

## Direct syntheses and complete characterization of halide-free tetrakis(dialkylamino)silanes

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Received 10 April 2006; accepted 23 April 2006

Available online 8 May 2006

### Abstract

Tetrakis(dialkylamino)silanes of the general formula  $\text{Si}(\text{NRR}')_4$  ( $\text{R} = \text{R}' = \text{CH}_3$ ,  $\text{CH}_2\text{CH}_3$ , or  $\text{R} \neq \text{R}' = \text{CH}_3$  and  $\text{CH}_2\text{CH}_3$ ) were prepared as halide-free, analytically pure compounds whose volatility scales with alkyl group size. The successful syntheses relied on the heavier silicon halides,  $\text{SiBr}_4$ , and  $\text{SiI}_4$ . In the case of  $\text{SiBr}_4$  incomplete amination with amines bulkier than dimethylamine ultimately led exclusively to  $\text{BrSi}(\text{NR}_2)_3$ , whereas  $\text{SiI}_4$  starting material afforded only homoleptic  $\text{Si}(\text{NR}_2)_4$  whose complete characterization is presented. The tetrakis(dialkylamino)silanes failed to react with alcohols, even at elevated temperatures, and only slowly hydrolyze. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Silicon; Amine; Precursor; Volatile; Halide

Chemical vapor deposition (in its many forms) and its related variant atomic layer deposition are accepted thin film fabrication techniques at semiconductor research and production levels. Essential to both processes is the availability of high-purity chemical sources that display appropriate chemistry and appreciable volatility [1,2]. One general precursor class that has recently generated significant commercial [3] and scientific [4] interest are hetero- and homoleptic pnictogenyl compounds of group 14 elements, of which tetrakis(dialkylamino)silanes are an important subset.

These compounds – recognized to always contain various levels of halide impurity typically resulting from incomplete amination of the  $\text{SiCl}_4$  starting material [3,5–7] – are under active exploration as silicon sources for binary oxides ( $\text{SiO}_2$ ) and higher-order silicates such as  $\text{Zr}_x\text{Si}_{1-x}\text{O}_2$  and  $\text{Hf}_x\text{Si}_{1-x}\text{O}_2$  [8–10]. Apart from their use

as gate dielectric precursors in vapor and liquid delivery solutions, they have also been considered promising metal–organic sources for IV/V films; specifically the growth of amorphous silicon nitride [6,7,11] whose expanding applications range from semiconductor diffusion barriers and passivation layers to antireflection coatings on silicon solar cells. Regardless of final application, minimizing halide content is essential, for their presence complicates process conditions or ultimately leads to device failure through the introduction of charge carriers or possibly even etching of the native silicon foundation.

In an effort to better understand and address the problematic halide content that plagued previous preparations, we initiated a synthetic study to both determine product distributions and evaluate routes toward halide-free homoleptic complexes using three different amino ligands – dimethylamino (DMA), diethylamino (DEA), and ethylmethylamino (EMA) – all of which are commonly used ligands in commercial precursor design [1]. Our initial efforts followed prior art and involved  $\text{SiCl}_4$  and the lithium salts of DMA and DEA as well as the free amine of

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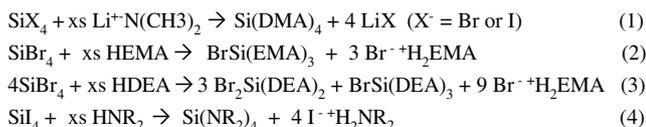
E-mail address: [jbelot2@unl.edu](mailto:jbelot2@unl.edu) (J.A. Belot).

EMA, although employing higher aromatic hydrocarbon boiling solvents than those previously reported [2,11]. In every attempted experiment, the chloride content could not be reduced below that of the monochlorosilane. For a number of reasons (vide infra) we then shifted our efforts to the heavier halide starting materials  $\text{SiBr}_4$  and  $\text{SiI}_4$ .

