*Materials Science-Poland, Vol. 23, No. 3, 2005*

# Chemical Vapour Deposition (CVD) of metallic layers prepared from silver carboxylates complexes with tertiary phosphines

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Silver fluorocarboxylate tertiary phosphine complexes $[Ag(O_2CR)(PR'_3)]$ (where R = $CF_3$, $C_2F_5$, $Me_3SiCH_2$; R′ = Me, Et) have been used as precursors in the *hot-wall* Chemical Vapour Deposition (CVD) of silver films. The pyrolysis of Ag(I) compounds and the thermal stability of metallic species transported in the gas phase were characterized by temperature variable IR (VT-IR) and MS (MS-EI) methods. Metallic films were produced between 403 and 423 K under the deposition pressure of 0.8–2.0 mbar, under an Ar atmosphere and on Si(111) substrates. They were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) integrated with EDX equipment.

Key words: *silver carboxylate; tertiary phosphine; silver films; chemical vapour deposition*

## 1. Introduction

Low resistivity and high thermal conductivity of silver result in numerous applications of Ag films, including ultra-fast optical switches [1], components of high-temperature superconducting materials [2], and infrared sensors [3, 4]. Chemical vapour deposition (CVD) has been widely used in the fabrication of ultra-thin metallic films at relatively low temperatures, when the appropriate precursors are available. Good silver CVD precursors should exhibit low vaporization and deposition temperatures, and provide high-purity metallic layers. Several inorganic and organometallic species, including AgF, $[Ag(C_4F_7)]_n$, fluorinated Ag(I) β-diketonates and their complexes [Ag(β-diketonate)L] where L is $PR_3$ (R is Me, Et), silanes (e.g., vinyltrimethylsilane, VTES) or diamines (e.g., tetramethylethylenediamine), have been used as CVD precursors [5–8]. In our studies, we focus on silver carboxylate complexes with tertiary phosphines ($[Ag(O_2CR)(L)]$, where R is a fluorinated, nonfluorinated or silylated

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alkyl, and L is a tertiary phosphine), which could be a new group of CVD precursors. In the present paper, the synthesis, mass spectra (MS) and variable temperature IR studies of volatile species and silver films obtained from $[Ag(O_2CCF_3)(PEt_3)]$ (**1**), $[Ag(O_2CC_2F_5)(PEt_3)]$ (**2**), $[Ag(O_2CCH_2SiMe_3)(PMe_3)]$ (**3**), and $[Ag(O_2CCH_2SiMe_3)(PEt_3)]$ (**4**) are described.

## 2. Experimental

The synthesis of complexes was performed in an argon atmosphere using standard Schlenk techniques. Trimethylphosphine (1.0 M soln. in THF) (Aldrich) and triethylphosphine (1.0 M soln. in THF) (Aldrich) were used without further purification. Silver (trimethylsilyl)acetate, and precursors (**1**) and (**2**) were synthesized as reported elsewhere [9–12]. Complexes (**3**) and (**4**) were obtained in the reaction of $Me_3SiCH_2COOAg$ (2.5 mmol) suspended in dry, deoxygenated ethanol (30 $cm^3$), with 2.5 mmol of $PR_3$ (R = Me (**3**) or Et (**4**) ). The mixture was stirred for 3 hours at room temperature in the dark, then filtered and evaporated on a vacuum line. Since (**4**) decomposes at laboratory conditions, it cannot be used in CVD experiments.

IR spectra were recorded with a FT IR Spectrum 2000 spectrometer (Perkin Elmer). Temperature variable IR (VT-IR) (303–523 K) spectra were measured with a SPECAC variable temperature cell, at the dynamic vacuum of $p = 10^{-2}$ mbar. Mass spectra (MS) were measured with a MS AMD-604, MASPEC using the EI method. Thermal analysis (TA) was conducted with a MOM OD-102 (Paulik and Paulik) Derivatograph in the following conditions: sample mass: 0.050 g, temperature range: 298–773 K, heating rate: 2.5 K/min, atmosphere: $N_2$, 20 $dm^3$/h.

