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# Preparation of Single Phase Gallium Nitride from Single Crystal Gallium Arsenide

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An analysis has been conducted on the final products obtained in attempts to prepare single phase gallium nitride from single crystal gallium arsenide. When the intermediate oxide phase was nitrided in pure ammonia it was found that (i) the lowest temperature at which rate of conversion of $\beta$-$Ga_2O_3$ to GaN became significant was in the range 600 to 700°C, (ii) over the temperature range 700 to 1000°C GaN was found to be the only crystalline phase present, (iii) above 1100°C $\beta$-$Ga_2O_3$ was the main constituent. In comparison, when the oxide phase was nitrided in a 50% $NH_3$-50% $N_2$ atmosphere it was found that (i) the lowest temperature at which conversion to GaN occurred lay between 700 and 750°C, (ii) there was only a narrow range of temperatures, 750 to 870°C, in which the final products were found to contain GaN as the only crystalline phase, (iii) samples nitrided above 870°C exhibited both GaN and $\beta$-$Ga_2O_3$ phases, the proportion of $\beta$-$Ga_2O_3$ increasing with increasing temperature.

## 1. Introduction

Interest has recently been aroused in the possible use of gallium nitride, GaN, as a material suitable for the production of efficient electroluminescent devices which operate throughout the visible region of the spectrum. GaN has a direct band-gap of approximately 3.4 eV at room temperature [11] which corresponds to radiation in the ultra-violet, but by the introduction of suitable dopants or by the application of conventional phosphors almost any visible radiation may be obtained. Little is known about the properties of GaN such as solubility, vapour pressure or melting point and for studies of these to be undertaken a suitable source of pure, bulk GaN is desirable.

Although it has been demonstrated that GaN may be prepared directly by reacting ammonia with pulverised gallium arsenide, GaAs, at 1000° C [1], a recent publication has shown that in order to convert bulk single crystal GaAs to GaN it is necessary to adopt a two-stage process in which the GaAs is first converted to gallium oxide, $\beta$-$Ga_2O_3$ [2].

GaAs is readily converted to $\beta$-$Ga_2O_3$ over the temperature range 600 to 1000° C [3-5]. If, however, the reaction is carried out in pure oxygen at temperatures above 850°C $GaAsO_4$ is formed in appreciable concentrations as a secondary product [5, 6].

Conversion of $\beta$-$Ga_2O_3$ to GaN has been shown to be accomplished in ammonia atmospheres in the temperature range 600 to 1100° C [7-9]. It has been found that the colour of the final product changes from a light yellow, at a preparation temperature of 600°C, to a light grey at 1090° C [7]. Although there appears to be no detectable difference in the composition of the various coloured products it has been suggested that the yellow coloration is due to the presence of oxygen in the lattice and the grey coloration to a nitrogen deficiency [10].

Recent attempts to form single phase GaN by nitriding, in atmospheres of both pure ammonia and 50% ammonia-nitrogen mixtures, $\beta$-$Ga_2O_3$ obtained initially by oxidation of GaAs crystals, are described and analysed in the present paper. The basic crystallographic character of the oxide and nitride products formed in such a conversion process have been described in a previous publication [2].

## 2. Experimental

Gallium arsenide slices, 1 to 2 mm thick and

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oriented in a <110> direction, were ground smooth with 1200 grit size alumina powder, chemically polished in a 1 : 3 : 1 solution of $H_2O$ : $H_2SO_4$ : $H_2O_2$, washed in distilled water and propan-2-ol and dried in a stream of warm nitrogen.

Chemical conversions were carried out in a standard 45 mm bore diffusion furnace. The slices were heated to the required temperature in a stream of pure nitrogen (total oxygen content $\leq$ 2 ppm) and allowed to come to thermal equilibrium before the reactant gases were admitted to the furnace tube. The standard oxidation treatment for all samples was 60 min at 870 °C $\pm$ 10°C in a stream of 50% oxygen in nitrogen, flowing at 2.0 l/min. All samples were nitrided with an ammonia flow rate of 0.5 l/min – those nitrided in a mixture had an additional nitrogen flow of 0.5 l/min. At the completion of each stage of the conversion the samples were cooled to at least 200° C in pure nitrogen before being removed from the furnace.

