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A Comparative Study Of A Series Of Dimethylgold(III) Complexes With S,S Chelating Ligands Used As MOCVD Precursors

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Abstract

Dimethylgold(III) complexes with S,S donor ligands having AuC_2S_2 coordination core are compared as precursors for gold MOCVD. Three of them are liquids, the fourth one is low-melting compound. They are non-sensitive to air and light, stable under storage, do not require special handling conditions, and show a good volatility and sufficient vaporization stability. Based on monitoring of the gas phase during the programmed heating of the compound vapor in vacuum, in hydrogen and in oxygen presence, the information concerning stability of the precursor in the gas phase and gaseous products of thermolysis was obtained. It was established that decomposition mechanism in the presence of the studied gas-reactants changed in comparison with vacuum only for diethyldithiocarbamate complex. MOCVD experiments have been performed within the temperature range 210-300 °C with and without hydrogen or oxygen. The films obtained in hydrogen presence were more thick indicating higher growth rate. Effect of gas-reactant on the morphology of the films deposited is discussed.

Keywords: gold films; MOCVD; volatile dimethylgold(III) complexes; thermolysis mechanism

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1. Introduction

Gold films are of interest due to their low resistivity and high corrosion stability; they have various applications in microelectronics, as an anticorrosive coating material, etc. Gold nanoparticles shows high catalytic activity in a variety of chemical processes [1-3]. Recently, gold-based nanostructure materials have become the object of intensive research in medicine [4]. Here we concern complexes of gold(III) with organic ligands and their application as precursors to obtain gold films and gold nanoparticles by metallorganic chemical vapor deposition (MOCVD). Such volatile dimethylgold(III) compounds as β-diketonates, carboxylates and others [5-9] have been tested as gold CVD precursors. This is a comparative study of volatile dimethylgold(III) complexes with S,S chelating ligands: liquid dimethylgold(III) dialkyldithiophosphates (**1**- $Me_2AuS_2P(OMe)_2$, **2**- $Me_2AuS_2P(OEt)_2$, $Me=CH_3$, $Et=C_2H_5$) dimethylgold(III) dialkyldithiophosphinate (**3**- $Me_2AuS_2P^iBu_2$, $^iBu=CH_2CH(CH_3)CH_3$) and low-melting diethyldithiocarbamate (**4**- $Me_2AuS_2CNEt_2$). These molecular compounds have the same coordination core AuC_2S_2. Their thermal behavior in the condensed phase was studied by thermogravimetric analysis (TGA). Results of such a study could be used to evaluate a suitability of the compound for MOCVD but they do not give insight into deposition mechanism of the precursor. We use an original mass spectrometry technique to study volatile complexes of metals with organic ligands on heated surface. It was used to identify the involving compounds, to evaluate their vaporization stability as well as to monitor the changes in the gas phase composition during the programmed heating of the compound vapor in vacuum, in hydrogen and in oxygen presence. In this way, we obtained the information concerning the thermal stability of the precursor in the gas phase, gaseous products of its thermolysis along with the temperature ranges of their formation. MOCVD experiments have been performed with and without hydrogen or oxygen to evaluate an effect of gas-reactant. Comparison of data on composition of gaseous products of decomposition with data on composition and morphology of the films deposited was performed.

2. Results and Discussion

Under standard conditions, **1-3** becomes transparent oily liquids, **4** – light yellow solid (M.p. 38°C). They were obtained in a high yield (>80%) without use of special synthesis and handling conditions [10, 11].

Mass spectrum of the compounds contains the molecular ion $[Me_2AuL]^+$, $[AuL]^+$ and $[L]^+$ (L = S_2POMe_2, S_2POEt_2, $S_2P^iBu_2$, S_2CNEt_2 for **1-4**, respectively). The absence of fragments of the mass greater than that of the molecular ion indicates that **1-4** are monomeric in the gas phase.

As revealed by TGA (atmospheric pressure, He 30-40 mL/min), **1-3** evaporate with partial decomposition (Fig. 1), the residue amounts were 7 % for the best complex (**2**), and 13 and 28 % for two others (**1**, **3**). Amount of residue increased with increasing the heating rate. **4** evaporates almost completely regardless of an environment and a heating rate. Under heating in oxygen presence (O_2-Ar 10-40 mL/min) as well as under heating in a helium flow at higher heating rate, **3** has two losses of weight producing a residue of about 60 % and 30 %, respectively. Thus, **4** shows the best thermal behavior in the condensed phase.

