Surface Reactivity of Alkylgold(I) Complexes: Substrate-Selective Chemical Vapor Deposition of Gold from $RAuP(CH_3)_3$ ($R = CH_2CH_3, CH_3$) at Remarkably Low Temperatures

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The reactivity of $CH_3CH_2AuP(CH_3)_3$ and $CH_3AuP(CH_3)_3$ is investigated on silicon, chromium, copper, PMDA–ODA polyimide, and silicon dioxide surfaces at temperatures ranging from 25 to 400 °C in an ultrahigh-vacuum chamber. By exploitation of the advantages of kinetically controlled reaction conditions and atomically clean surfaces, high-purity gold films are deposited at temperatures as low as room temperature. The surface reaction generating elemental gold is subject to an unusual level of control. Excursions to only moderately higher temperature serve to tune the process from one which is completely selective for metal and semiconductor surfaces to one which provides blanket deposition. Enhanced selectivity, allowing the discrimination between different metal substrates (e.g. Cr versus Cu or Au) is achieved by prior exposure of the substrate surface to inhibition agents such as $P(CH_3)_3$ and BF_3. The inhibition by BF_3 is essentially complete for deposition on Cr at 25 °C but is reversed by relatively mild heating of the substrate to 350 °C.

Introduction

The synthesis of metal films and wires plays a critical role in the manufacture of microelectronic devices. The many applications include contacts, interconnects, and wiring in multilayer and packaging structures. Gold is an attractive metal for these purposes because it is quite inert and has excellent conductivity and mechanical properties. For submicron patterning in very large scale integration (VLSI) technology, the low tendency of gold to electromigrate is also advantageous. However, in order to produce highly complex structures, any technique for deposition of gold must be controllable. Desirable characteristics include substrate-specific reaction, conformal coverage of textured surfaces, and deposition of pure material near ambient temperature.[1]

Gold films and wires for microelectronics have been generated by a variety of methods. Line-of-sight physical techniques, such as evaporation or sputtering, require masks to accomplish area-specific deposition and do not provide good conformal coverage. Laser-induced chemical vapor deposition (LCVD) of gold achieves area selectivity via specific decomposition of a precursor compound with a laser.[2] This technique is excellent for forming gold lines and patterns but has weaknesses in the areas of conformal deposition, can cause significant local heating,[3] and often has substantial impurity levels which degrade properties such as resistivity. In contrast, chemically driven methods, such as heterogenous redox reactions (so-called electroless deposition),[4] are capable of superior area selectivity and conformality. In this case, area selectivity is achieved through substrate-specific reactions. Electroless deposition is complicated by the use of multicomponent liquid solutions, the constituents of which may adversely interact with materials present on the substrate. There are also potential problems associated with purity in liquid solution and the necessity of using solvent.

In this paper we describe a method for producing elemental gold from very low temperature thermal reactions of $CH_3CH_2AuP(CH_3)_3$ (**1**) and $CH_3AuP(CH_3)_3$ (**2**)[5] with various substrates, i.e. thermal chemical vapor deposition (CVD) of gold. Thermal CVD permits highly conformal coverage and has been reported previously for gold using a variety of precursors. Puddephatt and co-workers have studied alkylgold complexes containing isocyanide and trialkylphosphine ligands ($RAuCNR$, $RAuPR_3$) as well as the fluoronated alkyl complex $CF_3AuCNCH_3$.[6] Gold films were generated by heating the substrate above the decomposition temperature of the organometallic precursor to temperatures of 200 °C or more. Colgate et al. reported substrate-selective deposition of gold on tungsten in the presence of native-oxide-covered silicon using $(CH_3CH_2)_3PAuCl$ and a substrate temperature of 500 °C.[7] Our goal in the work described here is to exploit the inherent difference in reactivity of chemically distinct surfaces by operating under conditions of kinetic control. In other words, gold films are formed in specific locations via substrate-selective reactions. Not only are the substrate temperatures well below those necessary to pyrolyze the organogold species but, since the reactions are performed in ultrahigh vacuum (UHV), the role of well-defined surfaces can be studied. The alkylgold complexes **1** and **2** which we examine also have the advantages of containing no potentially corrosive ligands (e.g. Cl) and of reacting at remarkably low temperature. Indeed, **1** and **2** have several likely low-energy reaction pathways leading to elemental gold not available to the chloride, including binuclear reductive elimination of alkane and, in the case of **1**, the possibility of β-hydride elimination. We find exquisitely controllable and, if desired, extremely selective reaction with metals, semiconductors, and insulators currently in use in the microelectronics industry.

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Experimental Section

Experiments were performed in a system of standard UHV chambers. Reaction chambers were pumped by 60 L/s turbomolecular pumps and titanium sublimators, giving base pressures of less than 1×10^{-9} Torr. However, after exposure to the organometallic compounds, base pressures were typically 5×10^{-9} Torr. Reaction chamber walls were at room temperature, and all gauges and other hot filaments were turned off during depositions. Analyses took place in a separate chamber, and all sample transfers were *in vacuo* via a transfer chamber. The analysis and transfer chambers were each fitted with an ion pump and a titanium sublimator, and both had base pressures of 2×10^{-10} Torr.

Deposition reactions were carried out on a variety of substrates, all of which were approximately 0.7 × 2.0 cm in size. Si(111) (±0.25°) wafers were obtained from Virginia Semiconductor precleaned using the RCA process. Pieces were cleaved from the 3-in. wafers, rinsed with absolute ethanol, and heated resistively to 1000 °C *in vacuo*. No carbon or oxygen (<1 atomic %) could be detected on the cleaned surfaces by X-ray photoelectron spectroscopy (XPS). Both p- and n-type silicon were used, giving identical results in all cases. Silicon dioxide films of approximately 40-Å thickness were prepared by exposing clean Si(111) substrates to 0.1 Torr of >99.9995% dioxygen for 20 min at 950 °C. The substrates were cooled to ambient temperature in oxygen to avoid pinhole formation.[8] Silicon dioxide films of 5000-Å thickness on silicon were obtained from Virginia Semiconductor and rinsed with absolute ethanol prior to use. Pyromellitic dianhydride oxydianiline (PMDA–ODA) polyimide films 2000 Å thick were prepared by spin casting from a solution of polyamic acid in *N*-methylpyrrolidone and cured under dinitrogen to 400 °C. The films could be used without further treatment. Polyimide films degassed at 350 °C for 10 min *in vacuo* prior to use behaved identically with non-degassed films. Chromium surfaces were prepared by sublimation of arc-melted chromium ingots held in a resistively heated tungsten basket in a reaction chamber with base pressure of 2×10^{-10} Torr. Copper surfaces were prepared in a similar fashion from the evaporation of copper ingots. Patterned substrate surfaces were created by covering either a silicon dioxide or PMDA–ODA polyimide substrate with a stainless steel mask possessing openings as small as 100 μm in diameter. Evaporation of chromium or copper through the mask produced surfaces containing metal dots of desired thickness.

