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Solvothermal synthesis: a new route for preparing nitrides

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Abstract

Solvothermal synthesis appears to be an interesting route for preparing nitrides such as gallium nitride and aluminium nitride, using ammonia as solvent. A nitriding additive is used to perform the reaction and, in the case of gallium nitride, is encapsulated by melt gallium. The syntheses are performed in the temperature range 400–800 °C and in the pressure range 100–200 MPa. The synthesized powders are characterized by x-ray diffraction and scanning electron microscopy. Finely divided gallium nitride GaN and aluminium nitride AlN, both with wurtzite-type structure, can be obtained by this route.

1. Introduction

III–V nitrides are very promising materials. Indeed, gallium nitride is a wide-bandgap semiconductor (3.5 eV) and exhibits very high thermal and chemical stability. Thus, this material is promising for many applications in micro- and opto-electronics such as light emitting diodes (LEDs), laser diodes (LDs), photodetectors etc. Moreover, aluminium nitride is also a wide-bandgap semiconductor (6.2 eV) and exhibits high thermal conductivity and electrical resistivity. These properties lead to dielectric or piezoelectric applications.

To produce high-performance devices, in particular for gallium nitride, single crystals are necessary; this has become a worldwide challenge [1, 2]. The high-pressure nitrogen solution process, developed by Porowski leads to very high-quality gallium nitride crystals but implies very high pressures (1–2 GPa) and temperatures (1400–1700 °C) [3]. The solvothermal crystal growth of III–V nitrides with reduced temperature and pressure conditions appears a suitable route, as developed in the case of α-quartz (replacing the solvent water by ammonia). Such a process is based on the solubility difference of a nutrient in an appropriate solvent, which

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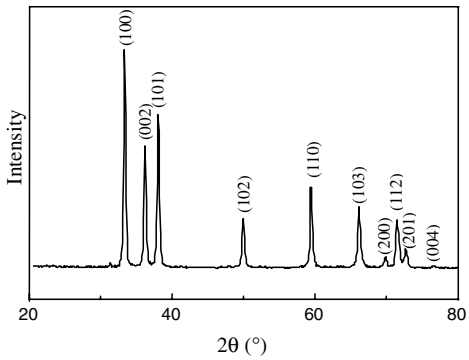

Figure 1. XRD pattern of aluminium nitride prepared with NH_2NH_3Cl (650 °C, 200 MPa and NH_2NH_3Cl/Al molar ratio = 1).

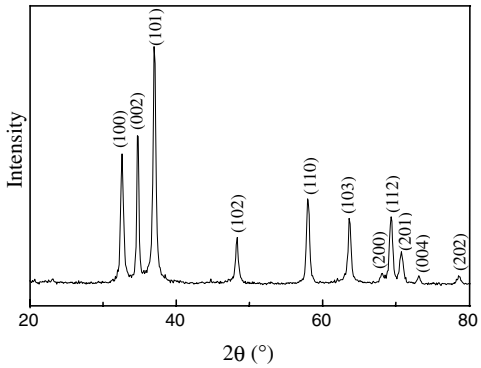

Figure 2. XRD pattern of gallium nitride prepared with NH_2NH_3Cl (650 °C, 200 MPa and NH_2NH_3Cl/Ga molar ratio = 1).

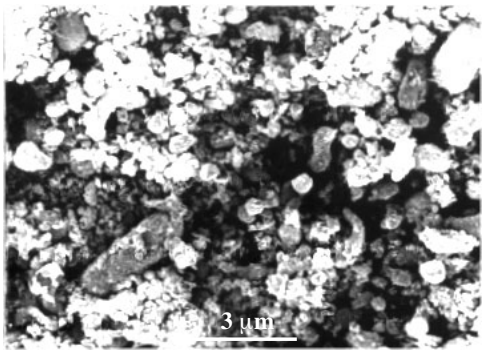

Figure 3. SEM image of aluminium nitride prepared with NH_2NH_3Cl (650 °C, 200 MPa and NH_2NH_3Cl/Al molar ratio = 1).

