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ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Synthesis, Characterization of Silicon (IV) Compounds Containing 2-alkyl-aminopyridine Ligands and Evaluation of them as CVD Precursors

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A family of silicon (IV) compounds, where the Si centers of trimethylsilyl (-$SiMe_3$) are linked with 2-alkyl-aminopyridine ligands, has been synthesized by reaction of corresponding lithium salt of these ligands and $SiMe_3Cl$ to a general procedure. They were characterized by ^1H NMR, ^{13}C NMR, ^{29}Si NMR, EI-MS and elemental analysis where necessary. Thereinto, ^{29}Si NMR and the synthesis of 2-*N*,*N*-bis(trimethylsilyl)aminopyridine were achieved for the confirmation of their coordination structures. Significantly, the evaluation of these silicon compounds containing 2-aminopyridinates as CVD precursors was discussed for the first time. Thermal stability, transport behavior and vapour pressures were assessed by simultaneous thermal analyses (STA). Chemical vapor deposition was accomplished in a hot wall CVD reactor system to qualitatively demonstrate the ability of them as CVD precursors.

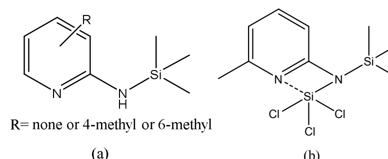
Introduction

2-Aminopyridinates are interesting amido ligands because of the flexibility of their binding mode and have found extensive utility in transition metal chemistry in recent years because they combine an anionic amide with a neutral pyridine in a chelate ring and offer a wide range of substitution patterns.[1] Such complexes are mostly known for early transition metals like titanium, vanadium and chromium, and only a few examples are known for the later first row transition metals like cobalt, nickel, copper and zinc. Moreover, the ligand “asymmetry” caused by the two different donor functionalities–the pyridine and amido function–might be considered as an additional interesting feature especially in comparison to the closest “relatives”, the amidinates.[2]

As is known, apart from the traditional silanes and halides, many silicon compounds have been investigated in regard to growing silicon-based thin films such as silicon nitride (SiN_x),[3] amorphous silicon (α-Si),[4] silicon carbide (SiC),[5] polycrystalline silicon[6], silicon carbonitride (SiCN),[7] silicon oxide (SiO_2)[8] and carbonin corporated silicon oxide (SiOC)[9], which have shown a wide range of properties and have various applications in microelectromechanical systems (MEMS) technology. The most widely studied of these compounds are hydrosilicons linked with alkyl and/or amino ligands, such as SiH_3CH_3, Et_3SiH, $SiH_2(CH_3)_2$, $SiH(NMe_2)_3$, $SiMe_2(NMe_2)_2$ and $(SiHMe_2)_2NH$.[10] Unfortunately, the introduction of gaseous reactant Me_2NH or Si-H units has increased the synthetic difficulty, hindering their industrialized application. The search for new silicon precursors is still a great challenge because the chemical and physical properties of the Si source can be adjusted by various ligands/substituents in order to obtain films with many particular properties and thereby satisfy different application requirements.[11] Thus, we have been intrigued by the question of whether such silicon compounds containing aminopyridinate ligands are applicable to a robust CVD process.

Only a handful of related silicon compounds linked with aminopyridinates have been reported, but they have been investigated as ligands (Scheme 1a) for further preparation of the transition metal complexes mentioned in the beginning or ancillary ligands for catalytic reactions.[12] That is, all of the research has focused on synthetic methodology or molecular geometry.[13] The potential application of these silicon compounds as CVD precursors is still an undeveloped field.

Scheme 1. Examples of previous related compounds



We are not aware of any other report concerning the synthesis of silicon compounds containing 2-alkyl-aminopyridine ligands and their evaluation as CVD precursors.

The precursor must meet several selection criteria in order to be a viable choice for industrial application.[14] The precursor must be

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Electronic Supplementary Information (ESI) available: [^1H NMR, ^{13}C NMR, ^{29}Si NMR spectra for **2a-2f**]. See DOI: 10.1039/x0xx00000x

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stable at room temperature, easily vaporized and generate a vapor that decomposes only at a high temperature. Additionally, the precursor must have a deposition rate suited to the application i.e., a low rate for precision IC technology and a high rate for robust coatings. The precursor should also decompose/chemically react at a temperature below the melting point/phase transformation of the substrate. It is also beneficial if the precursor is low in toxicity, non-explosive and non-pyrophoric. Moreover, the precursor should be cost-effective and either readily available at a high grade of purity or easily synthesized.

Many appreciable advantages can be obtained through the design and synthesis of these compounds as CVD precursors: i) saturated valence of Si (IV) center makes the precursors stable; ii) the synthesis method is well known as a salt elimination approach that is easily accomplished; iii) the specific -$SiMe_3$ groups enhance the volatility of these compounds;[15] iv) these 2-alkylaminopyridine ligands are either an easily sublimated solid or a volatile liquid that will facilitate the desorption of the byproducts from the surface;[16] and v) they are nontoxic, non-explosive and non-pyrophoric and are thus readily applicable to a robust CVD system.