Boron trifluoride (99.5%) was obtained from Matheson Gas Products and vacuum transferred to a stainless steel ampule. Oxidation of metal substrates occurred unless the material was freeze–pumped–thawed four times on a UHV manifold with a base pressure of 2×10^{-9} Torr or less. Trimethylphosphine (97%) was obtained from Aldrich, freeze–pump–thawed three times, and vacuum distilled from a sodium mirror into a stainless steel ampule. The trimethylphosphine was then subjected to the same UHV freeze–pump–thaw procedure as used for boron trifluoride.

Deposition of gold films was performed by exposing substrates to the vapor of either $CH_3CH_2AuP(CH_3)_3$ (**1**) or $CH_3AuP(CH_3)_3$ (**2**). The method of Schmidbaur and Shiotani was used to prepare **2**.[5a] The synthesis of previously unknown **1** is analogous to that of **2** and will be published along with full spectroscopic details shortly.[9] The organogold compounds were stored in stainless steel ampules held at room temperature and were introduced into the reaction chamber under unthrottled flowing conditions, resulting in reaction chamber pressures of 4.2×10^{-6} Torr for **1** and 1.2×10^{-6} Torr for **2** as measured by a water-cooled ion gauge.

The XPS spectrum of **1** was measured by condensing it onto Si(111) at −140 °C. The observed Au $4f_{7/2}$, P 2p, and C 1s core levels had binding energies of 86.2, 132.6, and 286.2 eV, respectively. These binding energies are uniformly greater than those expected on the basis of previous XPS measurements of gold phosphine complexes,[10] most likely due to charging effects in the condensed film. The trimethylphosphine C 1s binding energy should be approximately 285.3 eV. Correcting the observed binding energies by an offset of 0.9 eV gives 85.3 and 131.7 eV for Au $4f_{7/2}$ and P 2p, respectively. Both of these values are in close agreement with previous reports on similar Au(I) species.[10]

Surface characterization of samples was performed in the analysis chamber using a Riber ES 150 MAC 2 X-ray photoemission system employing Mg Kα X-rays ($h\nu = 1253.6$ eV). Samples were positioned normal to the spectrometer axis, and electrons were collected at 45° with respect to the surface normal with an imaged area of 4 × 10 mm. The angle-integrating nature of the MAC 2 analyzer makes it quite insensitive to the sample angle. Binding energies were calibrated using a separate gold foil sample stored in the analyzer chamber and defined with a Au $4f_{7/2}$ value of 83.8 eV, giving a reproducibility of ±0.1 eV.

Some samples were subjected to additional characterization which required removal from the above UHV system and exposure to air: Gold film thicknesses were measured with a Tencor Alpha-Step 200 profilometer. A Physical Electronics Model 600 scanning Auger microprobe was employed for depth-profiling and area-selective Auger spectroscopy. Patterned substrates were examined using a Surface Science Instruments SSX 301 XPS system, which permitted analysis of surface spot sizes of 150 μm.

Results and Discussion

In this investigation, we have explored the use of $CH_3CH_2AuP(CH_3)_3$ (**1**) and $CH_3AuP(CH_3)_3$ (**2**) for gold CVD on silicon, chromium, copper, PMDA–ODA polyimide, and silicon dioxide. Direct deposition of gold on these substrates poses some practical problems. Gold reacts and interdiffuses with silicon and copper, even at 25 °C.[11] On insulators, such as PMDA–ODA polyimide and silicon dioxide, the adhesion of deposited gold films is often poor. Both of these problems can be solved by employing chromium[12] or tungsten[13] as barrier and/or adhesion layers. But even these surfaces are complicated, since metal substrates are often readily oxidized, hence, the importance of carrying out the depositions under UHV conditions. Differences in reactivity of the various materials were exploited on patterned substrates with adjacent, chemically distinct surfaces to demonstrate completely selective deposition of gold at remarkably low temperatures. Patterned substrates of interest will not always contain only one type of metal for deposition, and an important feature of a deposition process would be the ability to deposit only on the desired metal, while leaving other metals in the structure gold free. Tuning the deposition chemistry on metallic substrates via the use of protecting groups (Lewis acids and bases) was also successfully demonstrated.

Reaction with Silicon. Exposure of a cleaned Si(111) surface to 4.2×10^{-6} Torr $CH_3CH_2AuP(CH_3)_3$ for 5 min (1.3×10^{-3} Torr s) at 25 °C resulted in the deposition of gold on the silicon substrate (Au $4f_{7/2}$ 84.9 eV). The initial binding energy of 84.9 eV is attributed to the combined effects of Au/Si alloy formation and island formation. No $P(CH_3)_3$ nor any other phosphorous-containing species could be detected by XPS, and only a trace of carbon was present on the surface.[14] Exposure for longer periods resulted in a changing Au/Si film composition as evidenced by a monotonic decrease in the binding energy of the Au 4f level and eventually (>1.5×10^{-2} Torr s) yielded a spectrum dominated by elemental gold features (Au $4f_{7/2}$ 83.8 eV), with small peaks remaining for the Si 2p and Si 2s core levels (Figure 1). The silicon peaks are attributed to a surface-segregated Au/Si alloy. Heating the sample to 700 °C resulted in the formation of a Au/Si alloy with no metallic gold remaining as evidenced by the Au$4f_{7/2}$ peak shifting to 84.8 eV. The behavior observed for gold deposited by CVD from **1** is consistent with that previously

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(14) Small C 1s peaks which we commonly observe in the XPS spectra of gold films grown on silicon and metals are due to carbon at the immediate surface of the film. Although the cross section for the C 1s peak is low compared to that for the Au 4f peaks, we are disproportionately sensitive to this carbon because sensitivity decays exponentially with depth below the surface. Consequently, the detected carbon corresponds to only trace levels. Ligands from the gold precursor which remain adsorbed on the film surface, particularly the alkyl ligands since no phosphorous is observed, may account for the C 1s peaks. However, no definitive identification from binding energies nor quantitative measurement of carbon coverages was obtained, so no specific conclusions regarding the deposition mechanism can be made on the basis of these data.

