

Syntheses of Liquid Phase [(efac)Ag(P(OR)₃)] Precursors and Their Application to the Preparation of Silver and Silver Selenide Thin Films

Hong-Ki Kim, Han-Cheol Jeong, Kyung Soo Kim, Seok Hwan Yoon, Seung Soo Lee, Kook Won Seo, and Il-Wun Shim*

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea

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Recently, the preparation of silver metal thin films through chemical vapor deposition (CVD) has been a research field of particular interest due mainly to their wide variety of applications, such as contact materials in microelectronic circuitry,¹ components of high T_c superconductors,² bactericidal coatings,³ and the development of electroluminescent materials.⁴ A central issue in the typical low-pressure CVD process for the preparation of silver films has been the development of thermally stable silver precursors; a number of Ag precursors has been reported but they often showed low volatility and thermal and/or photochemical instability. Among them, silver β -diketonate phosphine adducts were interesting since phosphine ligands could function as both anti-oligomerization and deoxygenating agents. The incorporation of the ancillary ligands is believed to give rise to coordination saturation around silver metal and to prevent oligomerization reaction. Also, the phosphine ligands are well known to reduce oxygen contamination in silver films. But many of the phosphine compounds are pyrophoric or air sensitive. Accordingly, in this study, various phosphites were chosen as an ancillary ligand because they are relatively more stable and easy to handle. Besides, such phosphite ligands are expected to be better π acceptors than phosphine ligands, leading to more thermally stable silver complexes. Also, silver selenide thin films have been extensively studied because of their potential applications to superionic conductors,⁵ solar cells,⁶ thermochromic materials, and photosensitizers.⁷

In this background, new phosphite adduct precursors of silver β -diketonate complexes were synthesized and characterized by various spectroscopic methods. Using them, silver metal films were deposited on glass or silicon substrates through MOCVD method. Then, those silver metal films were converted to Ag₂Se film by selenium vapor deposition.

Experimental Section

General. Infrared spectra were obtained on Jasco FT/IR-5300 spectrometer and NMR spectra were recorded on Varian Gemini 2000 NMR spectrometer. Thermal analyses, including TGA and DSC, were carried out with Setaram LABSYS, and mass spectra were obtained on Autospec EBE mass spectrometer. For the analyses of Ag and Ag₂Se thin films, Scintag XDS 2000 X-ray diffractometer, I.S.I.-DS 130, and a Philips XL30S FEG scanning electron micro-

scope equipped with a Phoenix Energy Dispersive X-ray spectrometer (EDAX) were used. Specific resistivities of silver films were measured with Alpha-step 500 surface profile and CMT-SR 1000N (4 point probe).

Syntheses of silver(I) precursors. Phosphite adducts of β -diketonate silver complexes were synthesized with AgNO₃, ethyl 4,4,4-trifluoroacetoacetate [H(efac)], trimethyl phosphite [P(OMe)₃], triethyl phosphite [P(OEt)₃], triisopropyl phosphite [P(OiPr)₃], and Na metal (from Aldrich Co.). Tetrahydrofuran, diethylether, and pentane were used as solvent after distillation to remove water molecules. For a typical preparation of [(efac)Ag(P(OEt)₃)], sodium β -diketonate was first made using 0.2 mol of Na metal and 0.21 mol of [H(efac)] in 30 mL of pentane solution at 0 °C. After stirring the solution until all sodium metal disappeared, the sodium salt precipitate was filtered and dried for 24 hours under vacuum. Meanwhile, silver nitrate was transformed to phosphite adduct by mixing 0.1 mol of triethyl phosphite and 0.1 mol of AgNO₃ in 20 mL of diethylether solution. After reaction, the mixture became a clear colorless solution. To this solution, 0.1 mol of sodium β -diketonate in 20 mL of THF was slowly added and the mixture was stirred for 2 hours. Then, a white precipitate of NaNO₃ was filtered off and after slow evaporation of solvent under vacuum, a brown-colored [(efac)Ag(P(OEt)₃)] was obtained in liquid phase. All other precursors were prepared with high yields in a similar manner.

