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Gallium Nitride formed by Vapour Deposition and by Conversion from Gallium Arsenide

K. R. FAULKNER, D. K. WICKENDEN
Semiconductor Laboratories

B. J. ISHERWOOD, B. P. RICHARDS, I. H. SCOBEY
Central Research Laboratories, GEC Ltd, Hirst Research Centre, Wembley, Middlesex, UK

Attempts to prepare single crystal gallium nitride in thin films and bulk form are reported. The thin films were prepared by reacting $GaCl_3$ and NH_3 and depositing on to single crystal silicon carbide substrates. The bulk gallium nitride was prepared by the conversion of single crystals of gallium arsenide using an intermediate oxide phase.

The structural perfection of the gallium nitride material thus formed has been assessed using X-ray diffraction and electron diffraction techniques. Both methods of preparation produced single phase gallium nitride exhibiting a high degree of structural disorder.

1. Introduction

Although considerable difficulty has been experienced in the preparation of single crystal gallium nitride, GaN, investigation of the luminescent characteristics of this material in polycrystalline form suggests that it could find useful application in the fabrication of junction electroluminescent devices.

Several attempts to grow such crystals have been described in the literature. Polycrystalline gallium nitride has been prepared by the reaction of ammonia with liquid gallium [1–4], and with a number of compounds e.g. $(NH_4)_3GaF_6$ [5], Li_3GaN_2 [6], GaP [7], GaAs and Ga_2O_3 [8–10]. Grimmeiss *et al* [11] claim to have produced single crystals of gallium nitride by reacting ammonia with the intermetallic compound LiGa. The crystals obtained by this process were, however, heavily contaminated with Li. In addition, the same workers prepared small single crystal whiskers by reacting gallium, diluted with an inert powder, with ammonia [11].

Lorenz and Binkowski have suggested that the difficulties encountered in the production of single crystal gallium nitride may be a consequence of the dissociation of this material, which has been reported to occur at temperatures as low as 600° C *in vacuo* [8]. The dissociation pressure of the gallium nitride was measured by Lorenz and Binkowski to be greater than 1 atm at 1000° C. These data, however, are somewhat in conflict with those obtained from experiments using thermal transportation [12] and torsion-effusion techniques [4, 13] to measure the vapour pressures of the solid. These experiments indicated that the dissociation pressure at 1000° C is several orders of magnitude below 1 atm.

The nature of the vapour species above the gallium nitride is also the subject of some controversy. Sime and Margrave [12] inferred that their results could be explained by the formation of a polymeric molecule $(GaN)_x$, but they could not detect an absorption spectrum of such a species in the range 300 to 700 $m\mu$. Gaseous dimeric species $(GaN)_2$, however, have been detected by Gordienko *et al* [14]. Munir and Searcy [4] have shown that gallium nitride sublimes congruently from a torsion-effusion cell when the ratio of orifice area to sample area is about 1:30, but no peaks attributable to gallium nitride molecules were detected in mass-spectrometric studies.

The presence of excess gallium has been shown to catalyse the dissociation of the nitride [13] suggesting that the stoichiometry of the material is a critical factor controlling dissociation kinetics.

The present paper describes the results of further attempts to prepare single crystal gallium nitride by two essentially different mechanisms.

Firstly, guided by the similarities between the crystal structures of gallium nitride and silicon carbide, epitaxial growth on silicon carbide as the deposition substrate was tried. A survey of the literature suggests that this attempt to grow films of gallium nitride is the first of its kind.

Secondly, the preparation of single crystal gallium nitride in bulk form by the conversion of single crystal gallium arsenide was attempted. Although references to this particular method are available in the literature [8–10], considerable doubt exists concerning the most favourable preparation conditions. This is mainly due, as indicated above, to the somewhat limited understanding of the factors influencing the dissociation of gallium nitride.

2. Experimental

2.1. Preparation of the Thin Films

Thin films of GaN (~ 0.1 to 0.5 μm) were prepared by vapour reaction in an open flow furnace tube system. Dry nitrogen carrier gas was passed over a silica boat containing $GaCl_3$, maintained at a temperature near its melting point of 77° C, the corresponding vapour pressure being 10 torr. Ammonia diluted with nitrogen (see table I for flow rates) was introduced via a separate tube into the hot zone of the furnace in the vicinity of the substrate. The ammonia was introduced well down-stream of the $GaCl_3$ in order to prevent the formation of $GaCl_3$—polyammoniates. In addition this arrangement favours a reaction at or near the substrate surface. The substrates were single crystal *p*-type silicon carbide which had been lapped, polished and chemically cleaned. In order to remove any surface damage a number of substrates were oxidised at 1200° C and the oxide layer was then removed in hydrofluoric acid. The substrates were placed on a silica support table and the films were deposited at temperatures in the range from 280 to 780° C. The temperatures were measured with a chromel/alumel thermocouple sealed into the support table. The majority of films were examined crystallographically in the as-grown state.

