VAPOR PHASE GROWTH TECHNIQUE AND SYSTEM

FOR

SEVERAL III-V COMPOUND SEMICONDUCTORS

by

J. J. Tietjen, R. Clough, A. B. Dreeben, and R. E. Enstrom

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SUMMARY

Research has continued on the vapor growth of GaN, $In_{1-x}Ga_xP$, and $Ga_{1-x}Al_xAs$ alloy layers. Several p-type conducting layers of GaN have been achieved by doping with Ge acceptor impurities, but reproducibility is a problem. Experiments designed to reduce the inherent donor concentration in the GaN to improve the p-doping reproducibility were not successful. However, as a result of these experiments the electronic mobility was increased to 150 cm^2/v-sec, which is the highest value yet observed. Rapid diffusion of Zn from the p-type $In_{1-x}Ga_xP$ alloy p-n junction layer into the GaAs substrate was eliminated by reducing the p- and n-type doping concentrations. As a result, $In_{1-x}Ga_xP$ electroluminescent diodes containing 40 and 88% GaP were prepared that emitted at 7300 Å and 5700 Å, respectively. An investigation of process variables showed that the composition of $In_{.2}Ga_{.8}P$ alloy samples is relatively insensitive to the temperature of the Ga and In sources and to the phosphine flow rate which indicates that control of alloy composition is best achieved by controlling the relative flows of HCl over the In and Ga sources. Efforts to improve the reproducibility of high AlAs content $Ga_{1-x}Al_xAs$ alloys by varying gas flow rates, substrate and source temperatures, and source size were not successful, but an improved understanding of the effects of these variables on the alloy growth was achieved.

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I. INTRODUCTION

The major emphasis of the research during the previous two quarters has been on the preparation and characterization of GaN, $In_{1-x}Ga_xP$, and $Ga_{1-x}Al_xAs$ alloy layers.

Initially GaN could be prepared only as a polycrystalline layer. However, a careful investigation of the growth parameters, expecially the gas purity and growth temperatures, led to the preparation for the first time of high quality single-crystalline GaN layers on sapphire substrates. Next, doping of the GaN layers during vapor growth with potential acceptor impurities to achieve conducting p-type materials was investigated in anticipation of preparing p-n junction structures. However, only highly conducting n-type or high resistivity p-type layers were obtained, although some promising results with Si-doping appeared.

In the case of $In_{1-x}Ga_xP$ alloys, problems were encountered in the preparation of a wide range of alloy compositions and p-n junctions. Progress was made in the first area by systematically studying the various experimental conditions used and in the second area by growing p-type alloy layers on a p-type GaAs substrate, followed by the growth of the alloy n-layer. Problems of crystallinity and contamination in the growth of $Ga_{1-x}Al_xAs$ alloy layers in the usual quartz growth tube appeared to be associated with attack of the quartz by aluminum compounds. Coating the inside of the tube with carbon reduced the attack, and reducing hydrogen carrier flow rates promoted the growth of single-crystalline layers. However, reproducibility of alloy composition and homogeneity continued to be a problem.

During the present quarter, emphasis on the preparation and characterization of GaN, $In_{1-x}Ga_xP$, and $Ga_{1-x}Al_xAs$ alloys has continued and good progress has been made. The details of this research are described in the following sections.

II.   TECHNICAL DISCUSSION

A.   Growth of GaN and $In_{1-x}Ga_xN$ Alloys

In Interim Technical Report No. 2, we reported that we had been able to prepare large area, colorless, single-crystalline layers of GaN on sapphire. However efforts to dope GaN with the potential acceptor impurities Zn, Hg, Mg, and Si did not provide uniformly doped conducting p-type material. As a result the work this quarter has included doping experiments with the additional potential acceptor impurities Sn and Ge. Also the growth of undoped layers of $In_{1-x}Ga_xN$ alloys has been initiated.

In the case of Sn-doping, only highly conducting n-type layers have been obtained. However with Ge-doping two p-type layers with resistivities of 0.01 and 0.94 ohm-cm for hole concentrations of 6 x 10^{19} and 6 x 10^{18} cm^{-3}, respectively, were achieved as shown in Table I. This result is encouraging since it demonstrates that a fundamental mechanism does not exist which prevents amphoteric doping of this compound. However, at present this result is difficult to reproduce, as evidenced by the two n-type samples in Table I, and the layers are still non-uniform with some areas of the sample being n-type. This is probably related to the very high inherent donor concentration typically greater than 1 x 10^{19} cm^{-3}, that must be compensated before a p-type sample with a high net acceptor concentration can be attained.