2.1. Thermal decomposition study

Built input system for the time-of-flight (TOF) mass spectrometer (MS) consisting of an evaporator and a temperature-controlled cell (thermal reactor) allowed us to study heterogeneous thermolysis under low-pressure (LP) CVD conditions with the *in situ* analysis of the gas phase. Compound in a glass ampoule was kept at constant temperature T_e (55, 60, 75, 90 °C for **1-4**, respectively) in the evaporator under dynamic vacuum conditions. The vapor of the compound passed into the reactor, which was heated from T_e to 350-450 °C with a rate of 5 °/min. Sampling was performed directly into the MS ion source through the 0.2 mm

effusive orifice of the reactor. From the full-range mass spectra (ionization electrons energy *ca.* 70 eV) the temperature dependences of the intensities of the ion peaks were derived. Such dependences look like classic kinetic concentration dependences (Fig. 2). The examination of the changes in the mass spectrum at different temperatures allowed us to reveal gaseous products. Upon reaching decomposition onset temperature, intensities of the peaks of Au-containing ions originating from the intact complex decrease while intensities of the ion peaks corresponding to the thermolysis products increase.
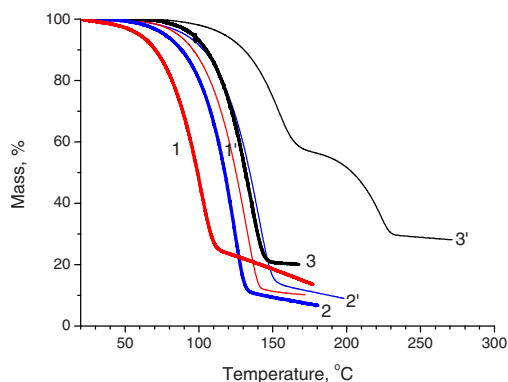

Fig. 1. TG curves (heating rate 1K/min): 1, 2, 3 – recorded for compounds **1**, **2**, **3** in He; 1', 2', 3' – recorded for compounds **1**, **2**, **3** in O_2.

The study was performed in the absence of gas-reactant (vacuum), in the oxygen and hydrogen presence. The gas-reactant was introduced directly into the reactor. Detailed report on study of thermolysis of **1-2** and **4** in vacuum is presented in [11] and [10], respectively.
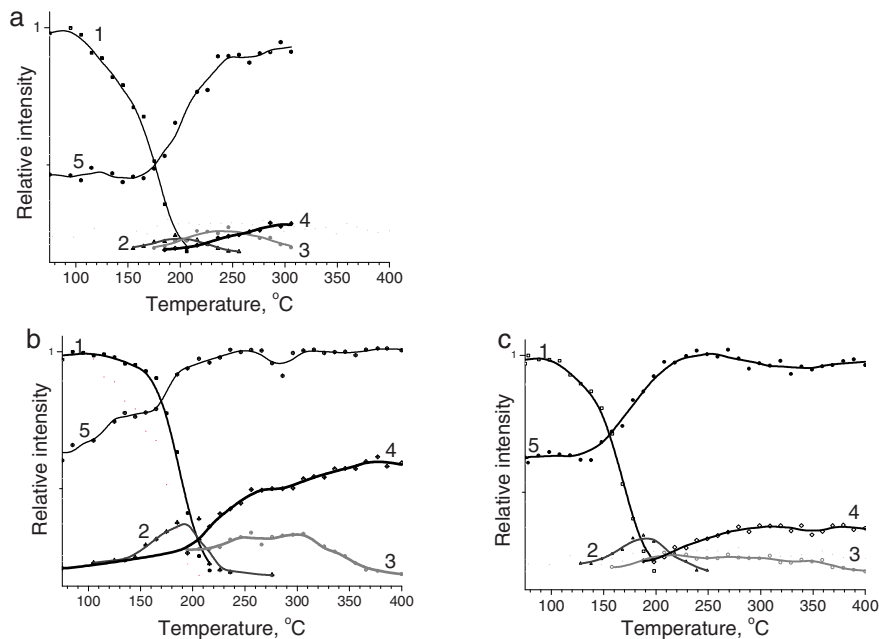

Fig. 2. Temperature dependence of the gas phase composition for the decomposition of **2** (a) in vacuum, (b) at H_2 presence, (c) at O_2 presence: 1- $[AuL]^+$, 2- $[HL]^+$, 3- ion at m/z 122, 4- ion at m/z 62, 5- $[C_2H_4]^+$.

