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Application Serial No.
Applicant(s): Calvert et al.

**PATENT APPLICATION**
Docket No.: N.C. 76,861

# SELECTIVE VAPOR DEPOSITION USING FILMS

## CROSS-REFERENCE TO RELATED APPLICATION

The present patent application is a continuation-in-part (CIP) of patent application of Serial No. 07/933,147 (hereinafter '147) filed on August 21, 1992 by Calvert et al., which '147 application is itself a continuation-in-part of prior application Serial No. 07/691,565 (hereinafter '565), filed by Calvert et al. on May 25, 1991, now abandoned, which '565 application is a CIP of S/N 07/182,123 filed on April 14, 1988 now issued as U.S. Patent No. 5,079,600 (hereinafter '600), which '600 patent is a continuation-in-part (CIP) of S/N 07/022,439 filed on March 6, 1987, now issued as U.S. Patent No. 5,077,085 (hereinafter '085). Further, another CIP of the '565 application of S/N 08/062,706 was filed by Calvert et al. on May 17, 1993, now issued as U.S. Patent No. 5,389,496 (hereinafter '496). All the aforementioned pending and abandoned patent applications and issued patents designated as '085, '600, '565, '147 and '496 are incorporated herein by reference in their entirety and for all purposes, respectively.

## BACKGROUND OF THE INVENTION

### FIELD OF THE INVENTION

The presently disclosed invention relates to a method of depositing materials (either selectively or non-selectively) such as metals, other conductors, semiconductors, insulators and other dielectric materials upon a variety of substrates. In a preferred embodiment, the presently disclosed inventions relates more particularly to a method of selectively depositing metals such as Cu°, Al°, Co°, Ni° and W°, to name a few, upon substrates such as diamond, single-crystal silicon, polycrystalline silicon, silicon nitride, quartz, alumina, platinum, tungsten, aluminum, poly(vinylphenol), poly(ethylene), epoxy, poly(ethersulfone) and others. The presently disclosed invention further relates to the products formed from the selective deposition of the various aforementioned materials such as metals upon the various aforementioned exemplary substrates.

## DESCRIPTION OF THE RELATED ART

Surfaces of substrates (e.g. Si, $SiO_2$, polymers, diamond etc.) modified with surface adherent ultra-thin film (UTF) layers of metals (e.g. Cu°, Al°, W° etc.) are increasingly sought for applications in microelectronic devices. For example, **Jain et al.**, in APPL. PHYS. LETT., 61, 2662 (1992) and in J. VAC. SCI. TECH., B11, 2107 (1993), respectively, report patterning Si wafers covered with an $SiO_2$ layer wherein holes are etched through the $SiO_2$ layer down to the underlying Si layer and wherein the holes are partially filled by W. Surface -OH groups generated upon the $SiO_2$ layer via $H_2O_2$ washing are coated with silanes such as $ClSi(Me)_3$ or $Cl_2Si(Me)_2$ to diminish the subsequent deposition of Cu°. The silanes (e.g. $ClSi(Me)_3$ or $Cl_2Si(Me)_2$) apparently passivate the $SiO_2$ surface -OH groups. Thus, wherever the silanes (e.g. $ClSi(Me)_3$ or $Cl_2Si(Me)_2$) passivate the surface -OH groups of the $SiO_2$ substrate, Cu° is less likely to deposit (i.e. on the silane passivated regions). Conversely, Cu° is more likely to deposit on the W patterned regions which are not passivated with the silanes.

A limitation of the **Jain et al.** process is that the selective deposition of Cu° is limited to substrates such as $SiO_2$ having surface -OH groups wherein the surface -OH groups are passivated with $ClSi(Me)_3$ or $Cl_2Si(Me)_2$, thereby, limiting the Cu° deposition to unpassivated surface -OH groups (or W coated Si regions). This limitation of the **Jain et al.** approach *confines or limits* the deposition of Cu° on substrates, such as $SiO_2$, that contain reactive unpassivated surface hydroxyl groups. In other words, a substrate having surface hydroxyl groups is subjected to **subtractive** passivation wherein the regions passivated (i.e. passivated with silanes or other blocking layers such as alkanethiols or polymers) resist subsequent deposition of metals such as Cu°. Thus, one cannot treat a substrate surface to enhance or promote Cu° deposition according to the **Jain et al.** process. One can only treat a substrate surface to inhibit or diminish Cu° deposition. Therefore, the **Jain et al.** process is, thus, considered a **subtractive** process.

