



Trimethylphosphite stabilized *N*-silver(I) succinimide complexes as CVD precursors

Xian Tao, Yu-Long Wang, Ke-Cheng Shen, Ying-Zhong Shen*

Applied Chemistry Department, School of Material Science & Engineering, Nanjing University of Aeronautics & Astronautics, Nanjing 210016, PR China

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ABSTRACT

The preparation of $[(\text{MeO})_3\text{P}_n \cdot \text{AgNC}_4\text{H}_4\text{O}_2]$ ($n = 1$, **2a**; $n = 2$, **2b**) is described. The molecular structure of **2a** was determined by using X-ray single crystal analysis. Complex **2b** was tested as Metal Organic Chemical Vapor Deposition (MOCVD) precursor in the deposition of silver for the first time. The thin films obtained were characterized using scanning electron microscopy (SEM) and energy-dispersion X-ray analysis (EDX). SEM and EDX studies show that the dense and homogeneous silver films could be obtained.

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In recent years, silver has received considerable attention in microelectronics, due to its lowest resistivity and highest thermal conductivity among all metals [1–5]. Further applications include the use of silver in the production of mirrors [6], as component of high-temperature superconducting materials [7], magnetics [8], or bactericidal coatings [9]. The deposition and characterization of Ag layers grown from new precursors therefore becomes an important research topic.

Various methods have been used to deposit silver thin films, such as sputtering [10], thermal evaporation [11], electron-beam evaporation [12], and chemical vapor deposition (CVD) [13]. Of these techniques, Metal Organic Chemical Vapor Deposition (MOCVD) is a very effective technique to produce high quality metal films with high deposition rates, good step coverage and higher aspect ratio in the multilevel metallization structure for the future generation of integrated circuits [14,15].

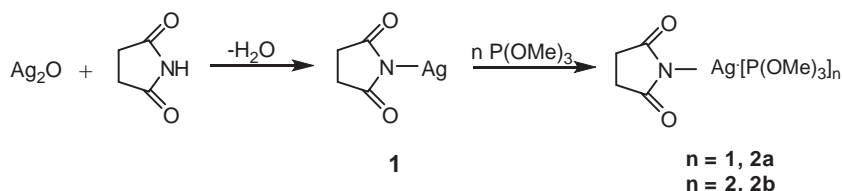
One of the major problems in silver-MOCVD is the availability of appropriate silver(I) precursors. They should be volatile, generally monomeric, easy to handle during the deposition processes, and storable for a long period of time without decomposition at room temperature. However, to date new silver(I) complexes which can be used as precursors in chemical vapor deposition are still not sufficiently available. In order to search for the new precursors for the growth of silver, we reported here the synthesis of trimethylphosphite stabilized *N*-silver(I) succinimide which were used as precursor for the deposition of silver by using MOCVD techniques. The single crystal structure of **2a** has been determined and discussed as well.

Metal organic silver precursors of type $[(\text{MeO})_3\text{P}_n \cdot \text{AgNC}_4\text{H}_4\text{O}_2]$ ($n = 1, 2$) were prepared [16,17] and used for this work. The solvent, dichloromethane (CH_2Cl_2) was purified by distillation from P_2O_5 under N_2 before use. Compound $[\text{AgNC}_4\text{H}_4\text{O}_2]$ (**1**) was synthesized by the reaction of succinimide with excessive Ag_2O in boiling water [18]. Complexes were synthesized by the interaction of $[\text{AgNC}_4\text{H}_4\text{O}_2]$ (**1**) with $\text{P}(\text{OMe})_3$ in stoichiometric ratios in CH_2Cl_2 as shown in Scheme 1.

