Adsorption Characteristics of Powders of Nanometric Gallium Nitride and Aluminium Nitride

L. Czepirski[1]*, J.F. Janik[1], E. Komorowska-Czepirska[1] and R.L. Wells[2] *(1) Faculty of Fuels & Engineering, University of Mining and Metallurgy, al. Mickiewicza 30, 30-059 Cracow, Poland. (2) Department of Chemistry, Duke University, Durham, NC 27708, USA.*

ABSTRACT: The results of studies on new precursors for the preparation of gallium nitride and aluminium nitride were presented. The samples obtained were characterised by argon adsorption at 77 K. The variation of the porous structure parameters with the pyrolysis temperature was discussed. The adsorption of water vapour and the selectivity of adsorption with respect to some gases at 298 K were also investigated.

INTRODUCTION

The thermal conversion of suitable chemical precursors via efficient elimination and condensation reactions may yield various forms of a number of ceramic and semiconducting materials. Thus, nanocrystalline metal nitrides, sulphides and oxides may be produced as fibres, whiskers, aerosol powders, foams, thin films and high surface area solids. In this regard, the syntheses and conversions of Group 13–15 (III–V) precursors have been of interest since the resulting products are very important for modern application.

In this report, the results of studies on new precursors for the preparation of gallium nitride and aluminium nitride are presented. Transamination/deamination reactions afforded a new polymeric gallium imide, $[Ga(NH_{3/2})]_n$, which was converted at appropriate temperatures to nanocrystalline powders of GaN. Similarly, nanocrystalline powders of AlN were obtained from the thermal decomposition of aluminium amide-imide, $[Al(NH_2)NH]_n$. In addition, precursor systems for the mixed nitrides AlN/GaN that afforded the composites of the nitrides with a complex phase character have been investigated.

Previous work showed that the pyrolysis temperature employed influenced the adsorption characteristics of the samples under study.

EXPERIMENTAL

The nanocrystalline nitride powder samples were prepared by synthesis procedures described by Janik and Wells (1996, 1997, 1998), the various steps employed being depicted schematically in Figure 1. Polymeric precursors from gallium or aluminium amides were pyrolysed at different temperatures and a series of nitride samples obtained.

The argon adsorption/desorption isotherms were determined at 77 K using a volumetric technique.

Water adsorption isotherms at 298 K were measured volumetrically for selected samples using a device which allowed simultaneous determination of the isotherms and the adsorption kinetics (Ciembroniewicz and Komorowska-Czepirska 1985).

*Author to whom all correspondence should be addressed. E-mail: czepir@nci.agh.edu.pl.
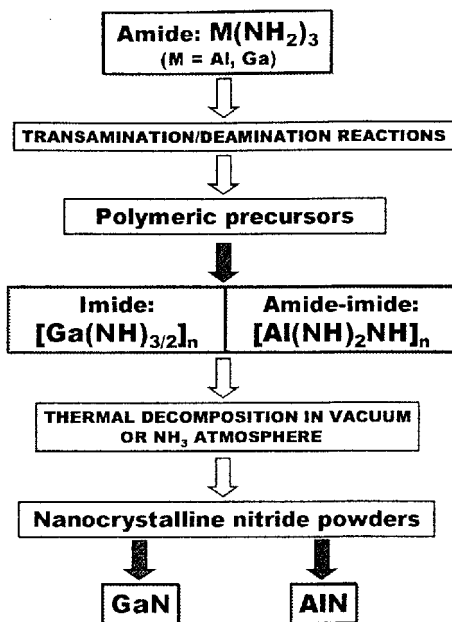
Figure 1. Synthesis routes for the preparation of nanocrystalline nitride powders.

The selectivity of adsorption with respect to some gases (nitrogen, oxygen, methane and carbon dioxide at 298 K) was also investigated.

RESULTS

Characterisation by argon adsorption

The argon adsorption/desorption isotherms (Figure 2) were typical for adsorbents exhibiting a combined micro- and meso-porous structure. According to the BDDT classification (Sing *et al.* 1985), the isotherm shape was type IV with a type H1–H2 hysteresis loop, characteristic of cylindrical pores.