Other processes for metal deposition are reported. According to **Schoer et al.** in LANGMUIR, 10, 615 (1994), a self-assembled monolayer film of octadecylmercaptan is deposited on Au(111) to diminish the deposition of Cu° on the Au surface. Thus, similar to the **Jain et al.** process, the **Schoer et al.** process is likewise considered a **subtractive** process. Neither **Jain et al.** nor **Schoer et al.** treat a substrate to *enhance or promote* the deposition of exemplary materials such as Cu° likened to an **additive** deposition process (as compared to the **subtractive** deposition process).

There are several advantages to an **additive** deposition process over a **subtractive** deposition process. **Additive** deposition processes provide greater control over the deposition process. Other advantages of additive deposition processes include obviating the need for removal of material, avoiding the use of etchants, decreased cost and fewer or no buried layers e.g. buried W layer under Cu layer. The greater control possible with the **additive** deposition processes provide greater control over the structures formed and linewidths of patterns formed. By enhancing or promoting deposition (i.e. **additive** deposition) of materials such as metals, dielectrics and others, these materials can be deposited at lower temperatures and with greater control, with fewer processing steps providing potential cost saving, allowing deposition on thermally sensitive substrate materials and forming patterns of deposited materials with higher resolution using a variety of lithographic techniques.

## SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to treat substrate surfaces, including diamond surfaces, to promote the additive deposition of materials to form a film or an UTF of the deposited material.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of materials to form a film pattern or an UTF pattern of the deposited material wherein the linewidth of the pattern so formed is about 1nm to about 1mm.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of materials to form a film pattern or an UTF pattern of the deposited material wherein the linewidth of the pattern so formed is about 10nm to about 20$\mu$m.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of materials to form a film pattern or an UTF pattern of the deposited material wherein the linewidth of the pattern so formed is about 25$\mu$m.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of materials to form a film pattern or an UTF pattern of the deposited material wherein the linewidth of the pattern so formed is about 1$\mu$m or less.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of materials to form a film pattern or an UTF pattern of the deposited material wherein the linewidth of the pattern so formed is about 0.1 - 0.5 $\mu$m.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of materials to form a film or an UTF of the deposited material upon a substrate at a temperature lower than the temperature at which a subtractive deposition process is carried out to form the same product.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of materials to form a film pattern or an UTF pattern upon the substrate of the deposited material at a temperature lower than the temperature at which a subtractive deposition process is carried out to form the same pattern.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of one or more metals to form a film pattern or an UTF pattern, wherein the linewidth of the pattern so formed is about 1 μm or less, at a temperature lower than the temperature at which a subtractive deposition process is carried out to form the same pattern.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of metals to form a film pattern or an UTF pattern, wherein the linewidth of the pattern so formed is about 0.1 - 0.5 μm or less, at a temperature lower than the temperature at which a subtractive deposition process is carried out to form the same pattern.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of thermally sensitive materials.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of one or more metals to form a film pattern or an UTF pattern at a lower cost than that of a subtractive deposition process to form the same pattern.

It is another object of the present invention to treat substrate surfaces to promote the additive deposition of one or more metals using chemical vapor deposition.

It is another object of the present invention to form film or UTF coated substrate products according to the process of the presently claimed invention.

It is another object of the present invention to form patterned film or patterned UTF coated substrate products resulting from the treatment of substrate surfaces to promote the additive deposition of metals.

It is another object of the present invention to form patterned film or patterned UTF coated substrate products having linewidths of about 1nm to about 1mm, the products resulting from the treatment of substrate surfaces to promote the additive deposition of metals.

It is another object of the present invention to form patterned film or patterned UTF coated substrate products having linewidths of about 10nm to about 20μm, the products resulting from the treatment of substrate surfaces to promote the additive deposition of metals.

It is another object of the present invention to form patterned film or patterned UTF coated substrate products having linewidths of about 25μm, the products resulting from the treatment of substrate surfaces to promote the additive deposition of metals.

It is another object of the present invention to form patterned film or patterned UTF coated substrate products having linewidths of 1.0 μm or less, the products resulting from the treatment of substrate surfaces to promote the additive deposition of metals.