Complex **2a** crystallizes in the monoclinic with space group $\text{P}2(1)/n$, which is composed of a dimer $[(\text{MeO})_3\text{P} \cdot \text{AgNC}_4\text{H}_4\text{O}_2]_2$, as shown in Fig. 1 and crystal data with refinement parameters is given in supporting information [19]. Complex **2a** is a dimer where a silver atom is coordinated by a phosphorus atom of $\text{P}(\text{OMe})_3$, a nitrogen and an oxygen atom from succinimide. The $\text{Ag}(1)\text{-N}(2)\text{-C}(5)\text{-O}(3)\text{-Ag}(2)$ plane is roughly perpendicular to the $\text{Ag}(1)\text{-O}(1)\text{-C}(1)\text{-N}(1)\text{-Ag}(2)$ plan with a dihedral angle of 77.3° . Four atoms $[\text{O}(1), \text{N}(2), \text{P}(1), \text{Ag}(1)]$ as well as $[\text{N}(1), \text{O}(3), \text{Ag}(2), \text{P}(2)]$ are in the same plane, forming a triangle geometry around silver. The structure features a metallophilic $\text{Ag} \cdots \text{Ag}$ contact of 3.089 between silver atoms which are in a planar three-coordinate configuration. The $\text{Ag}\text{-O}$ distances [2.470(3), 2.543(3)] are close to that of $[\text{Ag}_4\text{PH}_4(\text{P}(p\text{-tol})_3)_6]$ [2.440(5), 2.480(6)] ($\text{PH} = \text{C}_6\text{H}_5\text{-N}_2\text{O}_2$) [20]. The $\text{Ag}\text{-P}$ bond distances in complex **2a** [2.357(7), 2.356(8)] are shorter than the sum of covalent radii of the P and Ag atoms (2.44) [21]. The silver atom and the nitrogen atom of succinimide form $\text{Ag}\text{-N}$ bonds in complex **2a** [2.171(3), 2.142(3)] which are all shorter than that of $[(\text{Ph}_3\text{P})_3 \cdot \text{AgNC}_4\text{H}_4\text{O}_2]$ [2.313(4)] [22]. The angles of $\text{O}(3)\text{-Ag}(2)\text{-N}(1)$ [$99.2(3)^\circ$] and $\text{O}(1)\text{-Ag}(1)\text{-N}(2)$ [$103.3(4)^\circ$] are much larger than that of $[\text{Ph}_3\text{P} \cdot \text{AgO}_3\text{SCF}_3]$ [$90.1(1)^\circ$] [23].

ThermoGravimetry (TG) and Differential Scanning Calorimetry (DSC) studies are required to optimize the temperature at which the respective single silver precursor should be maintained during the

* Corresponding author. Tel.: +86 25 52112906x84765; fax: +86 25 52112626.
E-mail address: yz_shen@nuaa.edu.cn (Y.-Z. Shen).



Scheme 1. Synthesis of Complexes 2a – 2b.

CVD experiments. For an example, the TG and DSC curves of complex **2b** are shown in Fig. 2. It can be seen from the DSC curve that there is one apparent endothermic process with the peak temperatures at 107 °C and one continuous exothermic process with the peak temperatures at 185 °C from 89 °C to 319 °C and the silver precursor decomposes in this range. Firstly, it may lose a P(OEt)₃ from 89 to 160 °C with corresponding weight loss of about 27.30% which is close to the theoretical loss. It is very difficult to distinguish from one step to another and know the sequence of decomposition of another P(OEt)₃ and succinimide. The final percentage of the residue is 25.32%, which is little higher than the theoretical value of silver (23.76%). The thermal measurement is in good agreement with the structural analysis.