The primary motivation for using the heavier halides was to exploit the decreasing Si–X bond strengths when compared to Si–Cl; we felt this would be particularly important and advantageous in achieving complete amination if the substitution steps involved a dissociative mechanism, as proposed by Passarelli [5], further facilitated by anomeric effects [12] of the nitrogen lone-pair [13,14]. Secondly, both the HBr and HI by-products are slightly stronger acids than HCl, driving the non-aqueous acid-base equilibrium with excess amine further forward toward the ammonium precipitate,  $\text{X}^-\text{H}_2\text{NR}_2$  [15]. Ultimately, the steric bulk of the halide versus the incoming amine may also be important since recombination of any proposed cationic intermediate [5] with the larger halide anions will be less favored with bulkier amino alkyl groups [16–18]. The first attempts (1) using either  $\text{SiBr}_4$  or  $\text{SiI}_4$  with  $\text{Li}^+\text{N}(\text{CH}_3)_2$  (since dimethylamine is a gas we chose the alkali metal salt) afforded the desired homoleptic  $\text{Si}(\text{DMA})_4$  in >70% yield and analytical purity after a simple reduced-pressure distillation. This confirmed our hypothesis that the weaker Si–Br or Si–I bonds could afford the desired homoleptic compounds without halide residue (see Scheme 1).

Following this success we evaluated the reactions between  $\text{SiBr}_4$  and both protio HEMA and HDEA amines in toluene. For the reactions with HEMA only the monobromosilane compound,  $\text{BrSi}(\text{EMA})_3$ , was isolated from distillation (after removing the precipitate) in >80% yield and analytical purity, even if 128 equivalents of HEMA were used with respect to  $\text{SiBr}_4$ . The situation with HDEA immediately became more complex, and purification of the crude products yielded  $\text{Br}_2\text{Si}(\text{DEA})_2$  and  $\text{BrSi}(\text{DEA})_3$  in a 3:1 molar ratio. In attempts to drive these reactions to completion, all purified halogen-containing products were subjected to a neat reflux in the parent amine starting material. For  $\text{BrSi}(\text{EMA})_3$  and  $\text{BrSi}(\text{DEA})_3$  no reaction was observed, and only the monobromosilanes were reisolated. However, prolonged reflux (>24 h) of  $\text{Br}_2\text{Si}(\text{DEA})_2$  in excess HDEA ultimately removed a single bromide ion and provided nearly quantitative conversion to  $\text{BrSi}(\text{DEA})_3$ .

In an analogous approach to (2) and (3) the reactions between  $\text{SiI}_4$  and HEMA and HDEA were explored (4).



Scheme 1. Synthesis and product distributions from reactions using  $\text{SiX}_4$  as a starting material (X = Br or I).

It was found that the homoleptic products could be isolated in excellent yields and high-purity by first removing the ammonium precipitates by filtration through a filter aid followed by a simple vacuum distillation.<sup>1</sup> The isolated yields of colorless  $\text{Si}(\text{DMA})_4$ ,  $\text{Si}(\text{EMA})_4$ , and  $\text{Si}(\text{DEA})_4$  liquids were 70%, 80%, and 88%, respectively. The purified products never exhibited residual halide (ICP-MS and elemental analysis) and were, for the first time, fully characterized by common spectroscopic methods including mass spectroscopy and elemental analysis.

To assess stability we explored the propensity for homoleptic aminosilane alcoholysis with both MeOH and EtOH using  $^1\text{H}$  and  $^{13}\text{C}$  NMR to monitor the reaction. Surprisingly none of the tetrakis(dialkylamino)silanes reacted with either dried alcohol at ambient temperature and failed to undergo any significant spectroscopic changes at elevated temperatures (~40 °C) over a period of 8 hours. We attribute these observations to a robust Si–N bond [13,14] and significant steric crowding around the Si center. [16,17] Although stable toward small alcohols, the complexes were found to undergo hydrolysis at ambient temperature, with each being completely consumed by  $\text{H}_2\text{O}$  within 30 min at the rate  $\text{Si}(\text{DMA})_4 > \text{Si}(\text{EMA})_4 > \text{Si}(\text{DEA})_4$ . Qualitatively, at elevated temperatures the