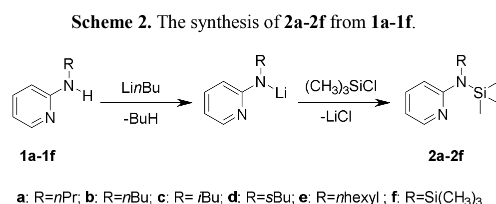
Based on these studies, we report the preparation and characterization of a family of silicon based compounds (**2a-2f**), where the Si centers of trimethylsilyl (-$SiMe_3$) are linked with 2-alkyl-aminopyridine (**1a-1f**), as presented in Scheme 2. The thermal behaviors of compounds **2a-2f** for evaluating them as CVD precursors were measured by simultaneous thermal analyses (STA) including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Further attempts at film deposition were made through a hot-wall CVD reactor, using **2a** as a representative precursor.

Results and Discussion

Synthesis and Characterization

The synthetic approaches involve the salt-elimination reaction of 1 molar equivalent to the in situ generated lithium salts with 1.2 molar equiv of $Si(CH_3)_3Cl$ in hexane (Scheme 2). All reactions proceeded easily under benign conditions. All of the compounds **2a-2f** were obtained as colorless liquids at high yields (>85%) and purified through distillation under vacuum.

Scheme 2. The synthesis of **2a-2f** from **1a-1f**.



a: R=*n*Pr; **b**: R=*n*Bu; **c**: R= *i*Bu; **d**: R=*s*Bu; **e**: R=*n*hexyl ; **f**: R=$Si(CH_3)_3$

Elemental analysis and high resolution mass spectrum of **2a-2f** were consistent with the proposed monomeric structures (Scheme 2). Furthermore, all results from ^{1}H NMR and ^{13}C NMR were simple and clear, implying the formation of these structures as shown in Scheme 2. Copies of all NMR spectra are listed in the supporting information.

The ^{29}Si NMR chemical shift is very indicative of the silicon coordination number. Thus, herein, the ^{29}Si NMR measurements of these compounds were accomplished at room temperature in $CDCl_3$. All ^{29}Si shifts appeared at 5.14~5.79ppm, evidently supporting tetracoordinate solution structures (commonly a lower magnetic field than -10ppm) as opposed to pentacoordinates (higher magnetic field to negative dozens of ppm) in the form of Si chelation with pyridine nitrogen atoms.[13,17] Furthermore, among these compounds **2f** is thet most instructive as a means to illustrate the structures. Unambiguously, as seen in Figure 1, the sole ^{29}Si signal at 5.45 ppm and the singlet with a ^{1}H [-$Si(CH_3)_3$, 18H] shift at 1.4 ppm also demonstrated the proposed structures.

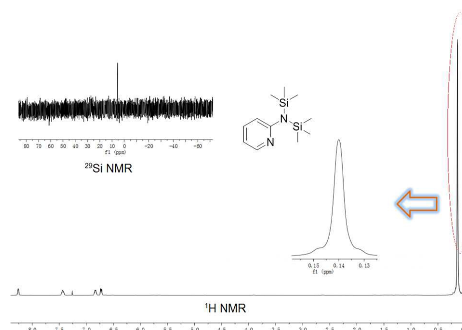


Figure 1. ^{1}H and ^{29}Si NMR spectrums of **2f**

Thermal Properties

The study of the basic parameters of precursors has not only scientific but also of great practical importance for understanding the chemistry of precursor preparation and their long-term stability as well as for the calculation of proper CVD precursor supply into the reactor for the preparation of the appropriate device structure. In particular, volatility data and a detailed vapour pressure equation are essential for controlled precursor dosimetry.

Thermogravimetric analysis (TGA) was employed in order to further confirm their thermal stability and volatility, which is the prerequisite for conventional CVD. The curves were obtained with an STA 449 F3 analyzer in argon at a heating rate of 10°C /min from 30° to 800°C. As is shown in the thermal curve in Figure 2, all evaporation occurs in a single step with very low residual mass (<1%), thus demonstrating that all of them have sufficient thermal stability for vaporization without significant decomposition.