CVD experiment using **2b** as precursor was performed in a hot-wall reactor using a continuous evaporation system. The deposition of Ag films was carried out in a reaction chamber (a hot-wall vertical cylindrical reactor). The precursor vessel was heated by a heating band. Carrier gas was introduced into the vessel to pick up the

precursor vapor and transport into the reaction zone. The substrate susceptor was in the reactor that can be heated by a resistive heating element. The reaction by-products were exhausted by a pumping system. In a typical CVD experiment silver was deposited onto pieces of a Si substrate at 350 °C. The precursor temperature was maintained at 75 °C with a nitrogen flow at 20 sccm. The run time was 1 h and the total pressure was maintained at 7.0×10^{-4} bar with nitrogen as carrier gas. No reducing agent such as H₂ was used in the deposition processes. The average film thickness was about 0.6 μm, giving a growth rate of 0.6 μm h⁻¹. The surface morphology and composition of the silver were examined by scanning electron microscopy (SEM) and energy-dispersion X-ray analysis (EDX).

The layer deposited is silver colored. SEM (Fig. 3) studies show that the dense and homogeneous silver layer was formed. The film is composed of many well isolated, granular particulates spreading all over the substrate surface. The sizes of silver grains are in the range of 20–40 nm.

The EDX spectrum (Fig. 3) of the deposited film shows Ag as a main component. Next to silver, silicon as substrate component was detected. This is due to the discontinuous Ag particles exposing the substrate and the relatively high penetration depth of the electron beam during the EDX analysis. The other light elements, such as C, O, and P, which might be present as impurities or formed by surface oxidation of silver, are below the detection limit.

In summary, a straightforward synthesis methodology for the preparation of trimethylphosphite stabilized *N*-silver(I) succinimide complexes was described. Complex **2b** was tested as MOCVD precursor for the deposition of silver for the first time. It has been demonstrated that the complex was a promising candidate as precursor for the deposition of Ag.

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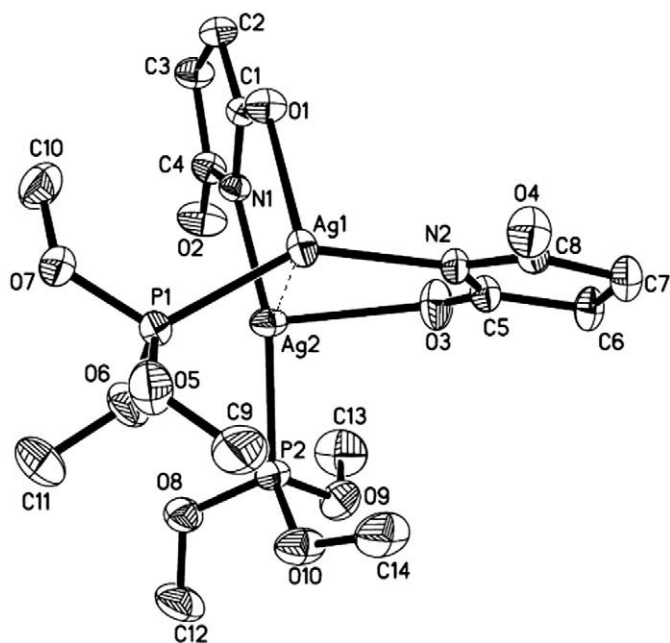


Fig. 1. The crystal structure of **2a**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)–N(2) 2.171(3), Ag(1)–P(1) 2.357(11), Ag(1)–O(1) 2.470(3), Ag(2)–N(1) 2.142(3), Ag(2)–P(2) 2.356(12), Ag(2)–O(3) 2.543(3), O(4)–C(8) 1.217(5), C(1)–O(1) 1.243(4), C(1)–N(1) 1.346(5), C(1)–C(2) 1.507(5), N(1)–C(4) 1.384(5), C(5)–O(3) 1.233(5), C(5)–N(2) 1.359(5), C(5)–C(6) 1.515(6), C(4)–O(2) 1.214(5), C(4)–C(3) 1.520(6), C(7)–C(8) 1.517(6), C(7)–C(6) 1.519(6), C(8)–N(2) 1.372(5), C(2)–C(3) 1.518(6); N(2)–Ag(1)–P(1) 144.4(9), N(2)–Ag(1)–O(1) 103.3(11), P(1)–Ag(1)–O(1) 110.1(8), N(1)–Ag(2)–P(2) 158.9(9), N(1)–Ag(2)–O(3) 99.2(12), P(2)–Ag(2)–O(3) 95.5(9), C(1)–O(1)–Ag(1) 123.5(2), C(5)–O(3)–Ag(2) 129.7(3), O(4)–C(8)–N(2) 125.0(4), O(4)–C(8)–C(7) 124.2(4), N(2)–C(8)–C(7) 110.7(4), O(1)–C(1)–N(1) 124.8(4), O(1)–C(1)–C(2) 122.7(3), N(1)–C(1)–C(2) 112.5(3), C(1)–N(1)–C(4) 109.8(3), C(1)–N(1)–Ag(2) 131.3(3), C(4)–N(1)–Ag(2) 118.7(3), C(5)–N(2)–C(8) 110.2(4), C(5)–N(2)–Ag(1) 122.4(3), C(8)–N(2)–Ag(1) 127.2(3), C(5)–C(6)–C(7) 103.6(4), C(1)–C(2)–C(3) 103.4(3).