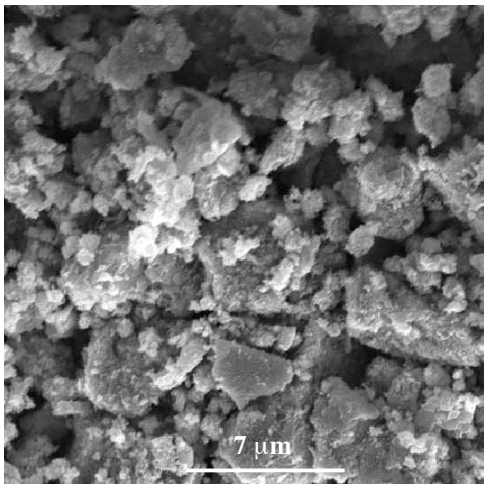

Figure 4. SEM image of gallium nitride prepared with NH_2NH_3Cl (650 °C, 200 MPa and NH_2NH_3Cl/Ga molar ratio = 1).

is governed by a temperature gradient ΔT in a reaction vessel [4]. In this way, Ketchum and Kolis [5] are working on the solubility of GaN in NH_3 with a mixture of KI and KNH_2 as mineralizers. The nutrient used in solvothermal crystal growth must be finely divided for improving the solubility and exhibit a good purity. The first step of solvothermal crystal growth is the synthesis of such a nutrient and we propose a route to obtain it: the solvothermal synthesis of nitrides at high pressure and low temperature.

2. Experimental details

The synthesis of aluminium nitride is realized by mixing particles of metallic aluminium and a nitriding additive. The mixture is introduced into a container, placed in a high-pressure vessel, filled with ammonia and heated by a furnace. This step is carried out in a glove box in order to prevent the oxidation or hydrolysis of the reagents. The tested nitriding additive is hydrazine hydrochloride NH_2NH_3Cl and the experimental conditions are 650 °C and 200 MPa.

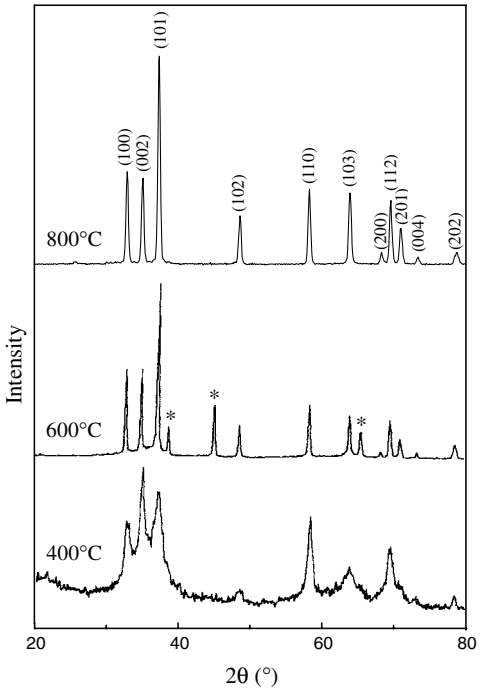

Figure 5. XRD pattern of gallium nitride prepared with NaN_3 (100 MPa, NaN_3/Ga molar ratio = 1.5).

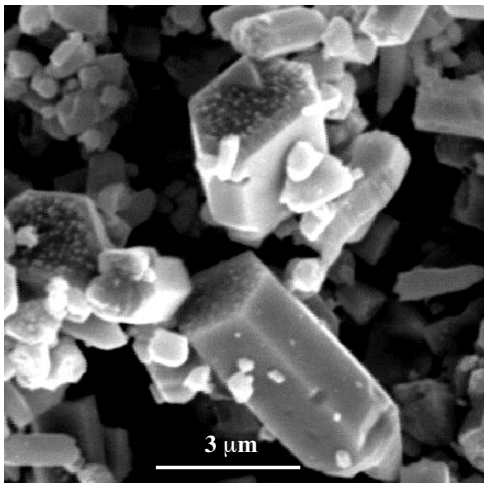

Figure 6. SEM image of gallium nitride prepared with NaN_3 (600 °C, 100 MPa and NaN_3/Ga molar ratio = 1.5).