As expected, the most similar thermal behavior is observed between dialkyldithiophosphate complexes **1** and **2** differing by alkyl group at oxygen atom. They have close thermal stability (decomposition onset within the range of 130-160°C). Dimethylgold dialkyldithiophosphinate **3** is slightly more stable (150-170°C).

Composition of gaseous thermolysis products revealed from the analysis of the temperature dependence of the mass spectra is given in the Table 1. If available, assignments of the ion peaks was done based on comparison of the mass spectra obtained with the reference from the NIST mass spectral library. Formation of the protonated HL and methylated MeL ligands is quite explainable as a result of intramolecular rearrangement in the precursor, *e.g.* such products have been recorded for dimethylgold(III) β-diketonates and their derivatives [12]. Evolution of ethane and ethylene is also expectable due to presence of Me groups bound to gold in the precursors. A feature of thermolysis of these complexes is the formation of a gaseous product giving in the mass spectrum molecular ion at m/z 94, 122, 178 for **1**, **2**, **3**, respectively. Formally, molecular formula of the product may be R_2S_2 (dialkyldisulfide) or/and $SP(H)R_2$ (dialkylphosphine sulfide) for **1-3**, besides, it may be $HP(OR)_2$ for **1-2**. Seems, occurrence of two maximums at the curve of temperature dependence of ion peak intensity indicates the formation of two species.

3 differs from **1** and **2** by the formation of product giving ion at m/z 258 in mass spectrum. It may be attributed to Me_2AuH_2P. Notice, such a thermolysis pathway results in non-effective use of precursor during gold CVD at temperature lower 350°C owing to part of the precursor does not produce elemental gold. Most probably, this could be overcome using higher deposition temperature.

Table 1. Composition of gaseous phase during the thermal decomposition of complexes **1-4**

complex	m/z	assignment
1, L= $S_2P(OMe)_2$	172	$[MeL]^+$ - methylated ligand
	94	$[R_2S_2]^+$ - dialkyldisulfide or/and $[SP(H)R_2]^+$ - dialkylphosphine sulfide
	47	$[PO]^+$
	30	ethane
	28	ethylene; (fragmentary ion from ethane)
2, L= $S_2P(OEt)_2$	186	$[HL]^+$ - protonated ligand
	122	$[R_2S_2]^+$ (dialkyldisulfide) or/and $[SP(H)R_2]^+$ (dialkylphosphine sulfide)
	62	$[POCH_3]^+$ $([SC_2H_5]^+)$
	47	$[PO]^+$
	30	ethane
	28	ethylene; (fragmentary ion from ethane)
3, L= $S_2P^iBu_2$	258	$[Me_2AuP]^+$ (fragmentary ion)
	210	$[HL]^+$ - protonated ligand
	178	$[R_2S_2]^+$ - dialkyldisulfide or/and $[SP(H)R_2]^+$ - dialkylphosphine sulfide
	177	$[SPR_2]^+$
	41	$[C_3H_7]^+$
	30	ethane
	28	ethylene; (fragmentary ion from ethane)
	15	$[Me]^+$
4, L= S_2CNEt_2	163	$[MeL]^+$ - methylated ligand
	149	$[HL]^+$ - protonated ligand
	131	$[MeSCNEt_2]^+$
	87	$[SCNEt]^+$ - ethylisothiocyanate
	76	CS_2 or/and $[HSNEt]^+$
	47	$[SMe]^+$
	34	$[H_2S]^+$ - hydrogen sulfide
	30	ethane
	28	ethylene

As to effect of oxidant and reductant gases to the thermolysis, general conclusion for complexes **1-3**, neither hydrogen nor oxygen presence change qualitative composition of gas phase, while relative amount of

the products in hydrogen presence is maximal, and it is minimal in vacuum. Fig. 2 illustrates this conclusion by the example of **2**.

