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Gold CVD Using Trifluorophosphine Gold(I) Chloride Precursor and Its Toluene Solutions

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The chemical vapor deposition (CVD) of gold using trifluorophosphine gold(I) chloride, a simple and volatile inorganic precursor, is presented. Both solid precursor and its toluene solutions were used as starting materials. With the solid precursor placed in a simple bubbler, adhesive and continuous gold thin films were grown on Ta/TaN/SiO₂/Si substrates with a growth rate of only 8 Å min⁻¹. However, with a liquid delivery system using 2.5% precursor solution in toluene with a volume rate of 0.3 mL min⁻¹, a growth rate of 200 Å min⁻¹ was achieved. Both H₂ and N₂ were used as carrier gas, but only in the case of H₂ were compact and highly pure 100–200 nm thick gold films grown on Ta/TaN/SiO₂/Si at deposition temperature as low as 110°C. The dependence of the deposition process and characteristics of gold deposited films, such as morphology, microstructure, and chemical composition, on deposition temperature and the nature of the carrier gas (N₂ or H₂) was also investigated. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2766648] All rights reserved.

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There has been much interest in the formation of thin films of metals using chemical vapor deposition (CVD).¹ These thin films have found applications in microelectronics, optical devices, wear protection, and catalysts.² Gold films are particularly interesting because of their low resistivity (2.44 $\mu\Omega$ cm) and high chemical corrosion resistance. However, gold CVD studies have not been developed extensively like copper because of the limited gold precursor resource. Some recent studies showed that gold may be deposited from either gold(I) precursors³⁻¹⁰ or gold(II) precursors.¹¹⁻¹⁵ Most of the known used precursors are metallo-organic compounds containing C or O atoms or both. Like other metals, gold demonstrates a high affinity for C and O and hence, these elements, when they are present in the precursor, are incorporated into the thin films as impurities. Therefore, the use of inorganic volatile precursors containing neither C nor O atoms could be an approach to solve this problem.¹⁶⁻¹⁸

The trifluorophosphine gold(I) chloride [AuCl(PF₃)], which was for the first time synthesized by Fuss and Ruhe¹⁹ and characterized recently by an X-ray structure,²⁰ has been tested with success for gold deposition by laser induced chemical vapor deposition (LCVD), electron-beam induced deposition (EBID) and local deposition in the tip-sample gap of a scanning tunneling microscope.²¹ However, blanket CVD studies using this precursor have not been published to date to our knowledge.

Under inert atmosphere, $AuCl(PF_3)$ decomposition may follow the same pyrolysis mechanism to form gold metal as the one determined for alkyl gold(I) trialkylphosphine precursors.^{6,22} However, when hydrogen is used as a coreagent, the precursor decomposition pathway might follow another reaction route as proposed following

$$\operatorname{AuCl}(\operatorname{PF}_3)_g \to [\operatorname{AuCl}(\operatorname{PF}_3)] \cdot S$$
 [1]

$$H_{2s} \to [H-H] \cdot S \to 2[H] \cdot S$$
[2]

$$[\operatorname{AuCl}(\operatorname{PF}_3)] \cdot S \to [\operatorname{AuCl}] \cdot S + [\operatorname{PF}_3] \cdot S \qquad [3]$$

$$[PF_3] \cdot S \to PF_{3g}$$

$$[4]$$

$$[\operatorname{AuCl}] \cdot S + [\operatorname{H}] \cdot S \to [\operatorname{Au}] \cdot S + [\operatorname{HCl}] \cdot S \qquad [5]$$

$$[HCl] \cdot S \to HCl_g$$
[6]

S indicates a surface adsorbed species, while g is a gaseous molecule. In the initial steps of the gold deposition, H_2 should be dissociatively adsorbed on the surface of the Ta substrate.^{23,24} The H_{ad} atoms then probably reduce [AuCI]·S to produce metallic gold. Hence, the Ta metal surface might be considered as a catalyst for the nucleation of gold when H_2 coreactant is used. Once a continuous gold film is deposited on the substrate surface, the growth of gold takes place on the surface of the growing film.⁶

In this paper, we report the study of gold metallic CVD thin film using the inorganic gold(I) precursor. Both hydrogen and nitrogen were used as carrier gas to evaluate the effect of their nature on the gold CVD process and thin-film production. Sublimation technique using the solid pure precursor in a bubbler and liquid injection of toluene precursor solutions were employed to vaporize and introduce this precursor into the reactor chamber.

