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Template assisted design of microporous gallium nitride materials†

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For the first time the synthesis of a porous gallium nitride material ($GaN_{1.15}H_{1.18}O_{0.06}C_{0.04}$) with narrow pore size distribution in the micropore regime using a nonylamine assisted sol–gel route is reported. The yellow solid has a very high micropore volume of 0.176 cm^3 g^{-1} comparable to that of zeolitic solids.

Gallium nitride (GaN) has been widely studied for the manufacture of blue light emitting diodes since cubic as well as hexagonal GaN are both direct wide band gap semiconductors (3.2–3.3 eV for *c*-GaN and 3.39 eV for *h*-GaN at 300 K).[1] The ternary systems (In,Ga)N are used for the fabrication of efficient green, blue or violet light-emitting diodes,[2] laser diodes and other electronic and optoelectronic devices.[3] They are typically grown as thin films by chemical vapor deposition (CVD) using organometallic precursors like $GaMe_3$ and ammonia.[4] Recently also gallium azides have been considered as single-source precursors for the synthesis of thin films and nanocrystalline GaN *via* detonation,[5,6] chemical vapour deposition (CVD),[7,8] solvothermal reaction[9] and decomposition at low temperature.[10] Polymer intermediates like $\{Ga(NCN)_{3/2}\}_n$ and $\{Ga(NH)_{3/2}\}_n$ were developed by Aldinger, Gladfelter and Wells for the generation of nanocrystalline and bulk GaN ceramics using $GaCl_3$ and $Me_3SiNCNSiMe_3$[11] for the carbodiimide polymer and cyclotrigallazane, $[H_2GaNH_2]_3$[12–15] or hexakis(dimethylamino)digallane, $Ga_2(NMe_2)_6$ for the imide polymer as precursors.[16–20]

Whereas these methods are focusing on the development of *dense* GaN materials for nanoparticular, ceramic or thin film applications, our interest is to produce inorganic nitrides as *porous* solids with high accessible surface area and well defined pore size for applications in heterogeneous catalysis or size selective adsorption.[21–24] One way to create porosity in such materials is to use primary aliphatic amines such as *n*-dodecylamine as templates in combination with sol–gel techniques.[22] The ammonolytic condensation of $(Me_2N)_3SiNH_2$ into $Si(NH)_2$, for example, affords microporous silicon nitride materials with well defined pore size in the micropore regime. They can be used as educt selective superbase catalysts.[22]

For the design of microporous gallium nitride materials, we have now successfully used this template assisted strategy. A transamination reaction of $Ga_2(NMe_2)_6$ in an aprotic solvent such as toluene affords a gallium imide gel. An additive such as nonylamine acts as a template and is occluded in the inorganic network during this gel formation. After filtration, hot toluene-extraction and drying under vacuum, the amine can be removed by heating the body in an ammonia flow reactor for 12 hours.

The resulting yellow powder (C_9-GaN) is highly porous according to nitrogen physisorption measurements carried out at 77 K (Fig. 1). The specific micropore volume (V_g = 0.176 cm^3 g^{-1}) is extremely high for a material with such a high density (ρ_{GaN} = 6.08 g cm^{-3}).[25] The isotherm is of type I and thus the majority of pores have a diameter below 2 nm. A hysteresis at $P/P_0 > 0.42$ is not observed, precluding the presence of mesopores. The mean pore diameter is 10.7 Å using Horvath-Kawazoe (HK) type analyses and the slit pore model. However, this number is only a rough approximation since interaction potentials and pore models for porous nitrides are still not well developed. Additionally, a smaller nitrogen take-up at $0.01 < P/P_0 < 0.3$ indicates the presence of a few wider pores (less than 10 %) that appear as a shoulder in the HK-pore size distribution (Fig. 1, inlay) with diameters ranging from 12 to 30 Å. Argon physisorption isotherms at 87.5 K give the same result (d_{HK} = 10.8 Å) but logarithmic plots do not allow the localization of an inflection point as observed for crystalline microporous solids, probably due to the presence of the wider pores.[26]