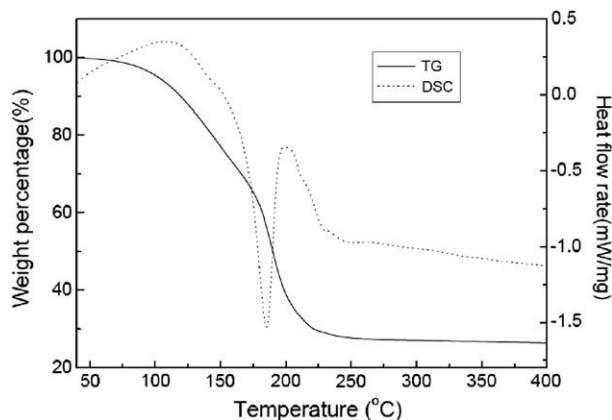


Fig. 2. TG and DSC curves of **2b** (heating rate 10 °C min⁻¹, nitrogen atmosphere).

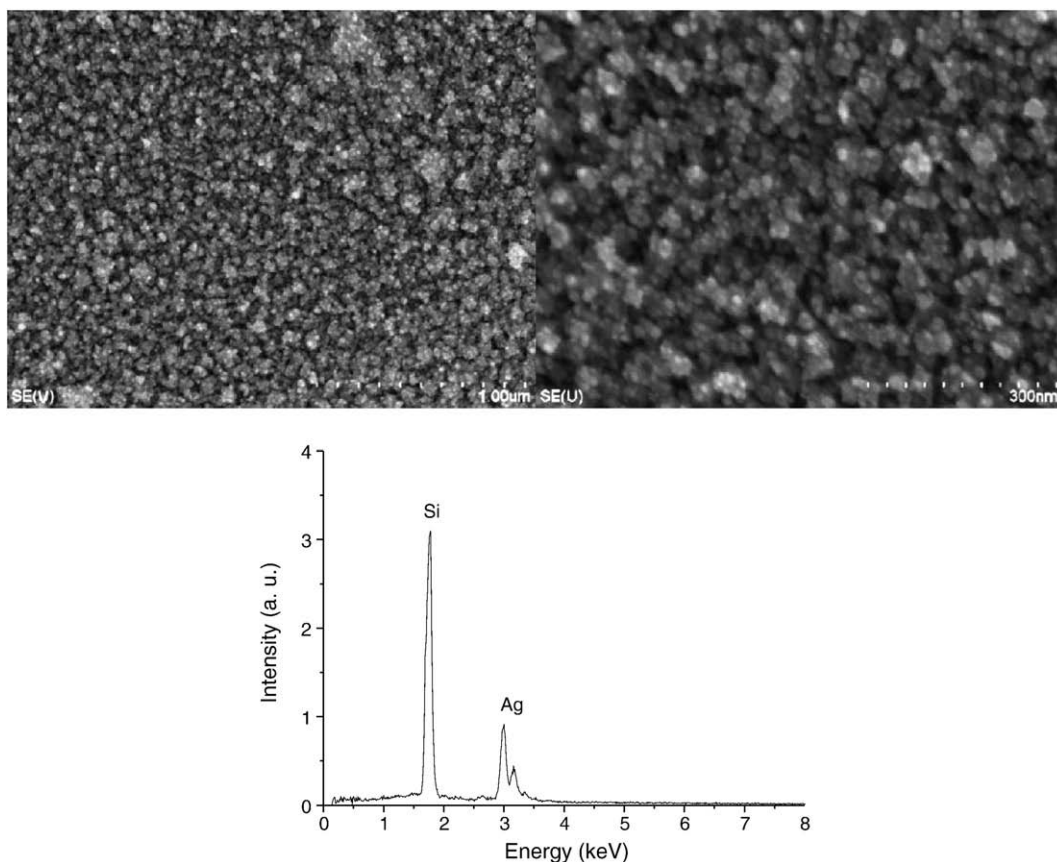


Fig. 3. SEM images showing the morphology and EDX spectrum of the silver deposit obtained from the MOCVD at 350 °C of sample **2b** deposited on a Si wafer.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2010.10.014.

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- [16] Complex **2a** was obtained by N-silver(I) succinimide (0.1379 g, 0.67 mmol) with trimethylphosphite (0.1661 g, 1.34 mmol) in CH₂Cl₂ at 0 °C. A white solid product was obtained after removing all volatiles in oil-pump vacuo. Yield: 0.29 g (95% based on N-silver(I) succinimide). Mp.: 170 °C dec. Anal. calcd. for C₁₄H₂₆O₁₀Ag₂P₂N₂: C, 25.48; H, 3.97. Found: C, 25.39; H, 3.83. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 2.61 (s, 4 H, CH₂-H), 3.66–3.68 (d, 9 H, CH₃-H, J_{PH} = 12.6 Hz). ¹³C{¹H} NMR (CDCl₃, 125 MHz, ppm): δ 32.1 (CH₂), 51.3 (CH₃/CH₃O-), δ 191.6 (C=O). IR (KBr) data (cm⁻¹): 