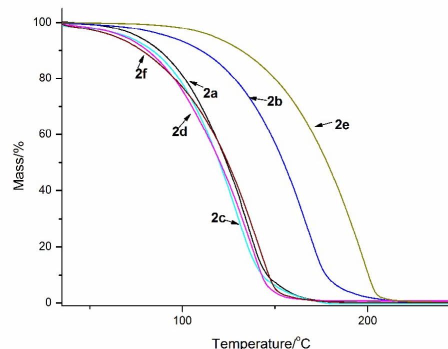


Figure 2. Thermogravimetric curves of **2a-2f**

The temperature of 50% mass loss derived from TGA data (T_{50}) has been shown to correlate with the volatility of the sample and is used to compare relative volatilities.[18] The combination of lower T_{50}

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with lower onset temperature derived from the TGA curve is usually a strong indication of the precursor's good volatility. As is shown in Table 1, the volatility of **2a** (R=*n*Pr), **2b** (R=*n*Bu) and **2e** (R=*n*hexyl) decreases with the increase in the molecular weight (M_w) of these compounds/ligands, which agrees with previous reports by other researchers.[19] Meanwhile, for compounds **2b** (R=*n*Bu), **2c** (R=*i*Bu) and **2d** (R=*s*Bu) with the same M_w, the branched construction of chelated ligands becomes the dominant factor in volatility. In other words, compounds with branched/bulky ligands possess better volatility (**2b**>**2c**≈**2d**). This is explained by the fact that the larger groups minimize intermolecular interaction by steric hindrance, which has stimulated the common method for increasing a molecule's volatility through the introduction of bulky groups.[20] Accordingly, compound **2f** has volatility that is approximately to that of **2c** and **2d,** but it has a relatively high molecular weight.

Based on the T_{50} results, all these compounds are sufficiently volatile for the typical bubbler system.

Table 1. STA data of **2a-2f**

No.	2a	2b	2c	2d	2e	2f
M/ $gmol^{-1}$	208	222	222	222	250	238
Onset temperature/°C	103	132	103	100	149	108
T_{50}/°C	123	155	125	121	171	127
Residual[a]/%	0.81	0	0.27	0.85	0	0.52
Sample size/mg	11.3	9.5	10.5	8.3	10.0	9.3

a. Mass residuals were measured at 250 °C.

Vapour-pressure data is very important for industrial process control and in manufacturing processes. Particularly, the film growth rate can be limited by the precursor vapor pressure. If the vapor-pressure/temperature plots could be known, it would be easy to select the right evaporation temperature at a given pressure so that the precursor flux could be maintained at the appropriate level.

Vapor pressure-temperature plots were obtained by thermogravimetry in accordance with the literature,[21] which is considered a rapid and convenient technique for the determination of vapor-pressure curves. The theoretical basis of the TG procedure is the Langmuir and Antoine equation, where benzoic acid was chosen as a standard.[21]

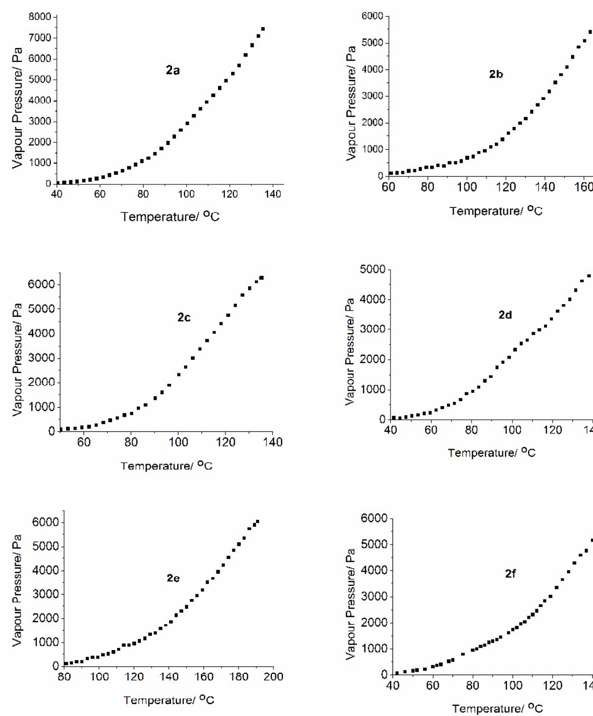
As seen from the curves (Table 2) for **2a-2f**, all of them possess appropriate vapor pressure in a range of temperatures that are relatively low. More specifically, all of **2a-2f** are nearly non-volatile at any temperature less than 40°C with extremely low vapor pressure. This is very beneficial to the safety for storage and freightage of these compounds as precursors. As temperature increases, the vapor pressure values (Pa) vary from single digits to thousands, which can meet the demand for different growth rates. Moreover, the above temperatures (40-200°C) cover the interval important for the CVD process.[14, 22]

According to the above description, a careful analysis of the TG plots and the vapor pressure-temperature curves can enable us to conclude the suitability of these compounds to be CVD precursors. It suggests the future strategy for the design of new, volatile CVD/ALD precursors.

Chemical Vapour Deposition

To further verify the applicability of these compounds as CVD precursors, **2a** was chosen as the representative to undergo a single precursor deposition process at temperature 600°C (1 Torr) for 240 minutes. As is shown in top-view of the as-grown film (Figure 3b), the compact and uniform surface morphology shows the proceeding of the deposition. And a thickness of approximately 390 nm (for a corresponding deposition rate of 1.6nm/min) was obtained by the cross-section SEM (Figure 3a).