For the synthesis of gallium nitride, the process is slightly different due to the very low melting point of gallium (29.8 °C). To increase its specific area and so its reactivity, melt gallium is mixed with the finely divided nitriding additive. Then the gallium encapsulates the nitriding additive. The following steps are the same as those that have been described previously for aluminium nitride. The tested nitriding additives are hydrazine hydrochloride NH_2NH_3Cl and sodium azide NaN_3. The experimental conditions are 650 °C, 200 MPa with NH_2NH_3Cl, and 400–800 °C, 100 MPa with NaN_3.

The synthesized products are washed according to the nitriding additive nature. With NH_3NH_2Cl as additive, the NH_4Cl residue easily sublimates by heating at 500 °C. The residues of the reactions with NaN_3 are eliminated by washing the powder with aqua regia and ethanol; the powder is then dried at 110 °C.

The nitrides are characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM).

3. Results and discussion

We first present the results obtained for the synthesis of aluminium and gallium nitrides with NH_2NH_3Cl.

The XRD patterns of aluminium and gallium nitride synthesized at 650 °C and 200 MPa are presented on figures 1 and 2 respectively. The samples are well crystallized and no impurity can be detected. The indexation of all the diffraction peaks is consistent with the wurtzite-type structure in both cases.

SEM images of these aluminium and gallium nitrides prepared at 650 °C and 200 MPa are presented in figures 3 and 4 respectively. The observed particles have micrometric size, which is consistent with a nucleation process enhanced in supercritical conditions.

The temperature effect is studied in the case of the synthesis of gallium nitride with NaN_3. Figure 5 presents the XRD patterns of gallium nitrides synthesized at 400–600–800 °C at 100 MPa. Whatever the temperature, no impurity can be detected and the indexation of all the diffraction peaks is consistent with the wurtzite-type structure. The peaks indexed with a star for the sample synthesized at 600 °C come from the aluminium sample holder.

Gallium nitride can be synthesized at 400 °C but the so-obtained material is poorly crystallized. One can remark that the full width at half-maximum (FWHM) of the diffraction peaks decrease while temperature increases. So increasing temperature allows a strong improvement of the crystallinity of the material. Nevertheless, 600 °C seems to be a sufficient temperature to obtain well crystallized gallium nitride.

An SEM image of gallium nitride prepared at 600 °C and 100 MPa is presented in figure 6. The crystallites exhibit various well defined morphologies with hexagonal shapes. The average size of these hexagonal crystallites increases at higher growth temperature, which underlines the beginning of a crystal growth process.

The comparison of the SEM micrograph of GaN prepared either with NH_2NH_3Cl or NaN_3 as nitriding additives suggests that the sodium metal resulting from the decomposition can play the role of a flux able to induce a crystal growth process [6].

4. Conclusion

Solvothermal reactions with ammonia are appropriate for the synthesis of finely divided nitrides. Such materials may be used as nutrients in a crystal growth process.

References

[1] Buboz J Y 2000 *C. R. Acad. Sci., Paris* **t1** 71–80
[2] Nakamura S 1998 *Proc. MRS Fall Meeting (Boston, MA 1998)*
[3] Porowski P 1995 *Proc. XXIII ISSC Acta Phys. Pol.* A **87** 295–302
[4] Demazeau G, Lafon F, Curtet J and Largeteau A 1994 *High Pressure Res.* **12** 329–35
[5] Ketchum D R and Kolis J W 2001 *J. Cryst. Growth* **222** 431–4
[6] Yamane H, Shimada M, Clarke S J and Di Salvo F J 1997 *Chem. Mater.* **9** 413–6