Synthesis, structural and thermal characterisation of titanium silylamido complexes

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A B S T R A C T

The titanium silylamido complexes [{R$_2$Si(N^{t}Bu)$_2$}$_2$Ti] (R = Me (**3**) and R = Ph (**4**)), [{(R$_2$Si(N^{t}Bu)$_2$)Ti(μ^2-N^{t}Bu)}$_2$] (R = Me (**5**) and R = Ph (**6**)) have been synthesised from the reaction of the lithio-silylamide ligands [{R$_2$Si(N^{t}Bu)$_2$}Li$_2$] (R = Me; (**1**), R = Ph; (**2**)) with TiCl$_4$ and [Ti(N^{t}Bu)Cl$_2$(Py)$_2$] respectively. In the case of complexes **2**, **3** and **5** the complexes have been structurally characterised by single crystal X-ray diffraction. The thermal profiles of the four silylamido (**3**–**6**) complexes have also been investigated by thermogravimetric analysis.

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Introduction

As the size downscaling of microelectronics continues, and the use of copper as an interconnect material in integrated circuitry has increased [1], the need for materials that can inhibit the fast diffusion of copper into the underlying silicon layers, and prohibit formation of highly resistive materials such as Cu$_3$Si, has also increased in turn [2]. Thin films of materials, based around early transition metal (Groups 4–6) nitrides, and specifically Ti–N, and produced by chemical vapour deposition (CVD) [3], or more recently atomic layer deposition (ALD) [4] has been an area of significant interest to those in the microelectronics industry for the last three decades and has continually been cited in the International Roadmap for Semiconductors as an area of considerable interest [5]. More recently materials such as Hf–N, Zr–N, Ta–N, Nb–N and W–N [3e,6] which combine properties such as, high conductivity, thermal stability and chemical inertness, have become increasingly important as diffusion barrier layers in ultra-large scale integration devices (ULSI).

However, one of the drawbacks of crystalline barrier materials, such as Ti–N, is the diffusion of Cu along grain boundaries [2,7]. Grain boundaries can also have a significant effect on properties such as conductivity, thermal stability and chemical inertness. As a result there is increasing attraction towards amorphous ternary materials such as M–Si–N (M = Ti, Ta, W, Mo) [8] and, to a lesser extent, M–B–N [9].

The efficacy of these films is sensitive to the relative M:N:Si ratios, with a high N content raising the temperature at which crystallization commences [10], while excessive amounts of Si encourages the formation of regions of resistive Si$_3$N$_4$ within the films [8b,11].

Ternary Ti–Si–N films have largely been deposited by physical techniques such as cathodic arc ion plating [12], or sputtering in a nitrogen atmosphere [13], although variations on CVD methods such as MOCVD [8a,11,14], PECVD [15], LPCVD [16], ALD [17] and various others [18] have all been performed using multiple source precursors.

We have previously reported the development of metal silylamido complexes as single-source precursors for the production of M–Si–N materials (M = Group 4 metals [3e] and Zn[19]). Several examples of possible precursors which claim the use of metal complexes of bidentate silylamides i.e. [{R$_2$Si(NR′)$_2$}$_x$MNR″$_2$], for the formation of M–Si–N thin film materials using CVD methods for a range of metals from Groups 4–6 are found in the patent literature [20]. However, details of the characterization of these complexes were not included in these patents. It is important to note that a successful single source precursor capable of depositing carbon and oxygen-free early transition metal MN or M–Si–N films has yet to be reported in a non-patent report. It is also important to note that precursors typically also require an external/additional

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reactive source of nitrogen (e.g. ammonia or hydrazine) to produce Ti−N or Ti−Si−N thin films. It is for these reasons that the development of new single source precursors represents a significant challenge.

Our interest in this area is the synthesis and development of single source precursors that contain pre-formed M−N−Si linkages for CVD purposes [21]. While there is a paucity of complexes developed specifically for utilization in CVD applications, it is important to note there are a wide range of complexes reported in the literature that have been developed for catalytic purposes [22] which contain both pre-formed M−N−Si linkages and an {MN$_4$} core: a key feature of precursor materials which has previously been reported to favour formation of M−N materials on decomposition [3e,23].