Table 2. Vapour pressure-temperature plots of **2a-2f**



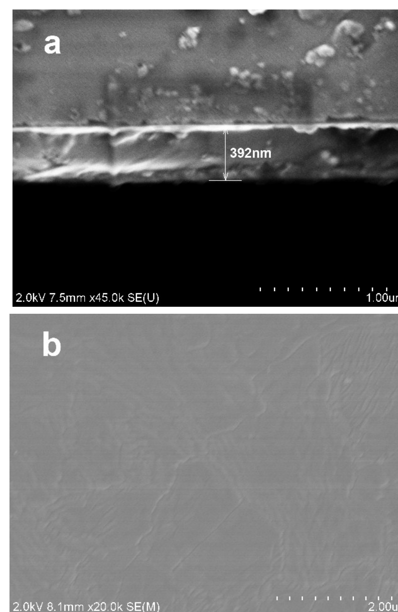


Figure 3. a) Top-view; b) cross-section images of the as-grown film by SEM.

Additionally, Figure 4 shows the X-ray photoelectron spectra (XPS) data acquired from the surface of the as-grown film at 600°C. The relative peak positions for the Si 2p, Si 2s and C 1s are 103.7,

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154.08 and 284.9 eV respectively, being consistent with earlier data reported[23] and thereby indicating the participation of the precursor in the film deposition. The peaks assigned to SiO_3–C (102.3 eV) and Si–O_2 (103.4 eV) from Si 2p electron orbital spectrum, together with the O–Si (532.6 eV) from O 1s electron orbital spectrum suggest the existence of Si-O bonding.[24] Meanwhile, the C-O formation is preliminary determined at 285.5 eV from C 1s electron orbital spectrum.[24] All of these narrow scans of C 1s, Si 2p, O 1s and their electron orbital spectra are present in supporting information. Thus the significant oxygen content (42%atom) observed here was assumed to be partly due to oxygen participation in preparation of thin film, which may be attributed to air introduction at relatively low vacuum degree (1Torr). Other contributions are surface oxidation or contamination.

Nevertheless, all of these results enable us to qualitatively conclude that these compounds have the potential to be CVD precursors.

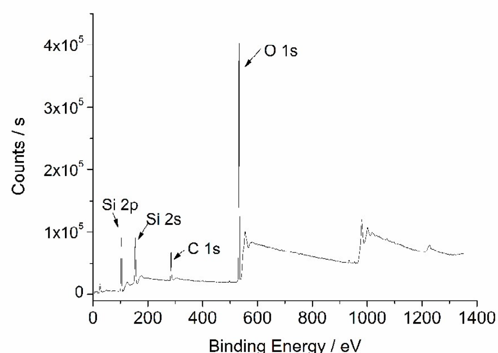

Figure 4. X-ray photoelectron spectra of the as-grown film.

Further work in regard to the deposition process such as optimization of conditions, quantitative analysis of the film component and mechanism will be presented in the subsequent report elsewhere.

Conclusions

In this study, a family of new silicon (IV) compounds containing 2-alkyl-aminopyridine ligands has been synthesized and characterized. ^{29}Si NMR and the special synthesis of 2-*N,N*-bis(trimethylsilyl)aminopyridine were performed for the confirmation of their coordination structures. Significantly, the evaluation, in which thermal stability, transport behavior and vapor pressures were assessed through simultaneous thermal analyses (STA) of these silicon compounds containing 2-aminopyridinates as CVD precursors has been discussed for the first time. Chemical vapor deposition was accomplished in a hot-wall CVD reactor system in order to qualitatively demonstrate their applicability as CVD precursors, where **2a** was chosen as the representative for the entire family, thus facilitating the formation of silicon-based film.

Further work in regard to the deposition process such as optimization of conditions, quantitative analysis of the film component and mechanism will be presented in the subsequent report elsewhere.

Experiment Section

General Consideration

All manipulations were carried out using standard Schlenk techniques or in a glove box under a nitrogen atmosphere. Prior to use, n-hexane was freshly distilled from Na. Other chemicals were purchased from Aldrich and used as received. NMR spectrum was collected on a Bruker ACF-400 spectrometer with deuterated chloroform as solvent and tetramethylsilane as internal standard (0.03% content as purchased). High-resolution electron impact ionization mass spectrometry (EI-MS) analyses were performed on the Waters Micromass GCT series time-of-flight mass spectrometer. The C, H, N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. **1a-1f** were obtained and purified according to the literature.[16]

