Journal of Crystal Growth 111 (1991) 594–598
North-Holland

The optimization of $In_xGa_{1-x}As$ and InP growth conditions by CBE

M.E. Sherwin, G.O. Munns, M.E. Elta, E.G. Woelk, S.B. Crary, F.L. Terry and G.I. Haddad

Center for High Frequency Micro-Electronics, Solid State Electronics Laboratory, 2435 EECS Building, The University of Michigan, Ann Arbor, Michigan 48109-2122, USA

Minimization of the number of experiments needed to fully characterize and optimize the growth of epitaxial material is the first important step in realizing state of the art device structures. While widely used in some fields such as chemical engineering, response surface modeling (RSM) has been little used in crystal growth applications. Using RSM, input parameters such as substrate temperature hydride injector temperature and V/III ratio, were simultaneously adjusted to characterize the crystal growth process. This technique identified interactions among parameters, minimized the number of experiments necessary to understand and optimize the process, and minimized the variability of the growth process. RSM has been applied to the CBE growth of InGaAs and InP with the purpose of generating an operating point at which both good surface morphology and high mobility material can be produced. Although the best 77 K InP mobility was 70,000 $cm^2/V \cdot s$, in order to improve the surface quality the input parameters were changed so that the final mobility was 37,000 $cm^2/V \cdot s$. Although the quality of the InGaAs layers showed a dependence on the reactor history, there did not appear to be any sensitivity to variations made in the operating conditions. The best 77 K InGaAs mobility was 62,500 $cm^2/V \cdot s$.

1. Introduction

Response surface modeling (RSM) is a powerful technique for process optimization [1,2] but has been little used in crystal growth applications. One of the primary advantages of RSM is its ability to reduce the number of experiments required to fully characterize and optimize a process. This can be very important for CBE growth, where the large number of possible material systems precludes a factorial design of experiments. An integral part of RSM is the design of experiments. The choice of experimental points has a profound effect upon the uncertainty in the results. All of the experiments carried out in this study were performed using a first generation Varian Gen II MOMBE reactor. Source materials used were TMI, TEG, AsH_3 and PH_3. During this study the flow rates of the group III elements were held constant. During InP growth, the TMI flow rate was 1.25 SCCM. During InGaAs growth, the TMI flow rate was 0.87 SCCM and the TEG flow rate was 1.13 SCCM. The control variables that were adjusted were: substrate temperature (T_{sub}), hydride injector temperature (T_{inj}), and V/III ratio. The goal was to find an operating point that produces high mobility InGaAs and InP with good surface morphology.

Grown layers were evaluated for mobility and background carrier concentration, surface morphology, composition and growth rate. All mobility measurements were carried out at room temperature and 77 K using patterned Hall samples. Surface morphology was evaluated by visual inspection of Nomarski photographs. By comparing sample photographs against a present standard a rough measure of hillock density was determined. Surfaces were rated from zero to ten, with ten indicating a perfect surface.

2. Design of experiments

A common approach to experimentation involves holding all parameters fixed, except the one being explored. The response would then be maximized with respect to the first variable, which would then be fixed at its "optimal" point while the second variable is varied. This process proceeds, cycling through all the variables, multiple

0022-0248/91/$03.50

times if necessary, until no further improvement in the response is observed. Unfortunately, this method can be very inefficient and there is no guarantee of finding the true maximal response [1]. One way of avoiding this problem is to set up a rectangular grid of operating points evenly distributed over the input parameter space. This has the disadvantage of requiring a large number of experiments.

