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The chemical preparation of gallium nitride layers at low temperatures

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The preparation and the physical and elecrical properties of gallium nitride layers prepared at temperatures in the region of 500° C is recorded.

1. Introduction

The potential uses of the III–V compound gallium nitride in light emitting diodes [1], acoustic surface wave devices [2] and microwave devices [3] has produced numerous contributions to the literature on its preparation and properties totalling at least fifty to date. The principal limitation of gallium is that it is not easy to prepare in single-crystal form since it decomposes when heated above 1000° C and the estimated melting conditions are at a temperature of 2000° C and a nitrogen pressure of 40 kbar [3]. As a result it has largely been prepared as crystalline layers on suitable substrates. The most widely used method of preparation is that of Maruska [1] which involves the reaction between gallium metal, hydrogen chloride gas and ammonia at temperatures between 800 and 1200° C. The presence of hydrogen chloride gas requires that the substrate on which the crystalline layers of gallium nitride are to be formed is chemically inert. Consequently the most frequently used substrate is single-crystal aluminium oxide. Other substrates tested have been single-crystal silicon carbide, although this material is itself difficult to obtain [4, 5] and silicon [5]. This limitation on substrates has led to attempts to prepare crystalline layers at lower temperatures, such attempts being supported by the observation that layers prepared above 800° C were always highly conducting and n-type. Reasons advanced for the latter property were impurity incorporation at high temperatures and the formation of nitrogen vacancies and gallium interstitials. It was hence presumed that both effects would be reduced at lower temperatures.

Chemical systems used at lower temperatures for layer preparation have been the gallium tribromide–ammonia complex [5] operating in the range 600 to 700° C and the trimethyl gallium complex operating at a lowest temperature of 750° C [6]. Active nitrogen produced by various methods has also been used operating at temperatures between 500 and 700° C [7–12].

The work below records the results of further attempts to produce crystalline layers of gallium nitride on suitable substrates at the lowest possible temperatures using chemical reactions in the vapour phase.

2. Experimental procedure

The substrates available for this work are silicon (cubic symmetry), gallium arsenide (cubic symmetry), gallium phosphide (cubic symmetry), sapphire (hexagonal symmetry), silicon carbide (hexagonal symmetry), quartz (hexagonal symmetry) and zinc oxide (hexagonal symmetry). The room-temperature lattice mismatches of hexagonal gallium nitride to these materials are in the order of 4.8%, 9%, 5.2%, 8.3%, 2.5%, 4.05% and 0.19%, respectively, defined as the minimum lattice difference between GaN and the lattice involved expressed as a percentage of the minimum GaN lattice spacing. From the list of available substrates a few were chosen. They were sapphire, quartz and zinc oxide from materials with hexagonal symmetry on the basis of availability and reasonable lattice mismatch, and gallium phosphide, gallium arsenide, silicon and indium phosphide from materials with cubic symmetry for the same reasons but in addition to test the possibility that gallium nitride can exist with cubic symmetry [12].

The chemical reactions chosen for investigation were similar to those successfully used by Born and Robertson [13] to produce large amounts of