Synthesis of 2a-2f

All of them were characterized by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, high-resolution electron impact ionization mass and elemental analysis where possible. Due to the similarities of preparing these compounds, only a detailed synthetic procedure for **2a** is described here. To a 100 mL Schlenk flask immersed at -78 °C and charged with **1a** (1.362 g, 10.0 mmol) in 40 mL hexane, 2.5 M n-butyllithium in n-hexane (4.0 mL, 10.0 mmol) was added. A white precipitate appeared after the addition started. The reaction mixture comprising lithium intermediate was warmed to room temperature and stirred for 2 h. Next, $SiMe_3Cl$ (1.341 g, 12 mmol) was added dropwise at -78 °C. After returnning to room temperature, the mixture was stirred overnight. Following filtration, the filtrate was concentrated until all volatiles were removed in vacuo. Vacuum distillation was operated to yield colourless liquid **2a** (1.896 g, 91% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 1H, -C_5H_4N), 7.43-7.38 (m, 1H, -C_5H_4N), 6.54-6.52 (m, 1H, -C_5H_4N), 6.51-6.46 (m, 1H, -C_5H_4N), 3.22-3.18 (t, J_{HH}= 8Hz, 2H, -NC$\mathbf{H}_2$), 1.58-1.49 (m, 2H, -C$\mathbf{H}_2$$CH_3$), 0.92-0.88 (t, J_{HH}= 8Hz, 3H, - CH_2C$\mathbf{H}_3$), 0.29 (s, 9H, -Si(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.09 (Py), 147.20 (Py), 137.08 (Py), 112.24 (Py), 106.41 (Py), 46.22 (*n*Pr), 22.50 (*n*Pr), 11.44 (*n*Pr), 1.43 ($SiMe_3$); ^{29}Si NMR (79 MHz, $CDCl_3$) δ 5.79; Anal. Calcd for $C_{11}H_{20}N_2Si$: C, 63.40; H, 9.67; N, 13.44; Found: C, 63.41; H, 9.83; N, 13.35. Mass (EI+, 70eV): 208.1395; Calc. Mass: 208.1396.

2b (colourless liquid, 87% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 1H, -C_5H_4N), 7.43-7.39 (m, 1H, -C_5H_4N), 6.54-6.52 (m, 1H, -C_5H_4N), 6.51-6.47 (m, 1H, -C_5H_4N), 3.26-3.22 (t, J_{HH}= 8Hz, 2H, -NC$\mathbf{H}_2$), 1.53-1.46 (m, 2H, -C$\mathbf{H}_2$$CH_2CH_3$), 1.37-1.28 (m, 2H, -$CH_2C\mathbf{H}_2$$CH_3$), 0.96-0.92 (t, J_{HH}= 8Hz, 3H, - CH_2CH_2C$\mathbf{H}_3$), 0.29 (s, 9H, -Si(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.07 (Py), 147.20 (Py), 137.09 (Py), 112.19 (Py), 106.32 (Py), 44.29 (*n*Bu), 31.63 (*n*Bu), 20.41 (*n*Bu), 14.01 (*n*Bu), 1.42 ($SiMe_3$); ^{29}Si NMR (79 MHz, $CDCl_3$) δ 5.14; Anal. Calcd for $C_{12}H_{22}N_2Si$: C, 64.81; H, 9.97; N, 12.60; Found: C, 64.83; H, 9.68; N, 12.52. Mass (EI+, 70eV): 222.1552; Calc. Mass: 222.1552.

2c (colourless liquid, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.05 (m, 1H, -C_5H_4N), 7.62-7.37 (m, 1H, -C_5H_4N), 6.58-6.55 (m, 1H, -C_5H_4N), 6.40-6.17 (m, 1H, -C_5H_4N), 3.11-3.08 (t, *J*= 6Hz, 2H, -NC$\mathbf{H}_2$), 1.98-1.84 (m, 1H, -C$\mathbf{H}$(CH_3)$_2$), 1.02-1.00 (d, *J*= 8Hz, 6H, -CH(C$\mathbf{H}_3$)$_2$), 0.28 (s, 9H, -Si(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.10 (Py), 146.73 (Py), 136.87 (Py), 112.29 (Py),

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106.96 (Py), 51.76 (*i*Bu), 26.86 (*i*Bu), 20.45 (*i*Bu), 1.77 ($SiMe_3$); ^{29}Si NMR (79 MHz, $CDCl_3$) δ 5.18; Anal. Calcd for $C_{12}H_{22}N_2Si$: C, 64.81; H, 9.97; N, 12.60; Found: C, 64.90; H, 9.98; N, 12.51. Mass (EI+, 70eV): 222.1550; Calc. Mass: 222.1552.

