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Homoleptic Gadolinium Guanidinate: A Single Source Precursor for Metal−Organic Chemical Vapor Deposition of Gadolinium Nitride Thin Films

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Received September 18, 2009; E-mail: roland.fischer@rub.de

Gadolinium nitride (GdN) is an emerging material that has recently become the object of theoretical and experimental studies due to its unique magnetic and electronic properties for applications in spintronics.[1] GdN films were grown by physical vapor deposition (PVD) methods, such as ion assisted deposition (IAD),[2a] Ar/N_2 mixed gas plasma radio frequency (rf) sputtering,[2b] and molecular beam epitaxy (MBE).[2c] However, deposition of GdN or any other rare earth nitride thin films by metal−organic chemical vapor deposition (MOCVD) or atomic layer deposition (ALD) has not been reported so far. These chemical deposition methods are particularly suitable for industrial applications and yield excellent coatings over large areas with a complex surface geometry but are strongly dependent on the underlying chemistry of the deposition process.[3,4] Thus, the properties of the metal−organic precursors need to be fine-tuned by the choice of the ligands.[5] This precursor engineering is a particular challenge for the deposition of nitride materials.[6] Below, we will present the homoleptic tris-guanidinato complex of gadolinium $[\mathrm{Gd}\{(^i\mathrm{PrN})_2\mathrm{CNMe}_2\}_3]$ (**1**) for MOCVD of GdN as an example of a homologous series of single-source precursors (SSPs) for rare earth nitrides (Figure 1).

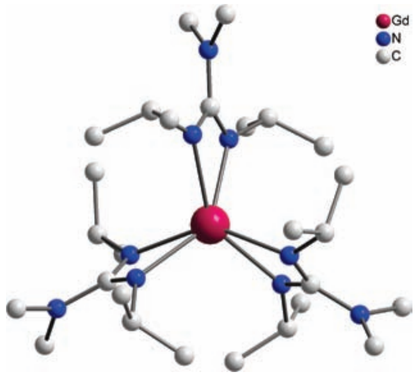

Figure 1. Molecular structure of $[\mathrm{Gd}\{(^i\mathrm{PrN})_2\mathrm{CNMe}_2\}_3]$ (**1**) in the solid state.[8]

All-nitrogen coordinated heteroleptic guanidinato group IV−VI transition metal complexes reveal very good precursor properties and applicability for MOCVD and ALD.[7] In addition to the possibility of growing oxide[7a] and oxynitride[7b] thin films in the presence of oxygen, compounds of the type $[\mathrm{M(NR_2)}\{(^i\mathrm{PrN})_2\mathrm{CNR}_2\}_2\mathrm{(NR)}]$ (M = Nb, Ta) are superior single-source precursors (SSPs) for MOCVD of NbN and TaN.[7c] We recently reported the synthesis of a series of related but homoleptic tris-guanidinato complexes $[\mathrm{M}\{(^i\mathrm{PrN})_2\mathrm{CNR}_2\}_3]$ (M = Y, Gd, Dy; R = Me, Et, ^{i}Pr).[8] Their excellent thermal properties motivated us to explore their application as SSPs for the growth of rare earth nitride thin films. The gadolinium compound **1** was chosen for the first case study (SI 1).