For the optimization of InGaAs a central composite design of experiments was used. It is recommended that all input variables be normalized [3], so that they range from roughly -1 to 1. This is especially true with this problem since T_{inj} can vary by $\pm 75\,^\circ C$ while the V/III ratio varies by only ± 5. By normalizing all variables, all changes will be of the same order of magnitude. Assuming that the responses, morphology and mobility, could be modeled by second order equations and with three input variables, T_{sub}, T_{inj} and V/III ratio, a central composite design requires a minimum of 15 experiments [1]. The experimental points are divided into three categories: cube, star and center points. The cube portion consists of eight points arranged in a first order 2^3 factorial design, $(\pm 1, \pm 1, \pm 1)$. The star portion consists of six points, $(0, 0, \pm \alpha)$, $(0, \pm \alpha, 0)$ and $(\pm \alpha, 0, 0)$. Although the choice of α is up to the experimenter, a value of 1.682 was used following the advice in ref. [2]. This choice of α results in spherical contours of the expected error in the response surface around the center point. This feature names the design rotatable. The minimum number of center points (0, 0, 0) is one, but for this experiment three center points were used to help obtain a better idea of the variance of the individual measurements. The 17 experiments were arranged in random order and conducted sequentially.

For the optimization of InP a minimum point near I-optimal design was used. Whereas a rotatable central composite design is arranged so that the response error is symmetrically distributed around the central point, an I-optimal design is arranged so as to minimize the average expected error in the response surface over the entire domain of the parameter space. As before, all input variables were normalized from -1 to 1. Being a minimum point design, only ten points were needed to model the second order response with three independent variables. One of the disadvantages of a minimum point design is its inability to provide a measure of the error of the fitted response surface. The ten experimental points were: $(0.96, 0.1, -0.1)$, $(-1, -1, -1)$, $(1, -1, 1)$, $(-0.1, 0.1, 0.96)$, $(-0.1, -0.96, -0.1)$, $(1, -1, -1)$, $(-1, 1, 0.25)$, $(1, 1, 1)$, $(-1, -0.25, -1)$ and $(0.26, 1, -1)$.

3. Results

The primary goal of this study is to determine a single operating point where both good InGaAs and InP can be grown. T_{sub} and T_{inj} are common variables for both InGaAs and InP, while the arsine and phosphine flow rates are independent for each material. The actual substrate temperature is estimated to be $55\,^\circ C$ below the setpoint [4]. The morphology scale is from zero to ten. In order to scale the mobility, the natural log of the mobility was linearly scaled so that 10,000 $cm^2/V \cdot s$ was equal to zero and 100,000 $cm^2/V \cdot s$ was equal to ten. All of the statistical analyses performed for this study were carried out using RS/1, a statistical package donated to the University of Michigan by BBN Software Products Corporation of Cambridge, MA.

3.1. InGaAs

The center point of the central composite design was: $T_{sub} = 580\,^\circ C$, $T_{inj} = 900\,^\circ C$ and the V/III ratio was 10.0. The distances from the cube center to the cube faces were $20\,^\circ C$ for T_{sub}, $50\,^\circ C$ for T_{inj} and 2.5 for the V/III ratio. The distance to the star points was the distance to the cube face multiplied by 1.682.

The highest mobility InGaAs grown had a 77 K mobility of 62,500 $cm^2/V \cdot s$, with a background carrier density of $5.3 \times 10^{14}\ cm^{-3}$. The 77 K mobility showed a linear increase with sample number, with no discernible dependence on any of the three input parameters. It is believed that this is due to the outgasing of the hydride injector. The last four experiments with drastically different operating conditions all showed 77 K mobilities over 50,000 $cm^2/V \cdot s$ while the surfaces of all 17 samples were featureless, showing no dependence on operating conditions. This indicates that the InGaAs is not very sensitive to the operating conditions.

Over the explored range of operating points, both the misfit and growth rate showed variation with the input parameters. The growth rate, as measured with a selective etch, showed a linear dependence on the V/III ratio and the injector temperature. This dependence is shown in fig. 1. The misfit, as measured by double crystal X-ray diffraction, is shown in fig. 2. The quadratic dependence of the misfit on the substrate temperature agrees with the findings of Andrews and Davies [5]. In determining the relationship for the misfit a small long term system drift observed earlier was ignored [4].