2d (colourless liquid, 86% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 8.10-8.09 (m, 1H, $-C_5H_4N$), 7.39-7.34 (m, 1H, $-C_5H_4N$), 6.66-6.63 (m, 1H, $-C_5H_4N$), 6.56-6.53 (m, 1H, $-C_5H_4N$), 3.59-3.50 (m, 1H, -NC**H**), 1.99-1.88 (m, 2H, -C**H**$_2$CH$_3$), 1.38-1.36 (d, J_{HH}= 8Hz, 3H, -CHC**H**$_3$), 0.89-0.85 (t, J_{HH}= 8Hz, 3H, -CH$_2$C**H**$_3$), 0.29 (s, 9H, -Si(C**H**$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.47 (Py), 146.89 (Py), 136.66 (Py), 112.53 (Py), 110.37 (Py), 52.99 (*s*Bu), 27.71 (*s*Bu), 20.20 (*s*Bu), 12.15 (*s*Bu), 2.40 ($SiMe_3$); ^{29}Si NMR (79 MHz, $CDCl_3$) δ 5.55; Anal. Calcd for $C_{12}H_{22}N_2Si$: C, 64.81; H, 9.97; N, 12.60; Found: C, 64.75; H, 10.08; N, 12.42. Mass (EI+, 70eV): 222.1550; Calc. Mass: 222.1552.

2e (colourless liquid, 87% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 8.11-8.10 (m, 1H, $-C_5H_4N$), 7.45-7.42 (m, 1H, $-C_5H_4N$), 6.59-6.56 (m, 1H, $-C_5H_4N$), 6.55-6.50 (m, 1H, $-C_5H_4N$), 3.28-3.24 (m, 2H, -NC**H**$_2$), 1.67-1.34 (m, 8H, $-CH_2CH_2CH_2CH_2-$), 0.95-0.91 (t, J_{HH}= 8Hz, 3H, -C**H**$_3$), 0.33 (s, 9H, -Si(C**H**$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.06 (Py), 147.18 (Py), 137.06 (Py), 112.18 (Py), 106.31 (Py), 44.57 (*n*hexyl), 31.71 (*n*hexyl), 29.45 (*n*hexyl), 26.92 (*n*hexyl), 22.70 (*n*hexyl), 14.01 (*n*hexyl), 1.43 ($SiMe_3$); ^{29}Si NMR (79 MHz, $CDCl_3$) δ 5.71; Anal. Calcd for $C_{14}H_{26}N_2Si$: C, 67.14; H, 10.46; N, 11.18; Found: C, 66.99; H, 10.38; N, 11.13. Mass (EI+, 70eV): 250.1862; Calc. Mass: 250.1865.

2f (colourless liquid, 90% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (m, 1H, $-C_5H_4N$), 7.46-7.41 (m, 1H, $-C_5H_4N$), 6.85-6.81 (m, 1H, $-C_5H_4N$), 6.74-6.71 (m, 1H, $-C_5H_4N$), 0.14 (s, 18H, [-Si(C**H**$_3$)$_3$]$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.11 (Py), 148.24 (Py), 136.72 (Py), 121.06 (Py), 117.71 (Py), 2.33 ($SiMe_3$); ^{29}Si NMR (79 MHz, $CDCl_3$) δ 5.45; Anal. Calcd for $C_{11}H_{22}N_2Si_2$: C, 55.40; H, 9.30; N, 11.75; Found: C, 55.31; H, 9.38; N, 11.51. Mass (EI+, 70eV): 238.1320; Calc. Mass: 238.1322.

Thermal analysis and CVD deposition

Thermal stability, transport behavior and vapor pressure of **2a-2f** were evaluated by thermogravimetric analysis (TGA) to confirm that this family of compounds is suitable CVD precursors preliminary. The TG curve was obtained with an STA 449 F3 analyzer in argon at a heating rate of 10°C /min from 30 to 800°C. Subsequently, chemical vapor deposition was accomplished in a simple system shown schematically in Figure 4, to further demonstrate the ability of these compounds as CVD precursors, where **2a** was chosen as the representative.

The furnace consists of a hot-wall tubular quartz reactor with a large (≈60 cm) isothermal (±5 °C) zone. The substrates used were 1 cm × 1 cm N-type Si (100)&(110)&(110) wafers doped with P with a resistivity of 0.01~0.02 Ωcm. Prior to the deposition, the wafers were treated by a $H_2SO_4 + H_2O_2$ (v/v = 7/3) mixture followed by HF etching, thoroughly rinsed with ultrapure water and then dried with N_2. The growth parameters used during the process were: total pressure: 1 Torr, 10 % H_2 /N_2 flow: 120 mL/min, deposition time: 240 min and temperature 600 °C. A 60 °C heating temperature of **2a** was kept during the whole deposition. After deposition, samples were cooled to room temperature at a rate of 5 °C/min in a N_2 (flow: 120 mL/min) atmosphere.

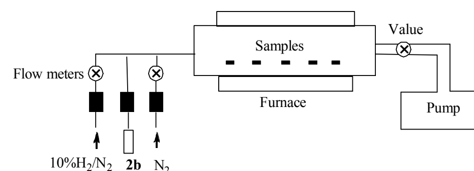

Figure 4. Experimental set-up of the hot-wall LPCVD reactor.