The silver films were deposited on Si(111) substrates prepared according to [13], using a horizontal *hot-wall* CVD reactor under Ar atmosphere; vaporization temperature $T_v$ was 303–433 K, decomposition temperatures $T_D$ 403–523 K, reactor pressure $p$ 0.3–2.0 mbar and deposition time $t$ 60–90 min. XRD diffraction data were collected with a Philips X'PERT diffractometer, using $CuK_\alpha$ radiation in the range of $2\Theta$ (30–80)°. The morphology of films was studied using a Scanning Electron Microscope (SEM) LEO 1460V with EDX equipment.

## 3. Results and discussion

The thermal stability of complexes (**1**)–(**3**) was studied by thermogravimetric analysis (TGA). The decomposition started at: 318 (**3**), 403 (**1**), and 423 (**2**) K being completed at 528 (**2**), 553 (**1**), and 618 (**3**) K, leaving metallic silver, what was evident from XRD studies of the residues.

VT-IR spectra of the gaseous products of (**1**) and (**2**) revealed $\nu$(C–H) bands at 2981 and 2902 $cm^{-1}$, a $\delta(PCH_2)$ band at 1401 $cm^{-1}$, and a $\delta_r(PCH_2)$ band at 893 $cm^{-1}$,

confirming that the phosphine species detach in the first step of decomposition (Fig. 1). Above 443 K, however, strong bands between 1000 and 1100 $cm^{-1}$ and at 1803 $cm^{-1}$ (**1**) and 1797 $cm^{-1}$ (**2**) were observed. The former bands can be assigned to C–F group vibrations, but the latter are typical of ester groups. Moreover, bands characteristic of $CO_2$ and CO were detected between 2350 and 2119 $cm^{-1}$.

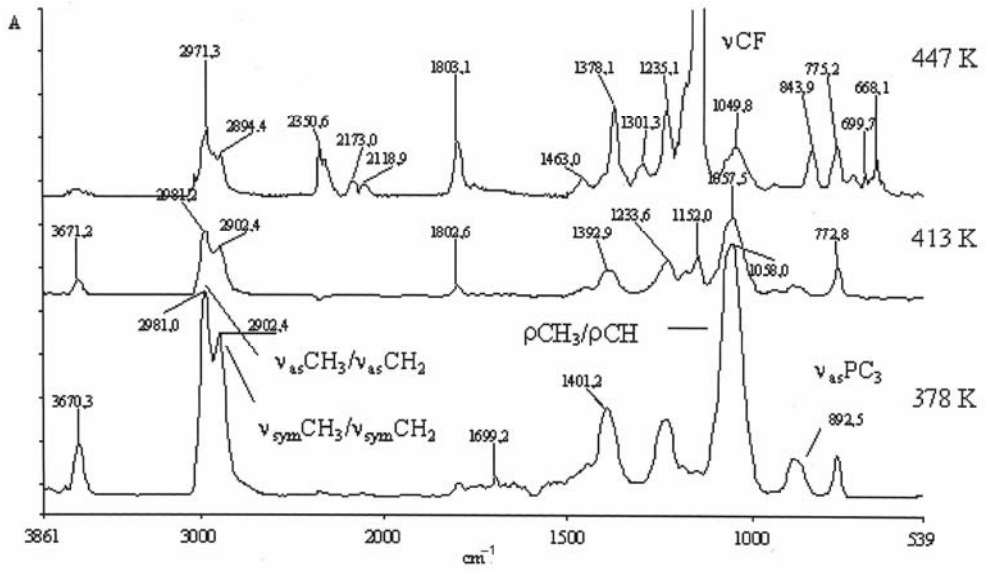


Fig. 1. VT-IR spectra of $[Ag(O_2CCF_3)(PEt_3)]$ (**1**) (gas phase, 318–513 K, KBr)