The effect of the template is most impressively shown by comparing the nitrogen physisorption isotherms of materials generated with (C_9-GaN) and without nonylamine additives (*NT*-GaN, Fig. 1). In contrast to C_9-GaN with a type I isotherm and a single point surface area of S_g = 372 m^2 g^{-1} (P/P_0 = 0.2) non-templated materials have type II isotherms, a characteristic feature of nanocrystalline powders with a somewhat broader particle size distribution. For *NT*-GaN the specific surface area is also high (S_g = 320 m^2 g^{-1} determined by BET analysis) but interparticle porosity is widely scattered. Thus for *NT*-GaN micropores contribute less than 30% to the cumulative pore volume whereas for C_9-GaN over 90% of the pores are below 2.0 nm. Clearly the addition of nonylamine during the imide gel formation is responsible for the well defined pore size distribution and microporosity of the product C_9-GaN.

Whereas for silicon nitride materials an increase in the micropore size was observed using amines of increasing chain length[22] so far we have been unable to prove this effect for gallium nitride materials probably due to superimposed sintering effects. The latter dominate at higher temperatures and with prolonged heat treatments necessary for the template removal and lead to an increasing number of secondary micropores.

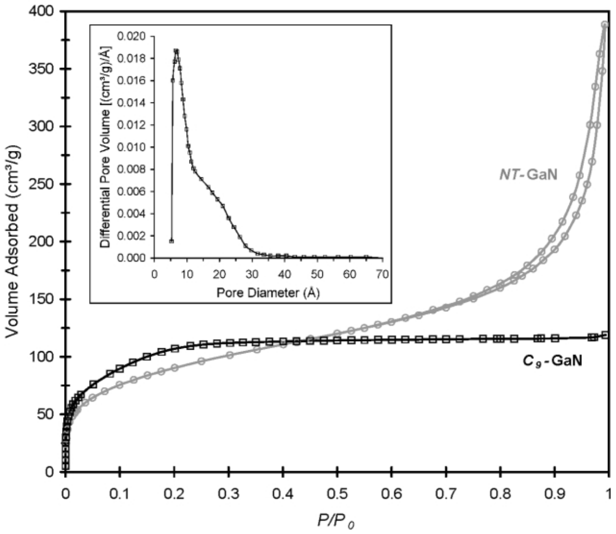

Fig. 1 Nitrogen physisorption isotherms at 77 K of C_9-GaN and *NT*-GaN and Pore Size Distribution of C_9-GaN (inlay).

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† Electronic supplementary information (ESI) available: experimental details, XRD powder patterns, UV/Vis and FTIR spectra. See http://www.rsc.org/suppdata/cc/b3/b300348e/

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The chemical composition of C_9-GaN is $GaN_{1.15}H_{1.18}O_{0.06}C_{0.04}$ with a N/Ga ratio higher than the expected 1.00 due to residual NH and NH_2 groups. They are clearly identified by FTIR spectroscopy with a broad band at 3204 cm^{-1} (ν(NH)), a weaker band at 1501 cm^{-1}, and a broad band at 950 cm^{-1}.[14] If the higher N content is assumed to be caused by surface NH_2 groups alone, the surface coverage would be approximately 4.2 nm^{-2}. In addition, traces of carbon (0.6 wt% for C_9-GaN) remain in the porous solids due to a small residual degree of incomplete transamination during processing (gel formation and calcination). According to the FTIR spectra these impurities are either NMe_2 groups (2962 and 1260 cm^{-1}) or $C\equiv N$ groups (2092 cm^{-1}). Oxygen contamination is relatively low in C_9-GaN if all synthetic steps are carefully carried out under rigorous exclusion of water and air.