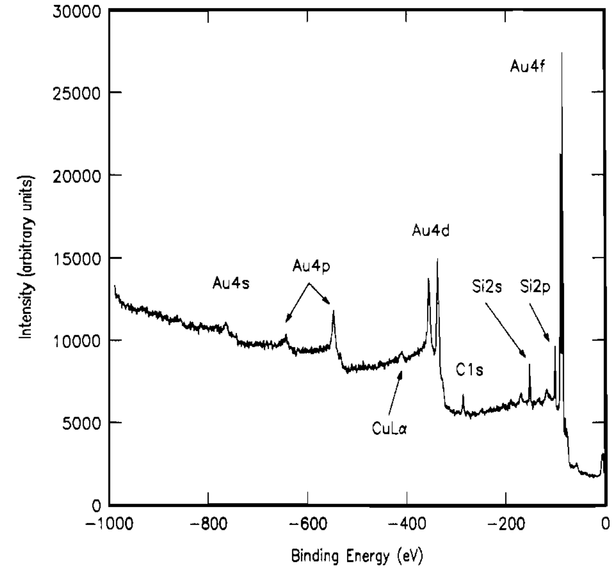

Figure 1. XPS survey spectrum of a Si(111) surface exposed to 6.0 × 10^{-2} Torr s $CH_3CH_2AuP(CH_3)_3$ at 25 °C.

reported for the evaporation of high-purity gold onto silicon substrates.[15] No evidence was seen for room temperature molecular adsorption of **1** or **2** on this or any other of the surfaces studied.

Reaction with Chromium, Copper, and Gold. The formation of Au/Si alloys and the diffusion of gold in various substrates has prompted the use of diffusion barriers between gold and silicon in device fabrication. Chromium is widely applied in this role for microelectronics applications, making it a good test substrate. Our chromium barrier films on Si(111) formed by evaporation of chromium ingots were estimated to be 30–40 Å thick on the basis of the attenuation of the Si 2p core level peak. When thicker chromium films were used, identical gold film growth behavior was observed. Submonolayer coverages of gold from **1** (e.g. 2.5 × 10^{-4} Torr s) on freshly prepared chromium surfaces were characterized by XPS spectra with a Au $4f_{7/2}$ binding energy of 84.4 eV, consistent with the formation of small islands of gold on the chromium surface.[16] Note that this binding energy is 0.5 eV less than that obtained for low coverages of gold on Si(111), where both island and Au/Si alloy formation occur. Exposures of greater than 3.0 × 10^{-2} Torr s generated continuous gold films with a Au $4f_{7/2}$ binding energy of 83.8 eV, identical to that of pure bulk gold (Figure 2). An exposure of 0.24 Torr s produced a film 500 Å thick, giving an average rate of 2.1 × 10^3 Å $Torr^{-1}$ s^{-1} at 25 °C. A film 850 Å was grown by heating the substrate to 230 °C and exposing for 4.5 × 10^{-2} Torr s, yielding an average rate of 1.9 × 10^4 Å $Torr^{-1}$ s^{-1}. The reaction of **2** was also studied in this context. Exposure of a chromium surface to **2** for 7.8 × 10^{-2} Torr s resulted in a film 150 Å thick, giving an average rate of 1.9 × 10^3 Å $Torr^{-1}$ s^{-1} at 25 °C.

These deposition rates, and all other rates reported in this paper, are average values determined by measuring the thickness of the film obtained after exposure of the surface in question to the organometallic precursor. For substrates like chromium which do not interdiffuse with gold, once sufficient gold has deposited to produce a continuous film, the reaction surface for the subsequent deposition is gold. The observed deposition rate therefore includes at least two distinct processes, the rate for gold film growth on the initial substrate (in this case chromium) and the rate for gold film growth on gold. However, similar rates have been obtained starting with gold as the initial substrate.[17] The presence of chromium as the initial surface does not appear to cause an induction period. It should be noted that the rates measured for substrates at elevated temperatures may be transport limited.

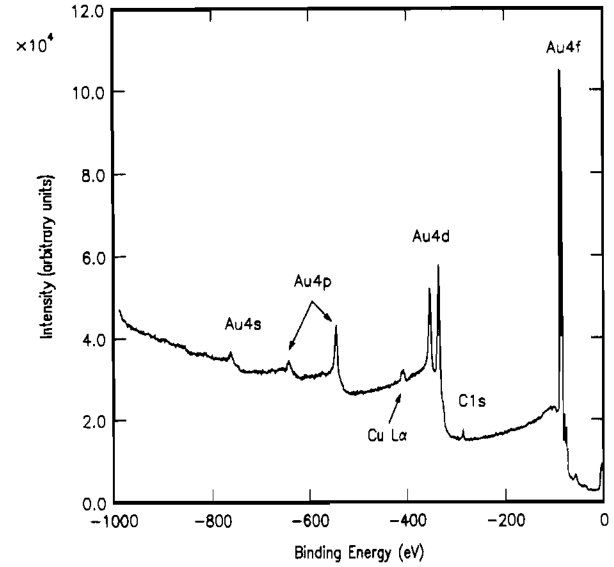

Figure 2. XPS survey spectrum of a chromium surface exposed to 3.0 × 10^{-2} Torr s $CH_3CH_2AuP(CH_3)_3$ at 25 °C.

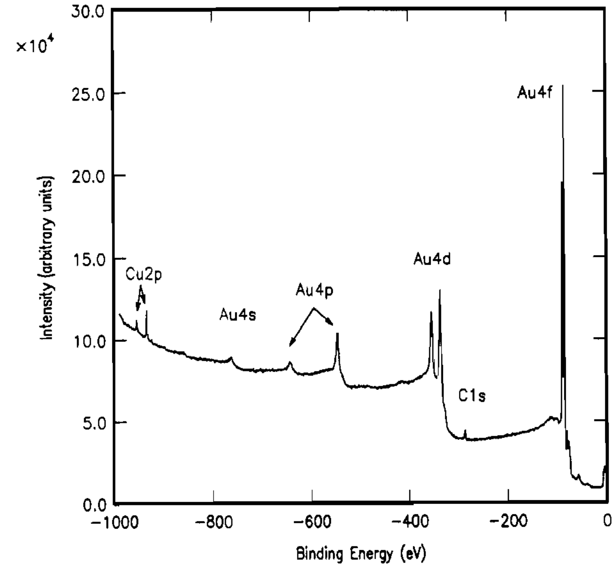

Figure 3. XPS survey spectrum of a copper surface exposed to 3.0 × 10^{-2} Torr s $CH_3CH_2AuP(CH_3)_3$ at 25 °C.

This reaction is very sensitive to the purity of the chromium surface, particularly with respect to oxidation. An oxygen or water background pressure in the chamber of 1 × 10^{-8} Torr was sufficient to oxidize the chromium surface and completely prevent gold deposition at 25 °C. Inhibition of low-temperature gold deposition upon oxidation of substrates is a recurrent theme in this study.