It is another object of the present invention to form patterned film or patterned UTF coated substrate products having linewidths of about 0.1 - 0.5 μm, the products resulting from the treatment of substrate surfaces to promote the additive deposition of metals.

These and other objects of the present invention are accomplished by:

(1) providing a substrate having polar surface groups including -OH, -COOH, -CO, -$O^-$, -$COO^-$ etc. or mixtures thereof;

(2) treating the surface groups of the substrate with ligating (**ligating means catalyst binding e.g. adsorption, coordination binding, hydrogen bonding, and/or electrostatic binding etc.**) film precursors such as exemplary silanes including silanes of the general formula $R_nSiX_{4-n}$ wherein R is a hydrocarbon moiety (the R groups may be the same or different), X is a halogen or an alkoxy moiety to from -O-Si-$R_n$ moieties on the surface of the substrate and wherein n = 0, 1, 2, or 3 to form a ligating film upon the substrate;

(3) attaching the ligating film on the surface of the substrate to a catalyst; and

(4) vapor depositing a material upon the catalyst coated ligating film.

To produce patterned deposition, the following steps may be carried out between steps (2) and (4) above, in the order presented below:

(2a) immediately after step (2) above, exposing the ligating film to a pattern of actinic radiation, to form a pattern of ligating film regions having linewidths of 1nm-1mm, 10nm-20$\mu$m, 25$\mu$m or less, 1.0 $\mu$m, 0.1 - 0.5 $\mu$m, or less, respectively;

(2b) immediately after step (2a) above, removing the lithographic mask used in step (2a);

(2c) exposing the surface of the ligating film to a catalyst to deposit the catalyst on the remaining unexposed ligating film; and

(2d) eliminating step (3) above and going directly to step (4) above.

In effect the process using a ligating film and catalyst comprises the steps of:

(I) providing a substrate having on at least a portion of its surface one or more chemical groups capable of ligating to a catalyst, said chemical groups comprising one or more moieties selected from the groups consisting of aromatic heterocycle, amino, phosphino, carboxylate and nitrile;

(II) contacting said substrate with said catalyst to ligate said catalyst to said chemical groups on said substrate; and

(III) vapor depositing said material upon said catalyst ligated to said chemical groups on said substrate.

Alternatively, with some materials, a catalyst is not necessary. Deposition of a material, such as diamond, may occur directly upon a film deposited onto the substrate surface. Accordingly, the catalyst-free process involves the following steps:

(i) providing a substrate having polar surface groups including -OH, -COOH, -CO, $-O^-$, $-COO^-$ etc. or mixtures thereof;

(ii) treating the surface groups of the substrate with film precursors such as exemplary silanes including silanes of the general formula $R_nSiX_{4-n}$ wherein R is a hydrocarbon moiety (the R groups may be the same or different), X is a halogen or an alkoxy moiety to from $-O-Si-R_n$ moieties on the surface of the substrate and wherein n = 0, 1, 2, or 3 to form a film upon the substrate; and

(iii) vapor depositing a material upon the film.

## BRIEF DESCRIPTION OF THE DRAWINGS

**Figure 1** is an exemplary schematic representation of the process steps carried out to practice the presently claimed process.

**Figure 2** contains plots labelled (a), (b) and (c) wherein each is a plot of surface atomic concentration obtained via alternating cycles of argon ion sputtering and X-ray photoelectron spectroscopic surface analysis. Each plot (a), (b) and (c) was made from the samples prepared according to the procedure of Example 5, *infra*.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Chemical vapor deposition (CVD) of materials is a powerful technique for forming a wide variety of thin films and devices. Chemical vapor deposition has significant advantages over traditional physical vapor deposition (PVD) techniques that include greater control over film properties, such as composition, thickness, uniformity, morphology, solid phase, crystal structures and orientations, electronic structure, the capability to form conformal films on complex structures, and the potential for selective deposition. *See* **Hitchman, M. L., and Jensen, K. F., Eds., <u>Chemical Vapor Deposition</u>, (San Diego: Academic Press, 1993)**, incorporated herein by reference in its entirety and for all purposes; *See* **Vossen, J. L., and Kern, W., Eds., <u>Thin Film Processes</u>, (New York: Academic Press, 1978)**, incorporated herein by reference in its entirety and for all purposes; *See* **Eden, J. G., <u>Photochemical Vapor Deposition</u>, (New York: John Wiley & Sons, Inc., 1992)**, incorporated herein by reference in its entirety and for all purposes; *See* **Gladfelter, W. L.,** ***Chem. Mater.*** **5, 1372** (1993), incorporated herein by reference in its entirety and for all purposes; *See* **Hampden-Smith, M. J., and Kodas, T. T., Eds., <u>The Chemistry of Metals CVD</u>, (VCH Publishers, New York, 1994)**, incorporated herein by reference in its entirety and for all purposes.

