Selective epitaxial growth of GaInP by low-pressure metal-organic chemical-vapor deposition using ethyldimethylindium as In source

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We have demonstrated the feasibility of selective epitaxial growth (SEG) of GaInP using low-pressure metal-organic chemical-vapor deposition (LPMOCVD) with the combination of ethyldimethylindium (EDMIn) and triethylgallium (TEGa) as the group-III sources. Complete selective epitaxy can be achieved at a growth temperature of 675 °C and a growth pressure of 40 Torr. The deposition of Ga-rich polycrystalline GaInP on Si_3N_4 film occurs at lower temperatures. Although the incorporation efficiency of TEGa into GaInP is much lower than that of trimethylgallium, the combination of EDMIn and TEGa has been found to be a good candidate for SEG of GaInP. Low-temperature photoluminescence shows that the selectively grown epitaxial layer has good optical quality and is useful for light emitting device applications. © *1994 American Institute of Physics.*

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 (e.g., quantum wires and dots). Several attempts have been made for SEG of GaAs,[1] InP[2], GaInAs,[3] GaInP,[4] and AlGaInP[5] on substrates patterned with SiO_2, Si_3N_4, or other insulators, using the metal-organic chemical-vapor deposition (MOCVD) process. For chloride vapor-phase epitaxy, where the growth takes place nearly at equilibrium, the deposition can occur only on the GaAs substrate.[6,7] In MOCVD processes, where reactions occur under highly nonequilibrium conditions, high-resistivity polycrystalline GaAs can be deposited on the SiO_2 mask.[7,8] Furthermore, ridge growth is observed on the GaAs substrate near edge of the opening. Therefore the thickness of the epitaxial layer is not uniform. In SEG of ternary alloys such as GaAlAs, GaInAs, and GaInP, not only the thickness but also the composition varies in the SEG area. This variation is believed to be caused by the migration of the reactant species on the mask to the edge of the opening or the lateral diffusion of them from the undepleted source region above mask into the opening.[7]

In this study, we have performed the SEG of GaInP by low-pressure MOCVD. Instead of a conventional solid trimethylindium (TMIn) source, the liquid ethyldimethylindium (EDMIn) source was adopted as the indium precursor because of its more stable vapor pressure. EDMIn has been investigated for the MOCVD growth of AlGaInP,[9] and it was compared with TMIn.

The reactor used in our experiment is a horizontal quartz tube containing a rotating graphite susceptor heated by rf induction with a rotation speed of 30 rpm. Triethylgallium (TEGa) was kept at 15 °C and the vapor pressure was 4 Torr. The vapor pressure of EDMIn has been reported by several groups[10–12] with values of 0.4 Torr at 10 °C, 0.56 Torr at 11°C, and 0.7 Torr at 18 °C. We used the vapor pressure of 0.4 Torr and the bubbler temperature was kept at 10 °C. There is some speculation that EDMIn may undergo a facile ligand exchange reaction to give TEIn and TMIn within the bubbler over time or when introduced into the source gas lines if maintained at a higher temperature than the bubbler. This will probably lead to run-to-run nonreproducibility and long term instability caused by a varying vapor pressure. However, Fry *et al.*[13] observed with mass spectrometry that EDMIn consisted only of a single compound, without any trace of TMIn or TEIn. The growth pressure we used was maintained at 40 Torr with total flow rate of 10 slm. The hydride sources were 100% AsH_3 and PH_3. The growth temperature ranged from 625 to 675 °C, and the V/III ratios were 100, 150, and 200. The flow rate of H_2 fed into the EDMIn bubbler was maintained constantly at 20 sccm, while that fed into the TEG bubbler ranged from 9.8 to 12.5 sccm. The substrates used were n-type (100) GaAs wafer, and patterned and unpatterned substrates were put side by side in each run for comparison. The Si_3N_4 film, prepared by plasma-enhanced chemical-vapor deposition (PECVD), was used as the masking material. The thickness of the Si_3N_4 film was about 100–150 nm. Patterns for selective epitaxy were defined by a conventional photolithographic method. The patterns were circles with a diameter of 500 μm and crosshatch with a width of 300 μm (Fig. 2). The surface morphology was observed by Nomarski microscopy and scanning electron microscopy (SEM). Photoluminescence (PL) measurement, high-resolution double-crystal x-ray diffraction (HRXRD), and energy dispersive x-ray analysis (EDX) were adopted for evaluation of the film quality and composition.