Copper was also employed as a substrate for the formation of gold films. Exposure of a copper surface freshly evaporated onto 5000-Å thick silicon dioxide to **1** for 3.0 × 10^{-2} Torr s at 25 °C resulted in the formation of a gold film (Au $4f_{7/2}$ 83.8 eV) (Figure 3). Small peaks for the Cu $2p_{3/2}$ core level with a binding energy of 932.6 eV remained, suggesting that a thin layer of copper was present at the surface of the otherwise pure gold film. This layer

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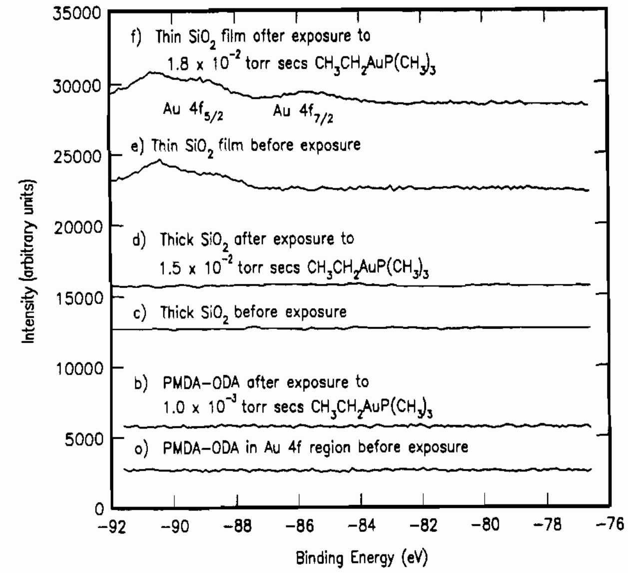

Figure 4. XPS spectra in the Au 4f core level region showing the inertness of insulating substrates toward reaction with $CH_3CH_2AuP(CH_3)_3$: (a) PMDA–ODA polyimide before exposure to **1**; (b) PMDA–ODA polyimide after exposure to 1.0×10^{-3} Torr s **1**; (c) thick (5000 Å) SiO_2 before exposure to **1**; (d) thick (5000 Å) SiO_2 after exposure to 1.5×10^{-2} Torr s **1**; (e) thin (40 Å) SiO_2 before exposure to **1**; (f) thin (40 Å) SiO_2 after exposure to 1.8×10^{-2} Torr s **1**.

persists even for films as thick as 3600 Å. Depth-profiling Auger spectroscopy confirmed the presence of a thin film of copper on this surface. Formation of structures in which copper is segregated on the surface of other metals in amounts on the order of a monolayer is well precedented and is important for the superior behavior of some bimetallic catalysts.[18] The result observed here is somewhat surprising though since the well-known phenomenon of gold and copper interdiffusion should lead to alloy formation rather than a layered structure.[19] Perhaps adsorbates derived from the ligands of the Au precursor are instrumental in segregating a thin layer of copper. The observed rate for gold deposition on copper was 1.0×10^3 Å $Torr^{-1}$ s^{-1}. This is a factor of 2 slower than the rate observed for gold growth on chromium. The simplest explanation for the slower rate is the presence of the copper overlayer. This will be discussed further in the section on mechanistic considerations.

Aside from traces of carbon[14] or copper at the immediate surface of deposited films, from the XPS evidence it appears that the bulk of the films deposited on metal substrates are pure, elemental gold. This was confirmed by depth-profiling Auger spectroscopy, which detected no carbon or phosphorus in the bulk of the gold. The purity of the films is also consistent with separate experiments[17,20] on larger substrates (3-in. wafers) for which we have determine that gold films deposited on metal substrates have resistivities near that of bulk gold. For specularly smooth gold films grown at 109 °C and above, the resistivity was found to be 3.2 ± 1.1 μΩ cm. Bulk gold metal has a resistivity of 2.20 μΩ cm.

Reaction with SiO_2 and PMDA–ODA Polyimide. Another important class of materials in the microelectronics industry, insulators, was also examined for reactivity with $RAuP(CH_3)_3$. Both 5000-Å thick silicon dioxide and PMDA–ODA polyimide films did not react at 25 °C with **1** or **2** (Figure 4). No trace of gold nor any phosphorus-containing species was noted after exposure of up to 0.3 Torr s. Thin silicon dioxide films (about 40 Å) prepared by *in situ* oxidation of Si(111) did react with **1** and **2** to give barely detectable amounts of gold on the surface as shown in Figure 4f (Au $4f_{7/2}$ 85.7 eV). The trace gold deposition is thought to occur at defect sites, but the nature of these sites has not been determined. Heating to 150 °C initiates film growth on both forms of silicon dioxide, while polyimide must be heated to over 400 °C. PMDA–ODA polyimide decomposes at approximately 400 °C, but it is not clear that decomposition of the polyimide film is responsible for initiation of gold deposition. Bombardment of polyimide with an argon ion beam is known to damage polyimide to an extent sufficient to make it conducting.[21] In an attempt to induce deposition, a 2000-Å PMDA–ODA polyimide film was exposed for 5 min to a focused argon ion beam. The pressure of argon in the gun was 1.1×10^{-4} Torr with a current of 25 mA and a potential of 2000 V. Subsequent exposure at 25 °C to **1** for 0.27 Torr s resulted in only trace amounts of gold both on and off the target area. Therefore, it seems more likely that at temperatures >400 °C, **1** is simply undergoing pyrolytic decomposition. A different mechanism must be operating on silicon dioxide, since deposition of gold begins at 150 °C. Again, surface defects may be responsible for nucleation of the gold deposits. However, it is clear that regardless of the operative mechanism, gold deposition with **1** can be tuned from a completely selective to a blanket CVD process.