In addition, CVD offers advantages over solvent-based film coating and electrochemical or electroless metal deposition, such as increased control over film properties, structure, and morphology, greater purity, reduced waste of solvents and reagents, and compatibility with other gas-phase or vacuum-based processing such as plasma etching.

Although this patent application describes a process for enhanced and controlled chemical vapor deposition (CVD), there are similar vapor-phase deposition processes, including, but not limited to, plasma-assisted chemical vapor deposition (PACVD), photochemical vapor deposition (photo-CVD), molecular beam epitaxy (MBE), and vapor-phase epitaxy (VPE), to which the present invention may be applied to control material film formation upon substrates.

Although electroless solution-based metallization can be carried out, the solution based metallization is limited to those materials (e.g., Au, Pd, Sn, Ni, Co, Cu) that can be deposited from an electroless solution. Exemplary chemical vapor deposition processes provide much greater control and range of choices of the composition, structure, phase, and other properties of deposited materials than does electroless deposition.

The following discussion is first directed to various materials that may be deposited upon a substrate according to the present invention. In conjunction, the precursors of the various materials sought to be deposited upon a substrate are also discussed below.

A variety of exemplary materials can be unselectively and/or selectively deposited upon exemplary substrates. For example, various metals may be plated or selectively plated (i.e. to form a patterned plated substrate coated with a metal) onto substrates, according to the present invention, including metals such as Co, Ni, Cu, Au, Pd, W, Al and alloys thereof and other alloys of Ni-Fe-B identified as permalloy.

There is an exemplary interest in material deposition, wherein the material is Cu, for forming high-conductivity, electromigration-resistant interconnects in multi-level microelectronic devices. *See* **Gladfelter, W. L.,** ***Chem. Mater.*** **5, 1372 (1993),** incorporated herein by reference in its entirety and for all purposes. *See* **Hampden-Smith, M. J., and**

**Kodas, T. T., Eds.**, **The Chemistry of Metals CVD**, **(VCH Publishers, New York, 1994)** incorporated herein by reference in its entirety and for all purposes. *See* **Shin, H. K., Chi, K. M., Hampden-Smith, M. J., Kodas, T. T., Paffett, M. F., and Farr, J. D.,** ***Adv. Mater.*** **3, 246 (1991)**, incorporated herein by reference in its entirety and for all purposes. *See* **Chi, K. M., Shin, H. K., Hampden-Smith, M. J., Kodas, T. T., and Duesler, E. N.,** ***Polyhedron*** **10, 2293** (1991), incorporated herein by reference in its entirety and for all purposes. *See* **Reynolds, S. K., Smart, C. J., Baran, E. F., Baum, T. H., Larson, C. E., and Brock, P. J.,** *Appl. Phys. Lett.* **59, 2332** (1991), incorporated herein by reference in its entirety and for all purposes. *See* **Shin, H. K., Chi, K. M., Hampden-Smith, M. J., Kodas, T. T., Paffett, M. F., and Farr, J. D.,** *Chem. Mater.* **4, 788** (1992), incorporated herein by reference in its entirety and for all purposes. *See* **Norman, J. A. T., Muratore, B. A., Dyer, P. N., Roberts, D. A., and Hochberg, A. K.,** *J. Phys.IV* (Paris), **1, C2-273** **(1991)**, incorporated herein by reference in its entirety and for all purposes.

