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Manganese half-sandwich complexes as metal-organic chemical vapor deposition precursors for manganese-based thin films

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ABSTRACT

The synthesis of compounds $[Mn(\eta^5\text{–}C_5H_4SiMe_3)(CO)_3]$ (**1**), $[Mn(\eta^5\text{–}C_5H_3\text{-1-}SiMe_3\text{-3-}Me)(CO)_3]$ (**2**), $[Mn(\eta^5\text{–}C_5H_4^tBu)(CO)_3]$ (**3**), $[Mn(\eta^5\text{–}C_5Me_5)(CO)_3]$ (**4**) and $[Mn(\eta^5\text{–}C_5H_7)(CO)_3]$ (**5**) and their potential use as metal-organic chemical vapor deposition (MOCVD) precursors for the deposition of manganese-based layers is reported. The thermal behavior of **1**–**5** was studied by thermogravimetry showing that these compounds evaporate in the temperature range of 363–498 K depending on the cyclopentadienyl substituents and the type of pentadienyl used. Vapor pressure measurements indicate that all compounds possess vapor pressures between 60 and 630 Pa at 353 K. Compounds **1**–**5** could be successfully applied in manganese-based film deposition without activation steps prior to the MOCVD experiments. The as-deposited thin layers were characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy and X-ray powder diffraction. Under comparatively mild conditions, whereas **5** possesses the lowest deposition temperature (553 K), dense and conformal layers with growth rates up to 7.0 nm min^{-1} (**5**) could be deposited. Metal carbonyls **1** and **2** featuring a $SiMe_3$ group produced Si-containing manganese-based films. The as-deposited layers from **1**, **2**, **4** and **5** contain carbon impurities (5–8.9 mol-%), while the films from **3** are carbon-free. The layers from **1** and **2** consist of mainly manganese silicate and manganese oxide, whereas those obtained from **3** to **5** are composed of manganese oxides.

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1. Introduction

Manganese-containing materials are of interest, *e.g.*, as catalysts in water oxidation reactions [1,2], as electrode materials for asymmetric super capacitors [3], as magnet data storage media [4,5], or as diffusion barriers between copper and the insulating SiO_2 layer in micro-electronics [6]. Due to the miniaturization in microelectronics and the use of copper interconnects in semiconductor industry, the conventional diffusion barriers are subjected to limitations [7]. According to the International Technology Roadmap for Semiconductors a barrier thickness of 1.9 nm is required for the 22 nm advanced technology node [8]. Referring to this challenge, future diffusion barriers need to be thinner and more effective to reduce the electric resistivity of the interconnect structure [9]. Materials that are currently used as diffusion barriers consist of TaN and WN_x, respectively [10,11]. So far, physical vapor deposition is used to fabricate the respective films [12,13]. However, a coating thickness of even less than 5 nm of these nitride-based materials does not prevent the copper diffusion effectively [9,14,15]. Due to this concern, several materials based on Mn [16], Cr [17], or Ru [18] have been explored and were used in the high temperature fabrication of devices such as complementary metal-oxide-semiconductor (CMOS) transistors [9]. It was found that manganese-containing films are promising candidates for future devices in the CMOS technology, not only from the economic point of view but also based on their properties. Recently, Nguyen et al. showed that 2 nm thin films of manganese silicate, $MnSi_xO_y$, prevent the diffusion of Cu efficiently [19]. Also Mn_xO_y layers are excellent diffusion barriers over a long period of time (100 h at 400 °C) [12]. Moreover, $MnSi_xO_y$ as well as Mn_xO_y thin layers exhibit a good adhesion on Cu and on SiO_2 [20]. These thin solid films were produced by either physical or chemical deposition techniques. Chemical methods such as chemical vapor deposition (CVD) and atomic layer deposition (ALD) are alternative techniques, since they allow the deposition of layers of isotropic nature, enable conformal coverage and, for example, appropriate film thicknesses [9].