<sup>1</sup> Tetrakis(dimethylamino)silane:  $\text{SiBr}_4$  (10.3 g, 29.6 mmol) in 40 mL dry  $\text{C}_7\text{H}_8$  was added dropwise to a suspension of  $\text{LiNMe}_2$  (10.0 g., 196 mmol) in 100 mL dry  $\text{C}_7\text{H}_8$  at 0 °C. Upon warming to room temperature, the mixture was heated at reflux for 24 h and then filtered through Celite. Both the flask and the precipitate were washed with pentane (30 mL) and the washings combined with the mother liquor. The volatiles were removed under dinitrogen and the light yellow crude product purified by vacuum distillation to give a colorless liquid of  $\text{Si}(\text{NMe}_2)_4$  (2.82 g, yield: 70%, b.p. 20–22 °C at 0.15 Torr).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  2.5 (singlet);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  38.6 (singlet); IR (neat,  $\text{cm}^{-1}$ ) 2972 (br, s), 1463 (m), 1291 (s), 1179 (s), 1069 (m), 987 (vs), 724 (s), 444 (m); Elemental Anal.: Calc. C, 47.01%; H, 11.84%; N, 27.41%; Observed. C, 47.24%; H, 11.79%; N, 27.53%. HR-EI M.S.: Calcd. mol. wt. 204.39, observed mol. wt. 204.177. Tetrakis(diethylamino)silane and tetrakis(ethylmethylamino)silane: In a representative procedure the amine was first dried overnight over  $\text{CaH}_2$  and distilled immediately before use. 12 mol excess of amine was added to 23 mmol of  $\text{SiI}_4$  stirring in 130 mL of dry  $\text{C}_7\text{H}_8$  in a 2-neck flask fitted with a reflux condenser and a septa. The reaction was then heated at reflux for 24 h and a white precipitate of  $\text{R}_2\text{NH}_2^+\text{I}^-$  salt formed upon cooling the solution to room temperature. The white precipitate was filtered using Celite, washed with  $\text{C}_5\text{H}_{12}$  and the washings combined with the filtrate. The volatiles were removed under dinitrogen and the crude products purified by vacuum distillation to give colorless tetrakis(dialkylamino)silanes. Tetrakis(ethylmethylamino)silane [ $\text{Si}(\text{NEtMe})_4$ ] – Yield: 80%; B.P. 68–70 °C at 0.15 Torr;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.06, (triplet, 3H), 2.503 (singlet, 3H); 2.81 (quartet, 2H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  15.0, 35.0, 44.7; IR (neat,  $\text{cm}^{-1}$ ) 2965 (br, s), 1473 (m), 1371 (ms), 1232 (s), 1175 (s), 1060 (m), 1007 (vs), 912 (s), 789 (m), 697 (s), 492 (m); Elemental Anal.: Calc.: C, 55.33%; H, 12.38%; N, 21.51%; Observed. C, 55.21%; H, 12.17%; N, 21.63%; HR-EI M.S.: Calcd. mol. wt. 260.5, observed mol. wt. 260.24. Tetrakis(ethylmethylamino)silane: [ $\text{Si}(\text{NEt}_2)_4$ ] – Yield: 88%; b.p. 120–123 °C at 0.15 Torr;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.06 (triplet, 3H), 2.95 (quartet, 2H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  15.2, 39.8; IR (neat,  $\text{cm}^{-1}$ ) 2930 (br, s), 1463 (ms), 1375 (s), 1292 (m), 1182 (br, s), 1023 (br, s), 928 (s), 779 (ms), 687 (s), 506 (ms); Elemental Anal.: Calcd. C, 60.7%; H, 12.73%; N, 17.7%; Observed. C, 60.46%; H, 13.11%; N, 17.62%; HR-EI M.S.: Calcd. mol. wt. 316.61, observed mol. wt. 316.3022.