Experimental

Precursor synthesis.— The precursor $AuCl(PF_3)$ was synthesized from $AuCl_3$ by the synthesis process reported in the literature.¹⁹ Because of its poor stability, being especially light and air-sensitive, conservation of this precursor for a long period is rather challenging. In our group, it could be kept for weeks in a darkened-sealed tube (under vacuum or under nitrogen) at approximately 0°C.

Substrates.— SiO₂/Si [thermal 100 nm of SiO₂ on Si(100) wafers] and Ta/TaN/SiO₂/Si substrates were used for these deposition experiments. Square samples 1×1 cm were cut in the 200 mm wafers and cleaned as follows.

 SiO_2/Si substrates were first immersed in an oxidizing solution of 0.5 M $Na_2S_2O_8$ in concentrated H_2SO_4 for 10–15 min, then washed extensively with water and dried with isopropanol vapors.

Ta/TaN (TaN: 20 nm, Ta: 15 nm) films were deposited on SiO_2/Si substrates by PVD. These substrates were cleaned by a flux of dry nitrogen gas for 10 min before use.

Gold films deposition using solid pure precursor.— A simple, vertical homemade CVD reactor (Fig. 1a) was used for this study. The reaction chamber was made of glass and had a diameter of about 180 mm and a height of about 220 mm. In a typical experiment, the bubbler of the CVD setup was charged with 30–50 mg of AuCl(PF₃) precursor and then purged several times with dry nitrogen. The substrate temperature was 200°C and the total pressure in the reactor was kept at 0.2 Torr. During deposition experiments the precursor was kept at room temperature while the outside of the reaction chamber was warmed to 30–40°C.

Gold film deposition using toluene precursor solutions.— The 2.5% precursor solution in dried and degassed toluene was prepared immediately before use and kept at room temperature during the deposition experiments. In a typical experiment, precursor solution was introduced into the vaporizer by an automatic injection system (Jipelec Inject) with a volume rate of 0.3 mL min⁻¹. The precursor vapor then was fed into the reaction chamber, 180 mm in diameter and 250 mm in height (Fig. 1b), with 100 sccm of hydro-

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Figure 1. (Color online) Schematic diagram of the CVD setups (a) using a bubbler and (b) using a liquid injection system.

gen or nitrogen carrier gas. The reaction chamber wall and the vaporizer were warmed to $30-40^{\circ}$ C. The total pressure was maintained at 2.2 mbar. The substrate temperature was chosen in the temperature interval of $110-210^{\circ}$ C.

In a separate experiment, the volatile reaction by-products from the CVD of 20 mL toluene precursor solution (at a substrate temperature of 140°C and 100 sccm H₂ carrier gas), was trapped at 77 K in a cold trap between the reaction chamber and the vacuum pump. The cold trap was disconnected from the CVD setup when the precursor injection was completed, and then 10 mL of distilled water was added into the trap. After this water addition, the trap was slowly warmed to room temperature in order to dissolve the trapped HCl, if produced in the decomposition reaction. At the end of experiment, the aqueous phase in the trap was separated from the toluene phase and analyzed.

The pH of the water solution was measured with a pH paper test. The presence of Cl⁻ anion in the solution is determined by the precipitation of AgCl after reaction with a silver nitrate solution.

Thin-film characterization.— A SEM-FEG LEO 1530 with a Gemini column scanning electron microscope (SEM) operating at an accelerating voltage of 3 kV was used to characterize the morphology of gold-deposited films. The XRD characterizations were carried out by an X-ray powder diffractometer with a θ -2 θ goniometer (Philips, PW 1080, graphite secondary monochromator) and Co K α radiation (40 kV, 30 mA). A 1° divergence slit and 0.1 mm receiv-



Figure 2. SEM pictures of CVD gold films deposited (a) on Ta/TaN/SiO₂/Si at 200°C using the solid precursor; (b) on Ta/TaN/SiO₂/Si at 140°C with N₂ carrier gas using toluene precursor solution; (c) on Ta/TaN/SiO₂/Si at 200°C with N₂ carrier gas using precursor solution; (d) on Ta/TaN/SiO₂/Si at 140°C with H₂ carrier gas using precursor solution; (e) on Ta/TaN/SiO₂/Si at 110°C with H₂ carrier gas using precursor solution; in an (f) on SiO₂/Si at 140°C with H₂ carrier gas using precursor solution;

ing slit were used. The data was collected in the angular range of 40–130 $2\theta_{Co}$, in the step mode with a step scan of 0.03° and 8 s per step. The X-ray photoelectron spectroscopy (XPS) experiments were performed on an ESCALAB 220i-XL, V.G. spectrometer. The Al K α ray of a dual Mg/Al source was used and the analyzed area was close to 3 mm². Photoelectrons were collected perpendicularly on the surface and treated in a constant analyzer energy code (20 eV). Scratch tests have been used to roughly evaluate the adhesion of the gold film. The resistivity of deposited gold films was measured at room temperature by a homemade four-points system. Each measurement was performed four times.