The surface morphology of the as-grown thin film was characterized by a Hitachi S-4800 scanning electron microscopy (SEM).

Acknowledgements

We gratefully acknowledge financial support of this work by the National Natural Science Foundation of China (No. 21371080) and “333 Talent Project” of Jiangsu Province (BRA2012165).

Notes and references

1 C. G. Glatz, S. Demeshko, G. Motz and R. Kempe, *Eur. J. Inorg. Chem.*, 2009, 1385; S. R. Boss, R. Haigh, D. J. Linton and A. E. H. Wheatley, *J. Chem. Soc., Dalton Trans.*, 2002, 3129; S. Deeken, S. Proch, E. Casini, H. F. Braun, C. Mechtler, C. Marschner, G.r Motz and R. Kempe, *Inorg. Chem.*, 2006, **45**, 1871; F. Ortu, G. J. Moxey, A. J. Blake, W. Lewis, and D. L. Kays, *Inorg. Chem.*, 2013, **52**, 12429; G. Glatz, T. Schmalz, T. Kraus, F. Haarmann, G. Motz and R. Kempe, *Chem. Eur. J.*, 2010, **16**, 4231; A. Noor, W. Kretschmer and R. Kempe, *Eur. J. Inorg. Chem.*, 2006, 2683; C. Jones, P. C. Junk, S. G. Leary and N. A. Smithies, *Inorg. Chem. Commun.*, 2003, **6**, 1126.
2 H. Nagashima, H. Kondo, T. Hayashida, Y. Yamaguchi, M. Gondoa, S. Masudaa, K. Miyazaki, K. Matsubara and K. Kirchner, *Coordin. Chem. Rev.*, 2003, **245**, 177.
3 F. L. Riley, *J. Am. Ceram. Soc.*, 2000, **83**, 245; H. Klemm, *J. Am. Ceram. Soc.*, 2010, **93**, 1501; Y. Q. Chen, X. N. Zhang, Q. Zhao, L. He, C. K. Huang and Z. P. Xie, *Chem. Commun.*, 2011, **47**, 6398.
4 H. Sirringhaus, *Adv. Mater.*, 2014, **26**, 1319; B. Rech and H. Wagner, *Appl. Phys. A*, 1999, **69**, 155.
5 N. G. Wright, A. B. Horsfall and K. Vassilevski, *Mater. Today*, 2008, **11**, 17; H. P. Phan, D. V. Dao, P. Tanner, J. S. Han, N. T. Nguyen, S. Dimitrijev, G. Walker, L. Wang and Y. Zhu, *J. Mater. Chem. C*, 2014, **2**, 7176.
6 J. K. Rath, *Sol. Energ. Mat. Sol. C*, 2003, **76**, 43; A. F. B. Braga, S. P. Moreira, P. R. Zampieri, J. M. G. Bacchin and P. R. Mei, *Sol. Energ. Mat. Sol. C*, 2002, **82**, 418; S. D. Brotherton, *Semicond. Sci. Technol.*, 1995, **10**, 721.
7 O. Flores, R. K. Bordia, D. Nestler, W. Krenkel and G. Motz, *Adv. Eng. Mater.*, 2014, 1; A. Badzian, T. Badzian, R. Roy and W. Drawl, *Thin Solid Films*, 1999, **354**, 148; A. Badzian, T. Badzian, W. D. Drawl and R. Roy, *Diamond Relat. Mater.*, 1998, **7**, 1519.
8 G. Lucovsky, *Adv. Mater. Opt. Electr.*, 1996, **6**, 55; A. Barranco, J. Cotrino, F. Yubero, J.P. Espinós, J. Benítez, C. Clerc and A. R. González-Elipe, *Thin Solid Films*, 2001, **401**, 150.
9 C. Y. Kim, H. S. Lee, C. K. Choi and Y. H. Yu, *J. Korean Phys. Soc.*, 2013, **62**, 1143; R. Navamathavan, R. Nirmala, C. Y. Kim, C. R. Lee and C. K. Choi, *J. Phys. Chem. Solids*,

