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The thermal stability of AlN

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The thermal stability of AlN powders and thin films has been investigated using reflection high-energy electron diffraction (RHEED) and X-ray diffraction. AlN powder was treated thermally and chemically to assess the oxidation resistance of this compound and to identify the phases formed. The results show that AlN is stable up to 1000° C in air and remains stable up to 1400° C *in vacuo*. γ-AlOOH is formed when AlN is treated with water at 100° C but AlN does not react readily with atmospheric moisture at room temperature. The thermal stability of thin films of AlN on GaAs has been evaluated at temperatures between 900 and 1100° C in a nitrogen atomosphere. It was found that AlN did not oxidize under these conditions. Pure AlN is a suitable encapsulant for GaAs at high annealing temperatures in an inert atmosphere.

1. Introdution

Aluminium nitride is currently of great interest as an encapsulant to protect ion-implanted GaAs during annealing. The chemcial reactivity of AlN under these conditions is thus of practical importance. Kubaschevski and Evans [1] have reported that AlN decomposes when heated in air at 940 to 950° C whereas Lyutaya *et al.* [2, 9] state that AlN oxidizes when heated in air above 800° C. In addition, the oxidation of crystals of AlN has been studied by Slack and Chelly [3] who found that at room temperature a protective oxide layer, about 10 nm thick, formed on single crystals of AlN in 1 day. Lavrenku *et al.* [4] showed that the oxidation rate of sintered AlN in oxygen at 800 to 1100° C was very low and that at 1100° C only 8% was oxidized. Thus it was thought necessary to investigate the stability of AlN under conditions likely to be encountered as a result of encapsulation and annealing of ion-implanted GaAs. X-ray diffraction (XRD), and reflection high energy electron diffraction (RHEED) have been used to study treated AlN powders and thin films were used to investigate bulk and surface phases formed.

2. Experimental details

AlN powder (99%) was supplied by Koch Light Limited (UK) and had a particle size of 50 μm and a dark grey colour, and by Alfa Products (West Germany) which had a light grey colour and a finer particle size. XRD analysis was carried out using a Debye–Scherrer camera of 11.486 mm diameter Cu$K\alpha$ radiation and glass specimen capillaries of 0.5 mm diameter. The RHEED analysis was carried out using an operating voltage of 40 kV at background pressure of 3 to 5×10^{-5} torr. The sample holder was an aluminium block (2 cm × 1 cm × 1 cm) with a wide, shallow groove into which the powder was pressed. The surface was made as smooth as possible before analysis.

Samples of AlN powder contained in porcelain boats were heated in air in a muffle furnace for 3 h at temperatures from 600 to 1400° C. The samples were allowed to cool in the furnace before being analysed. Other samples of AlN powder were placed in quartz capsules 7 cm long and 2 cm diameter, which were evacuated to about 10^{-4} torr and sealed. These capsules were heated in a muffle furnace for different times at temperatures [3] from 600 to 1400° C, and then allowed to cool in the furnace.

In order to study the wet oxidation of AlN and to identify any oxidation products, AlN powder was treated with 30 wt % hydrogen peroxide. About 0.5 g AlN was placed in a 250 ml beaker with 125 ml H_2O_2 solution, covered with a clock glass and either (a) heated to boiling point for 10 min, or (b) stirred for 5 min and left at room temperature for 24 h. The suspensions were then filtered and the residues left to dry uncovered at room temperature for 24 h. The reaction of AlN with water was studied by placing about 0.5 g AlN into 125 ml water and boiling for 10 min, when ammonia gas was liberated and a white precipitate formed which was removed by filtration and then dried for 24 h in air. Thin films of AlN were preapared by vacuum evaporation of aluminium metal in an atmosphere of nitrogen and ammonia [5]. The annealing of AlN films was carried out using a graphite strip heater for a very short time (30 sec) in flowing nitrogen and at a temperature of 900 to 1100° C. This process is typical for the rapid thermal annealing of ion-implanted GaAs.