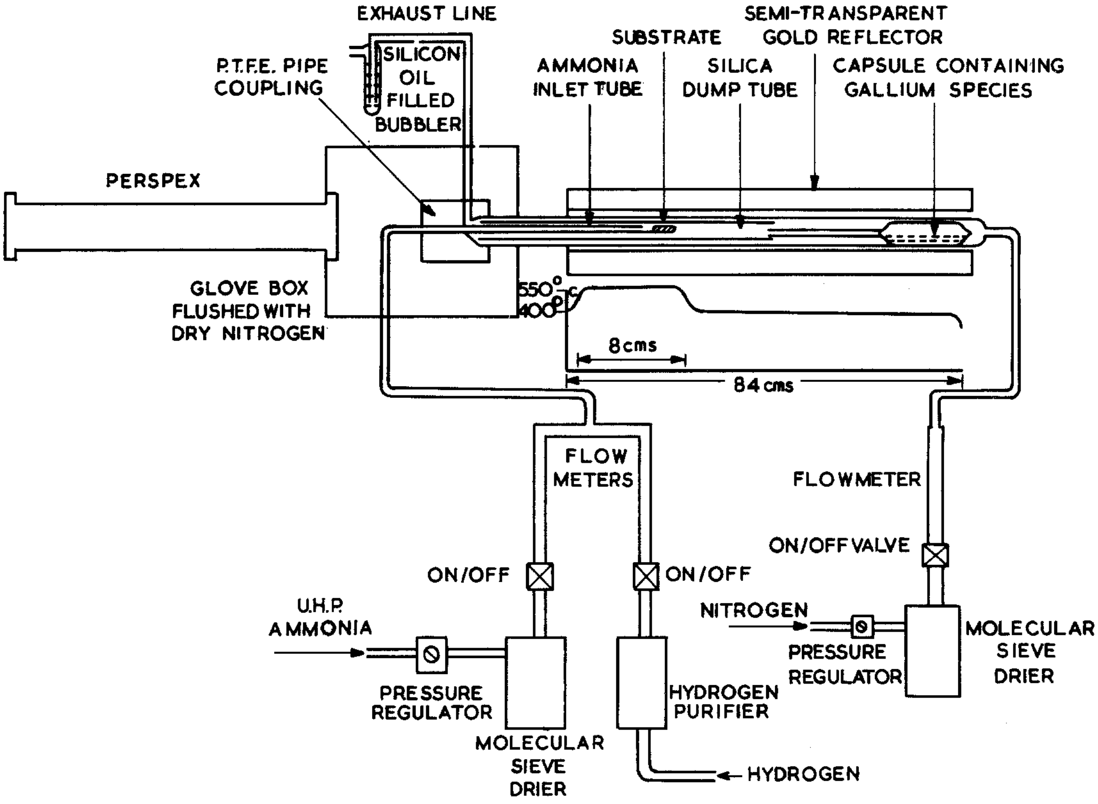

Figure 1 The vapour growth apparatus.

indium phosphide from chemical reactions in the vapour phase and were the direct reaction of the di- and tri-chlorides of gallium with ammonia gas.

The apparatus used is shown diagrammatically in Fig. 1 and consists of a wire-wound resistance furnace on a silica former 85 cm long. This furnace has three independently controllable heating zones. Lagging is provided by a gold coated silica tube reflector which permitted viewing of the interior of the furnace.

Since the halides used are hygroscopic they were supplied by the manufacturers in breaker seal pyrex tubes and were opened and loaded into the furnace via a glove box continually flushed with dry nitrogen gas.

The nitrogen carrier gas for the halide vapour entered the reaction tube at the end remote from the glove box and passed over the ampoule containing the halide. The ammonia gas entered the reaction tube at the glove box end and the tube carrying this reagent terminated in a horizontal platform on which the substrate was placed.

The substrates were prepared as follows. Sapphire, silicon and quartz substrates were cut on the selcted orientation, usually the basal plane in the case of sapphire and quartz and polished mechanically by the proprietary cyton process. The zinc oxide was mechanically polished and then subsequently chemically polished in phosphoric acid. The latter was necessary because examination of the surface in a scanning electron microscope showed channelling patterns to be present only on chemically polished surfaces, which indicates freedom from work damage. The gallium phosphide, gallium arsenide and indium phosphide were prepared by mechanical polishing using a 4 vol% bromine–methanol solution.

Electrical measurements were made on Maltese Cross shaped specimens abrasively machined from layer and substrate and contact made by using pressure bonded gold contacts. Cathodoluminecence measurements were made at room temperature using a suitably modified electron microscope.

3. Results

The results for the reaction of the four halides tested, gallium di- and trichloride and gallium diand tribromide were as follows. Gallium nitride was produced in all cases; for the dichloride the reaction temperature range was 500 to 650° C, and for the trichloride the reaction temperature range was 800 to 950° C. This confirms the results of Wickenden and co-workers [4]. In the case of the dibromide the reaction temperature range was 440 to 650° C and for the tribromide the range was similar to the trichloride. In all cases no reaction took place outside these temperature ranges, in other words, raising the furnace temperature at the point where deposition is taking place simply moves the deposition zone to another part of the reaction tube. The gallium nitride deposit in most cases was pale yellow but occasionally orange when the tribromide was used. Analysis of the product showed the main impurities to be halide at up to 20 ppm.