Reaction with Patterned Substrates. The facile room-temperature deposition of gold on semiconductors and metals contrasted with the need for elevated temperatures or defects in order to observe even trace deposition of gold on insulators demonstrates the extreme dependence of reaction rates of **1** and **2** on substrate surface composition. The disparity in rates is especially evident when one considers that growth of gold is autocatalytic; that is, once a metallic gold deposit is established, continued film growth is relatively rapid. For real device applications, however, both reactive and nominally unreactive surfaces must be exposed to the precursor molecule simultaneously. In order to demonstrate the complete selectivity of gold CVD using **1** or **2** under such conditions, we have employed patterned substrates with adjacent, chemically distinct surfaces. These substrates also test the possibility of diffusion from one surface to another that could lead to "spillover" of gold and degradation of selectivity. Some selective behavior with respect to insulators and conductors has been noted previously for gold and copper CVD processes but not under conditions as mild or with selectivity as complete as described here.[7,22]

A polyimide-coated silicon wafer was patterned via chromium evaporation through a mask. A spectrum of the resulting surface containing 100-μm chromium dots approximately 30 Å thick is shown in Figure 5a. Core level features for both the polyimide substrate and the chromium dots are indicated in the spectrum. This composite surface was exposed to **1** at 25 °C for 15 h (0.23 Torr s), forming gold dots 500 Å thick (Figure 5b). The spectrum once again shows features due to the polyimide substrate; however, the chromium peaks have been replaced by gold peaks, indicating that gold films now cover the dots. The deposition rate could be enhanced by heating to 230 °C without any degradation in selectivity. Area-specific Auger spectroscopy and small-spot XPS were used to quantify the selective nature of the reaction. Within the limits of the techniques (0.01 atomic % for small-spot XPS, slightly higher for Auger), no gold was deposited in the polyimide region in the temperature range 25–230 °C.[20] The optical microcope image in Figure 6 shows an example of a patterned sample after gold film formation. Identical results were obtained for **2** at 25 °C for the polyimide substrates patterned with

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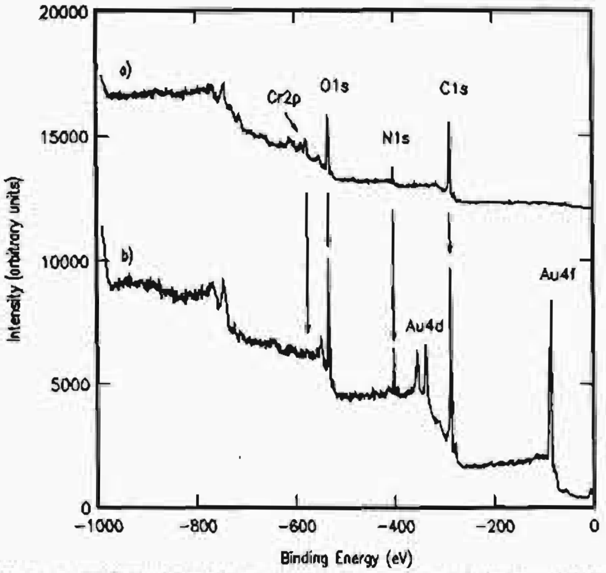

Figure 5. XPS survey spectra showing formation of 100-μm gold dots via selective reaction of $CH_3CH_2AuP(CH_3)_3$ with a chromium pattern on PMDA–ODA polyimide: (a) before exposure to **1**; (b) after exposure to 0.23 Torr s of **1**.

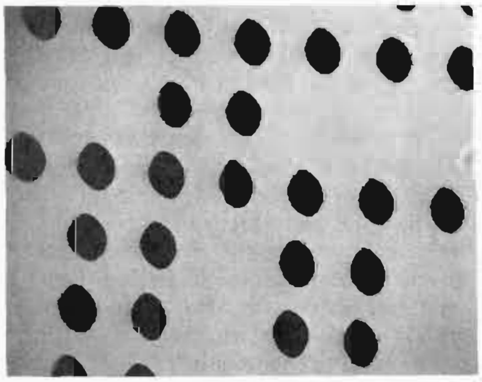

Figure 6. Optical microscope picture of a patterned substrate after gold deposition. The dots are ~100 μm in diameter.

chromium; an exposure of 7.8 × 10^{-2} Torr s of **2** produced gold dots 150 Å thick.[20]

Patterned substrates of chromium dots on silicon dioxide and of copper dots on polyimide were also constructed and treated with **1**. For the case of chromium on 5000-Å thick silicon dioxide, gold dots were grown with an exposure of 1.5 × 10^{-3} Torr s of **1**, and selectivity was maintained to at least 100 °C (Figure 7). A spectrum of a composite surface made up of copper dots on polyimide is shown in Figure 8a. An exposure of 8.1 × 10^{-2} Torr s of **1** at 25 °C yielded a completely selective 300-Å gold film deposited on copper only as shown in Figure 8b. The Cu 2p core levels again indicate the presence of a copper surface layer. Within 0.01 atomic %, no gold was found on the SiO_2 or polyimide regions of the patterns.[20]

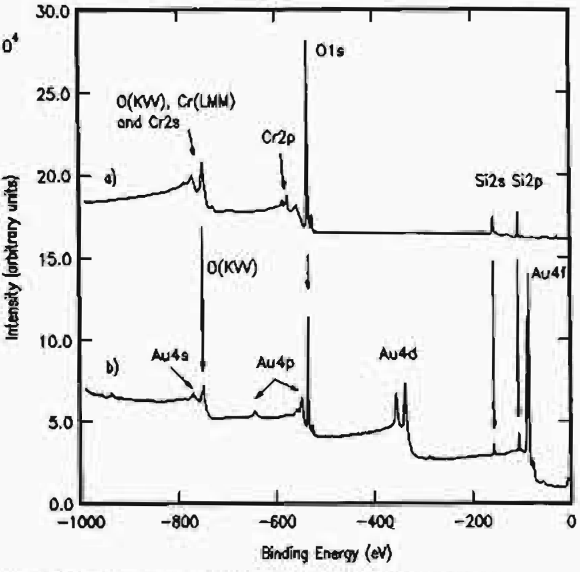

Figure 7. XPS survey spectra showing formation of 100-μm gold dots via selective reaction of $CH_3CH_2AuP(CH_3)_3$ with a chromium pattern on silicon dioxide: (a) before exposure to **1**; (b) after exposure to 1.5 × 10^{-3} Torr s of **1**.

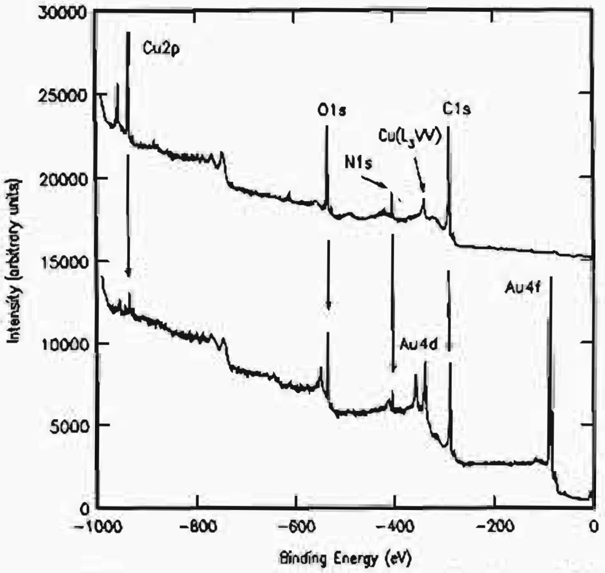

Figure 8. XPS survey spectra showing formation of 100-μm gold dots via selective reaction of $CH_3CH_2AuP(CH_3)_3$ with a copper pattern on PMDA–ODA polyimide: (a) before exposure to **1**; (b) after exposure to 8.1 × 10^{-2} Torr s of **1**.