In this paper, we report on the reactions of both TiCl$_4$ and [Ti(N^{t}Bu)Cl$_2$(Py)$_2$] respectively with lithio-silylamide systems [{R$_2$Si(N^{t}Bu)$_2$}Li$_2$] (R = Me (**1**), R = Ph (**2**)) and the structural and spectroscopic characterisation of the products. Thermogravimetric analysis has also been used in order to assess the potential utility of these complexes to form amorphous Ti−Si−N films.

Experimental

General information

All operations were performed under an atmosphere of dry argon using standard Schlenk line and glovebox techniques. Hexanes and toluene solvents were dried using a commercially available solvent purification system (Innovative Technology Inc.) and degassed under argon prior to use. Deuterated benzene (C$_6$D$_6$) and THF (d$_8$-THF) NMR solvents were purchased from Fluorochem and dried over potassium before isolating *via* vacuum distillation. All dry solvents were stored under argon in Young's ampoules over 4 Å molecular sieves. Me$_2$Si[N(H)^{t}Bu]$_2$ [21b], Me$_2$Si[N(Li)^{t}Bu]$_2$ [24], [Me$_2$Si(N^{t}Bu)$_2$]$_2$Ti (**3**) [25] and Ti(N^{t}Bu)Cl$_2$(Py)$_2$ [26] were prepared according to published procedures.

Solution ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a Bruker Avance 300 spectrometer, whilst [28] Si NMR spectra were recorded using a Bruker Avance 500 spectrometer. All spectra were obtained at ambient temperature (25 °C). ^{1}H and ^{13}C NMR chemical shifts are given in ppm and referenced internally to residual non-deuterated solvent resonances [27]. The following abbreviations are used: s (singlet), t (triplet), q (quartet), m (multiplet) and br (broad). Elemental analyses were performed externally by London Metropolitan University Elemental Analysis Service, UK. Thermogravimetric analysis (TGA) of the complexes was performed at SAFC Hitech Ltd, Bromborough, UK, using a Shimadzu TGA-51 Thermogravimetric Analyzer. Data points were collected every second at a ramp rate of 20 °C min^{-1} in a flowing (50 mL min^{-1}) N$_2$ stream.

Synthesis of [Ph$_2$Si(NH^{t}Bu)$_2$]

This compound was prepared based on a published procedure for the synthesis of [(2,6-^{i}Pr$_2$C$_6$H$_3$NH)$_2$SiPh$_2$] [28]. A stirred hexane (250 ml) solution of ^{t}BuNH$_2$ (10.5 ml, 100 mmol) was treated with ^{n}BuLi (2.5 M, 40 ml, 100 mmol) at −78 °C. The solution was allowed to warm to room temperature, then slowly refluxed for 30 min. Slow addition of Ph$_2$SiCl$_2$ (10.5 ml, 50 mmol) at −78 °C afforded a white precipitate. After warming the reaction mixture to room temperature the solution was filtered and washed with hexane. The filtrate was dried *in vacuo* to yield [Ph$_2$Si(NH^{t}Bu)$_2$], as a colourless liquid. Yield 11.07 g, 68%. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ_H 7.76−7.69 (br m, 2H, meta-C$_6$H$_5$), 7.20−7.08 (br m, 3H, ortho- and para-C$_6$H$_5$), 1.34 (s, 1H, NH), 1.16 (s, 9H, N^{t}Bu). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$): δ_C

140.4 (s, 1C), 135.3 (s, 2C), 129.1 (s, 1C), 127.9 (s, 2C), 50.0 (s, 1C, C(Me)$_3$), 33.7 (s, 3C, C(Me)$_3$). Analysis: calc for C$_{20}$H$_{30}$N$_2$Si: C 73.56, H 9.26, N 8.58%; found: C 73.62, H 9.40, N 9.05%.

Synthesis of [Ph$_2$Si(N[Li]^{t}Bu)$_2$] (**2**)

A stirred hexane (100 ml) solution of [Ph$_2$Si(NH^{t}Bu)$_2$], (9.78 g, 30 mmol) was treated with ^{n}BuLi (2.5 M, 24 ml, 60 mmol) at −78 °C. The solution was allowed to warm to room temperature, then slowly refluxed for 30 min. Volatiles were then removed *in vacuo*. Recrystallisation of the residue from hexane at −28 °C yielded [Ph$_2$Si(N[Li]^{t}Bu)$_2$], **2**, as colourless crystals. Yield 7.72 g, 76%. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ_H 8.14 (m, 2H, meta-C$_6$H$_5$), 7.47−7.27 (br m, 3H, ortho- and para-C$_6$H$_5$), 1.25 (s, 9H, N^{t}Bu). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$): δ_C 145.8, 136.2, 135.3, 128.7, 51.9, 37.1.

