Organometallic vapor phase epitaxial growth of high purity GaInAs using trimethylindium

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$Ga_xIn_{1-x}As$ lattice matched to the InP substrate ($x = 0.47$) has been grown by organometallic vapor phase epitaxy using trimethylindium (TMIn) and trimethylgallium (TMGa) as the group III sources and AsH_3 as the As source. In a simple, horizontal, atmospheric pressure reactor, the GaInAs growth proceeds without visible evidence of parasitic prereaction problems. The process yields homogeneous, reproducible GaInAs with a high growth efficiency and a solid/vapor In distribution coefficient of nearly unity. Most importantly, several layers with room-temperature electron mobilities of approximately 10 000 cm^2/Vs and carrier concentrations of approximately 10^{15} cm^{-3} have been produced. The 4-K photoluminescence shows a narrow (4–5 meV) band-edge emission peak and a low-intensity band acceptor peak at ~ 18 meV lower energy. Surface morphologies are routinely featureless as observed by high magnification interference contrast microscopy.

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GaInAs lattice matched to the InP substrate is one of the most promising new semiconductor materials. High electron mobility and peak velocity[1-3] and the ability to fabricate modulation-doped structures with InP[4] make this alloy ideal for ultrahigh-speed devices. The band gap of 0.75 eV (1.65 μm) is ideal for the fabrication of detectors for fiber-optic systems operating in the optimum wavelength range of 1.3–1.5 μm.[5]

It has now been demonstrated that very high quality $Ga_{0.47}In_{0.53}As$ can be grown with excellent properties by liquid phase epitaxy (LPE),[6,7] hydride vapor phase epitaxy (HVPE),[6,8] $AsCl_3$ VPE (ClVPE),[9] molecular beam epitaxy (MBE),[10] and organometallic VPE (OMVPE).[4,6] By each of these growth techniques, high room-temperature electron mobilities of $\geqslant$10 000 and 77 K electron mobilities of greater than 40 000 cm^2/Vs have been reported.

OMVPE appears to be a promising technique for many applications requiring the growth of large quantities of homogeneous, high quality material with multiple abrupt changes in composition and doping.[11] However, early results indicated severe problems with gas phase reactions occurring upstream from the substrate, leading to low growth efficiency and inhomogeneous alloy composition. Such problems have been observed using various combinations of reactants; triethylgallium (TEGa) and triethylindium (TEIn),[12] trimethylgallium (TMGa) and TEIn,[13] and TMGa and trimethylindium (TMIn).[14] Duchemin and coworkers,[4,15] have resorted to low pressure growth using TEGa and TEIn group III sources. This has resulted in the only OMVPE grown $Ga_{0.47}In_{0.53}As$ with electron mobilities of $\geqslant$10 000 cm^2/Vs reported until now. Other groups have developed adduct group III sources, such as TMIn-TEP[16] and TMIn-TMP[17] (TEP and TMP refer to triethyl and trimethyl phosphorus), which do not react upstream from the substrate to form In-containing polymers on the reactor walls. Since these adducts have low vapor pressures, this necessitates a slightly more complex apparatus, with all parts of the reactor downstream from the adduct source being heated to avoid condensation of the adduct on the walls.[18] In addition, no high electron mobility $Ga_{0.47}In_{0.53}As$ has been reported to date.

Recently, the growth of In-containing III/V compounds and alloys using TMIn at one atmosphere pressure has been reinvestigated. Possibly because of the higher purity of todays TMIn, two groups have independently found that no predeposition problems are observed. Sacilotti *et al.*[19] and Hsu *et al.*[20] have reported the growth of InP with electron mobilities of approximately 3500 cm^2/Vs, as compared with the highest values of > 5000 cm^2/Vs reported for growth using TEIn in a low pressure system.[4] $Ga_{0.47}In_{0.53}As$ alloys have also been successfully grown using TMIn by Sacilotti *et al.*[21] and by Kuo *et al.*[12] In the former case no mobility values were reported. Kuo *et al.*[12] reported low values of electron mobility due to the high doping level of 3×10^{17} cm^{-3}.

In this letter we describe the growth and properties of the first high purity $Ga_{0.47}In_{0.53}As$ to be grown by OMVPE at atmospheric pressure using TMIn, TMGa, and AsH_3. Room-temperature electron mobilities of $\sim$10 000 cm^2/Vs have been obtained repreatedly. The 4-K photoluminescence (PL) shows a single, sharp, near-band-edge emission peak with a much less intense peak at ~ 18 meV lower energy. The featureless surface morphology and sharp x-ray diffraction peaks (within the resolution limits of conventional x-ray measurements) are also indicative of the excellent homogeneity and high structural quality of the material.

