Journal of Crystal Growth 110 (1991) 452–456
North-Holland

Technical aspects of InGaAs MOMBE – shutter action, system drift, and material quality *

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Received 15 July 1990; manuscript received in final form 23 October 1990

Lattice matched $In_xGa_{1-x}As$ films were deposited on InP substrates using metalorganic molecular beam epitaxy (MOMBE) with trimethylindium (TMIn), triethylgallium (TEGa) and a solid arsenic source. The effect of growth temperature and molecular beam composition on growth rate and crystal composition was investigated. A long term drift of the molecular beam composition and an increasing difference between temperature readings of the thermocouple and the pyrometer were observed. The corrected data show a linear dependence of crystal composition on molecular beam composition. Shutter action on TMIn and TEGa was investigated. The results show the adverse effect of solely using the shutters to control the metalorganic molecular beam, leading to inferior material quality and rough surface morphology. Material grown in the optimized process consistently showed electron mobilities of $\mu_{300} \approx 9000$ cm^2/V·s and $\mu_{77} \approx 35{,}000$ cm^2/V·s at 1.2×10^{15} cm^{-3} n-type background concentration.

1. Growth conditions

Metalorganic molecular beam epitaxy (MOMBE) is a crystal growth method for As-containing compounds avoiding the use of highly toxic arsine (AsH_3). The advantages over conventional MBE are the reduction of oval defects density and virtually infinite group III sources which can be replenished without breaking the vacuum. The configuration of our Varian Gen II MOMBE growth system is shown in fig. 1. The alkyls are delivered from a pressure controlled stainless steel bubbler with a controlled flow of hydrogen used as carrier gas. All growth runs reported here were carried out on a quarter 2 inch (100) semi-insulating InP wafer. The wafers were cleaned in 5 : 1 : 1 $H_2SO_4 : H_2O_2 : H_2O$, methanol, 0.5% bromine methanol, then isopropyl alcohol and, after mounting with indium to a 3 inch silicon wafer, prebaked for about 30 min at 150°C in ultra-high vacuum. The gas manifold was set to the following parameters, of which bubbler pressure and H_2 flow were varied around the given values for most of the layers. Temperature of the TEGa bubbler was 6.4°C, H_2 flow through the TEGa bubbler was 11.2 SCCM, and the bubbler pressure was 23.2 Torr. The set point for the TMIn line was 19.9°C, 10 SCCM, and 18 Torr, respectively. This

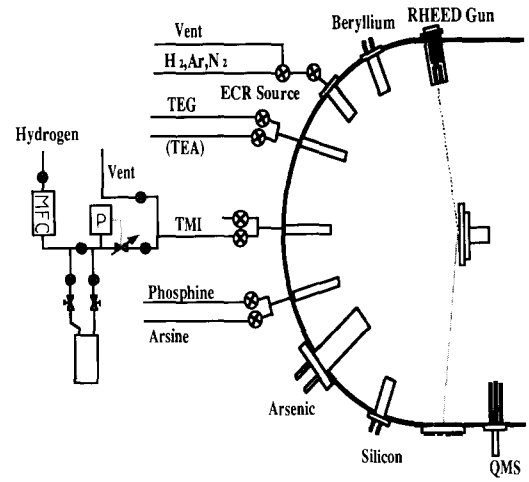

Fig. 1. Configuration of the growth system.

* This work was supported by the Army Research Office under the URI program, Contract No. DAAL 03-87-K-0007.

gave a total alkyl flow of about 2.2 SCCM or 1×10^{-4} mol/min. The vapor pressure values for this calculation were taken from the Alfa catalog [1] for TMIn and from Plass [2] for TEGa. The temperature of the arsenic effusion cell was adjusted to give a beam flux pressure of about 3.5×10^{-5} Torr which was measured by an ion gauge before and after the run. The growth rate at these conditions was found to be about 1 μm/h.