During the last years, organometallic and metal-organic manganese compounds such as $[Mn(Me)(CO)_5]$ [21], $[Mn(C(O)Me)(CO)_5]$ [22], $[Mn(\eta^5\text{–}C_5H_5)(CO)_3]$ [23], $[Mn(\eta^5\text{–}C_5H_4Me)(CO)_3]$ [3,24], $[Mn(\eta^5\text{–}C_5H_5)_2]$ [25], $[Mn(\eta^5\text{–}C_5H_4Et)_2]$ [6], $[Mn(acac)_3]$ [26], $[Mn(amd)_2]$ [27] and $[Mn(thd)_3]$ [28] (acac = acetylacetonate, amd = acetamidinate, thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) were used as manganese CVD precursors. The half-sandwich compounds $[Mn(\eta^5\text{–}C_5H_4R)(CO)_3]$

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(R = Me, H) follow a radical decomposition mechanism producing layers with minor carbon impurities [29]. Disadvantageous is, however, that the latter family of molecules possesses only low deposition rates due to their high stability [27]. To enhance the reactivity and decrease the deposition temperature the respective molecules need to be activated, for example, by electron bombardment in the gas phase prior to the deposition processes [30].

This prompted us to synthesize a series of manganese tricarbonyl half-sandwich compounds of composition $[Mn(\eta^5\text{–}C_5H_4SiMe_3)(CO)_3]$ (**1**), $[Mn(\eta^5\text{–}C_5H_3\text{-1-SiMe}_3\text{-3-Me})(CO)_3]$ (**2**), $[Mn(\eta^5\text{–}C_5H_4^tBu)(CO)_3]$ (**3**), $[Mn(\eta^5\text{–}C_5Me_5)(CO)_3]$ (**4**) and $[Mn(\eta^5\text{–}C_5H_7)(CO)_3]$ (**5**) (Scheme 1) and to apply them as MOCVD precursors in the deposition of thin manganese-based layers. Thereby, the main objective was to investigate the influence of various ligands in terms of the deposition parameters in the CVD process. Previous works in our group have shown that the substitution of sandwich complexes led to higher vapor pressure values and to lower decomposition temperatures [31]. Hence, species **1**–**5** are promising CVD candidates for manganese-based film formation, since they exhibit a low melting point. Furthermore, they are more reactive, and due to this no additional activation steps are necessary. Since the decomposition of such molecules is subjected to a radical mechanism, the respective pentadienyl substituents should allow better stabilizing effects on the corresponding (cyclo)pentadienyl-free radical during the decomposition process.

2. Experimental details

2.1. Instruments and materials

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were degassed prior to use. *n*-Hexane was purified by using the solvent purification system MS SPS-800 from MBraun. Anhydrous tetrahydrofuran was obtained by refluxing it over sodium/benzophenone ketyl. Compounds $C_5H_5^tBu$ [32], C_5HMe_5 [33], **1** [34], **3** [35], **4** [35] and **5** [36] were prepared by modified literature procedures (for more details see below). All other chemicals were purchased from commercial suppliers and have been used without further purification.

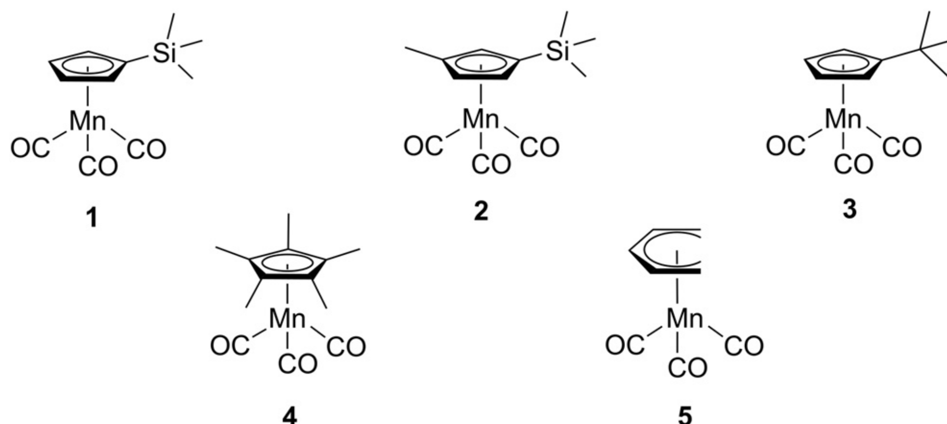
The nuclear magnetic resonance (NMR) spectra were recorded with a Bruker Avance III 500 spectrometer operating at 500.3 MHz for ^1H and at 125.8 MHz for $^{13}C\{^1H\}$ NMR in the Fourier transform mode. The chemical shifts are reported in δ units (parts per million) relative to tetramethylsilane for ^1H and $^{13}C\{^1H\}$ studies. The IR spectra were recorded with a FT Nicolet IR 200 spectrometer. High resolution mass spectra were measured with a micrO-Time-of-Flight (TOF) QII Bruker Daltonite workstation using electro-spray ionization (ESI). Thermogravimetric (TG) investigations were performed with a Mettler Toledo TGA/DSC1 1100 system equipped with an UMX1 balance.