Interestingly, the pore arrangements are not ordered but a low degree of crystallinity is detected using wide angle scattering which is unexpected since the pore walls must be only few nanometers in size. The X-ray powder pattern of C_9-GaN shows no peaks below 20° (2θ) but three broad reflections centered at 34.7, 58.0 and 68.5° (2θ) similar to those reported for materials prepared *via* transamination of $[H_2GaNH_2]_3$ and $Ga_2(NMe_2)_6$. They are assigned to the 111, 220 and 311 reflections of *c*-GaN respectively[18,19,27] or indicate a mixture of cubic and hexagonal GaN.[13,16] From the surface area (372 m^2 g^{-1}) an average particle diameter of 2.7 nm can be estimated assuming a bulk density of 6.08 g cm^{-3} for GaN and a powder consisting of spherical nanoparticles. Domains of such a small size are expected to cause significant size broadening in XRDs even if they are highly crystalline.

The extremely high porosity is confirmed by TEM studies of C_9-GaN (Fig. 2). They allow the nanometer-sized pores to be discerned. The worm like pores are evenly distributed in the bulk materials but higher magnifications are difficult to attain due to the high porosity giving rise to instabilities with increasing electron beam intensity.

UV/Vis spectra of C_9-GaN are similar to those of bulk GaN. A quantum size effect due to the small wall thickness was not observed but an additional shoulder close to the absorption edge was found comparable to the exciton feature reported by Benaissa *et al.* for nanocrystalline GaN.[28]

The role of the template is still not fully understood. In zeolite chemistry templates typically function as (hydrated) units that tend to organize the condensation of cluster units into an open framework. On the other hand, surfactant molecules can also cover the outer surface of nanosized particles and stabilize such colloids with uniform size distributions. Such particles may arrange and gradually condense into materials that display porosity in the micropore regime after surfactant removal.[29] In that respect, the microporous materials presented here may also be seen as well arranged nanoparticle assemblies with high and uniform interparticle porosity.

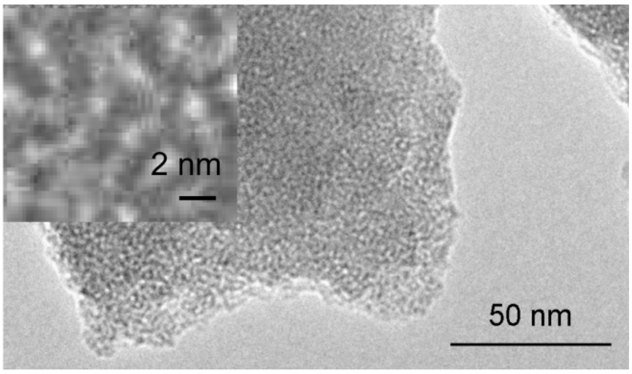

Fig. 2 TEM image of C_9-GaN.

Summarizing, we have for the first time prepared gallium nitride materials with very high specific micropore volume and well defined pore size distribution in the micropore regime using an oxygen free sol–gel route.