3. Results

Table I shows the results obtained for AlN heated in air for 3 h. The XRD analysis gives the composition of the bulk sample and the RHEED analysis gives that of the surface layer to a depth of a few nanometres. The typical RHEED pattern of the AlN powder at room temperature is shown in Fig. 1. For AlN heated to 1000° C the RHEED analysis revealed the presence of an unidentified phase (X, Fig. 2) which is possibly an oxide or oxynitride. However, on heating to 1200° C, the AlN was oxidized to α-Al_2O_3 (Fig. 3) but still

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TABLE I Effect of heating AlN powder in air* – bulk and surface

Temp (° C)	Phases present after heating for 3 h	
	XRD analysis (bulk)	RHEED analysis (surface)
600	AlN	AlN
800	AlN	AlN
1000	AlN	phase X
1200	α-Al_2O_3	phase X + α-Al_2O_3
1400	α-Al_2O_3	α-Al_2O_3

*Annealing *in vacuo* showed no sign of oxidation even for samples heated to 1400° C for more than 24 h.

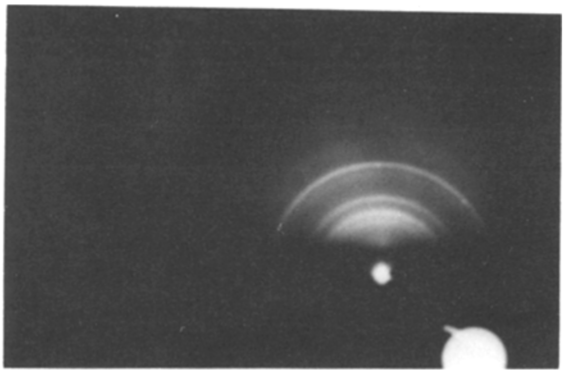

Figure 2 RHEED pattern for AlN powder heated at 1000° C.

contained a second phase on the surface which had a strong unidentified diffraction line at 0.288 nm (see Table II).

The samples of AlN heated *in vacuo* in quartz capsules for 24 h at temperatures from 600 to 1400° C contained only AlN when analysed by both XRD and RHEED. Table II shows the *d*-spacings of phase X obtained from the RHEED pattern of AlN heated in air at 1000° C and also shows the *d*-spacings obtained from AlN heated in air at 1200° C and *in vacuo* at 1400° C. Measured *d*-spacings of γ-AlOOH (Fig. 4) obtained from the surface of AlN reacted with boiling water, are also listed in the table and the standard patterns of AlN and α-Al_2O_3 are included for comparison. RHEED patterns from thin films of AlN on (1 0 0) GaAs are shown in Fig. 5. The diffraction pattern from the as-deposited AlN film (Fig. 5a) reveals the polycrystalline structure of the deposited layer and shows the presence of AlN only. This type of film, when annealed at 950° C, gave the RHEED pattern shown in Fig. 5b. Sharpening of the rings is clearly observed, but no change in the structure has occurred. An AlN thin film of the same type annealed at a higher temperature (1100° C) gave the diffraction pattern shown in Fig. 5c. Again, the diffraction lines are those of AlN alone, clearly demonstrating the oxidation resistance of the AlN thin film. However, some of the rings are "spotty" and this phenomenon may be explained as being due to recrystallization occurring in the layer at this temperature.

4. Discussion

AlN powder proved to be resistant to oxidation in air at temperatures up to about 1000° C. At higher temperatures an unknown phase, X, was formed on the surface. This phase could be an oxide or oxynitride of aluminium. The unknown phase, X, and α-Al_2O_3 seem to be related structures, but phase X is not α-Al_2O_3 since the strongest line of α-Al_2O_3 (0.346 nm) is absent in phase X. Furthermore, phase X was formed when thin films of aluminium were annealed at about 1000° C in nitrogen containing traces of air. On heating to 1200° C in air, AlN was transformed completely into α-Al_2O_3, although the pattern from the surface still contains weak traces of the line at 0.288 nm. When heated to 1400° C in evacuated capsules (10^{-4} torr) AlN powder did not react at the low oxygen pressure prevailing.