3.2. InP

The center point of the minimal point I-optimal design was: $T_{sub} = 580\,°C$, $T_{inj} = 900\,°C$ and the V/III ratio was 12.5. The excursions from the cube center to the cube faces were 25 °C for T_{sub}, 60 °C for T_{inj} and 5.0 for the V/III ratio. Initial data analysis after the 10 experiments were completed indicated that the quadratic models for mobility and morphology were unacceptable. Since there were only 10 data points and 10 terms in the quadratic equation, the equation would pass through each data point. This would be adequate if the system had very low noise. In order to improve the validity of the fitted equations, data from previously grown InP layers were added to the data set. Although the group III flow rate was somewhat different, it was felt that this variation was secondary to the three variables being explored. A total of 16 data points was used to obtain the final fits to the mobility and morphology. The growth rate, as measured by an interface stain, did not show any statistically significant variation over the operating conditions.

Both the mobility and morphology showed significant dependence on the input parameters, with no discernible dependence on reactor history. Table 1 shows the correlation matrix between the input parameters and the response variables, scaled mobility and morphology. The most striking feature is the difference in signs between the scaled mobility and the morphology correlations with all three input parameters. This is further borne out in the fitted equations given below.

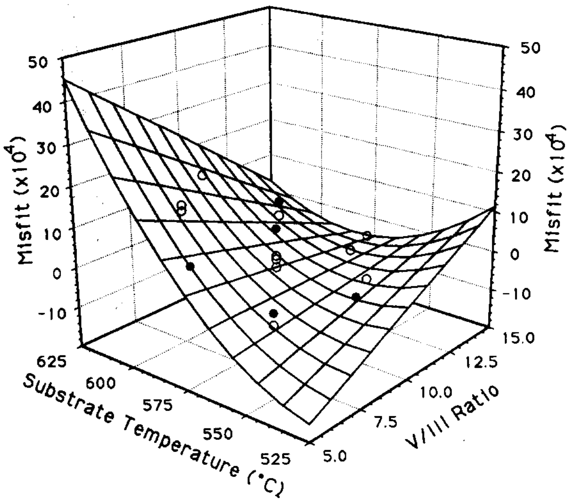

Fig. 2. InGaAs lattice misfit as a function of substrate temperature and V/III ratio. The filled symbols are above the fitted surface, while the empty symbols are below the fitted surface.

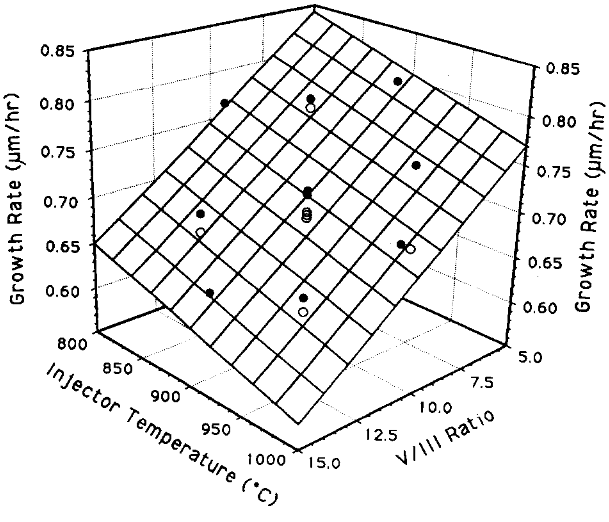

Fig. 1. InGaAs growth rate as a function of V/III ratio and hydride injector temperature. The filled symbols are above the fitted surface, while the empty symbols are below the fitted surface.