To facilitate comparison of the sorption properties of all the samples under study, the argon isotherms were used to determine the corresponding capillary structure parameters. Table 1 lists the total surface area (S_{BET}), micropore and mesopore volumes (V_{mi} and V_{me}), as well as the area (S_{me}) and mean radii (r_{me}) of the mesopores as determined by the procedure proposed by Dubinin (1960). The mean dimensions of the micropores (x_{mi}) were also calculated. In the designation of samples employed, the numeral denotes the pyrolysis temperature.
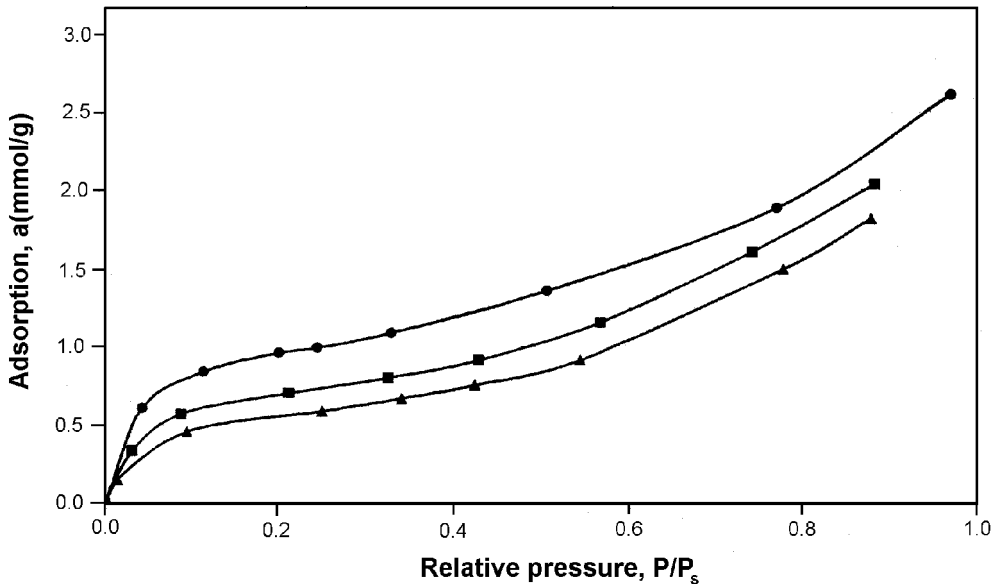
The results showed that the nitrides studied exhibited a wide range of porosity. In accordance with the volume of adsorbate sorbed, the characteristics of the porous structure changed when the pyrolysis temperature increased. This result was probably produced by the collapse of pores during thermal treatment.
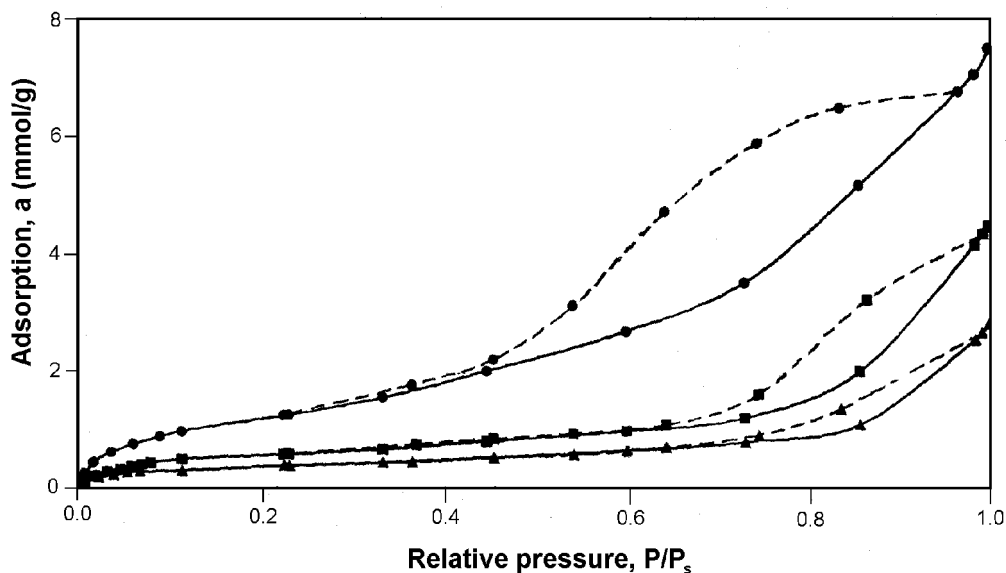
Figure 2. Argon adsorption/desorption isotherms measured at 77 K for selected aluminium nitride samples. Data points: ●, AlN900; ■, AlN1100; ▲, AlN1200.