From these results the dichloride and dibromide were selected for further use on the basis that deposition by these reagents could be obtained at the lowest temperature.

The procedure for layer preparation using the dichloride and dibromide is as follows. The substrates are heated to 650° C in ammonia prior to growth in the case of all substrates except indium phosphide. In the case of indium phosphide the substrate was heated to 540° C for 30 min in ammonia. The substrate temperature is reduced to 540° C and dichloride heated to 450° C maximum and the flow of undiluted ammonia commenced. The growth rate of the gallium nitride could be as high as 1.5 μm h^{-1}. However, the average growth rate was about 0.3 μm h^{-1} and this is fifteen times lower than values reported in the literature. The only by-product of the reaction is ammonium chloride or bromide and the reaction involved can be described by

$$2GaCl_2 + 2NH_3 = 2GaN + 4HCl + H_2.$$

All the layers deposited were polycrystalline and on the (1 1 1) plane of gallium phosphide, gallium arsenide and indium phosphide they consisted of a tightly-packed columnar structure with the diameter of the individual columns less than 40 Å (Fig. 2). The *c*-axis of the columns was normal to the plane of (1 1 1) GaP, the substrates as shown by X-ray examination. For other orientations of all substrates the *c*-axis of the columns was randomly orientated with respect to the plane of the substrate. The growth rate of the layers and the crystallite size was not affected by changes in ammonia concentration or gas flow rates. However, this parameter was affected by changes in dichloride or dibromide concentration, as shown in Table I, the halide concentration being changed by altering the capsule temperature. The results in Table I are for the dichloride but those for the dibromide were similar. The halide concentration was also changed with the number of layer preparations made and consequently the growth rate changed similarly. This is the result of ammonia gas entering the capsule and forming a chloroamide or bromoamide which is less volatile than the halides [5] from which it is derived.

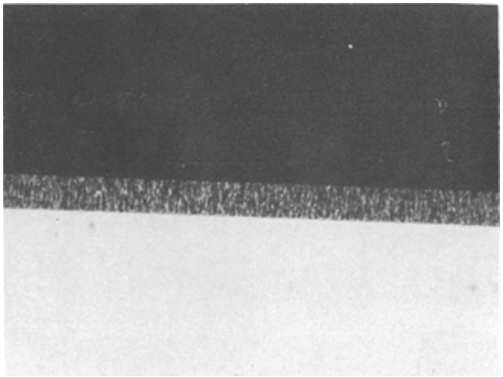

Figure 2 **An epitaxial layer of gallium nitride on gallium phosphide (×350).**

The electrical characteristics of the layers were affected, principally by the major impurity in the system which is water. This is present in the ammonia gas in which, even when supplied as very pure, the water content can be as high as 1000 ppm. This was substantially reduced by passing the ammonia through molecular sieve drying units. However, these have to be periodically re-activated and Table II shows the effect of increased moisture entering the reaction system causing low resistivity layers to be formed, followed by the effect of moisture content reduction after reactivating the drying units, which produced high resistivity layers. All results are again for the dichloride reaction.

No deposition of gallium nitride was obtained on sapphire in the reaction temperature range of the dichloride or dibromide and in the case of quartz deposition was only obtained at a temperature of 600° C. These latter layers did not adhere to the substrate, probably because of the strain caused by the quartz passing through its phase change at 573° C.