Results and Discussion

CVD using the solid precursor source.— Gold films 200 nm thick were deposited on substrates after 4 h of deposition. The gold deposited films are continuous, bright, and demonstrate the gold metal aspect. Gold films grown on Ta/TaN/SiO₂/Si passed the scratch test, in contrast with those deposited on SiO₂/Si, which are nearly all peeled off by the adhesive tape.

A typical film deposited on Ta/TaN/SiO₂/Si is shown in Fig. 2a. This film consists of considerably large grains (\sim 200 nm) which are mixed together with smaller ones (<20 nm).

The electron spectroscopy for chemical analysis (ESCA) revealed that this film contained C, O, Cl, F, and P near the surface. The C and O surface impurities came either from the film air exposure between the CVD process and insertion into the XPS spectrometer or from a residual H_2O in our CVD setup, whereas Cl, F, and P contaminants incorporated on the film are due to the adsorption and/or thermal decomposition of by-products. Nevertheless, a single argon ion sputter (4 kV, with a beam current of 1 μ A, for 10 min) is



Figure 3. (Color online) XPS spectrum after 10 min of Ar sputtering of a gold CVD film grown on Ta/TaN/SiO₂/Si at 200°C using the solid precursor AuCl(PF₃).

sufficient to completely remove the C, Cl, F, and most of the O and P impurities, leaving essentially pure Au metallic film (Fig. 3).

The good properties of deposited films using AuCl(PF₃) demonstrated that this inorganic complex is a valuable precursor for gold CVD production. However, the growth rate of a film deposited on Ta/TaN/SiO₂/Si is estimated to be as low as 8 Å min⁻¹, which means that long deposition periods are needed to obtain continuous films. In general, the growth rate can be improved by increasing the precursor concentration in the gas phase and hence, the sublimation temperature. This procedure is known to be useful for thermally stable precursors, which is not the case for AuCl(PF₃), which begins to decompose when exposed for more than 30 min at temperatures as low as 40°C.

However, because $AuCl(PF_3)$ is soluble in organic, very thermally stable solvents such as toluene or benzene, we chose to use a liquid delivery system in our more detailed studies on the deposition of gold metallic thin films employing this precursor. Using an injection system, the precursor solution should be introduced into the reaction chamber while the solution is kept at room temperature or lower to avoid maximally precursor decomposition. Furthermore, the precursor concentration in gas phase can be increased safely and easily by increasing the concentration and/or the volume rate of the precursor solution fed into the reaction chamber. Thus, this way should be favored to obtain sufficiently thick deposited films in shorter deposition periods.

Chemical vapor deposition using toluene solution.— Smooth gold films are obtained by CVD when a liquid delivery system is used. The growth rate of these films is clearly higher than that of films grown at the identical substrate temperature but employing a solid precursor source. With nitrogen as a carrier gas, a growth rate



Figure 4. (Color online) Gold CVD growth rate using AuCl(PF₃) toluene solutions on Ta/TaN/SiO₂/Si substrates as a function of the growth temperature with N_2 or H_2 as carrier gas.

of 200 Å min⁻¹ is achieved for a film deposited at 200°C on Ta/TaN/SiO₂/Si using 2.5% toluene precursor solution, which is 25 times higher than that estimated for a film deposited using AuCl(PF₃) solid precursor. Theoretically, even higher growth rates can be achieved if more concentrated solutions are used.

The deposition rate was found to be dependent on the carrier gas used. For example, at deposition temperature of 140° C, the growth rate obtained with H₂ is four times higher than that with N₂ (140 and 35 Å min⁻¹, respectively). Moreover, the minimal deposition temperature is lowered when H₂ is used. Continuous 100–200 nm thick films are deposited with a growth rate of 60 Å min⁻¹ at temperatures as low as 110° C under H₂, whereas under N₂, only small isolated grains are obtained at 130° C, even after a long deposition process.