1) [(efac)Ag(P(OMe)₃): yield 88%, brown liquid, EI-MS *m/z* 414 (M⁺), ¹H-NMR (300 MHz, CDCl₃): δ 4.97 CH (s, 1H), 3.99 CH₂ (q, 2H), 3.65 CH₃ (b, 9H), 1.99 CH₃ (t, 3H). IR 1671 cm⁻¹ (ν (C=O)), 1582 cm⁻¹ (ν (C=C)), 789 cm⁻¹ (ν (P-O)).

2) [(efac)Ag(P(OEt)₃): yield 91%, brown liquid, EI-MS *m/z* 456 (M⁺), ¹H-NMR (300 MHz, CDCl₃): δ 5.10 CH (s, 1H), 4.05 CH₂ (quintet, 6H), 4.04 CH₂ (q, 2H), 1.32 CH₃ (t, 9H), 1.23 CH₃ (t, 3H). IR 1678 cm⁻¹ (ν (C=O)), 1579 cm⁻¹ (ν (C=C)), 798 cm⁻¹ (ν (P-O): 798).

3) [(efac)Ag(P(OiPr)₃): yield 87%, brown liquid, EI-MS *m/z* 498 (M⁺), ¹H-NMR (300 MHz, CDCl₃): δ 5.12 CH (s, 1H), 4.64 CH (s, 3H), 4.06 CH₂ (q, 2H), 1.31 CH₃ (d, 18H), 1.23 CH₃ (t, 3H). IR 1679 cm⁻¹ (ν (C=O)), 1581 cm⁻¹ (ν (C=C)), 790 cm⁻¹ (ν (P-O)).

Silver and silver selenide thin films. Chemical vapor deposition experiments were carried out without H₂ gas, using the above precursors in a glass warm-wall reactor on

silicon [LG Siltron p-type (100)] or glass substrates as previously reported.^{8,9} Substrate temperature was controlled to 240–360 °C and bubbler to 80 °C. Working pressure during deposition was kept at about 0.1–0.5 torr, using argon as a flowing gas.

The experiments for the conversion of Ag films to silver selenides were performed by simply exposing the selenium vapor at 250 °C. After a 3 hour reaction, the silver metallic color of the films changed to dark gray.

Results and Discussion

All synthesized precursors were volatile liquid but quite stable toward thermal- or light-decomposition reactions to silver metal particles over more than several days. Thermogravimetric analyses conducted at atmospheric pressure under argon indicated that the silver precursors decompose in the temperature range of 169–203 °C, as shown in Table 1. It is noteworthy that the decomposition temperature range is somewhat lower than those of triorganic phosphine adducts of silver carboxylates or silver- β -diketonates.^{10,11} In the typical case of [(efac)Ag(P(OEt)₃)], it started to decompose

Table 1. Physical properties of synthesized Ag precursors

Precursors	State	Decomposition Temperature (°C)	Light Stability
[(efac)Ag(P(OMe) ₃)]	brown liquid	168.7	good
[(efac)Ag(P(OEt) ₃)]	brown liquid	202.7	good
[(efac)Ag(P(OiPr) ₃)]	brown liquid	190.1	good

good: stable, more than 3 days in the air

at 203 °C without significant volatilization of the intact complexes, and corresponding weight loss was about 76.5%, which is quite comparable to the calculated loss of 75.5%. This result is indicative of their relatively higher volatility and a decomposition process free of contamination, leading to the formation of very pure silver thin films.