TABLE I

Layer code	Halide source temp. (° C)	Seed temp. (° C)	Layer thickness (μm)	Growth rate (μm h^{-1})	Electrical characteristics (cm^{-3})	Substrate	Substrate orientation	Notes
GR109	375	550	–		1.0×10^8	semi-insulating GaP	1 1 1	–
GR115	375	550	–	0.87	1.7×10^4	as above	1 1 1	–
GR125	395	550	7.0	0.36	1.5×10^4	as above	1 1 1	–
GR126	430	550	9.8	1.38	1.3×10^4	as above	1 1 1	–
GR127	450	550	11.5	1.48	1.7×10^6	as above	1 1 1	Adhesion poor
GR138	400	550	10.0	0.37	1.5×10^5	as above	1 1 1	–
GR141	400	550	10.0	0.33	1.2×10^9	as above	1 0 0	–
GR142	400	550	7.5	0.24	4.6×10^6	as above	1 0 0	–
GR145	375	550	7.0	0.27	3.4×10^3	as above	1 1 1	–
GR116	375	550	10.0	0.47	5.8×10^2	as above	1 1 1	–
GR121	375	550	3.0	0.3	$\left.\begin{array}{r} N_D - N_A = 6 \times 10^{16} \\ u = 14 \end{array}\right\} -196^\circ \text{C}$	–	–	–
GR123	375	550	5.0	0.47	$\left.\begin{array}{r} N_D - N_A = 2.3 \times 10^{19} \\ u = 0.7 \end{array}\right\} -196^\circ \text{C}$	–	–	–
GR143	420	550	< 1	–	–	Quartz	Z-cut	Adhesion poor
GR144	350	550	7	1.04	–	Quartz	Z-cut	Adhesion poor
GR140	350	550	–	–	–	Zinc oxide	0 0 0 1	Adhesion poor
GR146	375	550	Very uneven	–	–	Zinc oxide	0 0 0 1	Adhesion poor
GR161	395	540	0.6	–	7.5×10^5	semi-insulating GaAs	1 0 0	–

TABLE II

Layer code	Halide source temp. (°C)	Seed temp. (°C)	Layer thickness (μm)	Growth rate ($\mu m\ h^{-1}$)	Electrical characteristics (cm^{-3})	Substrate	Substrate orientation	Notes
GR130	400	550	2.6	0.34	6.6×10^2	Semi-insulating	1 1 1	–
GR131	395	550	7	0.25	32	as above	1 1 1	–
GR132	380	550	11	0.45	4.5	as above	1 1 1	$GaCl_2$ capsule changed after this experiment
GR133	385	550	6	0.22	4.0	as above	1 1 1	poor layer
GR134	395	550	2	0.27	4.7	as above	1 1 1	–
GR135	395	550	6	0.23	3.5	as above	1 1 1	Ammonia gas driers reactivated after this experiment
GR136	385	550	4.6	–	4.3×10^2	as above	1 1 1	–
GR137	400	550	10.4	0.33	1.0×10^5	as above	1 1 1	–

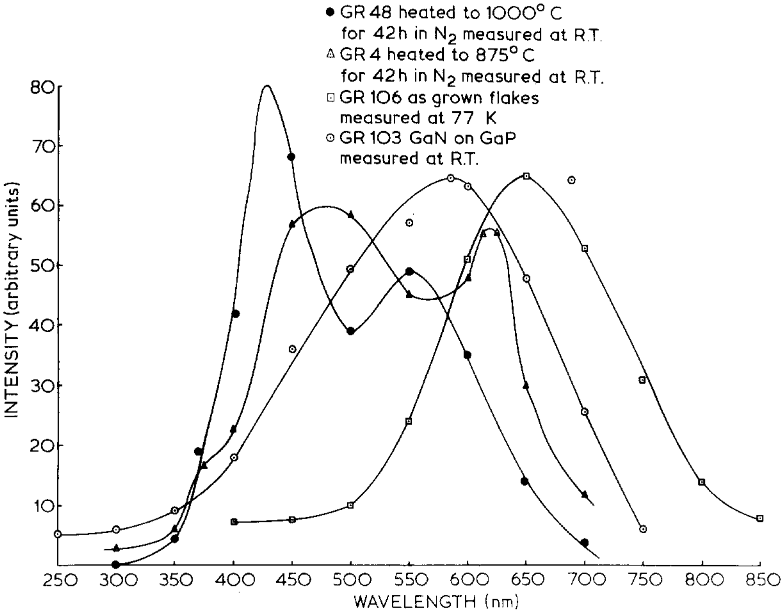

Figure 3 Cathodoluminescence of gallium nitride prepared in this work.

Layers were deposited on zinc oxide, gallium phosphide, gallium arsenide, silicon and indium phosphide in the reaction temperature range. In the case of zinc oxide there was chemical attack if the temperature was 600° C or above. These layers were pale yellow and up to 10 μm thick. However, adhesion of the layers was not good in the case of zinc oxide.

X-ray powder photographs of free gallium nitride from the reactor confirmed that the material possessed the reported structure and lattice constants.