Synthesis of [{Ph$_2$Si(N^{t}Bu)$_2$}$_2$Ti] (**4**)

Slow addition of TiCl$_4$ (0.54 ml, 5 mmol) to a stirred Et$_2$O (60 ml) solution of [Ph$_2$Si(N[Li]^{t}Bu)$_2$], **4**, (3.38 g, 10 mmol) at −78 °C afforded a precipitate. After stirring for 24 h the solution was filtered and dried *in vacuo*. Isolation from toluene at −28 °C yielded [{Ph$_2$Si(N^{t}Bu)$_2$}$_2$Ti] as a green powder. Yield 2.89 g, 83%. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ_H 8.10 (m, 2H, meta-C$_6$H$_5$), 7.66 (m, 3H, ortho- and para-C$_6$H$_5$), 1.32 (s, 9H, N^{t}Bu). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$): δ_C 138.0, 135.7, 130.2, 129.5, 61.0, 36.8. Analysis: calc for C$_{40}$H$_{56}$N$_4$Si$_2$Ti: C 68.93, H 8.10, N 8.04%; found: C 69.11, H 8.19, N 8.07%.

Synthesis of [{[Me$_2$Si(N^{t}Bu)$_2$]Ti(μ_2-N^{t}Bu)}$_2$] (**5**)

Slow addition of a Et$_2$O (20 ml) solution of [Ti(N^{t}Bu)Cl$_2$(Py)$_2$], (3.50 g, 10 mmol) to a stirred Et$_2$O (60 ml) solution of [Me$_2$Si(N[Li]^{t}Bu)$_2$], **1**, (2.17 g, 10 mmol) at −78 °C afforded a precipitate. After stirring for 24 h the solution was filtered and dried *in vacuo*. Recrystallisation of the residue from toluene at −28 °C yielded [{[Me$_2$Si(N^{t}Bu)$_2$]Ti(μ_2-N^{t}Bu)}$_2$], **5**, as green crystals. Yield 2.30 g, 72% (base on Ti). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ_H 1.61 (s, 6H, N^{t}Bu) 1.32 (s, 3H, μ_2-N^{t}Bu), 0.46 (s, 2H, SiMe). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$): δ_C 69.0, 59.8, 36.4, 6.4, 1.4. ^{29}Si NMR (99.35 MHz, C$_6$D$_6$): δ_{Si} −45.9. Analysis: calc. for C$_{28}$H$_{66}$N$_6$Si$_2$Ti$_2$: C 52.65, H 10.41, N 13.16%; found: C 51.31, H 9.57. N 12.89%.

Synthesis of [{[Ph$_2$Si(N^{t}Bu)$_2$]Ti(μ_2-N^{t}Bu)}$_2$] (**6**)

Slow addition of a Et$_2$O (20 ml) solution of [Ti(N^{t}Bu)Cl$_2$(Py)$_2$], (1.74 g, 5 mmol) to a stirred Et$_2$O (50 ml) solution of [Ph$_2$Si(N[Li]^{t}Bu)$_2$], **2**, (1.69 g, 5 mmol) at −78 °C afforded a precipitate. After stirring for 24 h the solution was filtered and dried *in vacuo*. Isolation of the residue from toluene at −28 °C yielded [{[Ph$_2$Si(N^{t}Bu)$_2$]Ti(μ_2-N^{t}Bu)}$_2$], **6**, as an orange−brown powder. Yield 1.53 g, 69% (base on Ti). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ_H 8.12 (m, 4H, meta-C$_6$H$_5$), 7.25−7.14 (br m, 6H, ortho- and para-C$_6$H$_5$), 1.28 (s, 18H, N^{t}Bu), 1.10 (s, 9H, μ_2-N^{t}Bu). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$): δ_C 136.2, 133.9, 128.4, 126.5, 59.3, 35.0, 32.4. Analysis: calc. for C$_{48}$H$_{74}$N$_6$Si$_2$Ti$_2$: C 64.99, H 8.41, N 9.47%; found: C 65.02, H 8.44. N 9.51%.

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in Table 1. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using MoKα radiation (λ = 0.71073 Å). Structure solution was followed by full-matrix least squares refinement and was