2.2. Preparation of Bulk Samples

Direct conversion of GaAs to GaN has proved to be impracticable since a thin surface layer of GaN is formed on the GaAs which inhibits further conversion. Consequently it has been necessary to adopt a two-stage process.

Slices of single crystal GaAs (1 to 2 mm thick) were heated to 880° C for 1 h in pure oxygen (or in an oxygen/nitrogen mixture) to form gallia. Conversion to the nitride was then accomplished by heating the intermediate oxide in ammonia (or in an ammonia/nitrogen mixture) at 880° C for 1 h. The reasons for the choice of a temperature of 880° C for formation of the nitride are discussed below.

Preparation of GaN was also attempted by direct conversion of single crystals of β-Ga_2O_3 using the nitriding conditions detailed above. Only a limited amount of surface conversion to the nitride, however, was effected. Severe specimen charging prevented reflection electron diffraction examination of the surface.

It is to be noted that these β-Ga_2O_3 crystals were of superior perfection, as shown by X-ray Laue patterns, to the β-Ga_2O_3 formed by oxidation of single crystal gallium arsenide. Imperfections detected were limited to twinning phenomena.

2.3. Examination of the Thin Films

Some of the samples were examined by glancing-angle X-ray diffraction. The resulting diffraction patterns, however, represented contributions from both the deposited film and the silicon carbide substrate, as the penetration depth of the CuKα X-ray beam was greater than the thickness of the film. Unambiguous interpretation of the patterns therefore presented difficulties owing to the crystallographic similarity of gallium nitride and silicon carbide. The deposited films were consequently investigated by glancing-angle electron diffraction, by which method penetration depth would be limited to approximately 200 Å.

2.4. Examination of the Bulk Samples

The products formed at the intermediate oxide and final nitride stages in the conversion of gallium arsenide crystals were examined by X-ray diffraction techniques.

In order to establish the constitutions of the intermediate oxide and the final nitride preparations, appropriate samples were crushed and examined by conventional X-ray powder diffraction.

The degree of development of a crystallographic structure in the products obtained at the two stages was ascertained using a back-reflection X-ray diffraction Laue technique.

The oxide and nitride preparations were also examined by glancing-angle electron diffraction techniques.

3. Results

3.1. Films Grown on SiC Substrates

All the deposited films examined consisted of polycrystalline gallium nitride only. Various types and degrees of preferred orientation, however, are exhibited in the samples, the details of which are listed in table I. Several points are worthy of note:

(*a*) For a given set of preparation conditions, the sharpness of the electron diffraction pattern improves with temperature of deposition, suggesting an increase in crystallite size at the surface of the film.

(b) At a substrate temperature of 445° C, orientation effects become noticeable, and in general, as the substrate temperature is raised the orientation becomes more pronounced. For temperatures in excess of ~ 700° C, however, the orientation condition becomes less marked.

(c) From the limited amount of data available, it appears that a change in the carrier gas from nitrogen to argon does not alter either the degree or type of orientation present in the resulting GaN films.

3.2. X-ray Examination of Bulk Samples

Examination by X-ray powder diffraction indicated that the intermediate oxide product consisted essentially of β-Ga_2O_3.

Some extra reflections on the powder patterns, not attributable to β-Ga_2O_3, were observed, but have not been satisfactorily explained up to the present. Arsenic in an estimated concentration of 0.1 to 1.0% was detected in the gallium oxide, sample 23, by X-ray fluorescence analysis.

Only one phase was detected in the final nitride preparation, namely that of hexagonal gallium nitride. The arsenic concentration was found by X-ray fluorescence examination to be very much lower ($\ll 0.1\%$) than that detected in the gallium oxide. The lattice parameters of the gallium nitride structure were measured to be $a_0 = 3.190 \pm 0.005$ Å and $c_0 = 5.17 \pm 0.01$ Å; in close agreement with the results of Juza and Hahn [15].

The back-reflection Laue patterns obtained from the (111) surface of the original gallium arsenide crystal and of the equivalent faces on the oxide and nitride preparations are reproduced in figs. 1, 2 and 3. The pattern from the oxide, fig. 2, has apparently near trigonal symmetry indicating a three-fold axis of rotation normal to

TABLE I Details of preparation and structural observations of films of GaN grown on *p*-type silicon carbide substrates