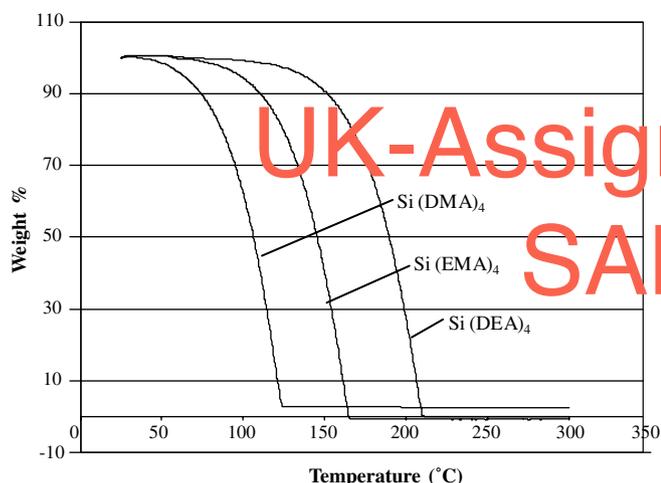


Fig. 1. TGA analysis of pure, halide-free  $\text{Si}(\text{DMA})_4$ ,  $\text{Si}(\text{EMA})_4$ , and  $\text{Si}(\text{DEA})_4$  at a ramp rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  and flowing  $\text{N}_2$  at 50 cc.

hydrolysis occurs more rapidly. No attempts were made to identify or analyze the final products from these reactions, however they lend credence to effectively using  $\text{H}_2\text{O}$  as a co-reactant in both vapor phase and solution (sol-gel) processing of these compounds.

One of the requirements for vapor phase processing and film growth is volatility. The boiling point of each compound increases with increasing amino steric bulk. At 0.15 Torr the boiling point ranges of  $\text{Si}(\text{DMA})_4$ ,  $\text{Si}(\text{EMA})_4$ , and  $\text{Si}(\text{DEA})_4$  are 20–22  $^\circ\text{C}$ , 68–70  $^\circ\text{C}$ , and 120–123  $^\circ\text{C}$ , respectively. Thus, addition of one ethyl group to each amine elevates the boiling point by approximately 50  $^\circ\text{C}$ . Atmospheric pressure thermogravimetric analysis (TGA, Fig. 1, ramp rate  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  under 50 cc flowing  $\text{N}_2$ ) reveals that both  $\text{Si}(\text{EMA})_4$  and  $\text{Si}(\text{DEA})_4$  volatilize to 0% residue, indicating complete evaporation and negligible decomposition. Although  $\approx 2\%$  residue remains for  $\text{Si}(\text{DMA})_4$ , this is most likely a handling artifact, since this compound undergoes the fastest hydrolysis.

In summary, this communication presents the definitive, high-yield, and straightforward syntheses and complete characterization of three homoleptic, volatile tetrakis(dialkylamino)silane derivatives –  $\text{Si}(\text{DMA})_4$ ,  $\text{Si}(\text{EMA})_4$ , and  $\text{Si}(\text{DEA})_4$ . The reactions between  $\text{SiBr}_4$  and the amine starting materials failed to give the desired compounds by equations (2) and (3), but ultimately and repeatedly yielded monobromosilanes of the general formula  $\text{BrSi}(\text{NR}_2)_3$  directly or by neat reflux with excess amine. However, switching to the heavier halide starting material,  $\text{SiI}_4$ , com-

pletely avoided mixed halide-amino species, and the title compounds presented themselves in high-yields and analytical purity (4); the reactions of either  $\text{SiBr}_4$  or  $\text{SiI}_4$  with  $\text{Li}^+\text{-N}(\text{CH}_3)_2$  afforded only the homoleptic complex  $\text{Si}(\text{DMA})_4$ . Furthermore, the amino complexes do not undergo appreciable alconolysis at ambient or elevated temperatures but do slowly hydrolyze upon exposure to  $\text{H}_2\text{O}$ , rendering them reactive and useful reagents for both vapor and solution phase processing. Although  $\text{SiCl}_4$  is admittedly more inexpensive than both  $\text{SiBr}_4$  or  $\text{SiI}_4$ , overall cost savings are gained through the use of any protio amine and the rapid isolation of analytically pure compounds.

### Acknowledgements

This work was supported in part by the MRSEC Program of the National Science Foundation under Award Number DMR-021380, the Nebraska Research Initiative, and NSF CHE-0415928. J.A.B. also thanks Prof. T.A. George (UNL) for insightful discussions.

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