Mass spectra of volatile metallated species should reveal characteristic signals due to the natural abundance of $^{107}Ag$ (51.8%) and $^{109}Ag$ (48.2%), hence fragments that contain one silver atom should display peaks pattern of 1 : 0.93, whereas disilver fragments should give three peaks with 1 : 1.86 : 0.86 relative intensities. The MS (EI, 453 K) of (**1**) and (**2**) exhibited the following fragments: $[PEtH_2]^+$ *m/z* = 62 (100% for both), $[OPEt_2]^+$ *m/z* = 106 (**1** – 9%; **2** – 15%), $[PEt_3]^+$ *m/z* = 118 (**1** – 49%; **2** – 55%), $[Ag(PEt)]^+$ *m/z* = 167 (**1** – 10%; **2** – 8%), and $[Ag(PEt_3)]^+$ *m/z* = 225 (**1** – 8%; **2** – 20%). Disilver fragments, $[Ag_2(O_2CCF_3)]^+$ (*m/z* = 279) and $[Ag_2(O_2CC_2F_5)]^+$ (*m/z* = 343), were noted as low intensity peaks (1–4%). According to TGA, VT-IR, and MS-EI data, thermal stability can be the main factor influencing the CVD process and the morphology of metallic layers.

In the case of (**3**), MS and VT-IR studies confirmed lack of silver volatile species, which suggests that this compound will not be useful for CVD. The most intensive bands were observed between 393 K and 453 K at 1835 $cm^{-1}$ and 1777 $cm^{-1}$, clearly indicating that one of the liberated compounds was acid anhydride (Fig. 2). We have nevertheless used (**3**) for *hot-wall* CVD, as it revealed the lowest decomposition onset temperature.

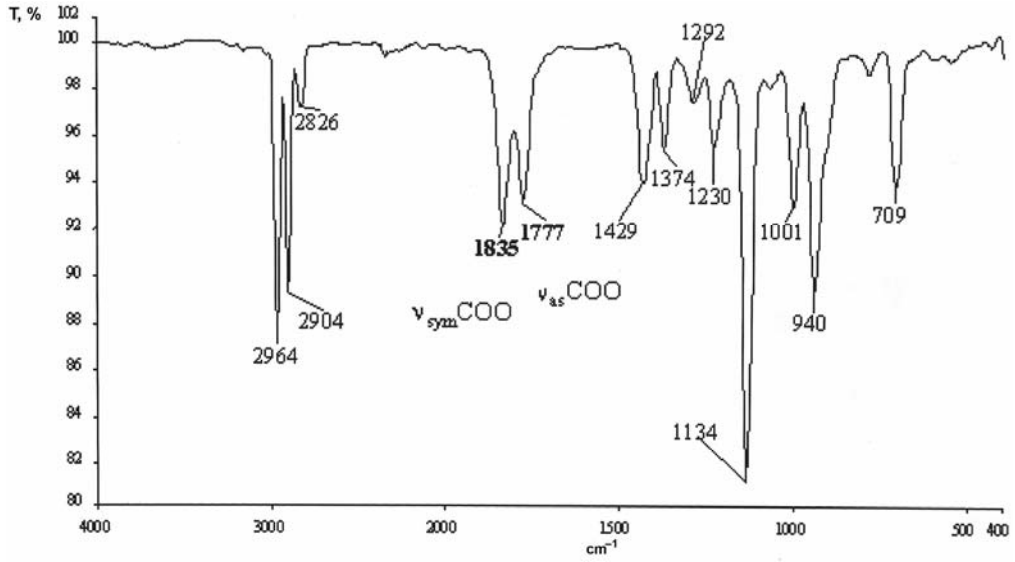


Fig. 2. VT-IR spectra of $[Ag(O_2CCH_2SiMe_3)(PMe_3)]$ (**3**) (gas phase, 453 K, KBr)

*Hot-wall* CVD experiments were performed using (**1**), (**2**), and (**3**). The silver films obtained from **1** and **2** revealed a cubic structure (Fig. 3), which was evident from XRD measurements (38.2 [111], 44.4 [200], 64.6 [220]).