The weights of the GaAs and final products were recorded, as were some of the intermediate oxide samples.

X-ray diffraction was used to identify the phases present in each of the final products. A number of the samples were also examined by X-ray fluorescence analysis to establish the level of any retained arsenic contamination. Due to the absence of a suitable standard for calibration, and the variable geometry of the slices, a quantitative determination of arsenic concentration was not practicable, but the results serve for a relative comparison.

## 3. Results

The relevant details of the preparations of each sample, the phases identified, arsenic concentration and the weights of the initial and final products are all summarised in tables Ia and Ib for the samples nitrided in pure ammonia and 50% ammonia-nitrogen, respectively.

The only crystalline phase present in the oxide preparations was that of $\beta$-$Ga_2O_3$, there being no evidence of any secondary phase of $GaAsO_4$. It should be noted that the highest concentration of arsenic found in any of the preparations was ~0.27% by weight, indicating a maximum possible concentration of $GaAsO_4$ to be only 0.7% by weight, and thus probably too small to have been detected by X-ray diffraction.

Inspection of table Ia indicates that the lowest temperature at which the rate of conversion of the oxide to the nitride of gallium in an atmosphere of pure ammonia becomes significant lies between 600 and 700° C. Above 700° C and up to approximately 1100°C the nitriding procedure adopted has resulted in the formation of single phase GaN bulk samples. Sample 8 prepared at 1210° C, however, was shown to contain a major phase of $\beta$-$Ga_2O_3$, with GaN as the minor constituent indicating that 1100°C represents the upper temperature limit for single phase preparation of GaN.

After nitriding, the measured weights of specimens 4, 5, 6 and 7 were found to be in very good agreement with the weights calculated for these samples assuming them to have been fully converted to GaN. That sample 3 was found to be heavier than the predicted weight for the nitride was consistent with the observation that the main constituent of this sample is $\beta$-$Ga_2O_3$.

The effect of the introduction of nitrogen into the nitriding gas atmosphere is illustrated by a comparison of the results, detailed above, with those obtained from $\beta$-$Ga_2O_3$ nitrided in the 50% $NH_3$-$N_2$ gas mixture. Under these conditions the lowest temperature at which there was a significant conversion of the oxide to the nitride was found to occur between 700 and 750°C, that is higher than the equivalent temperature in a nitriding gas of pure ammonia. For those samples, 13, 14 and 15, nitrided at temperatures in the range 750 to 870° C, the only crystalline phase detected was that of hexagonal GaN. Samples nitrided at 1000°C were found to contain in addition to a GaN phase a small concentration of $\beta$-$Ga_2O_3$ which increased until at 1100°C it represented the main constituent.

In contrast to the sample prepared in pure ammonia those prepared in the 50% $NH_3$-$N_2$ gas mixture show poor agreement between their final measured weights and those predicted assuming complete conversion to the nitride. In every case the measured weights of the samples were greater than predicted. For those samples which exhibited GaN as the only crystalline phase the difference between the final and predicted weights indicated that they also contain 10 to 20% by weight of non-crystalline material.

Samples nitrided in the $NH_3$-$N_2$ gas mixture contain, on average, a higher arsenic impurity concentration than those prepared in pure $NH_3$, table Ia and Ib. No correlation, however, was established between the measured arsenic levels and other parameters such as nitriding tempera-