Figure 1 shows the lattice mismatch between GaInP and GaAs vs Ga molar flow rate for GaInP grown by using TMGa or TEGa as the Ga source and EDMIn as the In source. At the growth temperature of 625 °C, and under the lattice-matched condition, the ratio of [TEGa]/[TMGa] is about 3.1. This indicates that the Ga incorporation efficiency from TEGa into GaInP is much lower than that from TMGa.

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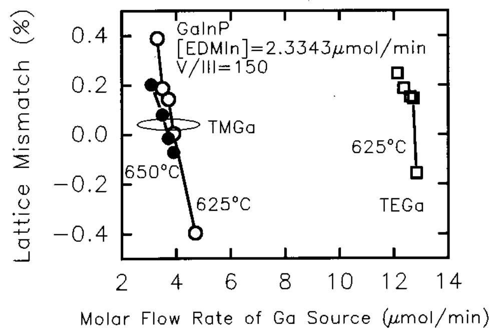

FIG. 1. Lattice mismatch between GaInP and GaAs vs molar flow rate of the Ga sources for TMGa or TEGa. EDMIn molar flow rate and V/III ratio maintained the constant values of 2.3343 μmol/min and 150, respectively.

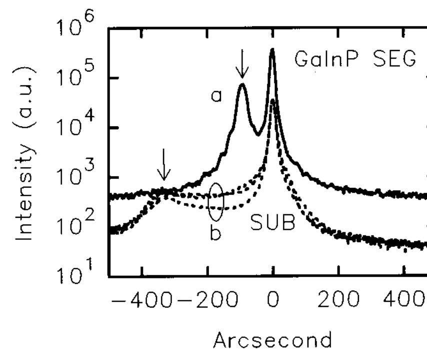

FIG. 3. Rocking curves (400 reflection) of GaInP grown on unpatterned (solid line) and patterned (dashed line) substrates. Solid line shows the Ga composition of 0.511. Dashed lines were measured in the circle pattern. The arrows indicate the peak positions of the curves.

The same trend is observed even when the growth temperature is increased.

The selectivity was observed by Nomarski microscopy at various growth temperatures. Samples grown at temperatures of 625 and 650 °C with a V/III ratio of 100 showed Ga-related particles and lateral overgrowth on the Si_3N_4 film. EDX analysis revealed that the particles were Ga-rich polycrystalline GaInP. The diameters of the polycrystalline GaInP grown at 625 and 650 °C were about 7–8 and 3.5–4.5 μm, respectively, and the density of polycrystalline GaInP on the Si_3N_4 film was higher at 625 °C. The decreasing size and density of GaInP polycrystals imply the decreasing probability of nucleation of the Si_3N_4 film at higher temperatures. The decomposition rate of group-III species is increased at higher temperatures and thus provides more nucleation sources. We have observed from the experimental results, however, that at high temperature the increase in the desorption of the adsorbed group-III species is greater than the increased decomposition driven nucleation.

Figure 2 shows the surface morphology of a sample grown at 675 °C with a V/III ratio of 150. The featureless

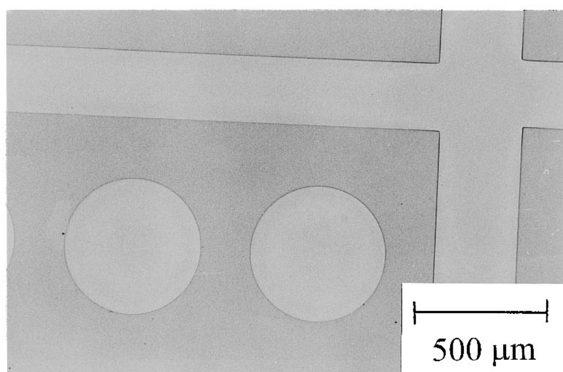

FIG. 2. Nomarski microscope photograph of substrate surface grown at 675 °C and V/III=150. The diameter of the circle pattern is 500 μm; the width of the cross is 300 μm.

surface indicates complete selectivity. There are two reasons for the complete selectivity. One is that there is sufficient kinetic energy for the migration of adsorbed Ga and In reactants to the open area; the other is that the desorption of group-III species on the Si_3N_4 film is enhanced at this temperature.