Thin films of AlN deposited on GaAs and then annealed in the temperature range 900 to 1100° C in a nitrogen atmosphere showed no sign of oxidation. However, at higher temperatures some sharpening of the arcs occurred. The appearance of spots in the arcs indicated recrystallization of some of the AlN at 1100° C. The stability of AlN at lower temperatures under various conditions was also investigated. AlN did not react with the oxidizing agent hydrogen peroxide, again indicating the stability of AlN towards oxidation. However, AlN reacted with hot water and the surface was converted to AlOOH (boehmite). Polycrystalline AlN did not form a surface oxide in air at room temperature, although Slack and Chelly [3] have reported that powders and single crystals form a protective layer of oxide 5 to 10 nm thick. Such a crystalline oxide was not detected in the

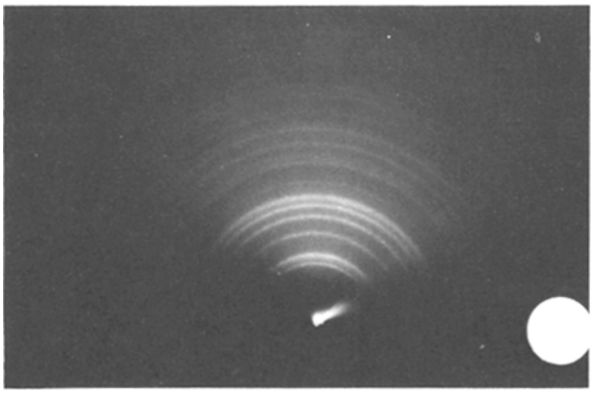

Figure 1 Standard RHEED pattern taken from powder AlN at room temperature.

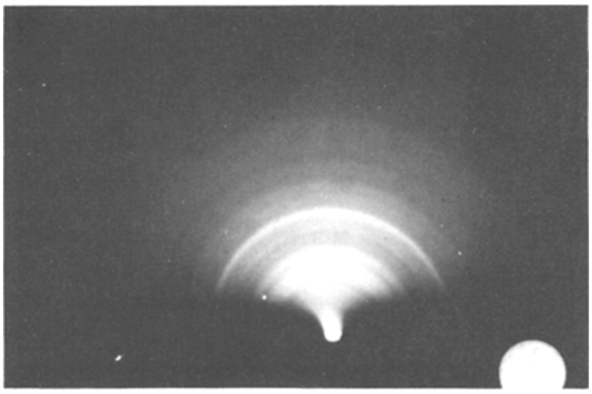

Figure 3 RHEED pattern obtained from AlN heated at 1200° C.

TABLE II Lattice *d*-spacings (nm) from RHEED patterns from surface of oxidized AlN

Standards				Results							
Standard RHEED pattern of AlN, room temp.		Standard RHEED pattern α-Al_2O_3, room temp.		AlN heated to 1400° C *in vacuo*		AlN heated in air at 1000° C		AlN heated at 1200° C in air		AlN reacted with H_2O at 100° C	
d (nm)	*I**	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*
		0.346	s					0.346	s		
										0.317	s
						0.290	s	0.288	s		
0.272	vs			0.272	vs						
0.250	m	0.252	s	0.250	m	0.250	vs	0.250	s		
0.238	vs			0.238	vs					0.235	s
		0.207	s			0.205	s	0.208	s		
0.183	s			0.184	s					0.188	vs
		0.175	m					0.176	m		
		0.159	m					0.159	m	0.165	m
0.155	s			0.155	s	0.155	w				
0.144	s	0.141	vs	0.141	s	0.144	vs	0.140	s	0.144	vs
0.131	s			0.131	s					0.132	vs
						0.122	w	0.122	w		
0.118	m			0.118	m						
0.115	m			0.115	m						
										0.113	m
Comments											
In good agreement with ASTM data card no. 25-1133		In good agreement with ASTM data card no. 10-173		Good agreement with AlN at room temperature		Unknown phase X formed		Mainly α-Al_2O_3, some unknown		γ-AlOOH boehmite formed	

*vs = very strong; s = strong; m = medium; w = weak.

present work. A crystalline oxide layer would have given its own RHEED pattern and an amorphous oxide layer woudl have blurred the RHEED pattern. The aluminium oxide hydroxide pattern obtained from the reaction with water showed that AlN does not dissolve readily in water to form aluminium hydroxide. The formation of the crystalline layer of AlOOH prevented further reaction of the AlN with water. It had previously been reported that treatment with water gave either $Al(OH)_3$ [6]:

$$AlN + 3H_2O \rightarrow NH_3 + Al(OH)_3$$

or α-Al_2O_3 [7]

$$2AlN(s) + 3H_2O(g) \rightarrow NH_3(g) + \alpha\text{-}Al_2O_3(s)$$

The present work shows that the probable reaction is:

$$AlN + 2H_2O \xrightarrow{100^\circ C} NH_3 + AlOOH$$

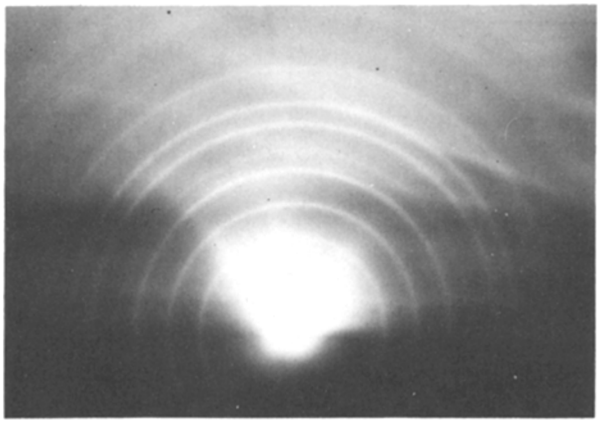

Figure 4 RHEED pattern obtained from AlN reacted with hot H_2O (γ-AlOOH).

5. Conclusions

AlN is suitable as an encapsulant for GaAs under non-oxidizing conditions up to 1400° C; this is at least 200° C higher than might be required in practice for annealing GaAs. Some recrystallization of the AlN thin film occurred between 950 and 1100° C. Polycrystalline AlN is also stable at room temperature under normal conditions of use.

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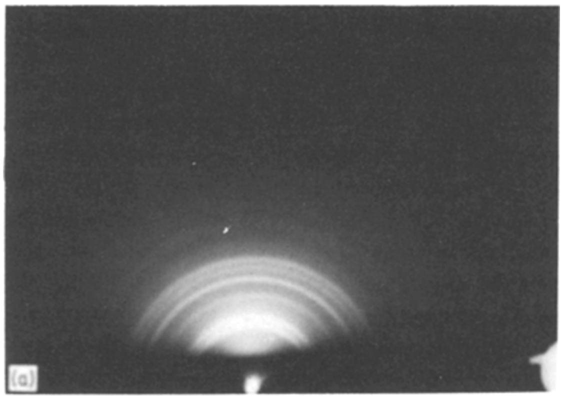

Figure 5 RHEED patterns obtained from thin AlN films on (1 0 0) GaAs. (a) As-deposited by vacuum evaporation of pure Al metal in N_2–NH_3 mixture at 3×10^{-3} torr. (b) Annealed at 950° C for 30 sec. (c) Annealed at 1100° C for 30 sec.

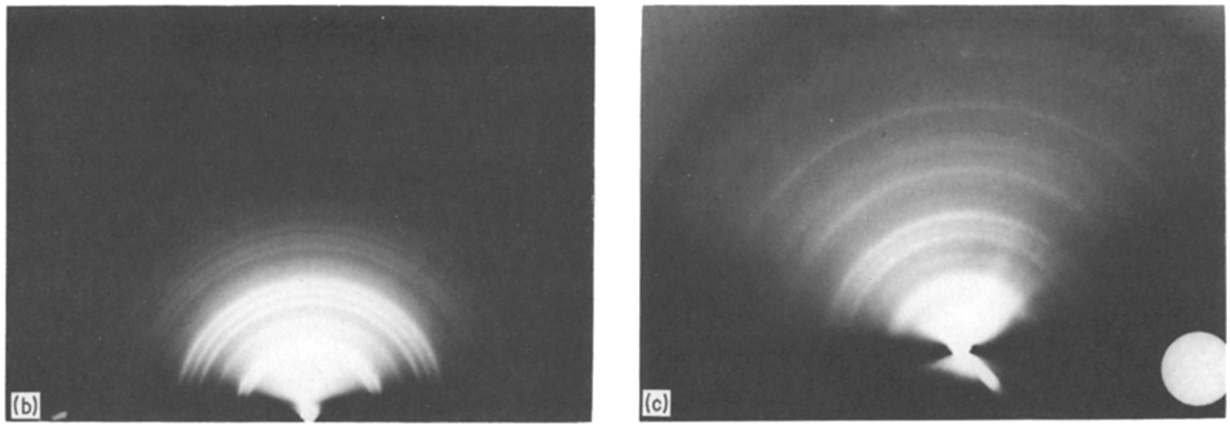

Figure 5 Continued.

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