TABLE 1. Capillary Structure Parameters of Samples Studied

Sample	S_{BET} (m²/g)	V_{mi} (cm³/g)	V_{me} (cm³/g)	S_{me} (m²/g)	r_{me} (nm)	x_{mi} (nm)
GaN300	129	0.057	0.024	19.6	2.47	0.93
GaN450	224	0.044	0.153	75.3	4.06	1.01
GaN600	148	0.034	0.127	57.0	4.46	1.13
GaN700	73	0.028	0.120	52.2	4.60	1.22
GaN900	16	0.006	0.032	11.3	5.61	1.17
GaN1100	6	0.005	0.004	1.3	5.80	2.15
AlN700	206	0.067	0.190	168.8	2.10	1.24
AlN900	113	0.032	0.187	149.3	2.50	1.13
AlN1000	54	0.023	0.177	81.0	4.68	1.37
AlN1100	50	0.017	0.163	49.3	6.61	1.21
AlN1200	33	0.011	0.099	27.0	7.36	1.06
AlGaN700	147	0.046	0.221	136.2	2.30	1.05
AlGaN900	74	0.033	0.156	96.5	4.57	1.39

Figure 3. Water vapour adsorption isotherms measured at 298 K for selected nitride samples. Data points: ●, AlGaN700; ■, AlGaN900; ▲, AlN1000.

Water sorption characteristics

As typical examples, the water vapour adsorption isotherms for samples AlGaN700 and AlGaN900 are shown in Figure 3. According to the IUPAC classification, isotherms of the kind depicted are of type II and indicate the multilayer sorption of water vapour over a wide range of relative pressure.

The water vapour isotherms were analysed by applying the modified BET equation in the form proposed by Kats *et al.* (1999):

$$a = \frac{a_m Ch[1 - h^{n-(2-d_{fs})}][1 + h^{n-(2-d_{fs})}]^{1/3}}{(1 - h)(1 - h + Ch)} \tag{1}$$

where a = adsorption capacity, h = relative pressure, a_m, C = BET constants, n = multilayer number and d_{fs} = sorbent fractal dimensions.

Using the BET C-constant obtained experimentally in the equation:

$$E_1 - E_L = RT \ln(C) \tag{2}$$

where E_1 = first layer heat of adsorption, E_L = heat of condensation, R = gas constant and T = absolute temperature, it was possible to calculate the first layer heat of adsorption. The results obtained are listed in Table 2.

TABLE 2. Parameter Values Obtained by Application of Modified BET Equation to Water Vapour Adsorption Isotherms Determined on Selected Samples

Sample	BET C-constant	a_m (mmol/g)	d_{fs}	E_1 (kJ/mol)
GaN450	89	0.541	2.51	46.5
GaN700	73	0.476	2.41	46.1
GaN900	62	0.375	2.75	45.6
AlN1000	67	0.547	2.77	45.8
AlGaN700	58	0.607	2.78	45.5
AlGaN900	48	0.464	2.65	45.0

It can be seen that the values of the monolayer capacity were in good agreement with the volume of the pores in the samples under study. The BET C-constant values given in Table 2 show that the strength of the vapour–adsorbent interactions decreased as the pyrolysis temperature increased. In conjunction with this decrease, the monolayer became less compact and it is probable that the shielding effect reduced the gas–solid interactions. The relatively high value of the monolayer adsorption energy suggests that the water vapour formed an oriented chemisorbed layer.