The atmospheric pressure, horizontal, IR heated OMVPE system used in this study was described previously.[12] The solid TMIn (obtained from Alpha/Ventron) was held in a temperature controlled bath at 10 °C and the TMGa was held at -11.5 °C. The purified H_2 flow rates through the two sources were 120 sccm and 0.9 sccm, respectively. The AsH_3 (diluted to 10% in H_2) flow rate was 60 sccm. These conditions give a growth rate of 0.05 μm/min. The (100) oriented InP substrates were prepared using a 4-min 5:1:1 A etch prior to introduction into the reactor.

Preliminary results[12] indicated that good morphology $Ga_{0.47}In_{0.53}As$ could be obtained only at low growth temperatures of below 550 °C, presumably due to P loss from the substrate during heat-up in the $H_2 + AsH_3$ atmosphere. Even though the PL is found to be strong under such conditions, it is apparently due to recombination through the carbon acceptor level rather than to free and bound exciton recombination. The 300-K electron mobility was also found to be less than 3500 cm^2/Vs. The impurity contamination was found to decrease with increasing growth temperature, but the surface morphology was found to deteriorate. To solve this problem, a two-step growth procedure was adopted. First, a very thin (~1000 Å) layer of $Ga_{0.47}In_{0.53}As$ is grown at a temperature of 540 °C. Then, the temperature is rapidly increased to 650 °C where the 1–2-μm $Ga_{0.47}In_{0.53}As$ layer is grown. This results in reproducibly excellent results. For a series of 20 runs, every surface was found to be mirror smooth to the naked eye and to have no observable features upon examination at high magnification using interference contrast microscopy.

The degree of lattice match and structural perfection of the layers were investigated using conventional x-ray diffraction measurements. The (400) diffraction results are illustrated by the examples shown in Fig. 1. These samples were chosen because the substrate and epilayer peaks could be readily distinguished. Other samples are so closely lattice matched that the epilayer and substrate peaks are indistinguishable. Typically, $\Delta a_0/a_0 < 2\times10^{-3}$. It is seen that the diffraction peaks from the substrate are nearly the same width as those from the substrate. Both are within the resolution limit of the conventional x-ray diffractometer.

A sample 4-K PL spectrum obtained at an excitation intensity of approximately 10 W/cm^2 from the 4880-Å Ar laser line is shown in Fig. 2. The spectrum is dominated by the narrow peak at 0.8138 eV which has a half-width of 4.5 meV. This is very similar to the peak observed by Goetz *et al.*[6] in high quality LPE and OMVPE $Ga_{0.47}In_{0.53}As$, which is attributed to a combination of several free and bound exciton peaks which cannot be resolved. Goetz *et al.* found the PL peak to occur at 0.808 eV for precisely lattice-matched layers. For a series of runs made under conditions specified above, the position of this peak was found to vary between 0.807 and 0.817 eV, which is a variation in composition of only $\Delta x = \pm 0.004$. This indicates the remarkable degree of composition control obtained using this process.

A small peak is observed at approximately 0.018 eV lower energy than the main peak. The results of Goetz *et al.*[6] indicate that this may be due to Zn. Pearsall *et al.*[23] reported the Zn ionization energy to be 19 meV from hole freeze-out experiments. A peak located at an energy 40–45 meV below the main peak is also sometimes observed. A notable feature of these spectra is the absence of any carbon related peak. Apparently the carbon concentration in $Ga_{0.47}In_{0.53}As$ grown using trimethyl source materials is low for growth temperatures of 650 °C. Earlier results[12] indicated that at 540 °C, carbon was a major source of contamination. As will

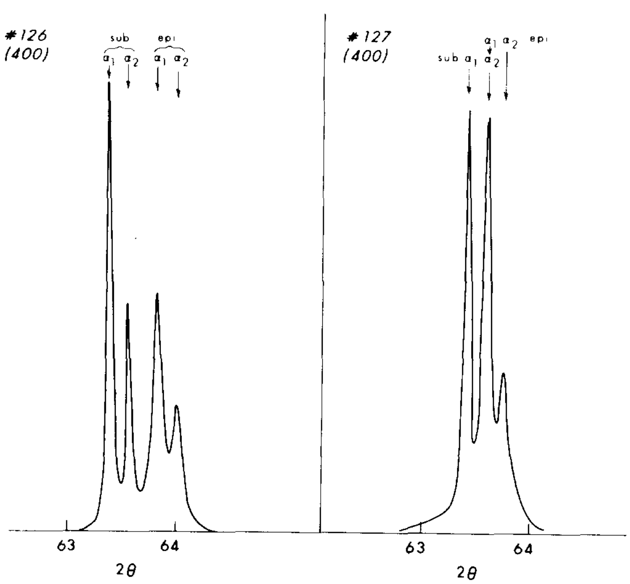

FIG. 1. (400) x-ray diffraction spectra for two samples of GaInAs grown on InP substrates. These samples were chosen because substrate and epilayer peaks could be clearly distinguished.