Figure 4 shows the gold CVD growth rate using AuCl(PF₃) toluene solution on Ta/TaN/SiO₂/Si substrate as a function of substrate temperature using either H₂ or N₂ carrier gas. The activation energy of the surface reaction can be deduced from the slope of the curve in the kinetically reaction-controlled regime. The values obtained are 69.5 kJ mol^{-1} and 35.0 kJ mol^{-1} for N₂ and H₂, respectively. Thus, the precursor pyrolysis reaction, which occurs when N₂ is used, is more strongly affected by the substrate temperature than the decomposition pathway when H₂ is used.

The transition temperature between the kinetic regime and the feed-rate-limited one for the surface decomposition reactions of the AuCl(PF₃) precursor is also strongly affected by the nature of the carrier gas used. The temperature was lowered when H₂ carrier gas was used; hence, the temperatures are 200 and 140 °C for N₂ and H₂, respectively.

A pH value of ~2 is measured for the aqueous solution separated from the decomposition by-products mixture by the separation process described in the Experimental section. In addition, the precipitation of AgCl is observed when AgNO₃ solution is added into the aqueous solution. These observations demonstrate that HCl byproduct is produced in the decomposition reaction of AuCl(PF₃) precursor when H₂ carrier gas is used.

The production of HCl by-product, together with the changes in the kinetic characteristics of the surface decomposition reaction (growth rate and activation energy), suggests that H_2 acts as a reductive coreactant in the decomposition of AuCl(PF₃) at the reported deposition conditions. The proposed mechanism, a reductiondecomposition process, seems to be a probable deposition pathway when reductive H_2 is used.



Figure 5. (Color online) Depth profile analyses of a gold film deposited on $Ta/TaN/SiO_2/Si$ at 200°C using AuCl(PF₃) toluene solution and N₂ carrier gas: (a) Au, C, O, Ta and (b) Cl, P, F impurities.

Characterization of gold films grown by the solution method.- The deposition temperature has a strong impact on the gold film morphology. Figure 2b shows the surface morphology of a film deposited on Ta/TaN/SiO₂/Si at 140°C with N₂ as a carrier gas. The film is formed by grains whose size distribution is quite narrow (50–70 nm). As growth temperature is increased, the grain growth and the surface diffusibility of the growth species increase. Thus, the size of gold grains also increases and their size distribution is broader. The morphology of a film grown at 200°C, which is given in Fig. 2c, reveals that considerably large grains ($\sim 200 \text{ nm}$) were mixed with the smaller ones (\sim 30 nm); a similar morphology has been observed for the film deposited at identical substrate temperature but using the solid precursor source (see Fig. 2a). Similarly, an increase in grain size with increasing substrate temperature was observed for the films deposited using H_2 coreagent (Fig. 2d and e). Increasing growth temperature resulted in not only an increase in average grain size but also a higher void concentration, therefore resulting in a decrease in intergrain connectivity into the films.

Average grain size was also dependent on the nature of carrier gas. The use of H_2 coreagent at the same substrate temperature gives larger grains than with N_2 (Fig. 2b and d). A similar observation had been reported for gold film deposition from $Me_2Au(hfac)$.¹²

The nature of the substrate materials also has an impact on the gold film production. Under identical deposition conditions, the nucleation rate of gold on SiO_2/Si substrate surface was lower than that on Ta/TaN/SiO₂/Si. Therefore, the corresponding thin films are less continuous and present higher void concentration, even though grain size was nearly identical (Fig. 2d and f).

Some C, O, Cl, F, and P impurities were found by XPS on the surface of deposited films. Nevertheless, a single argon ion sputter (4 kV, beam current of 1 µA, 10 min.) is sufficient to completely remove the C and most of the O impurities from the surface. Thus, the C and O contaminants were believed to come either from film air exposure after the deposition process or from residual H₂O in the CVD setup rather than, for the C impurities, from the thermal decomposition of toluene solvent during film production. A depth profile analysis of a film deposited on Ta/TaN/SiO₂/Si at 200°C using N_2 as a carrier gas is shown in Fig. 5. It can be seen that Cl contaminant disappeared after only 5 min of surface bombardment by argon ion, whereas for F impurities it was approximately 12 min and P contaminant was incorporated and detectable in all the film depth $(\sim 1.5\%)$. This last impurity species could be formed by the thermal disproportional decomposition of free PF₃²⁵ on the gold growing film. By contrast, the Cl and F species were believed to be contaminated on the surface of deposited films during the last steps of production, may be due to the by-products adsorption. Growth temperature and carrier gas nature were also found to have an impact on the concentration of surface impurities. Films deposited at higher temperature or with H₂ demonstrate lower surface impurity concentration (Table I). Particularly, neither P nor F was found on the surface of an extremely pure film deposited at 140°C in the presence of H₂.