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2012, **73**, 641; H. J. Kim, Q. Shao and Y. H. Kim, *Surf. Coat. Tech.*, 2003, **171**, 39.
10 I. Golecki, F. Reidingger and J. Marti, *Appl. Phys. Lett.*, 1992, **60**,1703; A. M. Wrobel, A. Walkiewicz-Pietrzykowska, M. Ahola, I. J. Vayrynen, F. J. Ferrer-Fernandez and A. R. Gonzalez-Elip, *Chem. Vap. Deposition*, 2009, **15**, 39; A. M. Wrobel, A. Walkiewicz-Pietrzykowska, M. Stasiak, T. Aoki, Y. Hatanaka and J. Szumilewicz, *J. Electrochem. Soc.*, 1998, **145**, 1060; A. M. Wrobel and A. Walkiewicz-Pietrzykowska, *Chem. Vap. Deposition*, 1998, **4**, 133; N. Fainer, A. Golubenko, Y. M. Rumyantsev and E. Maximovskii, *Glass Phys. Chem.*, 2009, **35**, 274; A. M. Wrobel, I. Blaszczyk-Lezak, P. Uznanski and B. Glebocki, *Chemical Vapor Deposition*, 2010, **16**, 211; R. D. Mundo, M. Ricci, R. d'Agostino, F. Fracassi and F. Palumbo, *Plasma Process. Polym.*, 2007, **4**, S21; G. Suchaneck, V. Norkus and G. Gerlach, *Surf. Coat. Technol.*, 2001, **142**, 808; A. M. Wrobel and I. Blaszczyk-Lezak, *Chemical Vapor Deposition*, 2007, **13**, 595; N. Fainer, A. Golubenko, Y. M. Rumyantsev and E. Maximovskii, *Glass Phys. Chem.*, 2009, **35**, 274.
11 M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354.
12 F. T. Edelmann, *Coordin. Chem. Rev.*, 2015, **284**, 124.
13 C. Jones, P. C. Junk, S. G. Leary, N. A. Smithies and J. W. Steed, *Inorg. Chem. Commun.*, 2002, **5**, 533.
14 A. Kafizas, C. J. Carmalt and I. P. Parkin, *Coordin. Chem. Rev.*, 2013, **257**, 2073; L. McElwee-White, *Dalton Trans.*, 2006, 5327.
15 P. Chadha, D. J. H. Emslie and H. A. Jenkins, *Organometallics*, 2014, **33**, 1467; I. Giebelhaus, R. Müller, W. Tyrra, I. Pantenburg, T. Fischer and S. Mathur, *Inorg. Chim. Acta*, 2011, **372**, 340; H. C. Aspinall, J. F. Bickley, J. M. Gaskell, A. C. Jones and G. Labat, *Inorg. Chem.*, 2007, **46**, 5852; R. Anwander, F. C. Munck, T. Priermeier and W. Scherer, *Inorg. Chem.*, 1997, **36**, 3545.
16 B. Basu, S. Das and B. Mandal, *Indian J. Chem.*, 2008, **47B**, 1701; S. T. Liddle and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 2001, 402.
17 A. A. Ahdab, G. Rima, H. Gornitzka and J. Barrau, *J. Organomet. Chem.*, 2001, **636**, 96; J. Wagler, U. Bohme, E. Brendler and G. Roewer, *Organometallics*, 2005, **24**, 1348; B. M. Kraft and W. W. Brennessel, *Organometallics*, 2014, **33**, 158.
18 M. F. Richardson and R. E. Sievers, *Inorg. Chem.*, 1971, **10**, 498; Z. Li, A. Rahtu and R. G. Gordon, *J. Electrochem. Soc.*, 2006, **11**, C787.
19 E. G. Gillan, S. G. Bott and A. R. Barron, *Chem. Mater.*, 1997, **9**, 796; T. Chen, C. Xu, T. H. Baum, G. T. Stauf, J. F. Roeder, A. G. DiPasquale and A. L. Rheingold, *Chem. Mater.*, 2010, **22**, 27.
20 M. Putkonen and L. Niinistö, *Topics in Organometallic Chemistry*, 2005, *9*, 125-145.
21 S. F. Wright, D. Dollimore, J.G. Dunn and K. Alexander, *Thermochim. Acta*, 2004, **421**, 25.
22 W. Hunks, P. S. Chen, T. Chen, M. Stender, G. T. Stauf, L. Maylott, C. Xu and J. F. Roeder, *Mater. Res. Soc. Symp. Proc.*, 2008, **1071**, F09.
23 J. H. Boo, S. B. Lee, K. S. Yu, M. M. Sung and Y. Kim, *Surf. Coat. Technol.*, 2000, **131**,147; M. B. J. Wijesundara, G. Valente, W. R. Ashurst, R. T. Howe, A. P. Pisano, C. Carraro and R. Maboudiana, *J. Electrochem. Soc.*, 2004, **151**, C210; B. P. Swain and N. M. Hwang, *Appl. Surf. Sci.*, 2008, **254**, 5319.
24 C. Y. Kim, S. H. Kim, R. Navamathavan, C. K. Choi and W. Y. Jeung, *Thin Solid Films*, 2007, **516**, 340; M. V. Sopinskyy, V. S. Khomchenko, V. V. Strelchuk, A. S. Nikolenko, G. P. Olchovyk, V. V. Vishnyak and V. V. Stonis, *Nanoscale Res. Lett.*, 2014, **9**, 182.

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