Sample no.	Thickness, μm	Substrate temperature, °C	Time, h	Nitrogen bleed, *l*/min	Nitrogen carrier gas, *l*/min	Comments on electron diffraction pattern
1	0.1	280	1.0	3.0	1.0	diffuse bands at $\langle h0\bar{h}0\rangle$ maxima
2	0.1	330	1.25	3.0	1.0	weak diffuse unoriented pattern
3	0.1	375	1.0	3.0	1.0	weak diffuse unoriented pattern
4	0.16	445	1.5	3.0	1.0	diffuse pattern with slight $\langle 000l\rangle$ and $\langle h0\bar{h}0\rangle$ orientations
5	0.30	640	1.0	3.5	1.0	oriented polycrystalline pattern; degree of orientation makes unambiguous differentiation between $[11\bar{2}2]$ and $[20\bar{2}3]$ difficult
6	0.50	750	2.25	3.0	1.0	polycrystalline pattern with slight $\langle h0\bar{h}0\rangle$ orientation
7	0.08	620	2.0	3.0	0.15	fairly well developed basal orientation, together with slight development of $[20\bar{2}1]$ orientation
8*	0.08	620	2.0	0.7	0.0	as sample 7
9	0.28	620	15.5	2.7	0.15	fairly well developed $[20\bar{2}1]$ orientation, together with a slight development of a basal orientation
10	0.35	780	5	3.0	0.15	polycrystalline pattern with slight basal orientation
11	0.10	700	15.5	0.0	2.0	polycrystalline pattern with basal orientation
12	0.50	700	2.0	2.0†	0.12†	as sample 10
13	0.45	700	2.0	2.0	0.14	polycrystalline unoriented pattern
14	0.40	700	2.0	2.0	0.15	as sample 10
15	0.08	700	2.0	2.0†	0.15†	as sample 10

*Annealed for 12 h at 750° C
†Argon substituted for nitrogen.

the crystal surface. The breadth (diffuseness) of the diffraction "spots" can be interpreted as a measure of the disorder present in the structure of the sample, and in this instance it is considerably worse than that expected from a sample classified as a single crystal, e.g. from the gallium arsenide crystal, fig. 1.

All the gallium nitride samples were very similar in the type and degree of their crystallographic orientation. It is evident from the Laue pattern, fig. 3, which is typical of all the samples, that the gallium nitride shows even greater disorder and departure from single crystal character than the β-Ga_2O_3 growth. Although more accurately described as trigonal, the symmetry of the Laue pattern reproduced in fig. 3 closely resembles the expected hexagonal symmetry characteristic of the [0001] direction of the GaN structure.

Figure 1 Back-reflection Laue photograph from gallium arsenide crystal.

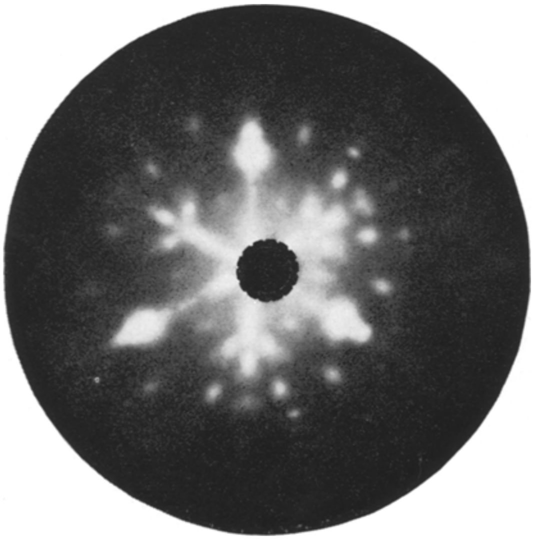

Figure 2 Back-reflection Laue photograph from gallium oxide (β-Ga_2O_3).

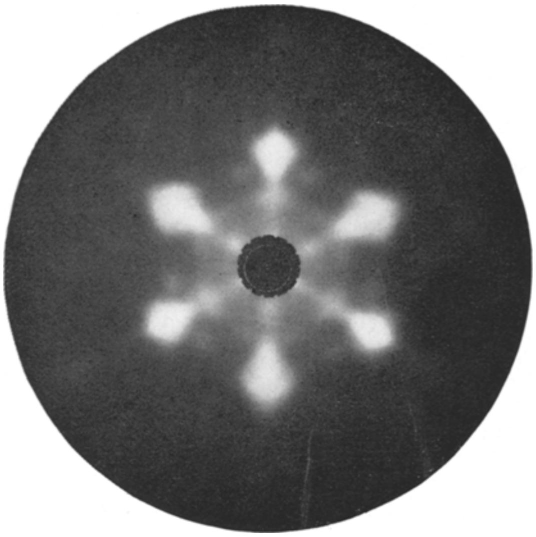

Figure 3 Back-reflection Laue photograph from gallium nitride sample.

3.3. Electron Diffraction Examination of Bulk Samples

The surfaces of all the samples examined consist of polycrystalline GaN only. Detailed results of the type and degree of orientation observed in the samples by electron diffraction are given in table II. The results of this examination are, with the exception of sample 20, in good agreement with those of the X-ray diffraction examination (see section 3.2). In the case of sample 20, the polycrystalline pattern recorded was characteristic of the GaN surface layer and not of the bulk of the GaN structure, which exhibited considerable directional orientation.