Complex **4** in gas phase is considerably more stable than phosphorus-containing complexes **1**-**3,** and its stability in hydrogen and oxygen presence is higher than in vacuum: changes in the mass spectrum are observed at T>260°C (H$_2$, O$_2$) and 210°C (vacuum). In addition, composition of gaseous products of thermolysis in the presence of both gases differs in comparison to vacuum. Products giving peaks at m/z 87 (SCNEt) and m/z 76 (HSNEt) were recorded in mass spectrum upon thermolysis in hydrogen and oxygen presence, while neither metylated ligand nor MeSCNEt$_2$ was observed.

2.2. Thin films study

Gold films were obtained after 30 min of deposition in a stagnant-flow, vertical cold-wall reactor under the following conditions: evaporator temperature T$_e$ = 55, 60, 75, 90 ^{o}C for **1-4**, respectively, deposition temperature T$_d$ = 210, 250 and 300 ^{o}C depending on the precursor used, total pressure - 10 Torr (1.33*10^3 Pa), argon (25 sccm) was used as the carrier gas, oxygen or hydrogen were used as gas-reactant (25 sccm). Gold films were deposited onto oxidized silicon (100) wafers. During deposition time full evaporation of 20 mg of the precursor occurred. Gold deposited films are continuous and show the gold metal aspect. The formation of gold films upon MOCVD within the temperature range 250-300 ^{o}C using the involving precursors was confirmed by means of XPS and XRD analysis. Fig. 3 shows an example of XPS spectrum. It should be noted that nanoparticles or non-continuous films have been obtained at lower deposition temperature. The thicknesses of the films deposited from the various precursors measured using interference microscopy with a laser profilometer Zigo 6300 New View are within the range 3 to 175 nm (Table 2). The presence of hydrogen results in increase in the average thickness.

Analysis of SEM images (JEOL-JSM 6700 F scanning electron microscope) showed that all the precursors give small-grain films at lower deposition temperature (210 ^{o}C for **1** and **2** and 250 ^{o}C for **3** and **4**). Fig. 4 shows selected SEM data. Increase in deposition temperature results in coalescence and increased thickness. For precursors **1** and **2**, film grains are larger under deposition in H$_2$ presence, however film deposited from **2** is less porous. Films deposited from **4** in H$_2$ presence are more porous and considerably thicker. Films obtained at the same deposition conditions from **3** are of worse quality comparing with **4**. For all the precursors, the growth rate in hydrogen presence is higher. It could be suggested that this is due to the fact that the growing surface is more efficiently released from the reaction products, which follows to the mass spectrometric results. It could be due to formation of well adsorbing products during thermolysis of **3** on the surface. Average grain size was dependent on gas-reactant. Presence of hydrogen gives larger grains than with argon or oxygen. A similar observation has been reported for gold CVD from toluene solution of trifluorophosphine gold(I) chloride precursor [13].

Thus, the deposition temperature to obtain films of good quality is lower for dialkylphosphinates. The thickest films are deposited from diethyldithiocarbamate complex.

Table 2. Thickness of the films obtained at different deposition conditions

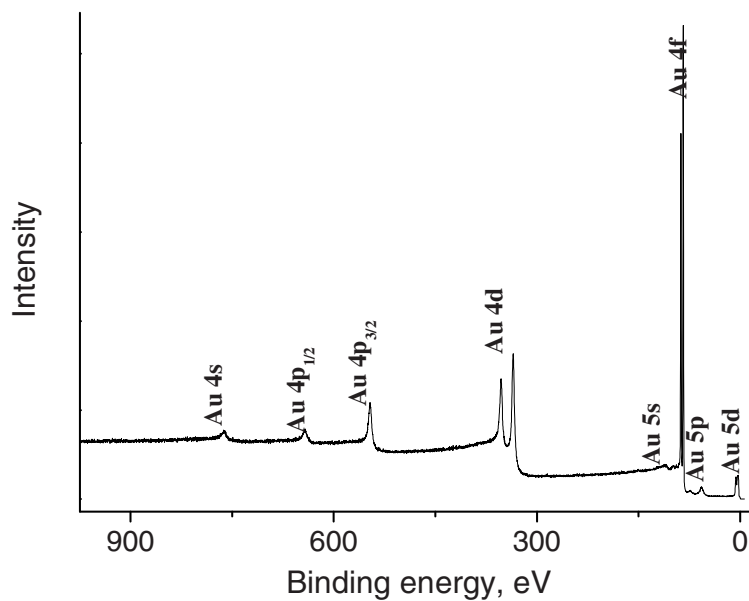| Complex	Thickness (nm)								
	210 ^{o}C			250 ^{o}C			300 ^{o}C		
	Ar	H$_2$	O$_2$	Ar	H$_2$	O$_2$	Ar	H$_2$	O$_2$
1	7	10	3-4	15	21	12			
2	7	7	3-4	28	35	13			
3							5	15	5
4							95	175	90