Figure 2 shows the electron impact ionization mass spectrum of **1**. The molecular ion peak $[\mathrm{M}]^{+\bullet}$ at *m*/*z* 668 is clearly seen and indicates the intact evaporation of **1** (confirmed by high resolution MS; see SI 5). All peaks with $m/z < 668$ could be attributed to defined fragments of **1** (SI 2−5). An important peak is at *m*/*z* 343. It is assigned to the imido fragment $[\{(^i\mathrm{PrN})_2\mathrm{CNMe}_2\}\mathrm{GdNH}\}]^{+\bullet}$, which is unambiguously confirmed by the high resolution MS results (SI 5). The base peak centered at *m*/*z* 327/328 is composed of two components. The minor component at *m*/*z* 328 is assigned to $[\{(^i\mathrm{PrN})_2\mathrm{CNMe}_2\}\mathrm{Gd}]^{+\bullet}$. The major component and actual base peak at *m*/*z* 327 is attributed to $[\{(^i\mathrm{PrN})_2\mathrm{CNCH}_2\}\mathrm{GdNH}]^{+\bullet}$, which is formed by CH_4 loss from the parent Gd-imido fragment at *m*/*z* 343. Note that Gd−O and Gd−C species were not detected. At this point it is noteworthy to mention that defined fragmentation patterns (as by **1**) and the presence of several imido fragments are also observed for analogous tris-guanidinato complexes of Sc, Y, Dy, and Er (SI 6). This is interesting, since it points to the possible participation of such species in the process of e.g. GdN film growth and the particularly favorable properties of the guanidinato ligand as efficient source for NH-species attached to the rare earth ion. Although care must be taken in extrapolating EI-MS data to the MOCVD, EI-MS proved to be a valuable tool in investigating the decomposition of MOCVD precursors.[9]

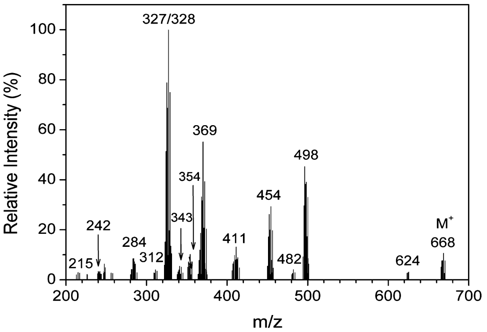

Figure 2. Electron impact mass spectrum (70 eV) of **1**.

For GdN MOCVD with **1** as an SSP, a horizontal cold wall screening reactor was employed at 1 mbar with N_2 as the carrier gas in the absence of ammonia or other reactive nitrogen sources. The precursor was heated to 125 °C. Conformal films were deposited on Al_2O_3 substrates in the temperature range 650−850 °C with typical growth rates of 1.8 μm/h. Due to the extreme air sensitivity of the GdN material, which is known to fully oxidize within a few tens of seconds when exposed to ambient conditions,[2] the as-deposited GdN films were subsequently covered with a protective capping layer of copper (SI 7). It is expected that such a layer will prevent/slow down oxygen and moisture diffusion, thus allowing sample manipulation/analysis in ambient conditions for a limited period of time (Figure 3).

10.1021/ja907952g CCC: $40.75

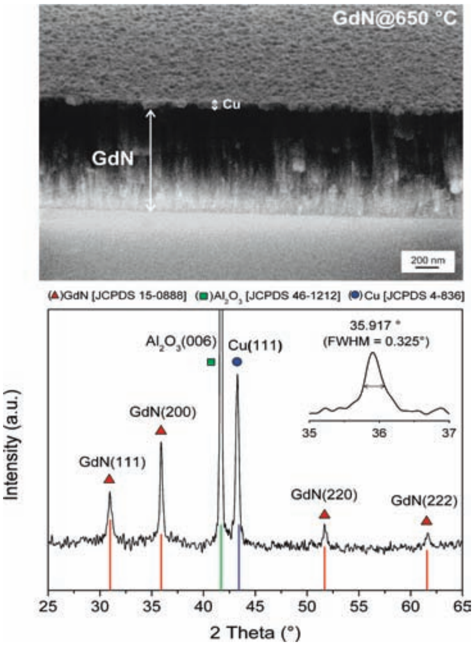

Figure 3. *Above:* SEM cross section of GdN (ca. 900 nm) film grown at 650 °C on Al_2O_3 using **1**. A protecting layer of Cu (ca. 70 nm) was deposited from [(hfac)Cu(vtms)] at 180 °C. *Below:* XRD pattern of GdN films MOCVD deposited at 850 °C on Al_2O_3(0001) substrate using **1**.