It is evident from table II that the presence of nitrogen in the gas atmosphere (NH_3:N_2::1:5) is highly beneficial to the establishment of extensively developed orientation on the surface of the resulting GaN. When nitrogen is not present, the surfaces of the resulting GaN are essentially unoriented.

TABLE II Details of preparation and results of ED examination of GaN grown by conversion from GaAs

Sample no.	Oxide preparation Ga_2O_3	Nitride preparation GaN	Comments on electron diffraction patterns*
16	$N_2 : O_2 :: 1 : 1$ 880° C; 1.5 h	$NH_3 : N_2 :: 1 : 5$ 880° C; 1 h	highly developed basal orientation
17	$N_2 : O_2 :: 1 : 2$ 880° C; 1.5 h	$NH_3 : N_2 :: 1 : 5$ 880° C; 1 h	highly developed basal orientation
18	O_2; 880° C; 1.5 h	$NH_3 : N_2 :: 1 : 5$ 880° C; 1 h	highly developed basal orientation
19	O_2; 880° C; 1.5 h	NH_3; 880° C; 1 h	unoriented polycrystalline pattern with superimposed highly oriented basal pattern
20	O_2; 880° C; 1.5 h	NH_3; 880° C; 1 h	unoriented polycrystalline pattern
21	O_2; 880° C; 1.5 h	NH_3; 880° C; 1 h	unoriented polycrystalline pattern with superimposed highly oriented basal pattern
23	O_2; 880° C; 1.5 h	—	no pattern due to excessive specimen charging

*N.B. X-ray diffraction patterns of these samples were all very similar indicating imperfect GaN with [0001] roughly parallel to [111] of original GaAs.

4. Discussion

The data listed in table I indicate that the procedure of growing gallium nitride on silicon carbide substrates produces thin films of the nitride, the perfection and orientation of which are temperature-dependent. Under the experimental conditions used, the highest degree of preferred orientation was obtained in the temperature range 600 to 700° C. As the substrate temperature is raised above about 700° C the orientation condition in the GaN films becomes less marked. This phenomenon is probably associated with the onset of dissociation of the nitride at these temperatures.

The procedure described above for the preparation of gallium nitride from single crystals of gallium arsenide, via an intermediate phase of gallium oxide, has been shown to be successful in that the final material formed is "single phase" gallium nitride.

The choice of 880° C for the preparation of the nitride from the oxide phase was established from an X-ray diffraction analysis of samples prepared over the temperature range 600 to 1100° C. This analysis showed that with an NH_3/N_2 gas mixture the lowest temperature at which conversion of β-Ga_2O_3 to GaN occurs is approximately 750° C and that dissociation of GaN becomes noticeable at temperatures in excess of 1000° C. A temperature of 880° C was therefore adopted as a convenient nitriding temperature.

The X-ray diffraction study has indicated that the transformation of GaAs to GaN through an intermediate stage of β-Ga_2O_3 is of a topotactic character. The atomic rearrangements are such that a $\langle 111 \rangle$ direction of GaAs, normal to the crystal surface, becomes a $\langle 100 \rangle$ direction of the intermediate β-Ga_2O_3 phase, and this in turn becomes the [0001] direction of the GaN product.

The breadth of the reflections in the X-ray diffraction powder photographs, the diffuseness of the "spots" and the absence of true hexagonal symmetry in the Laue photographs indicates that the GaN thus prepared remains structurally and texturally very imperfect. The pale yellow colour of the nitride samples suggests, according to Lorenz and Binkowski [8], that they contain excess oxygen. The grey colour is possibly due to nitrogen deficiency [16]. Such defects may well have a deleterious influence on perfecting the structure of the GaN phase and may account for much of the observed disorder.

It is apparent from the electron diffraction evidence given in table II that the presence of excess nitrogen in the nitriding gas mixture is required for the development of a high degree of directional orientation at the surface of the GaN. Absence of nitrogen from the gas mixture results in an essentially unoriented surface condition. As discussed above all the bulk samples of GaN exhibit degrees of orientation which are similar in character, and unaffected by the presence of nitrogen in the nitriding gas mixture. It is apparent, therefore, that the nitrogen affects only the surface condition of the GaN prepared under these conditions.

5. Conclusions

The preliminary results reported above are encouraging in that both preparation methods attempted have produced single phase gallium nitride.

In the case of the thin films deposited on to single crystal silicon carbide substrates, the degree of orientation suggests that the preparation of near single crystal material by this method is a practical possibility. The degree of structural distortion present in the bulk gallium nitride, however, is such that further work is required to assess the potentialities of this method of preparation.

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