Since the diffusion constants in the gas phase above the masking film and migration lengths of Ga and In species on the masking film are expected to be different,[14] the composition in the SEG area will vary due to the extra flux of reactants from the surrounding mask region. Figure 3 shows the rocking curves of HRXRD measurement of the sample grown at 675 °C. Curve (a) is measured on an unpatterned substrate for reference with the measured Ga composition of 0.511 and full width at half maximum (FWHM) of 28 arc sec. The thickness of the $Ga_{0.511}In_{0.489}P$ layer was about 0.8 μm. The other plots in curve (b) are measured by scanning the x-ray spot (spot size of 250×250 μm) within the area of the 500 μm circle patterns. The broadening of these curves indicate the composition variation of the patterned substrates. The peak values of these curves from the SEG layer show that the Ga composition is 0.499±0.002. Caneau *et al.*[15] have found the In enrichment in SEG GaInP and GaInAs using TMIn and TEGa, or TMIn and TMGa as the group-III sources, and concluded that the In enrichment of SEG GaInP and GaInAs was lowered by using TMIn and TEGa. This can be attributed to a similar decomposition temperature of TEGa (260 °C) and TMIn (290 °C), and they are considered to be more suitable than TMIn and TMGa (420 °C) if the reduction of lattice mismatch in SEG is required. The shift of the Ga composition of their SEG GaInP was about 0.025 mol fraction deduced from the In mole fraction from the mask edge against a 0.2 mm wide masked area. The maximum shift of the Ga composition of SEG GaInP in our experiment between patterned and unpatterned substrates is about 0.012 mol fraction. The smaller In enrichment implies that the combination of EDMIn and TEGa may be more suitable than TMIn and TEGa. This can probably be attributed to the decomposition temperature and molecular structure of EDMIn. The EDMIn source is comprised of an indium atom bonded to two methyl radicals (CH_3) and a single

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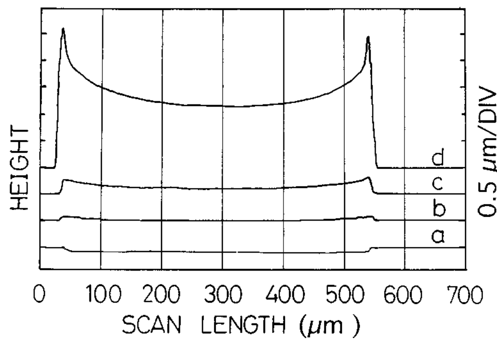

FIG. 4. Surface profiles of samples grown for (a) 1, (b) 5, (c) 10, and (d) 60 min under the lattice-matched condition with $T=675$ °C and V/III=150. The measurement was performed along the diameter of the 500 μm circle pattern.

ethyl radical (C_2H_5), and is slightly less thermal stable than TMIn. It can decompose into ethyl- and methyl-composition fragments. The larger size of the ethyl fragments produces smaller effective diffusion coefficients above the mask, and thus abates the In enrichment. Figure 4 shows the surface profiles of the samples grown for 1, 5, 10, and 60 min. These profiles indicate that the growth rate enhancement occurs near the edges of the SEG area with the thickness decreasing monotonically from the pattern edge.

The optical quality of the SEG GaInP was investigated by low-temperature PL. Figure 5 shows the 20 K PL emission of the unpatterned reference sample and that of the patterned sample in which the laser spot is located at the center of the 500 μm circle. The reference sample exhibits a PL peak at 1.918 eV with a FWHM of 14.8 meV which is attributed to the near-band-edge emission of the undoped GaInP layer. There are no obvious low-energy signals related to impurities.[16] The patterned sample shows a PL peak at 1.895 eV with a FWHM of 16.5 meV, and there is no impurity-related transition emission either. The shift of the SEG GaInP emission peak toward lower energy indicates its stoichiometry has moved toward a In-rich composition. The broadening of the FWHM is caused by the nonuniform composition in the area of laser spot.

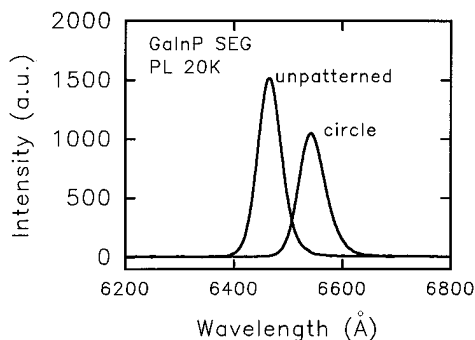

FIG. 5. 20 K PL spectra of unpatterned and patterned substrates.

In summary, we have demonstrated the SEG GaInP using EDMIn and TEGa as the group-III sources. By comparison of epitaxial growth of GaInP on an unpatterned substrate, TMGa is found to be more efficient than TEGa. However, TEGa is more suitable than TMGa for GaInP selective epitaxy if suppression of the In enrichment is required. Furthermore, the combination of EDMIn and TEGa seems to a good candidate for SEG of GaInP. Using photoluminescence, we have found that the SEG layer was redshifted with respect to the unpatterned substrate, indicating a change in composition. Strong PL intensity demonstrates that the SEG layers have good potential in manufacturing light emitting devices.

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