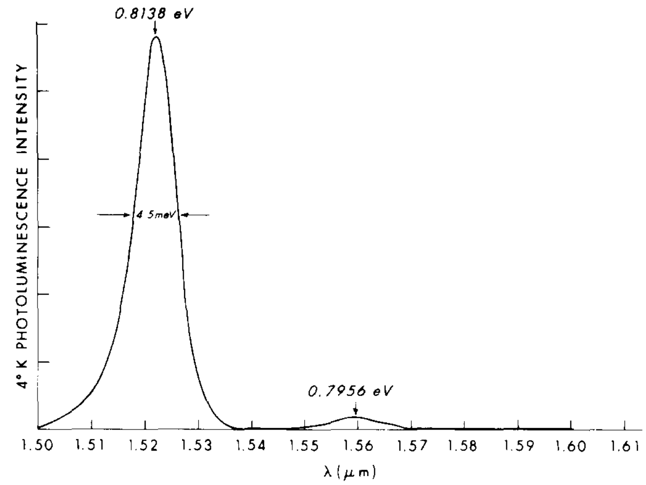

FIG. 2. Liquid helium temperature photoluminescence spectrum for a sample of $Ga_{0.47}In_{0.53}As$ grown on an InP substrate. The excitation intensity was 10 W/cm^2. The detector was a Ge pin cooled to 77 K.

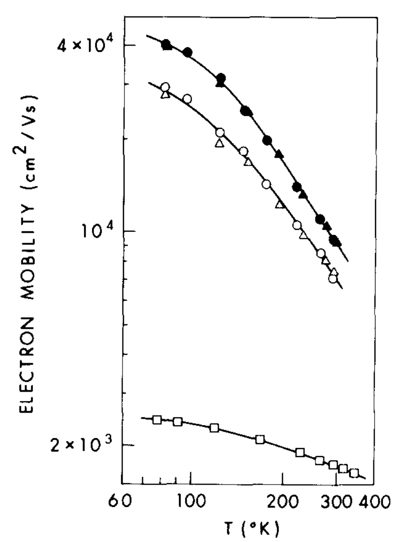

FIG. 3. Electron mobility vs temperature for several samples of $Ga_{0.47}In_{0.53}As$ grown on semiinsulating InP substrates at temperatures of 650 °C (○, ●, △, ▲) and 540 °C (□).

be seen, this is consistent with the electrical properties of the layers grown at 540 °C in contrast with those grown at 650 °C.

The electrical properties of these undoped $Ga_{0.47}In_{0.53}As$ layers, which are all 1.0–2.0 μm thick, are summarized in Fig. 3. The carrier concentrations are reproducibly approximately 10^{15} cm^{-3}. The 300-K mobilities range from 7500 to 10 000 cm^2/Vs, and the 77-K mobilities are in the range from 30 000 to 40 000 cm^2/Vs. The temperature dependence of mobility is qualitatively as expected for a combination of optical phonon and ionized impurity scattering. It should be noted that these are the first room-temperature electron mobilities in the 10 000-cm^2/Vs range to be reported for layers grown using TMIn, either by itself or in adduct form. The $Ga_{0.47}In_{0.53}As$ layers grown at 540 °C have lower mobilities. As seen in Fig. 3, they show the $T^{-1/2}$ temperature dependence previously attributed to scattering by carbon in GaAs and AlGaAs samples.[22] It should be noted that this sample was grown using TMAs rather than AsH_3.

In summary, the quality of $Ga_{0.47}In_{0.53}As$ grown by OMVPE using TMIn in an atmospheric pressure reactor is shown to be excellent with properties similar to those of the best samples produced by LPE, HVPE, CIVPE, MBE, or low pressure OMVPE using TEIn. The key growth parameter leading to the high material quality is the relatively high substrate temperature of 650 °C. To avoid morphological problems apparently associated with the decomposition of the InP substrate, a very thin layer of $Ga_{0.47}In_{0.53}As$ is grown at 540 °C before the substrate temperture is increased to 650 °C. This procedure has produced a number of epilayers with excellent surface morphologies, narrow x-ray diffraction linewidths, 4-K PL spectra dominated by a single, narrow, exciton-related line, and room-temperature electron mobilities of $\sim 10\,000$ cm^2/Vs.

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