The major components of the gas mixture from the decomposition processes were easily identified to be CO₂, C₂H₄, CF₃COCH₃, and a small amount of CO on the basis of known gas phase FT-IR spectra.¹² Adhesion of the Ag films to the substrates was good, and the deposition rate was about 0.2 nm/min at a substrate temperature below 240 °C. But at high substrate temperature above 300 °C, the decomposition increased to about 1.5 nm/min. Average grain sizes in diameter increased from 50 to 1700 nm as the substrate temperatures increased from 240 °C to 360 °C. Figure 1 shows that as the substrate temperature increases, the silver metal particle sizes increase drastically due to their nucleation and following crystal growth process.

Average resistivities of the silver films by the four-point probe method greatly depended on the degree of nucleation or the grain size of metal particles. When they were grown at a substrate temperature of 240 °C, the resistivity was 5.3 $\mu\Omega\text{cm}$, indicating that there was large contact resistivity due to relatively smaller silver particles. But at a substrate temperature exceeding 330 °C, it became 1.61 $\mu\Omega\text{cm}$, which is quite close to that of pure silver metal (1.60 $\mu\Omega\text{cm}$). This result was corroborated by their X-ray diffraction patterns (JCPDS 04-0783), as shown in Figure 2. Also, EDAX analyses showed that there were no appreciable amounts of O, F, and P impurities in the films.

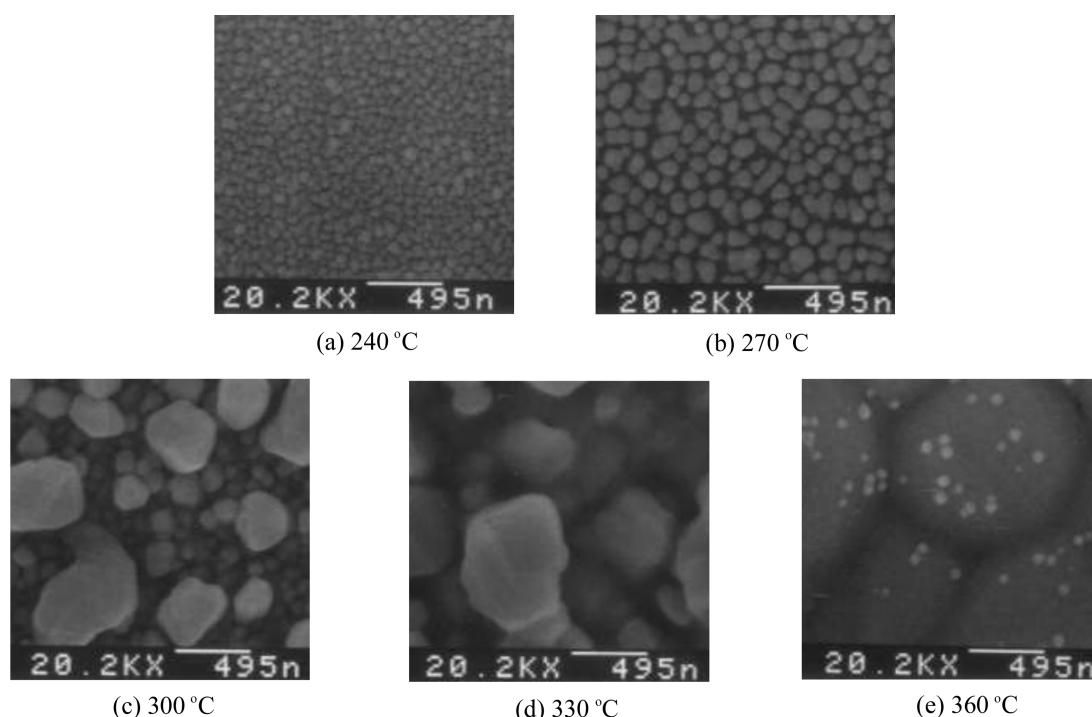


Figure 1. SEM image at 15 kV of Ag films on Si substrate at different substrate temperatures using [(efac)Ag(P(OEt)₃)] precursor.