High purity, exemplary copper films can be deposited from copper precursors of the general form ($\beta$-diketonate)-$Cu^{I}$-$L_x$, where L is a Lewis base and **x** is zero or a positive integer, preferably, an integer indicating the number of the bases (Ls) coordinated to the exemplary $Cu^{I}$ of the exemplary precursor. It is believed that these precursors (i.e. ($\beta$-diketonate)-$Cu^{I}$-$L_x$) exploit the differences in the electrical conductivity or electron donating capability of solid surfaces to achieve selectivity. Without being limited by theory, it is further believed that copper deposits preferentially on conducting and semiconducting surfaces, but not on insulators, via a disproportionation reaction:

$$2\ (\beta\text{-diketonate})\text{-}Cu^{I}\text{-}L_x\ (g)\ \text{---->}\ Cu^0\ (s) + Cu^{II}(\beta\text{-diketonate})_2\ (g) + 2x\ L\ (g) \qquad (1)$$

wherein (s) indicates an adsorbed species and (g) indicates a gaseous species. Though not fully understood, the electrically conductive surfaces apparently facilitate the electron transfer required for the disproportionation.

A variety of $Cu^I$ precursors include precursors of the following general formulas:

(hfac)Cu(triorganophosphine) **(2)**

(hfac)Cu(olefin) **(3)**

(hfac)Cu(alkyne) **(4)**

and mixtures thereof. The above general formulas **(2)**, **(3) and (4)** can be classified as the formula given below:

(N)Cu(L) **(5)**

wherein N includes the following: N =hfac=1,1,1,5,5,5-hexafluoroacetylacetonate, N=tfac=trifluoroacetylacetonate, N=acac=acetylacetonate or N=mixtures thereof and wherein L includes the following: L=trimethylphosphine ($PMe_3$), L=triethylphosphine ($PEt_3$), L=1,5 cyclooctadiene (1,5-COD), L=triethylvinylsilane (TEVS), L=trimethylvinylsilane (TMVS), L=2-butyne, L=2-pentyne, L=bis(trimethylsilyl)acetylene, L=CO and mixtures thereof.

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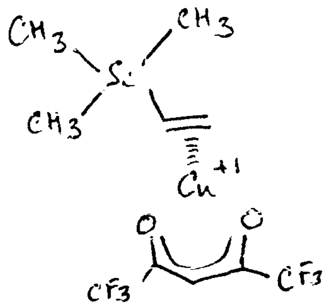
Note that the structure of (hfac)Cu$^I$(tmvs) is as described below (*See* U.S. Patent Nos. 5,322,712; 5,144,049; 5,085,731, each patent incorporated herein by reference in its entirety and for all purposes; Note that (hfac)Cu$^I$(tmvs) is available under the name CupraSelect from Schumacher Co.):



Other suitable metal precursors which may be used with the present invention are given in **Hampden-Smith, M. J., and Kodas, T. T., Eds.,** <u>**The Chemistry of Metals CVD**</u>**, (VCH Publishers, New York, 1994)**, *supra*, at pages 175-327.

Other examples of disproportionation reactions are also given below:

$$2\ (\text{acac})\text{-Cu}^{I}\text{-}(\text{NH}_3)_{25}\ (g)\ \text{---->}\ \text{Cu}^0\ (s) + \text{Cu}^{II}(\text{acac})_2\ (g) + 5\text{NH}_3\ (g) \qquad \textbf{(6)}$$

$$2\ (\text{hfac})\text{-Cu}^{I}\text{-}(\text{CO})\ (g)\ \text{---->}\ \text{Cu}^0\ (s) + \text{Cu}^{II}(\text{hfac})_2\ (g) + 2\text{CO}\ (g) \qquad \textbf{(7)}$$

wherein (s) indicates an adsorbed species and (g) indicates a gaseous species.

Exemplary high-purity, exemplary conductive copper films can be deposited selectively at about 393-523 K using hfac-Cu$^I$-tmvs wherein hfac = hexafluoroacetylacetonate and tmvs = trimethylvinylsilane, and similar monovalentcopper precursors of the general form ($\beta$-diketonate)-$Cu^I$-$L_x$, wherein L is a Lewis base and wherein **x** is zero or a positive number, preferably, an integer indicating the number of the bases (Ls) coordinated to the exemplary $Cu^I$ of the exemplary precursor. *See* **Norman, J. A. T., Muratore, B. A., Dyer, P.N., Roberts, D. A., Hochberg, A. K., and Dubois, L. H.,** ***Mat. Sci. and Eng.*** **B17, 87 (1993)**, incorporated herein by reference in its entirety and for all purposes. *See* **Jain, A., Farkas, J., Chi, K. M., Hampden-Smith, M. J., and Kodas, T. T.,** *Appl. Phys. Lett.* 61, 2662 (1992), incorporated herein by reference in its entirety and for all purposes. *See* **Jain, A., Kodas, T. T., Jairath, R., and Hampden-Smith, M. J.,** ***J. Vac. Sci. Tech. B*** **11, 2107 (1993)**, incorporated herein by reference in its entirety and for all purposes.