In general, electrical resistivity of the gold film depends on its morphology as well as its chemical composition. Thus, the minimal resistivity of 9.6 $\mu\Omega$ cm, without any post-treatment (as opposed to 2.44 $\mu\Omega$ cm for bulk gold), was obtained for a compact film grown on Ta/TaN/SiO₂/Si at 110°C with H₂. In contrast, a film deposited on SiO₂/Si having a high void concentration and low intergrain connectivity has a maximal resistivity of 24.5 $\mu\Omega$ cm. The carrier gas nature has an impact on the film impurity concentration, therefore affecting the film's electrical properties. As an illustration, a resistivity of 16.5 $\mu\Omega$ cm is measured for films grown on Ta/TaN/SiO₂/Si at 140°C with N₂ carrier gas, while for films grown with H₂ at the same substrate temperature only 12.0 $\mu\Omega$ cm is obtained.

After an annealing step (2 h, 400°C and, under a reduced pressure of 1 mTorr), the resistivities of the deposited gold films are lowered to 2.5–4 times that of bulk gold. A significant drop in resistivity is observed for the film deposited on Ta/TaN/SiO₂/Si at 140°C with N₂ carrier gas while less difference is seen for the one grown at 110°C with H₂, the resistivities of these annealed films being 8.5 and 6.0 μ Ω cm, respectively. The SEM micrograph (not given here) of the former film shows an evident coalescence of the small particles into larger grains and a significant decrease in the void density upon annealing. The change in morphology of the latter film is less evident. Annealing for longer periods and at higher temperatures gives no further enhancement of the continuity of the films; thus, no additional improvement in film properties is observed.

XRD was used to evaluate whether a preferred film growth orientation exists on Ta/TaN/SiO₂/Si, using the intensity ratio $I_{(111)}/I_{(200)}$ of the Au(111) and Au(200), respectively. Figure 6 shows a typical XRD pattern of a film deposited at 200°C with N₂. For all deposition temperatures, gold films were polycrystalline and demonstrate a higher intensity ratio $I_{(111)}/I_{(200)}$ than that of randomly orientated gold powder (1.92).²⁶ This intensity ratio is maximal for a film grown at 150°C and decreases for films deposited at higher or

Table I. Impurities concentration of films deposited at different
temperatures with N ₂ or H ₂ carrier gas using AuCl(PF ₃) toluene
solution. ^a

Sample	ESCA	Cl (%)	F (%)	P (%)
200°C, N ₂	Surface	2.0	2.8	5.3
	After 15 min of Ar sputtering	_	—	1.5
140°C, N ₂	Surface	6.0	3.0	8.4
	After 15 min of Ar sputtering	_	_	4.7
140°C, H ₂	Surface	4.5	_	_
	After 15 min of Ar sputtering	—		—

^a Note: (—) indicates that elemental concentration was below 1%.





lower substrate temperatures (Fig. 7). Because the Au(111) texture is expected to limit electromigration, as in the case of Cu (111),²⁷ the films grown at relatively low temperatures (140–160°C) would show high resistance to failure.

Conclusion

Gold metallic thin-film deposition using solid pure trifluorophosphine gold(I) chloride precursor or its toluene solutions has been reported in this study. Adhesive, continuous films having Au(111) preferred texture were deposited on Ta/TaN/SiO₂/Si in the deposition temperature interval of 110–210°C using N₂ or H₂ carrier gas. The Cl and F impurities were slightly incorporated on the surface of grown films only at the last deposition process steps, whereas the P contaminant was detected in the film thickness (1.5-4.7%). The carrier gas nature had a strong impact on the deposition process conditions and on obtained film characteristics. The precursor surface decomposition reaction followed the reduction decomposition



Figure 7. Variation of the I_{111}/I_{200} intensity ratio with growth temperature of films deposited on Ta/TaN/SiO2/Si using precursor toluene solution and N2 carrier gas.

mechanism rather than the pyrolysis when N2 carrier gas was replaced by H₂ coreactant, which led to a lowering of the activation energy in the kinetically controlled regime, and a minimization of the required deposition temperature. Moreover, the use of H₂ carrier gas resulted in production of higher purity gold films with higher growth rate and lower electrical resistivity.

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