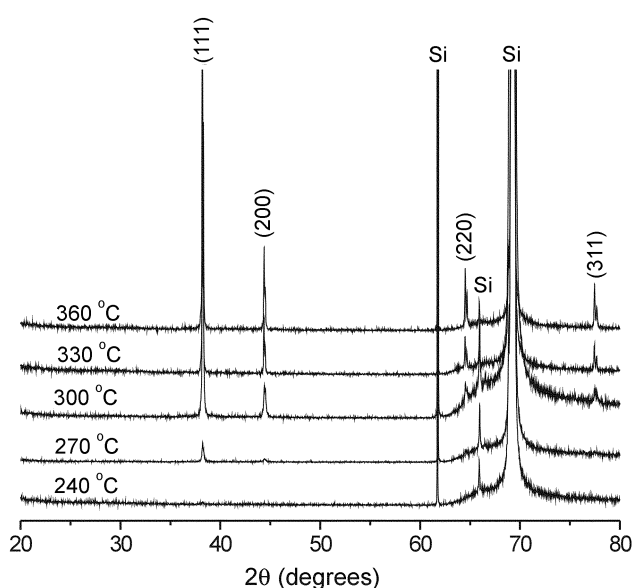


Figure 2. X-ray diffraction patterns of Ag films at different substrate temperatures.

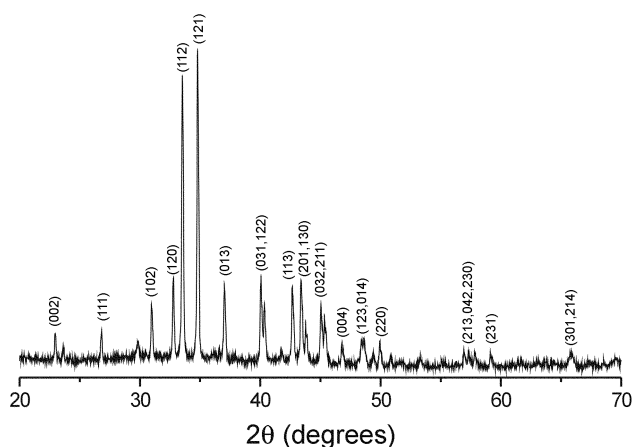


Figure 3. X-ray diffraction pattern of Ag_2Se thin film.

The experiment for the conversion of Ag thin films to Ag_2Se was implemented by simply exposing the silver thin film (substrate temperature 120 °C) to selenium vapor at 250 °C. After 3 hours, the silver metallic color of the films changed to dark gray and the X-ray diffraction patterns of the resulting films accorded quite well with that of Ag_2Se (JCPDS 24-1041) as shown in Figure 3, revealing that the silver selenide is in β -orthorhombic structure.¹³⁻¹⁵ Also, it should be noted that there were no other peaks that could be related to possible impurities such as Ag, Ag_2O , and Se. In the scanning electron microscopy (SEM), the micrograph of the Ag_2Se thin films showed that the average particle sizes are about 1.26 μm in diameter after gas phase selenization

reaction. According to EDAX measurements with a power source of 30 kV, the composition of the film corresponds to the stoichiometric composition of Ag_2Se . Analogous Ag and Ag_2Se thin films were successfully obtained by using other two silver precursors under similar conditions.

Conclusion

New Ag precursors containing neutral phosphite ligands were synthesized in high yields and characterized by various spectroscopic methods. These precursors were quite volatile liquids and useful in the preparation of silver thin films through bubbler type MOCVD without H_2 gas for reduction. In the typical case of $[(\text{efac})\text{Ag}(\text{P}(\text{OEt})_3)]$, very pure silver thin films were obtained under relatively mild conditions in the substrate temperature range of 240-360 °C without any appreciable amounts of F, O, and P impurities. These silver thin films were easily converted to silver selenide in β -orthorhombic phase by simple selenium vapor deposition method at 250 °C. In SEM analysis, the average particle size of the latter was found to be about 1.26 μm with relatively narrow size distribution.

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