It is possible that this high donor concentration arises from a high concentration of nitrogen vacancies. Therefore, several approaches have been investigated for reducing the net donor concentration in GaN by suppressing the nitrogen vacancy concentration in order to provide effective p-type doping of this material. Two samples were annealed in an autoclave under ammonia pressures of 3 and 7 atmospheres at 800 and 900°C, respectively, for 18 hours. However, in each case the specimen decomposed, probably because excessive ammonia decomposition occurs at these temperatures. The decomposition products of ammonia, nitrogen and hydrogen, are not effective in preventing GaN decomposition. In another set of experiments, GaN was grown at temperatures as low as 775°C instead of the usual 850°C. However, the net donor concentration was not reduced in these growths, and was sometimes slightly higher than the usual values. In addition, attempts to dope these layers with Ge did not produce homogeneous p-type material. In a third experiment, the ammonia was introduced into the reaction tube in close proximity to the deposition zone to prevent premature decomposition of the ammonia. Although this change doubled the growth rates and resulted in higher mobility values (150 cm^2/v-sec), it did not effect lower donor concentrations.

In order to better characterize the defect structure of these GaN layers and in particular to see if experimental evidence exists for high vacancy concentrations, a study is now being initiated to examine these crystals by transmission electron microscopy.

Measurements of the optical properties of GaN have recently been refined and now place the bandgap and reflectivity respectively at 3.39 eV and, 18% over the range 4000 - 6000 Å.

Table I

Electrical Properties of Some Representative GaN Samples

Sample	Dopant	Type	Carriers cm^{-3}	ρ ohm-cm	μ $cm^2/v\text{-}s$
3·31·69:M	Ge	p	6.3×10^{19}	.010	9
4·8·69:M2	Ge	n	1.0×10^{19}	.005	104
4·9·69:M	Ge	p	6.0×10^{18}	.940	1
4·21·69:M	Ge	n	1.9×10^{19}	.0026	126
5·19·69:M	none	n	3.5×10^{19}	.0011	150
5·26·69:M	none	n	5.1×10^{19}	.0010	123

$In_{1-x}Ga_xN$ alloys have never been prepared before and it is possible that such alloys with a bandgap smaller than GaN can be more easily doped with acceptor impurities than can pure GaN. For the growth of the $In_{1-x}Ga_xN$ alloys, a growth-tube similar to that used for the preparation of $In_{1-x}Ga_xP$ is being used. The growth of a clear, single-crystalline GaN layer has demonstrated proper operation of this new tube, and efforts to prepare $In_{1-x}Ga_xN$ will now begin.

B. Growth of $In_{1-x}Ga_xP$ Alloys

Work has continued on the growth of $In_{1-x}Ga_xP$ alloys for potential application as an efficient visible electroluminescent source. During this quarter work has been directed toward optimizing the doping levels in the n- and p-type layers and on investigating the effect of process variables on the alloy composition.

The previously reported problem of rapid diffusion of Zn from the p-type $In_{1-x}Ga_xP$ alloy layer through the alloy n-type layer and then into the GaAs substrate, which results in diodes emitting infra-red rather than visible light, has been completely eliminated by reducing the dopant concentrations to p ∼ 5 x 10^{18} cm^{-3} and n ∼ 5 x 10^{17}. Using these doping concentrations,

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$In_{1-x}Ga_xP$ alloy p-n junction structures were prepared on n-type GaAs substrates, and emission at 7300 Å and 5700 Å was observed without a special heat treatment step for structures containing 40 and 88% GaP, respectively. In addition, for the latter alloy, uniform emission over the entire surface of the diode was achieved for the first time.

Typically the diode efficiencies have been low, i.e. about 10^{-6} at 300°K and 10^{-4} at 77°K, and these low quantum efficiencies may be related to metallurgical imperfections. In fact, the rapid diffusion of Zn observed at high Zn concentrations is undoubtedly related to a high density of defects, particularly dislocations. Indeed, transmission electron microscopic examination of several alloy layers has shown a high density of dislocations ($>10^7$ cm^{-2}) and a well-developed subgrain structure. This high dislocation density could result from either lattice mismatch, thermal expansion mismatch, or both. While it would be possible to minimize the lattice constant mismatch by growing alloys having compositions near $In_{.43}Ga_{.57}P$ on GaAs, the thermal expansion mismatch would still be fairly large. The best procedure would be to grow these alloys on either InP or GaP and then grade the composition of the material from that of the substrate to the final alloy composition. To accommodate this process, since bulk single-crystalline InP or GaP are not currently available, an RCA supported program to pull these crystals from the melt using an oxide-encapsulated Czochralski technique is in progress. Until these crystals are available, studies will continue of the vapor growth conditions in order to obtain full control of the composition and uniformity of these materials. In this regard, the effects of source temperature and gas phase composition on the alloy composition have been investigated.