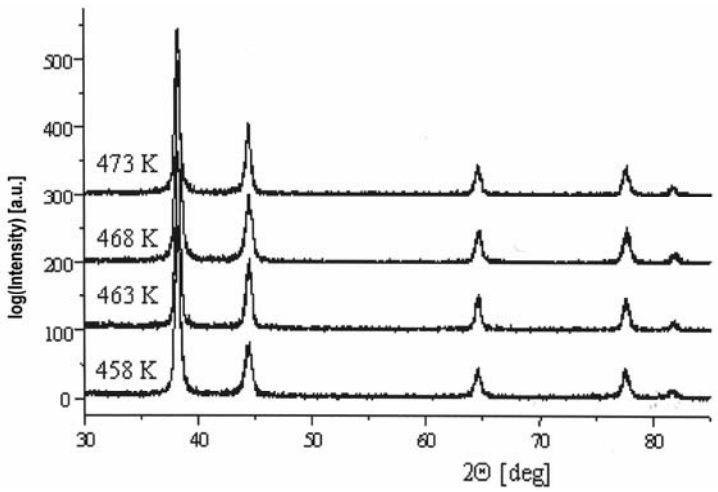


Fig. 3. XRD $\Theta$–$2\Theta$ scans of silver films deposited at various temperatures on Si(111) from $[Ag(O_2CC_2F_5)(PEt_3)]$ (**2**)

The SEM micrographs of films produced from (**1**)–(**3**) were studied. The most promising deposition results were obtained for layers deposited from (**2**), where SEM micrographs reveal a rough and cluster structure (Fig. 4) and EDX spectrum are char-

acteristic of metallic silver. It can be noted that films produced from (**1**) demonstrated a lower density and higher non-uniform thickness. The layer morphology of films deposited from (**3**) and the lack of signals in the EDX spectrum that could be assigned to metallic silver suggest that only condensed organic impurities on the substrate surface were present.

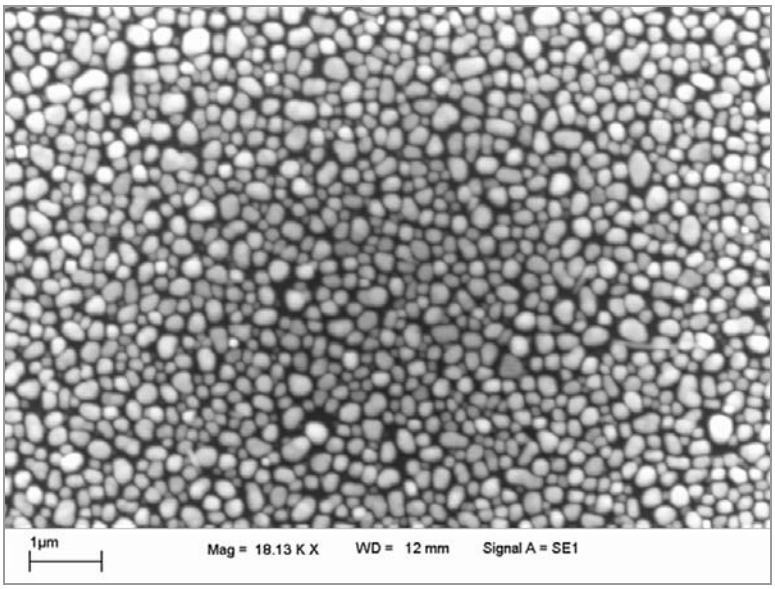


Fig. 4. SEM micrograph of a silver film deposited from (**2**) (Si(111), *hot-wall* CVD, $T_v$ = 433 K, $T_D$ = 523 K)

## 4. Conclusions

Results of CVD experiments revealed that **1** and **2** are promising precursors for silver films, since both compounds exhibit good volatility and sufficient thermal stability. Variations in the pyrolysis pathway and vapour composition appeared to be the main factors influencing the morphology of the silver films.

**Acknowledgements**

The authors wish to acknowledge the Polish Committee for Scientific Research for financial support (grant no. 4T08C 039 23).

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*Received 16 December 2004*
*Revised 15 April 2005*