Notes and references

1 H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov and M. Burns, *J. Appl. Phys*, 1994, **76**, 1363.
2 S. Nakamura, *Science*, 1998, **281**, 956.
3 S. J. Pearton, F. Ren, A. P. Zhang and K. P. Lee, *Mater. Sci. Eng., R*, 2000, **30**, 55.
4 D. A. Neumayer and J. G. Ekerdt, *Chem. Mater.*, 1996, **8**, 9.
5 A. C. Frank and R. A. Fischer, *Adv. Mater.*, 1998, **10**, 961.
6 A. C. Frank, F. Stowasser, H. Sussek, H. Pritzkow, C. R. Miskys, O. Ambacher, M. Giersig and R. A. Fischer, *J. Am. Chem. Soc.*, 1998, **120**, 3512.
7 R. A. Fischer, A. Miehr, E. Herdtweck, M. R. Mattner, O. Ambacher, T. Metzger, E. Born, S. Weinkauf, C. R. Pulham and S. Parsons, *Chem.-Eur. J.*, 1996, **2**, 1353.
8 H. Sussek, O. Stark, A. Devi, H. Pritzkow and R. A. Fischer, *J. Organomet. Chem.*, 2000, **602**, 29.
9 L. Grocholl, J. J. Wang and E. G. Gillan, *Chem. Mater.*, 2001, **13**, 4290.
10 J. McMurran, J. Kouvetakis, D. C. Nesting, D. J. Smith and J. L. Hubbard, *J. Am. Chem. Soc.*, 1998, **120**, 5233.
11 D. Rodewald, J. Bill, U. Beck, M. Puchinger, T. Wagner, A. Greiner and F. Aldinger, *Adv. Mater.*, 1999, **11**, 1502.
12 J. W. Hwang, S. A. Hanson, D. Britton, J. F. Evans, K. F. Jensen and W. L. Gladfelter, *Chem. Mater.*, 1990, **2**, 342.
13 J. W. Hwang, J. P. Campbell, J. Kozubowski, S. A. Hanson, J. F. Evans and W. L. Gladfelter, *Chem. Mater.*, 1995, **7**, 517.
14 J. A. Jegier, S. McKernan and W. L. Gladfelter, *Chem. Mater.*, 1998, **10**, 2041.
15 J. A. Jegier, S. McKernan, A. P. Purdy and W. L. Gladfelter, *Chem. Mater.*, 2000, **12**, 1003.
16 J. F. Janik and R. L. Wells, *Chem. Mater.*, 1996, **8**, 2708.
17 J. F. Janik, R. L. Wells, J. L. Coffer, J. V. St John, W. T. Pennington and G. L. Schimek, *Chem. Mater.*, 1998, **10**, 1613.
18 K. E. Gonsalves, G. Carlson, S. P. Rangarajan, M. Benaissa and M. JoseYacaman, *J. Mater. Chem.*, 1996, **6**, 1451.
19 K. E. Gonsalves, G. Carlson, S. P. Rangarajan, M. Benaissa and M. JoseYacaman, *Nanostruct. Mater.*, 1997, **9**, 237.
20 O. I. Micic, S. P. Ahrenkiel, D. Bertram and A. J. Nozik, *Appl. Phys. Lett.*, 1999, **75**, 478.
21 S. Kaskel, D. Farrusseng and K. Schlichte, *Chem. Commun.*, 2000, 2481.
22 D. Farrusseng, K. Schlichte, B. Spliethoff, A. Wingen, S. Kaskel, J. S. Bradley and F. Schüth, *Angew. Chem., Int. Ed.*, 2001, **40**, 4204.
23 S. Kaskel and K. Schlichte, *J. Catal.*, 2001, **201**, 270.
24 S. Kaskel, K. Schlichte and B. Zibrowius, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1675.
25 F. Rouquerol, J. Rouquerol and K. Sing, *Adsorption by Powders & Porous Solids*, Academic Press, San Diego, 1998.
26 S. Storck, H. Bretinger and W. F. Maier, *Appl. Catal., A*, 1998, **174**, 137.
27 K. E. Gonsalves, S. P. Rangarajan, G. Carlson, J. Kumar, K. Yang, M. Benaissa and M. JoseYacaman, *Appl. Phys. Lett.*, 1997, **71**, 2175.
28 M. Benaissa, M. JoseYacaman, J. M. Hernandez, Bokhimi, K. E. Gonsalves and G. Carlson, *Phys. Rev. B*, 1996, **54**, 17763.
29 G. Pacheco, E. Zhao, E. D. Valdes, A. Garcia and J. J. Fripiat, *Microporous Mesoporous Mater.*, 1999, **32**, 175.
30 H. Nöth and P. Konrad, *Z. Naturforsch., B*, 1975, **30**, 681.
31 K. M. Waggoner, M. M. Olmstead and P. P. Power, *Polyhedron*, 1990, **9**, 257.