Table 1
Correlation matrix for InP 77 K scaled mobility (μ) and surface morphology (M) versus T_{sub}, T_{inj} and the V/III ratio

	T_{sub}	T_{inj}	V/III	μ	M
T_{sub}	1.0	0.065	0.196	0.347	−0.217
T_{inj}	0.065	1.0	0.107	−0.519	0.244
V/III	0.196	0.107	1.0	−0.211	0.353
μ	0.347	−0.519	−0.211	1.0	−0.358
M	−0.217	0.244	0.353	−0.358	1.0

$$\begin{aligned}
\text{Morphology} &= 8.8892 - 0.03862(T_{sub} - 580) \\
&\quad + 0.01004(T_{inj} - 900) \\
&\quad + 0.3399(\text{V/III} - 12.5) \\
&\quad + 0.00531(T_{inj} - 900)(\text{V/III} - 12.5) \\
&\quad - 0.00438(T_{sub} - 580)^2 \\
&\quad - 0.04824(\text{V/III} - 12.5)^2,
\end{aligned}$$

$$\begin{aligned}
\mu &= 5.1347 + 0.036178(T_{sub} - 580) \\
&\quad - 0.01905(T_{inj} - 900) \\
&\quad - 0.1343(\text{V/III} - 12.5) \\
&\quad + 0.01104(T_{sub} - 580)(\text{V/III} - 12.5) \\
&\quad - 0.00298(T_{inj} - 900)(\text{V/III} - 12.5) \\
&\quad - 0.02203(\text{V/III} - 12.5)^2.
\end{aligned}$$

A graphical representation of this equation is difficult to obtain since this would require a four-dimensional graph. It is very important to take great care in trying to visualize this information [6]. A series of three-dimensional graphs with one of the input parameters chosen as a grouping variable is the best option.

These equations indicate that good morphology and high mobility do not occur at the same operating point. The highest 77 K mobility measured was 70,000 $cm^2/V \cdot s$, with a background carrier concentration of 1.0×10^{15} cm^{-3}, but the sample had a very rough surface. The strong relationship between the surface morphology and the hydride injector temperature would involve a reaction with only partially decomposed phosphine as proposed by Karlicek et al. [7]. Using the above equations and the optimization routine available in RS/1, we were able to determine an operating point that had both acceptable morphology and good mobility. This operating point was: $T_{sub} = 580°C$, $T_{inj} = 894°C$ and the V/III ratio = 14.2. Confirmation runs at this operating point gave a 77 K mobility of 37,000 $cm^2/V \cdot s$ with good morphology. Both the surface quality and the 77 K mobility agreed well with the predicted values.

Some further work will be done to determine the effects of substrate misorientation and growth rate. It is anticipated that with these additional parameters it should be possible to obtain a good surface at the highest mobility available.

4. Conclusions

The results presented here show the applicability of response modeling techniques to the CBE growth process. As shown by the problems encountered with the minimum point near I-optimal design, it appears necessary to perform additional experiments to be able to test the model and to determine the error of the fit. Using RSM, a compromise operating point has been found which produces both good InP and InGaAs for future heterostructure work. A future effort will also involve modeling those elements of the growth process that drift in time.

Acknowledgments

The authors would like to thank 3-D Visions for their assistance in developing methods of visualizing some of the data. This work was supported by the US Army Research Office, URI Program, Contract DAAL03-86-K-0007.

References

[1] G.E.P. Box, W.G. Hunter and J.S. Hunter, Statistics for Experimenters (Wiley, New York, 1978).

[2] G.E.P. Box and N.R. Draper, Empirical Model-Building and Response Surfaces (Wiley, New York, 1978).
[3] A.I. Khuri and J.A. Cornell, Response Surface (Dekker, New York, 1987).
[4] E.G. Woelk, M.E. Sherwin and G.O. Munns, J. Crystal Growth 107 (1991) 1074.
[5] D.A. Andrews and G.J. Davies, J. Appl. Phys. 67 (1990) 3187.
[6] P. Hirsch, Sci. Computing & Automation 6 (1990) 19.
[7] R.F. Karlicek, Jr., D. Mitcham, J.C. Ginocchio and B. Hammarlund, J. Electrochem. Soc. 134 (1987) 470.