TABLE Ia GaAs nitrided in pure ammonia

| Sample number | Nitriding temperature, °C | Time at nitriding temperature, h | Phases present | Approx. arsenic concentration, % by weight | Sample weighings, grms | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | GaAs | $Ga_2O_3$ | | GaN | |
| | | | | | | Expected | Obtained | Expected | Obtained |
| 1 | 500 | 23.0 | $\beta$-$Ga_2O_3$ | — | 0.336 | 0.212 | 0.224 | 0.195 | 0.213 |
| 2 | 550 | 23.0 | $\beta$-$Ga_2O_3$ | — | 0.367 | 0.231 | — | 0.213 | 0.233 |
| 3 | 600 | 20.0 | $\beta$-$Ga_2O_3$ +GaN | 0.27 | (1) | 0.188 | — | 0.173 | 0.187 |
| 4 | 700 | 20.0 | GaN | none detected | (2) | 0.175 | 0.180 | 0.161 | 0.162 |
| 5 | 800 | 7.0 | GaN | none detected | 0.288 | 0.181 | 0.198 | 0.167 | 0.167 |
| 6 | 1000 | 3.0 | GaN | 0.08 | 0.312 | 0.196 | 0.215 | 0.181 | 0.179 |
| 7 | 1100 | 2.0 | GaN | none detected | 0.300 | 0.189 | — | 0.174 | 0.179 |
| 8 | 1210 | 0.5 | $\beta$-$Ga_2O_3$ +GaN | — | 0.291 | 0.183 | 0.195 | 0.169 | 0.180 |

(1) Starting $Ga_2O_3$ obtained from sample no. 9.
(2) Starting $Ga_2O_3$ obtained from sample no. 10.

TABLE Ib GaAs nitrided in 50% ammonia-nitrogen gas mixture

| Sample number | Nitriding temperature, °C | Time at nitriding temperature, h | Phases present | Approx. arsenic concentration, % by weight | Sample weighings, grms | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | GaAs | $Ga_2O_3$ | | GaN | |
| | | | | | | Expected | Obtained | Expected | Obtained |
| 9 | 600 | 19.5 | $\beta$-$Ga_2O_3$ | — | 0.590 | 0.382 | 0.406 | 0.352 | 0.384 |
| 10 | 700 | 8.0 | $\beta$-$Ga_2O_3$ | 0.21 | 0.570 | 0.370 | 0.393 | 0.336 | 0.371 |
| 11 | 725 | 18.0 | $\beta$-$Ga_2O_3$ | 0.15 | 0.324 | 0.204 | 0.214 | 0.188 | 0.206 |
| 12 | 750 | 22.0 | $\beta$-$Ga_2O_3$ +GaN | — | 0.356 | 0.223 | 0.236 | 0.206 | 0.219 |
| 13 | 750 | 19.0 | GaN | — | 0.552 | 0.358 | 0.377 | 0.320 | 0.335 |
| 14 | 800 | 7.0 | GaN | — | 0.590 | 0.372 | 0.409 | 0.343 | 0.350 |
| 15 | 870 | 3.0 | GaN | 0.08 | 1.4 | — | — | 0.8 | 0.9 |
| 16 | 1000 | 3.0 | GaN +$\beta$-$Ga_2O_3$ | 0.17 | 0.574 | 0.362 | 0.398 | 0.334 | 0.398 |
| 17 | 1100 | 2.5 | $\beta$-$Ga_2O_3$ +GaN | — | 0.558 | 0.352 | 0.381 | 0.324 | 0.352 |

ture, time at temperature, or the constitution of the final product.

The occurrence of a particular phase was associated with a distinctive sample coloration. Those preparations which had been shown to be single phase $\beta$-$Ga_2O_3$ were white in colour, both over the external surfaces and throughout the bulk, whilst those constituted of GaN were yellow. The surfaces of those samples prepared at high temperatures and which contained appreciable concentrations of both $\beta$-$Ga_2O_3$ and GaN phases tended to have a mottled, yellowish-white appearance. Furthermore, examination of cross-sections of these high temperature samples revealed that they had developed a complex lamella-like structure. Typically, around the edge of a slice and parallel to its surfaces was a band of pale yellow coloured material within which was a region of closely spaced, concentric, alternate light and dark bands, extending almost

to the centre of the specimen. Further investigations of this phenomenon, for which no unambiguous explanation has yet been proposed, are being undertaken.

Although this investigation was performed on <110> oriented GaAs slices, similar results were obtained on oxidation and nitriding of crystals cut in other orientations.

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