1h is about 1 μm in diameter. Complete selectivity can be achieved at 650°C with improved surface morphology in the SEG area. Nevertheless, some random-distributed particles is found on the masking film which may be caused by unclean surface. Figure 2 shows the rocking curves of unpatterned (upper curves) and patterned (lower curves) samples under In-rich ([TEG] / [TMI] = 1.01), near-lattice-matched ([TEG] / [TMI] = 1.12), and Ga-rich ([TEG] / [TMI] = 1.23) conditions. The spectra from the unpatterned substrates are the classical results of a substrate with a thin epitaxial layer. The tails of the SEG spectra extended toward the low angle side indicate that there is a grading and enhancement of In composition.

Figure 3 shows the rocking curves of unpatterned (upper curves) and patterned (lower curves) substrates grown using TMG+TMI under In-rich ([TMG] / [TMI] = 0.8475) and Ga-rich ([TMG] / [TMI] = 1.1771) conditions. Complete selectivity can be achieved at 650°C. It is found that the spectrum (In-rich) tail of the patterned substrate is extended more toward the low angle side, and spreads over about 650 arcseconds which is wider than the spreading ranges of the spectra from samples using TEG+EDMI and TEG+TMI. This extension indicates that the In enrichment and the compositional variation in SEG GaInP using TMG+TMI are larger than that using TEG+EDMI and TEG+TMI.

Figure 4 shows the rocking curves of unpatterned (upper curves) and patterned (lower curves) samples using TMG+EDMI under the In-rich ([TMG] / [EDMI] = 1.6774) condition. An additional spectrum ([TEG] / [TMI]=1.25) from sample grown by using TEG+TMI at 650°C is attached for reference. It is found that not only the spectrum tails are extended toward the low angle side but also the positions of the spectra are obviously shifted to the low angle direction. This imply that the In enrichment and the compositional variation in SEG GaInP using TMG+EDMI are more larger than using TEG+TMI.

4. COMPARISON OF THE IN ENRICHMENT IN SEG AREA

The In enrichment can be attributed to the decomposition temperatures of TEG (260°C), TMI (290°C), and TMG (420°C), while EDMI is slightly less thermally stable than TMI. The extent of decomposition is related to the decomposition temperature of the source reagents. Since the decomposition temperature of TEG is markedly lower than that of TMG, the decomposed TEG fragments would be expected to be more than that of TMG, and thus reduce the In enrichment. EDMI can decompose into ethyl- and methyl-related fragments and the larger size of ethyl fragments may reduce the effective diffusion constant of the decomposed fragments above the masking film.

In epitaxial growth of GaInP using TEG+EDMI, it is found that a serious parasitic reaction occurs, leading to heavy deposits on the side wall upstream from the substrate. This causes low Ga incorporation efficiency from TEG into GaInP. The excess TEG and the adducts of the precursors are also thought to affect the effective diffusion constant of the In-containing species above the masking films. By observation of the HRXRD measurements for SEG using TEG+TMI and TEG+EDMI, it is found that the tail of the spectra using TEG+TMI is more smoothly and deeply inclined into the low angle side than using TEG+EDMI. This means that the In enrichment of SEG GaInP using TEG+TMI is slightly higher than using TEG+EDMI. Obviously, the spectrum from SEG GaInP grown by using TMG+TMI shows more In enrichment than that using TEG+TMI and TEG+EDMI. On the other hand, by comparison of the spectra of SEG GaInP using TMG+EDMI and TEG+TMI, larger In enrichment occurs in the SEG GaInP using TMG+EDMI.

5. CONCLUSIONS

In summary, we have demonstrated the selectively epitaxial growth of GaInP by LP-MOCVD using EDMI, TMI, TEG, and TMG as the group III sources. Complete selectivity can be achieved at growth temperatures of 675°C, 650°C, 650°C, and 650°C for TEG + EDMI, TEG + TMI, TMG + TMI, and TMG + EDMI, respectively. Polycrystalline GaInP appears more easily when TEG and EDMI are used as the group III sources, which is related to its heavy parasitic reaction. Compositional variation occurs in all cases. The In enrichment is specially large using TMG+TMI and TMG+EDMI. This will induce more strain and poor surface morphology near the edge of the SEG area, while for TEG+EDMI and TEG+TMI, the In enrichment is suppressed.

6. REFERENCES

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7. FIGURES

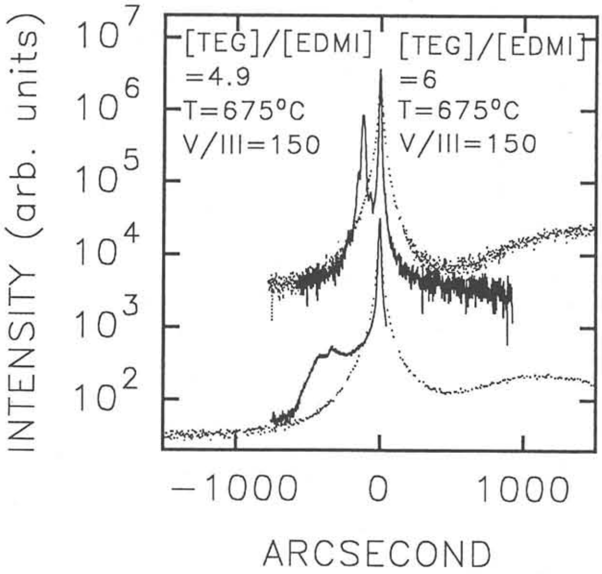

Fig. 1 Rocking curves (400 reflection) of GaInP grown using TEG+EDMI on unpatterned (upper curves) and patterned (lower curves) substrates under Ga-rich and near-lattice-matched conditions. The Ga-rich conditions are T=675°C, V/III= 100, and [TEG] / [EDMI] = 6, while the lattice-matched conditions are T = 675°C, V/III = 100, and [TEG] / [EDMI] = 4.9.