2. Growth system characteristics

Good control of crystal composition is required for electronic devices. This is particularly true for $In_xGa_{1-x}As$ since the lattice constants change greatly with composition leading to unwanted strain in the layers or even incommensurate growth. The initially poor correlation between the composition x_s (=x) as determined by double crystal X-ray diffractometry and the molecular beam composition x_g as calculated from vapor pressure data and system set points lead to the suspicion that long term drift of the sources might be present. Since the variation of x_g and x_s is small we assume a linear dependence between them. The ratio x_g/x_s should therefore be constant for all runs. As seen in fig. 2, however, x_g/x_s shows a slow decrease besides the unreproducibility of the system of $\pm 2\%$. Thus the content of TMIn in the molecular beam increases or, equivalently, the TEGa content decreases from run to run. Since the duration of all runs was about the same, the run number is a rough linear time scale for the service time of the MO sources. The possible reasons for this drift remain speculative: we would suspect a changing MO-bubbler rather than

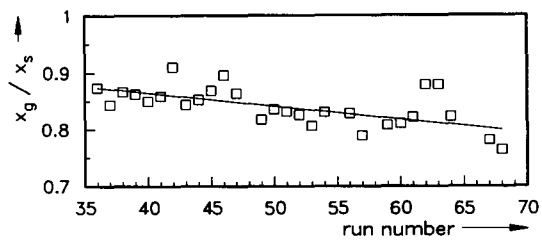

Fig. 2. Long term drift of the molecular beam.

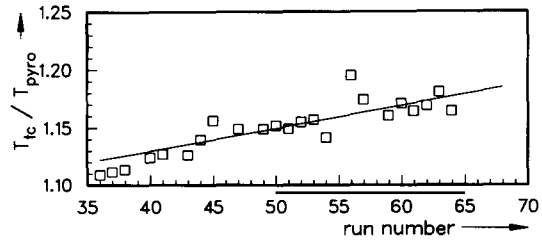

Fig. 3. Long-term drift of pyrometer reading.

a long-term drift in the electronics or the gas flow components.

In much the same way the temperature reading of the pyrometer (maximum sensitivity at $\lambda = 0.91$ to 0.97 μm) of our system changed from run to run compared to the thermocouple reading which is used in the feedback loop of the substrate heater. Fig. 3 shows the ratio of thermocouple reading T_{tc} and pyrometer reading T_{pyro} plotted over the growth runs. Since the pyrometer reading decreases from run to run we assume changing absorption by increasing coating of the viewport through which the measurement is taken. Fig. 4 shows T_{pyro} corrected for the long-term drift plotted against the thermocouple readings. The dependence is linear with a slope of only 0.81. This leads us to the assumption that the change of the temperature of the growing surface is smaller than the thermocouple reading suggests. Some indirect indications allow the statement that T_{pyro} (corrected) is fairly close to the real surface tem-

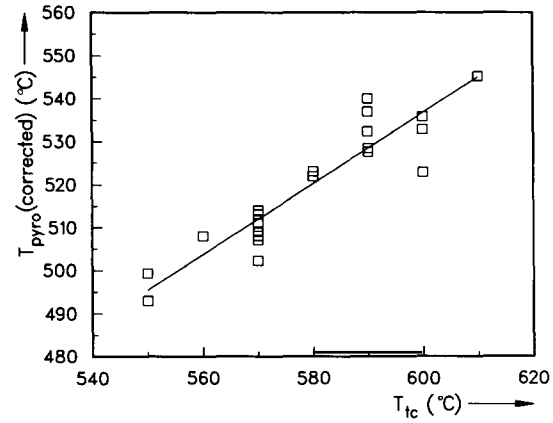

Fig. 4. Pyrometer reading (after correction) versus thermocouple reading.

perature in our case. First, at the congruent sublimation temperature of GaAs assumed to be 620°C the thermocouple reading was 55°C higher than the pyrometer reading. This calibration was done in the virgin system with clear windows. Secondly, the very weak dependence of crystal composition on the growth temperature (see below) which is known to occur between 500 and 540°C [3].

