Inorganica Chimica Acta 363 (2010) 1077–1083

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Bis(cyclopentadienyl) zirconium(IV) amides as possible precursors for low pressure CVD and plasma-enhanced ALD

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A R T I C L E I N F O

Article history:
Received 28 April 2009
Received in revised form 30 June 2009
Accepted 5 July 2009
Available online 9 July 2009

Dedicated to Prof. Jonathan R. Dilworth

Keywords:
Zirconium amide
CVD
ALD
Zirconium carbide
Zirconium nitride

A B S T R A C T

Low pressure chemical vapour deposition (LPCVD) of $[ZrCp_2(NMe_2)_2]$ (**1**), $[ZrCp_2(\eta^2\text{-}MeNCH_2CH_2NMe)]$ (**2**), $[ZrCp'_2(NMe_2)_2]$ (**3**) and $[ZrCp'_2(NEt_2)_2]$ (**4**) (Cp = η^5-cyclopentadienyl, Cp′ = η^5-monomethylcyclopentadienyl), onto glass substrates at 600 °C, afforded highly reflective and adhesive films of zirconium carbide and amorphous carbon. Powder XRD indicated that the films were largely amorphous, although small, broad peaks accounting for ZrC and ZrO_2 were present, suggesting that the remaining carbon was due to amorphous deposits from the cyclopentadienyl ligands. SEM images showed an island-growth mechanism with distinct crevices between the concentric nodules. Plasma-enhanced atomic layer deposition (PEALD) of compounds **1** and **2** showed that the precursors were not sufficiently stable or volatile to give a good rate of film growth.

1. Introduction

As demand for smaller electronic devices increases, the need for smaller circuits and electronic components also increases. Modern components contain a conducting barrier layer between the semiconducting silicon and the copper or aluminium connects in order to prevent the diffusion of the metal into the silicon and the consequent destruction of the component functionality. The challenge arises due to the ever smaller dimensions required for the barrier layer [1–3]. Deposition techniques for such a layer include physical vapour deposition (PVD) [4], chemical vapour deposition (CVD) and atomic layer deposition (ALD) [5,6]. Highly conformal and adhesive films at a high growth rate can be grown *via* CVD, whereas ALD, a pulsed dual-source method, gives greater control over film thickness and growth because of the self-limiting nature of this process, although growth rates are lower when compared to CVD. In CVD and ALD the precursors are introduced into the reaction chamber in the gas phase [7]. The method of obtaining gaseous precursors can be varied to suit the conditions required for specific applications, or the nature of the precursor. For example, in atmospheric pressure CVD (APCVD) the precursors are sublimed or evaporated into an inert gas flow and are carried to the substrate. Low pressure CVD (LPCVD) involves a similar process although the reduced pressure is generally sufficient to carry precursors to the reaction chamber. However, the low pressure requirements restrict the size of the apparatus, which means it is suitable for batch production and deposition over small areas, such as in circuitry. Where the precursors are of low volatility, more appropriate CVD methods are: aerosol-assisted CVD (AACVD), where a solution of the precursor is nebulised with a piezo-electric crystal and the resultant solution droplets are carried through the system by an inert gas [8,9]; or liquid injection CVD/ALD, where a precursor solution is injected into a hot zone, where it vaporises before travelling to the substrate under vacuum [10,11].

Zirconium nitride has both conducting (ZrN) and metastable insulating (Zr_3N_4) forms, the latter being the result of metal vacancies in the face-centred cubic lattice [12,13]. However, it is ZrN that is of interest for use in barrier layers due to its low bulk resistivity of 17–22 μΩ cm at 20 °C [14], although other uses include hardness coatings for machinery as an alternative to TiN [15] and decorative alternatives to gold plating [16]. Zirconium carbide, ZrC_x ($x = 0.55–0.99$), adopts only the face-centred cubic structure and its bulk resistivity is comparable to that of ZrN (35–55 μΩ cm at 20 °C), but shows less resistance to chemical attack [17]. Due to

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doi:10.1016/j.ica.2009.07.004

their respective resistivities, a solid solution of ZrN and ZrC_x would still be suitable as a barrier layer.

There are few examples of precursors for the CVD of zirconium nitride reported to date [18], although potential nitrogen-containing precursors have been used in the presence of oxygen to form ZrO_2 thin films, such as $[Zr\{\eta^2\text{-}N(Me)NMe_2\}_4]$ [19] and $[Zr(NEtMe)_2\{\eta^2\text{-}({}^iPrN)_2CNEtMe\}_2]$ [20]. However, deposition of zirconium nitride using the homoleptic amido compound, $[Zr(NR_2)_4]$ (NR_2 = NMe_2, NEtMe, NEt_2), has been reported. Both APCVD [21,22] and ALD [23] in the presence of ammonia gave Zr_3N_4, which is unsuitable for use as a barrier layer due to its aforementioned insulating properties. Recently, we described the use of bis(cyclopentadienyl) zirconium(IV) guanidinate complexes as precursors to zirconium carbonitride thin films [24].