3437 (m), 3285 (m), 2939 (m), 2839 (w), 1701 (m), 1618 (s), 1439 (m), 1359 (s), 1269 (s), 1249 (s), 1182 (m), 1012 (s), 790 (m), 761 (m), 669 (m), 571 (w), 526 (m), 451 (m). ³¹P{¹H} NMR (CDCl₃, 121 MHz, ppm): δ 126.8.
- [17] Complex **2b** was synthesized by N-silver(I) succinimide (0.1132 g, 0.55 mmol) with trimethylphosphite (0.2046 g, 1.65 mmol). After appropriate work-up, complex **2b** was obtained as a colourless liquid. Yield: 0.29 g (91% based on N-silver(I) succinimide). Anal. calcd. for C₁₀H₂₂O₈Ag₂P₂N₂: C, 26.45; H, 4.88. Found: C, 26.31; H, 4.73. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 2.62 (s, 4 H, CH₂-H), 3.64–3.66 (d, 18 H, CH₃-H, J_{PH} = 12.1 Hz). ¹³C{¹H} NMR (CDCl₃, 125 MHz, ppm): δ 32.3 (CH₂), δ 50.7 (J_{PC} = 5.5 Hz, CH₃/CH₃O-), δ 192.1 (C=O). IR (KBr) data (cm⁻¹): 3458 (m), 2952 (m), 2843 (s), 1710 (m), 1590 (s), 1439 (m), 1352 (s), 1291 (s), 1250 (s), 1183 (m), 1013 (s), 793 (m), 675 (m), 523 (m), 450 (m). ¹P{¹H} NMR (CDCl₃, 121 MHz, ppm): δ 134.4.
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