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

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Abstract

Tetrakis(dialkylamino)silanes of the general formula Si(NRR')₄ (R = R' CH₃, CH₂CH₃, or R ≠ R' = CH₃ and CH₂CH₃) were prepared as halide-free, analytically pure compounds whose volatility scales with alkyl group size. The successful syntheses relied on the heavier silicon halides, SiBr₄, and SiI₄. In the case of SiBr₄ incomplete amination with amines bulkier than dimethylamine ultimately led exclusively to BrSi(NR₂)₃, whereas SiI₄ starting material afforded only homoleptic Si(NR₂)₄ whose complete characterization is presented. The tetrakis(dialkylamino)silanes failed to react with alcohols, even at elevated temperatures, and only slowly hydrolyze.

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 SiCl₄ starting material [3,5–7] – are under active exploration as silicon sources for binary oxides (SiO₂) and higher-order silicates such as ZrₓSi₁₋ₓO₂ and HfₓSi₁₋ₓO₂ [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 SiCl₄ and the lithium salts of DMA and DEA as well as the free amine of
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, SiBr₄ and SiI₄.

The primary motivation for using heavier halides was to exploit the decreasing Si–X bond strength when compared to Si–Cl; we felt this would be particularly important and advantageous in achieving complete reduction if the substitution steps involved a dissociative mechanism, as proposed by Passarelli [5], further facilitated by anomic effects [12] of the nitrogen lone-pair [13,14]. Secondly, both the HBr and HI by-products are slightly weaker acids compared to excess amine further forward toward the ammonium precipitate, X⁺H₂NR₃ [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 SiBr₄ or SiI₄ with Li⁺N(CH₃)₂⁺ (since dimethylamine is a gas we chose the alkali metal salt) afforded the desired homoleptic Si(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 SiBr₄ and both protio HEMA and HDEA amines in toluene. For the reactions with HEMA only the monobromosilane compound, BrSi(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 SiBr₄. The situation with HDEA immediately became more complex, and purification of the crude products yielded BrSi(DEA)₂ and BrSi(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 BrSi(EMA)₃ and BrSi(DEA)₃ no reaction was observed, and only the monobromosilanes were reisolated. However, prolonged reflux (>24 h) of BrSi(DEA)₂ in excess HDEA ultimately removed a single bromide ion and provided nearly quantitative conversion to BrSi(DEA)₃.

In an analogous approach to (2) and (3) the reactions between SiI₃ and HEMA and HDEA were explored (4).

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\begin{align*}
\text{SiX₄} + xx \text{Li}^+\text{N(CH₃)₂} & \rightarrow \text{Si(DMA)₄} + 4 \text{LiX} \quad (X = \text{Br or I}) \\
\text{SiBr₄} + xx \text{HEMA} & \rightarrow \text{BrSi(EMA)₃} + 3 \text{Br}^+ \cdot \text{HEMA} \\
4\text{SiBr₄} + xx \text{HEDA} & \rightarrow 3 \text{BrSi(DEA)₄} + \text{BrSi(DEA)₃} + 9 \text{Br}^+ \cdot \text{HEDA} \\
\text{SiI₃} + xx \text{HNR₃} & \rightarrow \text{Si(NR₃)₂} + 4 \text{I}^- \cdot \text{HNR₃}
\end{align*}
\]

Scheme 1. Synthesis and product distributions from reactions using SiX₄ 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. The isolated yields of colorless Si(DMA)₄, Si(EMA)₄, and Si(DEA)₄ liquids were 70%, 80%, and 88%, respectively. The purified products were used without further purification in a number of spectroscopic tests (vide infra). We then shifted our efforts to all attempted experiments, the chloride content could 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. Although stable toward small alcohols, the complexes were found to undergo hydrolysis at ambient temperature, with each being completely consumed by H₂O within 30 min at the rate Si(DMA)₄ > Si(EMA)₄ > Si(DEA)₄. Qualitatively, at elevated temperatures the...
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 H2O 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 Si(DMA)4, Si(EMA)4, and Si(DEA)4 are 20–22 °C, 68–70 °C, and 120–123 °C, respectively. Thus, addition of one ethyl group to each amine elevates the boiling point by approximately 50 °C. Atmospheric pressure thermogravimetric analysis (TGA, Fig. 1, ramp rate 10 °C min⁻¹ under 50 cc flowing N2) reveals that both Si(EMA)4 and Si(DEA)4 volatilize to 0% residue, indicating complete evaporation and negligible decomposition. Although ≈2% residue remains for Si(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 – Si(DMA)4, Si(EMA)4, and Si(DEA)4. The reactions between Si(ema) 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 BrSi(NR2)3 directly or by neat reflux with excess amine. However, switching to the heavier halide starting material, SiI4, completely avoided mixed halide-amino species, and the title compounds presented themselves in high-yields and analytical purity (4); the reactions of either SiBr4 or SiI4 with Li+[NR3]2 afforded only the homoleptic complex SiD(DMA)4. Furthermore, the amino complexes do not undergo appreciable alcoholysis at ambient or elevated temperatures but do slowly hydrolyze upon exposure to H2O, rendering them reactive and useful reagents for both vapor and solution phase processing. Although SiCl4 is admittedly more inexpensive than both SiBr4 or SiI4, overall cost savings are gained through the use of any protio amine and the rapid isolation of analytically pure compounds.

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References

[17] H. Breederveld, H.I. Waterman, Research 6 (1953) 1S–3S.