Adsorption of gases at room temperature

Some selected samples were used for investigating the adsorption of gases at 298 K over the pressure range 0–500 Torr. All samples studied showed good equilibrium selectivity with respect to methane, carbon dioxide, nitrogen and oxygen. The isotherms for sample GaN450 are depicted in Figure 4.
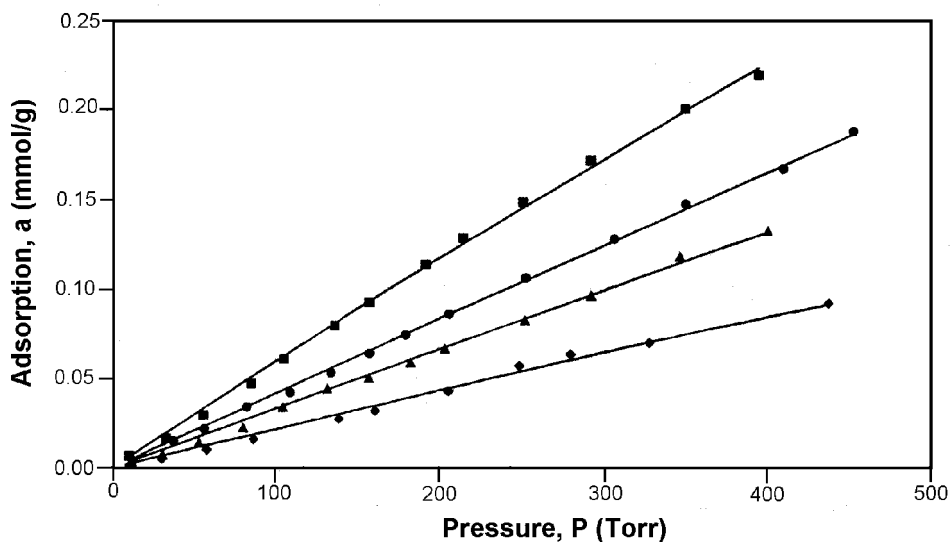
Figure 4. Adsorption isotherms for selected gases as measured at 298 K for sample GaN450. Data points: ■, CO_2; ●, N_2; ▲, CH_4; ◆, O_2.

TABLE 3. Parameters of Langmuir Equation and
Selectivity of Adsorption for Gases Studied

(a) Langmuir parameters

Gas	m	$10^5 b$	$10^6 K_H$
N_2	0.2558	2.271	5.809
CH_4	0.1611	3.293	5.305
CO_2	0.1446	20.000	28.920
O_2	0.1939	1.764	3.420

(b) Selectivity of adsorption

CO_2/N_2	5.0
CO_2/CH_4	5.5
CO_2/O_2	8.5

It was concluded that the Langmuir isotherm gives a good representation of the adsorption data. The parameters of the Langmuir equation for sample GaN450, as well as the selectivity calculated from the Henry constants, are listed in Table 3.

CONCLUSIONS

By varying the synthesis/pyrolysis conditions in a systematic fashion, the pore structure and adsorption properties of gallium and aluminium nitrides can be altered over a fairly wide range. The main factors influencing the adsorption properties of the nitrides are the type of precursor employed, as well as the temperature and conditions used for its decomposition.

The preliminary results reported show that the pore structure may be manipulated to yield products with desirable properties. A number of processing parameters remain to be explored to optimise the pore structure for particular applications. In addition, a thorough study of the properties of these unique materials remains to be undertaken.

ACKNOWLEDGEMENTS

REFERENCES

Ciembroniewicz, A. and Komorowska-Czepirska, E. (1985) *Przem. Chem.* **66**, 265.
Dubinin, M.M. (1960) *Chem. Rev.* **60**, 235.
Janik, J.F. and Wells, R.L. (1996) *Chem. Mater.* **8**, 2708.
Janik, J.F. and Wells, R.L. (1997) *Inorg. Chem.* **36**, 4135.
Janik, J.F. and Wells, R.L. (1998) *Chem. Mater.* **10**, 1613.
Kats, B.M., Kutarov, V.V. and Kutovaya, L.V. (1999) *Colloids Surf. A* **157**, 95.
Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J. and Siemieniewska, T. (1985) *Pure Appl. Chem.* **57**, 603.