Selective Reversible Inhibition. The highly controllable nature of gold CVD with **1** and **2** is already evident from the substrate selectivity of the process as well as the temperature dependence. For purposes of constructing more complicated structures, the ability to reversibly inhibit the deposition of gold on specific metals would make the CVD process even more versatile. We have found in our deposition experiments on chromium and copper that if these metals are oxidized due to exposure to air, they become inert to **1** and **2**; i.e., no gold is deposited at 25 °C. Unfortunately, inhibition by oxidation is not easily reversed under mild conditions, particularly for chromium. Ideally, inhibition would involve treatment of one metal with some gaseous reagent at room temperature which passivates that metal to CVD of gold. An adjacent surface of a second metal would remain unaffected, and gold could still be deposited on the second metal. Subsequent treatment of the substrate, e.g. by mild heating, would reactivate the first metal surface, upon which the deposition could be reinitiated. To this end, we have examined the efficacy of trimethylphosphine and boron trifluoride as agents for the reversible inhibition of gold deposition on chromium surfaces, with a view to achieving selectivity in this inhibition with respect to Cu and Au surfaces. As we shall show below, boron trifluoride substantially satisfies the criteria for an ideal inhibition agent, while trimethylphosphine is somewhat less successful.

The role of trimethylphosphine, a species already present during the course of the reaction due to the decomposition of **1**, was explored by treating chromium surfaces with various amounts of $P(CH_3)_3$ prior to initiation of the deposition reaction (Figure 9). As shown in Figure 9a for a chromium surface previously saturated with $P(CH_3)_3$, gold coverage after exposure to 2.5 × 10^{-3} Torr s of **1** is only submonolayer. Clearly, exposure of the chromium surface to $P(CH_3)_3$ results in significant inhibition, but even saturating the surface does not stop the eventual formation of a

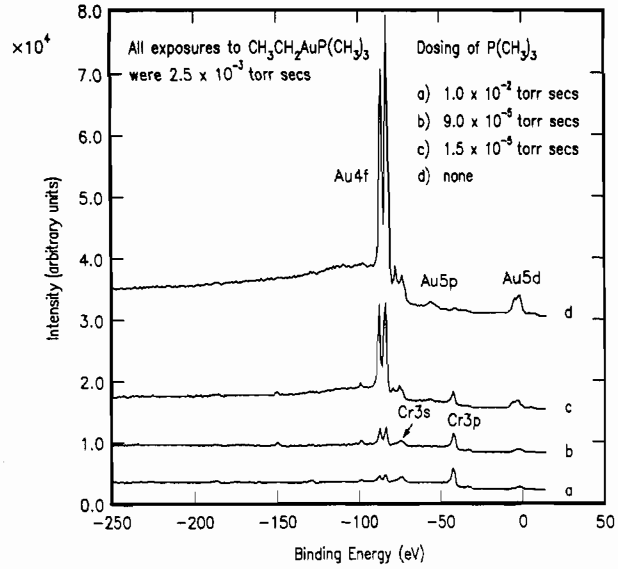

Figure 9. XPS spectra in the Au 4f core level and valence band regions showing the effect of trimethylphosphine upon gold film growth from $CH_3CH_2AuP(CH_3)_3$: (a) chromium surface exposed to 1.0×10^{-2} Torr s $P(CH_3)_3$ followed by 2.5×10^{-3} Torr s **1**; (b) chromium surface exposed to 9.0×10^{-5} Torr s $P(CH_3)_3$ followed by 2.5×10^{-3} Torr s **1**; (c) chromium surface exposed to 1.5×10^{-5} Torr s $P(CH_3)_3$ followed by 2.5×10^{-3} Torr s **1**; (d) chromium surface exposed to 2.5×10^{-3} Torr s **1** only (no $P(CH_3)_3$ exposure).

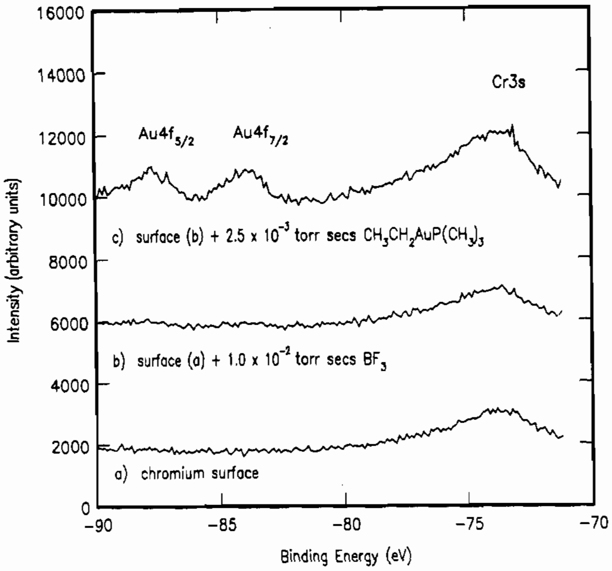

Figure 10. XPS spectra in the Au 4f core level region showing the inhibition by boron trifluoride of gold film growth from $CH_3CH_2AuP(CH_3)_3$: (a) chromium surface before exposure to **1**; (b) chromium surface exposed to 1.0×10^{-2} Torr s BF_3; (c) chromium surface exposed to 1.0×10^{-2} Torr s BF_3 followed by 2.5×10^{-3} Torr s **1**.

continuous gold film. After 2 h (3.0×10^{-2} Torr s of **1**), all samples had formed a film thicker than 40 Å.