Layers on gallium phosphide, gallium arsenide, silicon and indium phosphide were shiny and transparent and could be produced up to 30 μm thick, (Fig. 2). Adhesion of the layers was good up to a thickness of 10 μm but thicker layers adhered less well. Cathodoluminescence measurements were made on the layers and on free gallium nitride from the reactor. The measurements were made both at 27° C and − 196° C using a 20 keV electron beam giving a 10 μsec pulse every 500 μsec. These samples produced broad-band emission with peaks centred near 600 nm, as shown in Fig. 3. On cooling to − 196° C no change was observed in the nature of the spectra, although the peak

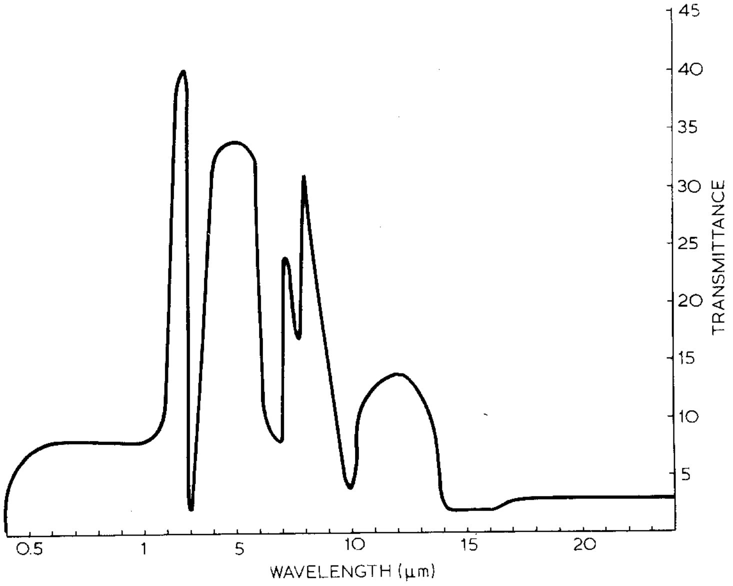

Figure 4 Transmission spectra of gallium nitride prepared in this work.

position was nearer 650 nm. When samples of substrate-free gallium nitride from the reactor were subjected to heat treatment for 42 h in sealed silica ampoules evacuated to 10^{-6} torr and then re-examined by cathodoluminescence, a progressive change in the spectra was observed, and this is also shown in Fig. 3. Heating to 1000° C caused the broad-band to shift towards shorter wavelengths and also produced a strong emission at 429 nm. These results were unchanged by cooling to − 196° C. Samples heated to 1200° C dissociated completely.

Electrical measurements of the layers showed wide variations were possible and as stated these resulted from changes in growth conditions. In those layers where the resistivity was low the free electron concentration was high and the electron mobility was low. The range of transmission of layers freed from the substrate is shown in Fig. 4.

4. Discussion

The processes described readily produce crystalline gallium nitride at low temperatures and this can be deposited on semiconductor substrates much more readily than on substrates which contain oxygen. However, the layers deposited are invariably polycrystalline. For hetero-epitaxy it is generally considered that the preferred properties of the substrate are a structure match, a close lattice match and a close thermal expansion match. The substrate with such properties in relation to gallium nitride is zinc oxide. This substrate cannot be used in the Maruska process since it is chemically attacked. However, even under the conditions described where chemical attack was minimized, gallium nitride layers were not deposited. Layers were also not deposited on the normal substrate alumina or silica. It is evident therefore that deposition at lower temperatures is governed by a factor other than those listed above. This appears to be, from the results, the availability of nucleation sites on the substrate at these low temperatures and these are apparently much more numerous on the semiconductor surfaces than on the alternative surfaces. This is supported by the very small grain polycrystalline nature of the layers. This nature also makes lattice and thermal expansion match much less important. The change in the nature of the cathodoluminescence spectrum on heating shows that the emission characteristics of gallium nitride are related to the stoichiometry of the compound and hence it is likely that the electrical characteristics are similarly affected.

5. Conclusions

In conclusion, it has been shown that layers of gallium nitride can be produced at temperatures of 550° C by chemical reaction. The layers are polycrystalline and can have resistivities ranging from 1.0 Ω cm to 10^8 Ω cm.

Acknowledgement

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