We have been investigating a range of metal complexes as precursors to metal nitride thin films *via* CVD, including TaN and NbN [25,26], TiN and TiN_xC_y [27–32], VN [33], GaN [34], ZrN and HfN [35], WN_xC_y [36] and ZrN_xC_y [24]. This study examines and compares four bis(cyclopentadienyl) zirconium(IV) amide complexes: $[ZrCp_2(NMe_2)_2]$ (**1**), $[ZrCp_2(\eta^2\text{-}MeNCH_2CH_2NMe)]$ (**2**), $[ZrCp'_2(NMe_2)_2]$ (**3**) and $[ZrCp'_2(NEt_2)_2]$ (**4**) (Cp = cyclopentadienyl, Cp′ = monomethylcyclopentadienyl) as potential LPCVD precursors to zirconium carbonitride. The plasma-enhanced atomic layer deposition (PEALD) of compounds **1** and **2** was also investigated.

2. Experimental procedures

2.1. General procedures

All reactions were performed under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques and an Mbraun Unilab glove box. Nitrogen (99.99%) was obtained from BOC and used as supplied. All solvents were stored in alumina columns and dried with anhydrous engineering equipment, such that the water concentration was 5–10 ppm. All reagents were procured from Sigma Aldrich, except for $ZrCl_4$, $[ZrCl_4(THF)_2]$ and zirconocene dichloride, which were purchased from Strem. $[Zr(NMe_2)_4]$ and $[Zr(NEt_2)_4]$ were donated by SAFC Hitech Ltd. [NaCp′(THF)], $[ZrCp'_2Cl_2]$ and $[ZrCl_2(NR_2)_2(THF)_2]$ (R = Me, Et) [37] were prepared by published procedures. *N,N′*-dimethylethylenediamine was degassed and stored over 3 Å molecular sieves under nitrogen. All other compounds were used without further purification.

2.2. Physical measurements

Microanalytical data were obtained at University College London (UCL). NMR spectra were recorded on Bruker AMX500 or ADVANCE III 600 spectrometers, referenced to C_6D_6 distilled over benzophenone or dried and degassed deuterated dimethyl sulfoxide (DMSO-d_6). ^1H and $^{13}C\{^1H\}$ chemical shifts are reported relative to $SiMe_4$ (δ = 0.00 ppm). FT-IR spectra were recorded on a Perkin Elmer Spectrum RX I instrument, over the range 4000–400 cm^{-1}. Mass spectra were recorded on a Micromass ZABSE instrument. Thermogravimetric analysis (TGA) was performed on a Netzsh STA 449C instrument. The TGA was carried out in aluminium pans at atmospheric pressure, under a flow of helium gas. The rate of heating was 10 °C min^{-1}. Vapour pressure measurements were carried out at SAFC Hitech Ltd. on custom-built apparatus. X-ray diffraction (XRD) was carried out on a Bruker AXS D8 Discover machine using monochromatic Cu Kα radiation (λ_1 = 1.54 Å). WDX was performed on a Philips XL30ESEM machine. Scanning electron microscope (SEM) images were obtained on a JSM-6301F Scanning Microscope Field Emission machine. UV–Vis spectra were recorded in the range 300–2500 nm using a Helios double beam instrument.

2.3. Synthesis of $[Li_2(MeNCH_2CH_2NMe)]$

${}^nBuLi$ (59.0 cm^3, 1.6 M in hexane, 94.40 mmol) was diluted with hexane (40 cm^3). This was added dropwise to a stirred colourless solution of *N,N′*-dimethylethylenediamine (5.0 cm^3, 4.10 g, 46.51 mmol) in hexane (60 cm^3), which was cooled to −78 °C. A white precipitate formed after about 30 s. The mixture was stirred for 4 h, after which time it was cooled to −20 °C for 18 h. The supernatant solution was decanted off and the precipitate was dried under vacuum, affording a white powder (yield = 4.38 g, 94%). *Anal.* Calc. for $C_4H_{10}N_2Li_2$: C, 48.03; H, 10.08; N, 28.01. Found: C, 48.69; H, 10.66; N, 27.18%. ^1H NMR δ/ppm (DMSO-d_6, 600 MHz): 2.21 (s, 6H, NCH_3), 2.48 (s, 4H, CH_2NMe). $^{13}C\{^1H\}$ NMR δ/ppm (DMSO-d_6, 600 MHz): 36.1 (NCH_3), 50.9 (CH_2NMe). FT-IR and mass spectrometry data are not available due to the highly air-sensitive nature of this compound.