The XRD analysis of the Cu capped GdN films deposited at 650 °C revealed their amorphous nature. As the GdN deposition temperature was increased to 850 °C, crystalline films were obtained with reflections that were unambiguously indexed and assigned to rock salt type GdN using the known diffraction pattern (Figure 3). No impurity phase was observed in any of the samples. The presence of significant amounts of crystalline Gd_2O_3 was excluded since the known lattice parameters for both the cubic and the monoclinic phases are much different than that of GdN (SI 8). The same conclusion is drawn concerning the existence of gadolinium carbide, dioxycarbonate, etc. The lattice parameter for the GdN films as calculated from the positions of the GdN(200) reflection was $a = 4.995 \pm 0.005$ Å. This value concurs with that of unstrained bulk rock salt GdN (4.999 Å) and is comparable to the data on GdN thin films reported by Gerlach et al. for ion-assisted deposition (IAD) grown GdN thin films capped with a GaN protecting layer ($a = 4.97 \pm 0.06$ Å).[2a] Based on the full width at half-maximum (fwhm) of the GdN(200) reflection, the mean dimension of the GdN crystallite coherence length was ~26 nm, as calculated using the Scherrer equation.

Secondary neutral mass spectroscopy (SNMS) analysis was performed to characterize the bulk composition of the deposited GdN material (SI 9). The species and respective signals chosen for the analysis were GdN and GdO. The depth profile of a 900 nm thick GdN film deposited at 650 °C and capped with ca. 70 nm Cu shows comparably sharp interfaces between the layers and constant element distribution throughout the bulk of the film, indicating a homogeneous composition and sustainable MOCVD process. Further, GdN and GdO signals of comparable intensity with a slight GdO dominance at the Cu/GdN interface were observed throughout the volume of coating. At this stage no quantitative N/O atomic ratio can be presented. Nuclear reaction analysis (NRA) and/or time-of-flight elastic recoil detection analysis (TOF-ERDA) data are needed to determine the sensitivity factors for the chosen fragments for SNMS. However, in a previous SIMS study of IAD deposited GdN films the sensitivity for the oxide fragment was found to be ~10 times higher than that for the nitride.[2a] Further, it is known from the literature that the lattice parameter of the GdN phase is very indicative of the oxygen impurity in the crystal.[1a] Thus, based on the accuracy of our lattice parameter determination ($a = 4.995 \pm 0.005$), the oxygen level of the deposited GdN crystallites is expected to be low and on the same order of magnitude as those in the films grown using IAD ($a = 4.97 \pm 0.06$), where the average N/O ratio was ~30.[2a] Nevertheless, exclusion of O-contamination will be a technical (reactor design, sample handling) but not a chemical problem.

In conclusion, we presented $[Gd\{(^{i}PrN)_2CNMe_2\}_3]$ (**1**) as the first example of a single source precursor for MOCVD of a rare earth nitride material. The presence of phase-pure cubic rock salt GdN in the films deposited at 850 °C was established by XRD. This result is encouraging, since a homologous series of rare earth compounds similar to **1** is available.[8] Note, that such tailored all-nitrogen coordinated SSPs allow MOCVD or ALD of superior quality metal nitride films if optimized (small) amounts of additional ammonia (or hydrazine, etc.) are used in a two-stream experiment (SI 10).[6] Finally, apart from the possibility of growing rare earth nitride thin films, the new precursors may be interesting for various other applications including doping for diluted magnetic semiconductors (DMS) like GaGdN and GaDyN[10] and modifying the optical properties of nitride semiconductor nanoparticles.[11]

Acknowledgment. We thank the German Science Foundation (DFG-DE-790-3) and the Ruhr-University Research School for financial support.

Supporting Information Available: Precursor and GdN film characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA907952G