We determined the fate of the predosed trimethylphosphine following gold film growth by both XPS and depth-profiling Auger spectroscopy. No trimethylphosphine is trapped in the bulk of the gold film as it is grown from **1**, whether or not the chromium is predosed with $P(CH_3)_3$. A gold film grown under normal conditions, i.e. no pretreatment with $P(CH_3)_3$, has no detectable signal for phosphorus and carbon at the Cr/Au interface by depth-profiling Auger spectroscopy. However, depth-profiling Auger spectroscopy shows that significant amounts of carbon and phosphorus are buried at the Cr/Au interface if the chromium surface is saturated with trimethylphosphine prior to reaction with **1**. The phosphorus/carbon ratio was 1 to 3.4 ± 0.3, just slightly higher in carbon than the 1 to 3 ratio expected for trimethylphosphine. XPS spectra of a trimethylphosphine-saturated chromium surface showed a single very broad peak for P 2p (130.0 eV, 3.9 eV fwhm) and two peaks for C 1s (284.9, 282.4 eV) in a 7 to 1 ratio assigned as chemisorbed $P(CH_3)_3$ and an unidentified decomposition product, respectively. After heating to 150 °C, there are still two C 1s peaks but now in a 4 to 1 ratio with binding energies of 284.3 and 282.4 eV, respectively. The 0.6-eV shift in the first peak is probably due to formation of an intermediate decomposition product and indicates that by 150 °C all of the trimethylphosphine has decomposed. Upon heating to 300 °C, two C 1s peaks (284.1, 282.4 eV) in a 1 to 2.8 ratio are present. The change in the C 1s spectra is mirrored by the formation of a single narrower peak for phosphorus at 150 °C (128.6 eV, 2.7 eV fwhm) which persists at 300 °C (128.6 eV, 2.0 eV fwhm). The P 2p and C 1s core level spectra support the initial adsorption of intact trimethylphosphine on the chromium surface accompanied by approximately 12% decomposition. This decomposition may well be the key to the failure of trimethylphosphine to suppress eventual film formation. The Auger measurement of carbon and phosphorous at the interface in the stoichiometric ratio appropriate to trimethylphosphine is evidence that the part of the chromium surface covered by intact molecules remains passivated and that these areas are simply buried by gold, the nucleation of which is initiated elsewhere. Locations where trimethylphosphine decomposition has occurred are logical candidates for the sites for this nucleation to take place.

In contrast to $P(CH_3)_3$, BF_3 appeared to chemisorb entirely in an intact molecular form and provided a much more robust inhibition. Reaction of BF_3 with a chromium surface resulted in the appearance of only a single B 1s (199.4 eV) and a single F 1s (686.8 eV) peak, as expected for molecular chemisorption. Like $P(CH_3)_3$, the reaction with BF_3 was self-limiting; exposures of 1×10^{-4} Torr BF_3 for 30 s saturated the surface. Subsequent exposure for 2.5×10^{-3} Torr s to **1** resulted in a small amount of gold depositing on the surface (Figure 10c), approximately half the amount of gold seen for the same exposure of **1** on a trimethylphosphine-saturated surface. However, in contrast to the case of $P(CH_3)_3$, these deposits appear to be insufficiently reactive to serve as nuclei and do not promote the formation of continuous films. Exposure of the boron trifluoride-saturated chromium surface to 3.0×10^{-2} Torr s of **1** still yields only submonolayer coverages of gold, as illustrated in Figure 11a. The Au $4f_{7/2}$ binding energy of 84.0 eV is 0.2 eV shifted from the value for bulk gold, indicating that small islands of gold are present. In the absence of any pretreatment of the surface, these conditions would have generated a continuous gold film 60 Å thick.

The inhibiting effect of BF_3 can be partially reversed by heating the BF_3-covered surface to 350 °C. This results in a shift of +0.4 eV in the B 1s binding energy, and a second, very broad B 1s peak begins to grow in at about 190 eV. The F 1s peak decreases in intensity by approximately a factor of 2 and shifts by +1.2 eV. The growth of B 1s peaks in the 190-eV region suggests the formation of chromium borides and/or elemental boron. Subsequent exposure to **1** results in gold film growth at a rate intermediate between that of the clean chromium surface and the boron trifluoride-saturated surface.

Neither $P(CH_3)_3$ nor BF_3 served to inhibit the deposition process on either Au or Cu surfaces, making the inhibition selective with respect to these two metals. The behavior of the gold and copper surfaces toward these molecules was, however, rather different. Neither $P(CH_3)_3$ nor BF_3 adsorbed in detectable quantities on a gold surface at 25 °C, and while both species do bind to copper, they had no apparent effect on the rate of film formation. Presumably, both of these molecules are readily displaced from the Cu surface by **1**.

Mechanistic Considerations. The selectivity and low-temperature reactivity of $RAuP(CH_3)_3$ raise the question of what is the mechanism of decomposition to elemental gold. Given our inability to identify any intermediate decomposition products on the surface, it is impossible to draw definitive conclusions in this regard. Nonetheless, it is interesting to compare our observations with the conclusions drawn by Tamaki and Kochi regarding the thermal decomposition of several alkyl(triphenylphosphine)gold(I) complexes ($RAuPPh_3$).[23] These authors convincingly argue that, at least for the case of CH_3AuPPh_3, gold–alkyl bond homolysis to produce free alkyl radicals is not an important decomposition pathway, either for the neat solid or in liquid solution. They propose the mechanism shown in Scheme 1. Loss of the phosphine ligand in eq 1 is thought to be rate limiting, a conclusion supported by first-order thermolysis kinetics and strong retardation in rate by added PPh_3. Eq 4 is a competing reaction which may contribute to the retardation of decomposition. Tamaki and Kochi have no evidence for the "coupling product," and it is left unspecified.

Scheme 1

$$CH_3AuPPh_3 \rightleftharpoons [CH_3Au] + PPh_3 \qquad (1)$$

$$[CH_3Au] + CH_3AuPPh_3 \rightarrow \text{“coupling product”} \qquad (2)$$

$$\text{“coupling product”} \rightarrow CH_3CH_3 + 2\,Au + PPh_3 \qquad (3)$$

$$CH_3AuPPh_3 + PPh_3 \rightleftharpoons CH_3Au(PPh_3)_2 \qquad (4)$$

If the CVD of gold from **1** is thought of as being analogous to Scheme 1, then a reasonable mechanism can be hypothesized for a continuously growing film of gold, as indicated in Scheme 2. It should be noted of course that there may be some variation in the details of this surface mechanism. For example, it is entirely plausible that the reaction steps in eqs 5 and 6 are concerted. Likewise, eq 7 is a combination of several processes, including surface diffusion and reductive coupling of alkyl groups, for which many possibilities exist.