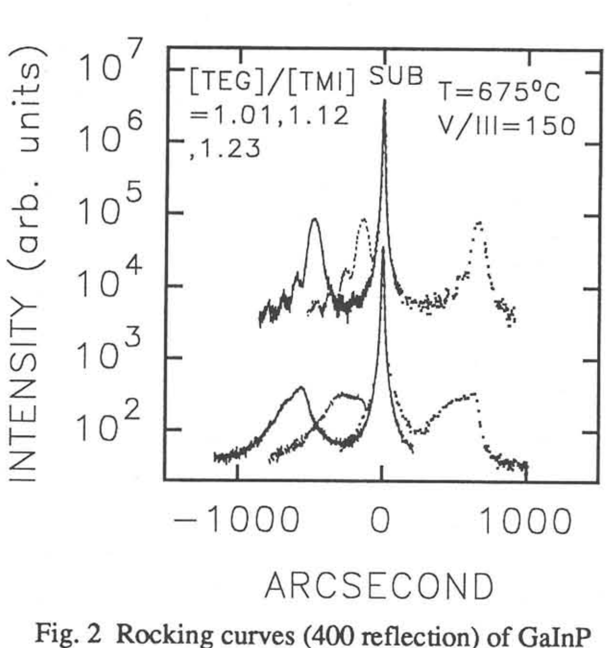

Fig. 2 Rocking curves (400 reflection) of GaInP grown using TEG+TMI under the conditions of T = 675°C and V / III = 150 on the unpatterned (upper curves) and patterned (lower curves) substrates. Solid curves, short dash curves, and dot curves represent the growth under the conditions of [TEG]/[TMI]=1.01, [TEG]/[TMI] = 1.12, and [TEG] / [TMI] = 1.23, respectively.

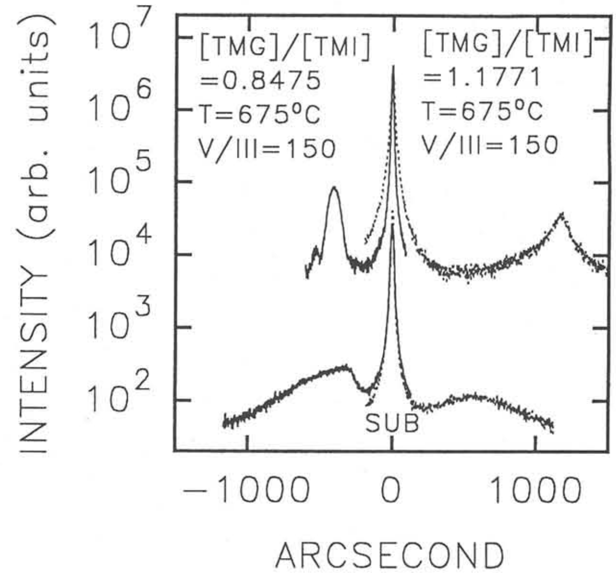

Fig. 3 Rocking curves (400 reflection) of GaInP grown using TMG+TMI on unpatterned (upper curves) and patterned (lower curves) substrates. Solid curves represent the substrates grown under the conditions of T = 675°C, V / III = 150, and [TMG] / [TMI] = 0.8475. Dot curves represent the substrates grown under the conditions of T = 675°C, V/III = 150, and [TMG] / [TMI] = 1.1771.

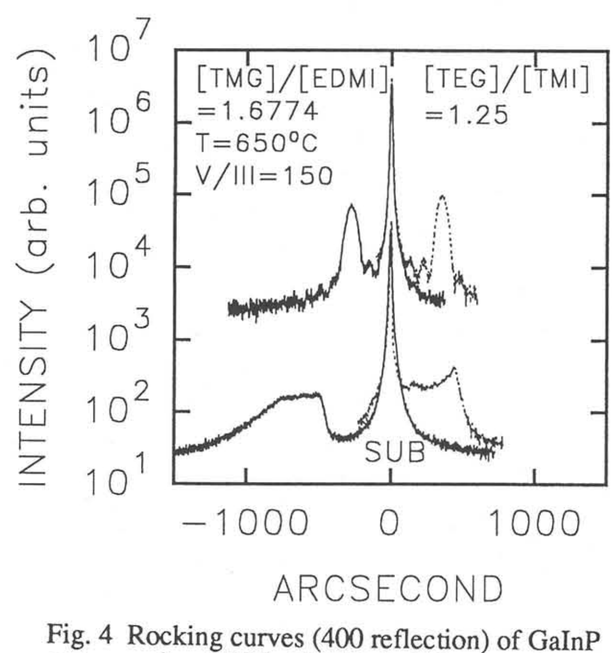

Fig. 4 Rocking curves (400 reflection) of GaInP grown using TMG+EDMI (solid curves) and TEG+TMI (dot curves) on unpatterned (upper curves) and patterned (lower curves) substrates. Solid curves represent the substrates grown under the conditions of T = 650°C, V / III = 150, and [TMG] / [EDMI] = 1.6774. Dot curves represent the substrates grown under the conditions of T = 650°C, V / III = 150, and [TEG] / [TMI] = 1.25.