Fig. 3. General XPS spectrum of gold film deposited from **2**, O$_2$, T$_d$ = 250 ^{o}C.
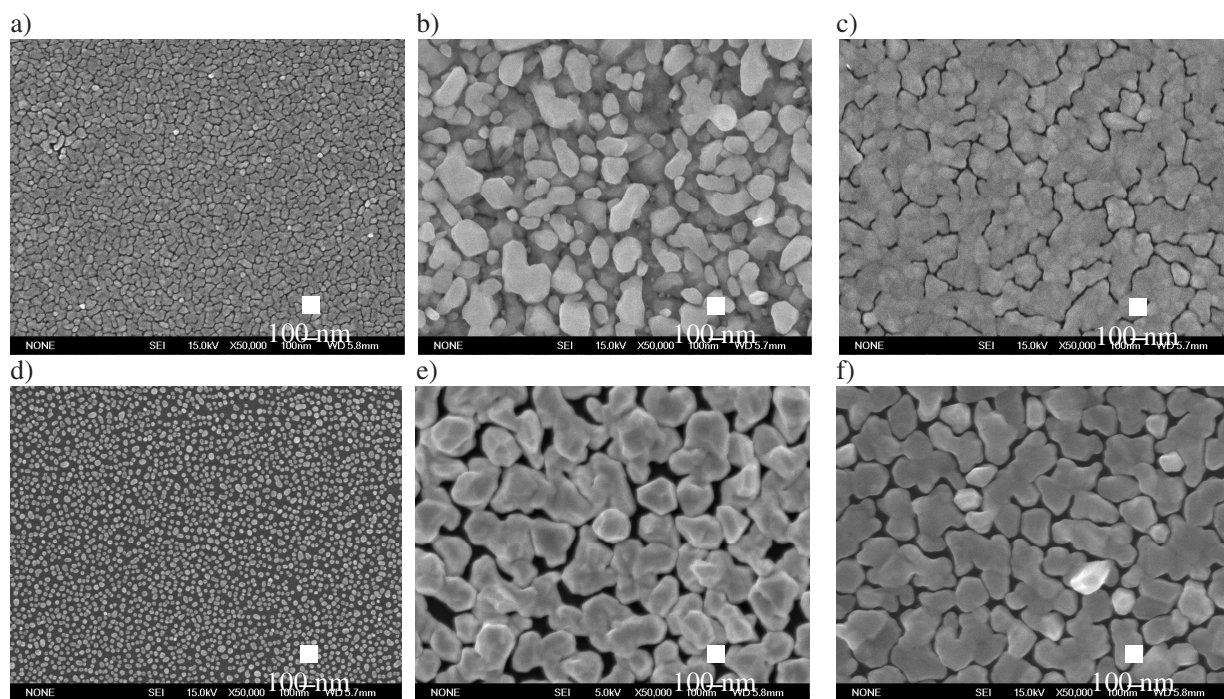
Fig. 4. SEM images of CVD gold films: (a) **1**, O$_2$, T$_d$=210°C; (b) **1**, H$_2$, T$_d$=210°C; (c) **1**, H$_2$, T$_d$=250°C; (d) **4**, H$_2$, T$_d$=250°C; (e) **4**, H$_2$, T$_d$=300°C; (f) **4**, O$_2$, T$_d$=300°C.

2.3. Summary

We performed a comparative study of vapor phase behavior for dimethylgold(III) complexes with S,S donor ligands. The reported complexes give continuous gold films of different morphology during MOCVD within the range of 210-300 ^{o}C. The correlation of results of mass spectrometric study and CVD experiments allows concluding that the composition of gas phase and solid products does not depend much on the nature of the studied gas-reactants. However, for hydrogen co-reactant a typical increase in the growth rate and grain size was observed. These phenomena we explain by the increased amount of growth centers due to the ability of hydrogen to remove the reaction products from the surface irreversibly, providing no self-retardation of gold deposition.

Acknowledgements

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