CVD experiments were carried out in a home-built vertical cold-wall reactor equipped with a continuous evaporation system (for more details see reference [31]). For all film depositions a heater dimensioned with a 20 × 60 mm surface was utilized (BACH Resistor Ceramics GmbH). A heat capacity of up to 793 K could be realized, controlled by a Gefran 600 module, which is connected with a Pt100 thermo sensor. The carrier gas flow (N_2, 40 sccm) and the reactive gas flow (O_2, 20 sccm) were controlled by MKS type 247 mass flow controllers connected to the reactor by heated copper lines. The continuous evaporation of the MOCVD precursors was conducted by a molecular pump (EXC 120) from Edwards vacuum. The pressure within the reactor was controlled with an Edwards Active Gauge Controller (PKR 251).

The surface morphology of the as-deposited films was investigated by field-emission scanning electron microscopy (SEM) using a ZEISS Supra60 SEM microscope with an operating voltage at 1 kV for surface and 3 kV for cross-section images. Energy-dispersive X-ray (EDX) analyses were carried out using a Bruker Quantax 400 system attached to the SEM with an XFlash detector 5030 (operating voltage: 10 keV and 3 keV). X-ray photoelectron spectroscopy (XPS) measurements were examined using a PREVAC XPS system kept at ultrahigh vacuum conditions (1×10^{-4} Pa). Monochromatic aluminium K_α radiation (1486.6 eV) was provided by a VG Scienta MX 650 X-ray source and a monochromator system. The energy distribution of the photoelectrons was measured by a VG Scienta EW3000 XPS/UPS/ARPES analyzer. This analyzer was operated at 200 eV pass energy. Concentration quantification was done using standard single element sensitivity factors [37]. The binding energy scale was calibrated with respect to the C1s peak at 284.6 eV. *Casa XPS 2.3.16 Pre-rel* software was used to calculate the atomic concentration of each element. X-ray powder diffraction (XRPD) measurements were carried out with a STOE-STADI-P diffractometer equipped with a Germanium(111) monochromator and Cu $K_{\alpha 1}$ radiation ($\lambda = 0.15406$ nm, 40 kV, 40 mA). All samples were analyzed by the grazing incidence technique with an applied incident angle of 3°.

2.2. Synthesis of trimethylsilylcyclopentadienylmanganese tricarbonyl (*1*) [34]

A solution of cyclopentadienylmanganese tricarbonyl (**6**) (0.36 g, 1.74 mmol) in tetrahydrofuran (40 mL) was treated with a 1.9 M *n*-hexan solution of ^{t}BuLi (0.91 mL, 1.74 mmol) at −80 °C and stirred for 30 min at −50 °C. After warming up the solution to −40 °C, trimethylsilyl chloride (0.88 mL, 6.96 mmol) was added dropwise to the mixture. Afterwards, the solution was slowly heated to ambient temperature and stirring was continued for 1 h. All volatiles were evaporated and the red oily residue was chromatographed (column size 2.5 × 30 cm, alumina, *n*-hexane). Complex **1** was isolated as a pale yellow oil in a yield of 91% (based on **6**, 0.44 g, 1.58 mmol).



Scheme 1. Compounds **1**–**5**, MOCVD precursors for the deposition of manganese-based thin layers.

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