2.4. Synthesis of $[ZrCp_2(NMe_2)_2]$ (1)

Adapted from the literature [38]. A Schlenk flask was charged with zirconocene dichloride (10.00 g, 34.21 mmol) and $LiNMe_2$ (4.36 g, 85.25 mmol). Hexane (400 cm^3) was cooled to −78 °C and was then added slowly to the reagents with stirring. The pale yellow mixture was allowed to warm to room temperature and was then heated under reflux for 18 h. The yellow mixture was allowed to cool and settle, and the amber solution was filtered off. This was then reduced to dryness under vacuum to give a crude amber product. The product was then sublimed at 85 °C onto a cold finger at 0.1 Torr affording a canary yellow powder (yield = 5.37 g, 51%). *Anal.* Calc. for $C_{14}H_{22}N_2Zr$: C, 54.32; H, 7.16; N, 9.05. Found: C, 52.39; H, 7.13; N, 9.40%. ^1H NMR δ/ppm (C_6D_6, 500 MHz): 2.83 (s, 12H, $N(CH_3)_2$), 5.85 (s, 10H, C_5H_5). $^{13}C\{^1H\}$ NMR δ/ppm (C_6D_6, 500 MHz): 49.3 ($N(CH_3)_2$), 109.8 (C_5H_5). FT-IR cm^{-1} (KBr disc, nujol): 3087 w, 2941 s, 2924 vs, 2854 s, 2810 sh w, 2759 w, 1592 br w, 1458 sh m, 1456 m, 1444 sh m, 1378 m, 1262 m, 1230 w, 1116 m, 1093 m, 1057 m, 1015 s, 939 m, 793 s, 738 sh m, 651 w, 635 w, 528 w, 425 s, 410 s. Mass spec. *m/z* (CI+, methane): 265 $[M-NMe_2]H^+$, 309 $[M]H^+$. TGA: mass loss 67% (calc. ZrN, 67%; Zr_3N_4, 65%) at 590 °C.

2.5. Synthesis of $[ZrCp_2(\eta^2\text{-}MeNCH_2CH_2NMe)]$ (2)

A Schlenk flask was charged with zirconocene dichloride (10.00 g, 34.21 mmol) and $[Li_2(MeNCH_2CH_2NMe)]$ (3.76 g, 37.56 mmol). Hexane (400 cm^3) was cooled to −78 °C and was then added slowly to the reagents with stirring. The pale pink mixture was allowed to warm to room temperature and was then heated under reflux for 18 h. The resulting deep red mixture was allowed to cool and settle and the red solution was filtered twice. This was then reduced to dryness under vacuum to give a deep red glassy solid (yield = 6.01 g, 57%). *Anal.* Calc. for $C_{14}H_{20}N_2Zr$: C, 54.67; H, 6.55; N, 9.11. Found: C, 53.49; H, 6.47; N, 7.36%. ^1H NMR δ/ppm (C_6D_6, 600 MHz): 2.50 (s, 6H, NCH_3), 3.24 (s, 4H, CH_2NMe), 6.03 (s, 10H, C_5H_5). $^{13}C\{^1H\}$ NMR δ/ppm (C_6D_6, 600 MHz): 43.9 (NCH_3), 60.0 (CH_2NMe), 111.8 (C_5H_5). FT-IR cm^{-1} (KBr disc, nujol): 3085 w, 2941 s, 2923 s, 2854 s, 2756 w, 1600 br w, 1456 m, 1378 m, 1261 m, 1152 sh w, 1090 m, 1918 m, 937 w, 932 w, 861 w, 797 s, 733 sh w, 630 w, 427 vs, 408 s. Mass spec. *m/z* (CI+, methane): 220 $[M-MeNCH_2CH_2NMe]H^+$, 241 $[M-Cp]H^+$, 255, 263 $[M-CH_2NMe]H^+$, 305 $[M-H]H^+$, 306 $[M]H^+$. TGA: mass loss 70% (calc. ZrN, 66%; Zr_3N_4, 64%) at 590 °C.

2.6. Synthesis of $[ZrCp'_2(NMe_2)_2]$ (3)

A pink solution of [NaCp′(THF)] (4.90 g, 28.13 mmol) in THF (100 cm^3) was added dropwise to a stirred solution of