Finally, to assess the ability of our Varian II MOMBE system to perform fast gas changes we monitored the concentration of gaseous species in the growth chamber using the quadrupole mass spectrum (QMS) analyzer (UTI 100). To monitor the TMIn concentration we used dimethylindium (145 amu). At the mass of TMIn (160 amu) no signal could be detected. This highly unstable compound is probably completely cracked in the ionizer of the mass spectrometer. To monitor the TEGa concentration mass 129 was selected which could be hyrdogenized diethylgallium. No further attempt was made to verify this assumption. Fig. 5 shows the effect of the shutters on the gas concentration in the growth chamber. Water, rather than the more commonly utilized liquid nitrogen, was used to cool the source shroud. The intention of the two minute pre-run with the shutters closed had been to bring the gas system to a steady state without growing the crystal. As shown by this study the shutter is not able to keep TMIn and TEGa completely from reaching the surface. With the gasses running and the shutters closed there

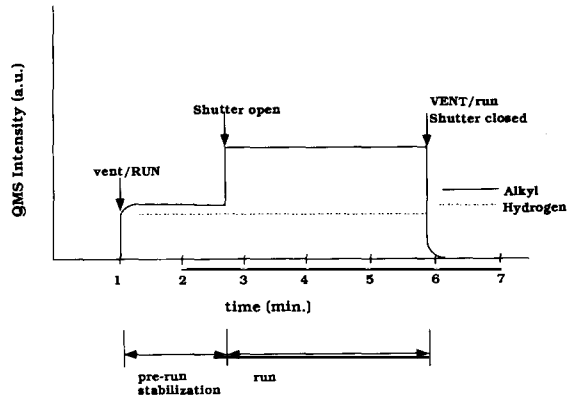

Fig. 5. Effect of shutter on gas concentration near the substrate.

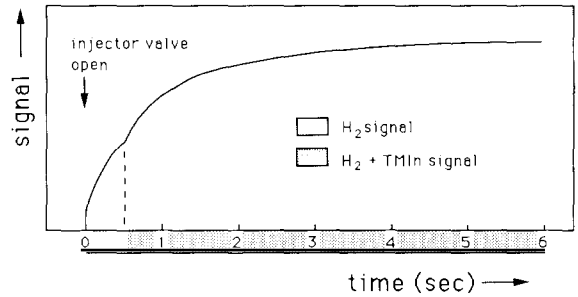

Fig. 6. TMIn concentration transients after switching using the vent/run manifold.

exists an undesired uncontrolled gas composition in the very important first instances of growth. The dotted line is the contribution of hydrogen to the signal which is the same at 145 amu and 129 amu and is not affected by the shutters. Fig. 6 shows the performance of the system if the vent/run manifold is used. On a different time scale it shows that it takes about 5 s to reach steady state. This transition can be accounted to the poor pressure balance between vent and run line and the ≈ 40 cm^3 volume of the growth chamber–gas manifold connection tube which experiences a pressure transient after switching. The lower bulge in the rising part of the curve can be attributed to the fast diffusing hydrogen and the upper bulge to the alkyl arriving about 0.5 s later.

3. Layer properties

The layers grown had a thickness of ≈ 1.5 μm. Morphology inspection, Hall measurements and double crystal X-ray diffraction were carried out. Fig. 7 shows the crystal composition dependence on the drift-corrected gas phase composition and growth temperature as determined by the thermocouple. It is a linear around lattice matching which is $0.51 \leq x \leq 0.55$. The scatter of $|\Delta a/a|$ is in the range of $\pm 2\%$ and can therefore be attributed to the irreproducibility of the gas handling system which is the combined repeatability of the gas handling components. However, the crystal composition can be controlled to $|\Delta x| \leq 0.01$ which is sufficient for most devices. The temperature

dependence of crystal composition in the investigated range was found to be negligible [4].

Since the ratio of TMIn to TEGa molecules is lower than the In content in the crystal it appears that the sticking coefficient of the particular growth sustaining In compound(s) is higher than that of the corresponding Ga compound(s). That is opposite from what is usually observed in the MOVPE of InGaAs where the gas phase composition x_g is usually higher than the crystal composition x [5] and might be due to the absence of parasitic reactions reducing the concentration of growth sustaining In compounds at the growing surface.

The growth rate can be controlled by adjusting the total flow of the group III elements. Fig. 8 shows that the growth rate depends linearly on the total group III flow and is virtually independent of the growth temperature in the range of $550 \leq T_{tc} \leq 610$°C (see comments in section growth system characteristics). The slope is 165 μm/mol which is about an order of magnitude less than with atmospheric pressure MOVPE systems [6]. Thus the highly efficient use of group V elements in MOMBE and CBE is accompanied by very low efficiency of the group III elements.