The standard conditions used for the growth of $In_{1-x}Ga_xP$ alloy samples containing about 80 mole percent GaP are given in Table II. The effects on the composition of variations of the gallium temperature, the indium temperature, and the phosphine flow rate are given in Tables III, IV, and V, respectively. It may be seen that these parameters have only a slight effect on the composition. In fact, the composition is quite reproducible for similarly prepared samples e.g. a gallium temperature of 850°C (79.3% GaP), and indium temperature of 980°C (82-86% GaP), and a pure phosphine flow rate of 60 ml/min (83.3% GaP). Previously it had been found that the phosphorus partial pressure played a significant role in determining the composition for InP-rich alloys but the present results demonstrate that, this is not the case for GaP-rich alloys. The results, to date, indicate that control of alloy composition should result from providing good control of the relative flow of HCl over the In and Ga sources, and this possibility will now be investigated.

Table II

Standard Conditions for Growth of $In_{.2}Ga_{.8}P$ Alloy Layers

Furnace	Temperature, °C	Gas	Flow Rate, ml/min
Gallium Zone	850	HCl over indium	4.0
Indium Zone	980	Hydrogen carrier gas	300
Center Zone	1000	HCl over gallium	0.4
Growth Zone	775	Hydrogen carrier gas	30
		Phosphine (100%)	60
		Hydrogen carrier gas	540

Table III

Effect of Gallium Zone Temperature on $In_{1-x}Ga_xP$ Composition

Gallium Temperatures (°C)	Composition (% GaP)
900	82.9
850	79.3
770	78.8
650	77.7

Table IV

Effect of Indium Zone Temperature on $In_{1-x}Ga_xP$ Composition

Indium Temperature (°C)	Composition (% GaP)
1100	82.6
950	86.5-94.1
800	90.0

Table V

Effect of Phosphine Flow Rates on $In_{1-x}Ga_xP$ Composition

Flow Rate of Pure PH_3 (ml/min)	Composition (% GaP)
22	81.0
60	83.3
290	83.3

C. Growth of $Ga_{1-x}Al_xAs$ Alloys

As reported previously, $Ga_{1-x}Al_xAs$ alloys with up to 30 mole percent AlAs have been prepared, but reproducibility has been a problem.

In an effort to improve the reproducibility of high AlAs content $Ga_{1-x}Al_xAs$ alloys new combinations of gas flow rates, substrate temperature, aluminum source temperature, and a larger aluminum source have been examined during this quarter but without success. More effective transport of aluminum was achieved with the larger source but this in turn caused increased attack of the quartz tube in spite of the use of a heavier carbon coating. Accordingly, the use of a carbon foil or an alumina protective liner within the quartz tube will be investigated to miminize this attack.

The growth of AlAs has been initiated using the single-metal-source quartz growth tube (carbon coated for the growth of AlAs) used previously for the preparation of GaAs, in conjunction with the larger aluminum source. Good transport of aluminum was observed, as with the alloy tube, and deposits judged to be AlAs from their brown color have been obtained on GaAs substrates at growth temperatures between 800 and 940°C. Thermal decomposition of the substrate at the higher temperatures is avoided by the use of a higher arsine flow rate.

III. CONCLUSIONS AND RECOMMENDATIONS

Some success was achieved with Ge-doping of GaN to prepare p-type conducting material. However, the layers are non-uniform and difficult to reproduce probably because of the high inherent donor concentration in the GaN.

The rapid diffusion of Zn from the p-type $In_{1-x}Ga_xP$ alloy layer into the GaAs substrate can be eliminated by optimizing the dopant concentrations in the p- and n-type alloy layers. Also, a better understanding of the effect of process variables on the $In_{1-x}Ga_xP$ alloy composition and the growth of $Ga_{1-x}Al_xAs$ has been reached that will be useful in preparing improved alloy layers.

During the next quarter, work will be initiated on the growth of $In_{1-x}Ga_xN$ alloy layers. In addition, work will continue on the growth of $In_{1-x}Ga_xP$, $Ga_{1-x}Al_xAs$, and Al As layers.

IV. NEW TECHNOLOGY APPENDIX

A. Title: Ge-Acceptor Doping of Single Crystal GaN

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   Comments: The preparation of p-n junction structures in GaN requires that the high inherent n-type impurities be compensated before a conducting p-type sample can be achieved. Conducting p-type GaN has been prepared for the first time by doping with Ge-acceptor impurities.