Scheme 2

$$\text{(Au surface)} + CH_3CH_2AuP(CH_3)_3(g) \rightarrow CH_3CH_2Au(\text{surface}) + P(CH_3)_3(\text{surface}) \qquad (5)$$

$$P(CH_3)_3(\text{surface}) \rightarrow \text{(Au surface)} + P(CH_3)_3(g) \qquad (6)$$

$$2CH_3CH_2Au(\text{surface}) \rightarrow CH_3CH_2CH_2CH_3(g) + \text{(Au surface)} \qquad (7)$$

In this analogy, the dissociative chemisorption to produce surface ethylgold fragments and trimethylphosphine (eq 5) corresponds to the coupling in eq 2. In solution, the forward reaction in eq 1 is necessary to generate the coordinatively unsaturated $[CH_3Au]$ intermediate capable of attacking another CH_3AuPPh_3 molecule. No such reaction is included in Scheme 2 since the reactive surface of the growing gold film plays the role of the coordinatively unsaturated species and reacts directly with $CH_3CH_2AuP(CH_3)_3$. In the neat solid or in solution, the major hydrocarbon products for $RAuPPh_3$ decomposition are, except for highly branched alkyl groups such as 2-propyl and 2-methyl-2-propyl, almost entirely the R–R coupling products and not the alkane and alkene (RH and R(–H)) disproportionation products. Accordingly, Tamaki and Kochi posited the existence of the "coupling product" and its subsequent reductive elimination of ethane (eq 3). A surface covered with a number of alkylgold moieties is analogous to this "coupling product", and eq 7 is the counterpart of eq 3. We have preliminary mass spectroscopic evidence that butane is produced in the reaction of **1** with silicon surfaces. Butane would most likely be formed by the association of two surface-bound ethylgold moieties and would not involve reaction with a molecularly adsorbed reactant complex. Finally, the reaction in eq 6 is expected to be quite facile if it is indeed separate from eq 5, since trimethylphosphine does not bind to gold surfaces at room temperature. In other words, the loss of surface phosphine should be essentially irreversible, particularly since it is continually pumped away, and no self-retardation of gold deposition should occur. The lack of inhibition by trimethylphosphine for deposition on gold surfaces supports this conclusion. This contrasts with the situation in solution, where the reactive species responsible for decomposition, $[CH_3Au]$, can be tied up with excess phosphine (the back-reaction in eq 1 and perhaps the forward reaction in eq 4), consequently retarding the rate. Only on virgin chromium surfaces, where trimethylphosphine is bound strongly, is analogous inhibition observed.

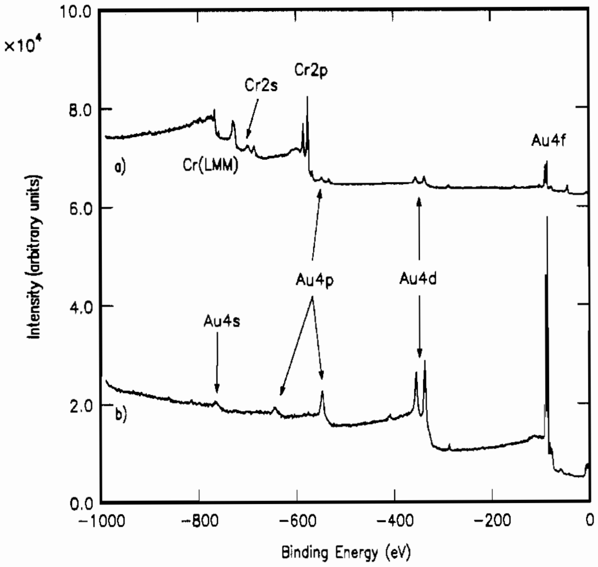

Figure 11. XPS survey spectra comparing inhibition of gold film growth by $P(CH_3)_3$ and BF_3: (a) chromium surface presaturated with BF_3 and then exposed to 3.0×10^{-2} Torr s **1**; (b) chromium surface presaturated with $P(CH_3)_3$ and then exposed to 3.0×10^{-2} Torr s **1**.

If free alkyl radicals are ruled out as transient intermediates present in any significant amount, β-hydride elimination may account for formation of disproportionation products. As was pointed out in the Introduction, the possibility of β-hydride elimination as a low-energy reaction pathway for **1** was a motivation for considering this species for gold CVD. We tested this hypothesis by comparing the reactivity of $CH_3AuP(CH_3)_3$ (**2**); the β-hydride elimination pathway is not available for this otherwise similar molecule. The rates of gold deposition on chromium for **1** and **2**, 2.1×10^3 and 1.9×10^3 Å Torr^{-1} s^{-1}, respectively, are the same within experimental error, suggesting that the same mechanism is operative for both species. If this is the case, β-hydride elimination is not a major pathway in the decomposition mechanism of **1**, and reductive coupling of ethyl fragments to give butane is probably more likely. This conclusion is in agreement with our preliminary mass spectroscopic evidence for reaction of **1** with silicon surfaces, which suggests that butane is a major decomposition product. Moreover, the rate difference between deposition on copper versus gold may result from interaction of surface ethyl groups with the thin layer of surface-segregated copper. In particular, the kinetic parameters (activation energy and frequency factor) may be different for reductive elimination to form butane on copper. The barrier to diffusion of the alkyl fragments across the surface may also be different

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[23] Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1973**, *61*, 441–450.

on copper. Further investigations are currently underway to address the detailed mechanism of the gold deposition reaction.

Conclusion

We have shown that by operating under UHV conditions, so as to maintain atomically clean substrate surfaces, the organogold species $CH_3CH_2AuP(CH_3)_3$ (**1**) and $CH_3AuP(CH_3)_3$ (**2**) can be used to deposit pure gold films selectively at room temperature on metals and semiconductors. The key to the selectivity of this process is the maintenance of a reactive (i.e. nonoxidized) substrate which allows the initiation of reaction without resorting to pyrolysis of the source gas, an inherently nonselective process. This kinetically controlled method of gold deposition generates films with resistivities which are superior to those formed via pyrolytic methods, either thermal or laser induced. The poorer resistivity of gold films grown via pyrolytic CVD likely results from the generation of a plethora of very reactive decomposition products, some of which are inevitably trapped within the growing film. In contrast, the kinetically controlled, low-temperature process is far more likely to produce only stable byproducts, such as trimethylphosphine and alkanes. Insulators appear inert to **1** and **2** at 25 °C but will react to form gold films upon heating to the pyrolysis threshold. Thus, the reaction can be tuned for selective or blanket gold films. Further molecular control of the deposition process can be effected via the use of protecting groups, such as boron trifluoride, to achieve selectivity for one metal over another, allowing deposition on Cu in the presence of Cr surfaces. The reactivity of surfaces thus inhibited can largely be restored by simple mild heating.

Given the manifest advantages inherent in kinetically controlled reactions between suitable precursor molecules and substrates whose sufficient reactivity may be ensured by the simple maintenance of cleanliness, it is ironic to note that many surveys of precursor materials for CVD of metals have made use of reactors operating at 1×10^{-4} torr with glass substrates as deposition targets. Such conditions are clearly inappropriate to distinguish those precursor candidates which most fully exploit all of the potential advantages of CVD processes.

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