Electrical properties and morphology had greatly been improved by the change in the way the molecular beam was admitted to the growth chamber. Using the sequence depicted in fig. 5 the surface showed elongated scars at unreproducible density where the very high density layers appeared as oriented orange peel. The density of the scars was found to be related to the Hall mobilities; samples with very low density or absence showed mobilities of up to 10,000 $cm^2/V \cdot s$ at 300 K and 36,000 $cm^2/V \cdot s$ at 77 K, whereas samples with higher density showed mobilities around 5000 $cm^2/V \cdot s$ at 300 K and little improvement at lower temperature. This shows how sensitive the growth of bulk InGaAs is to the growth of the first few monolayers. If TMIn and TEGa arrival at the substrate is not coincident the growing surface shows varying density of three dimensional nucleation defects. After eliminating the pre-run stabilization with the shutters closed, the surfaces of the layers were featureless and consistently showed mobilities of $\mu_{300} \approx 9000$ $cm^2/V \cdot s$ and $\mu_{77} \approx 35{,}000$ $cm^2/V \cdot s$ at 1.2×10^{15} cm^{-3} background concentration.

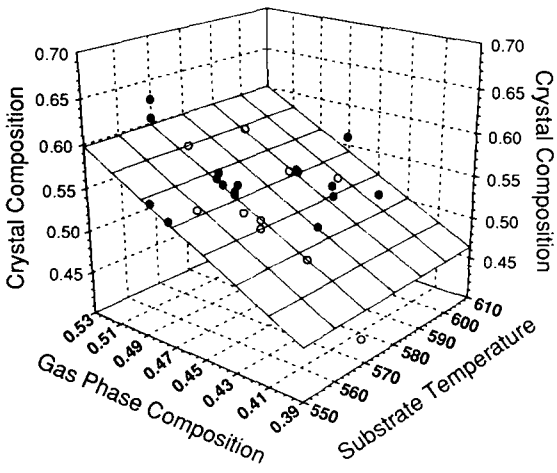

Fig. 7. Crystal composition versus gas phase composition and thermocouple temperature; (●) above surface; (○) below surface.

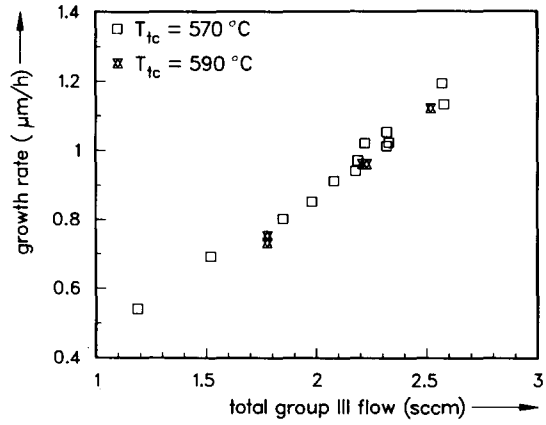

Fig. 8. Growth rate versus total group III total flow.

4. Conclusion

The growth of InGaAs on InP substrate is particularly sensitive to the performance of the growth system. Characterizing the material grown and relating this information to the system settings, we observed a long term drift of molecular beam composition. At higher run numbers the beam composition became TMIn-rich, calling for

a reduction of carrier gas flow through the TMIn bubbler.

Temperature readings as obtained by an infrared pyrometer and a thermocouple correlated well after a correction for increasing window coating. The corrected pyrometer reading shows that the uncertainty of the temperature of the growing surface is about $\pm 10°C$.

MBE shutters should not be used to modulate beams in a MOMBE system. Uncontrolled gas phase compositions are present near the substrate and lead to undesirable growth of material.

The composition of InGaAs was found to be linearly dependent on the molecular beam composition. The temperature dependence of composition was found to be weak. After process optimization the mobility of the layers was 10,000 and 36,000 $cm^2/V \cdot s$ at 300 and 77 K, respectively, at unintentional doping of 1.2×10^{15} cm^{-3}. The surface of these layers was featureless.

Acknowledgments

The authors wish to express their thanks to Drs. M.E. Elta and T.J. Drummond, and F. Sequin, J. Fournier and S. Sostrom for their contributions to the development and the installation of the MOMBE system. This work was supported by the Army Research Office under the URI program, Contract No. DAAL 03-87-K-0007.

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