According to the present invention, for the selective deposition of exemplary metals from their respective precursors such as (2), (3), (4) **and/or** (5), *supra*, a deposition catalyst solution is needed for facilitating the unselective and/or selective deposition of the exemplary metal, which deposition is suspected to occur via the disproportionation reaction denoted as (1), (6) **and/or** (7), *supra*. Although Pd/Sn catalysts have been used in electroless solution based metallization and may be successfully used in conjunction with the present invention, such Pd/Sn catalysts require at least "acceleration" prior to commencement of metal deposition. (*See* U.S. Patent No. 5,389,496 at Column 2, lines 64-70). Therefore, Sn-free Pd catalysts are preferred for use in conjunction with the presently disclosed invention.

A variety of exemplary metallization catalysts may be employed, including tin-free catalysts, with $Pd^{II}$ compounds and compositions preferred for the generally superior catalytic activity those catalysts provide. A substrate is preferably treated with a solution of the metallization catalyst, for example, an aqueous solution or a solution of an organic solvent. The catalyst solution preferably comprises other materials such as ancillary ligands, salts and buffers to enhance the stability of the catalyst solution and thereby to provide suitable catalyst activity as well as convenient use and storage of the solution.

A variety of compounds may be employed as the catalyst in accordance with the present invention such as catalysts of palladium, platinum, rhodium, iridium, nickel, copper, silver, gold, and mixtures thereof, respectively. Palladium or palladium containing compounds and compositions generally provide superior catalytic activity and therefore are preferred. Particularly preferred palladium species include derivatives of palladium dichloride and $Na_2PdCl_4$. Other salts of $PdCl_4^{2-}$ should also be suitable.

The vapor deposition or chemical vapor deposition (CVD) metallization catalysts useful in the processes of the present invention are preferably applied to the substrate (the substrate having a ligating film on its surface, *infra)* as a solution, for example, as an aqueous solution or a solution of an organic solvent. Suitable organic solvents include dimethylformamide (DMF), toluene, tetrahydrofuran (THF) and other solvents in which the metallization catalyst is soluble at effective concentrations.

Means for contacting a substrate with a catalyst solution may vary widely and include immersion of the substrate in a solution as well as a spray or puddle application. The catalyst solution contact time required to provide complete metallization of the contact area can vary with catalyst solution composition and age.

A variety of catalyst solutions have been successfully employed, with solutions stabilized against decomposition preferred. Thus, the catalyst solution may comprise ancillary ligands, salts, buffers and other materials to enhance catalytic activity. Though not wishing to be bound by theory, it is believed many of the catalyst solutions useful in the present invention change over time by oligomerization and formation of insoluble oxo-compounds. For example, as such catalyst oligomers increase in molecular weight, their solubilities decrease and precipitation of the catalyst can occur. Exemplary conditions for an active oligomerized Pd catalyst is found in the '496 patent, *supra*.

Many substrates or substrate surfaces capable of being coated or plated, according to the present invention, intrinsically contain chemical groups, or appropriate precursors of chemical groups, that are able to ligate an exemplary plating catalyst. These chemical groups are referred to as the catalyst ligating functionality or catalyst ligating group present upon the substrate itself.

Upon encountering a substrate surface lacking a catalyst ligating group or readily convertible precursor thereof, an intervening ligating film is attached to the surface of the substrate via an exemplary chemical reaction. For example, substrate surface -OH groups of an exemplary substrate are chemically reacted with an exemplary organosilane to form a siloxy (-Si-O-) bond between the ligating film precursor (the exemplary organosilane) and the substrate surface -OH groups. The attached organosilane comprises an exemplary **ligating film** upon the substrate via the formation of the exemplary siloxy bond. For example, the reactive portion of the exemplary organosilane is referred to as the **substrate binding group** of the ligating film precursor, the organosilane. Note that a variety of organic percursors can be used to form the ligating film such as organotitanates, organothiols, organosulfides, carboxylic acids, organoaluminates etc.

That portion of the ligating film (e.g., organosilane attached to the substrate surface via siloxy bonds) which is capable of binding an exemplary catalyst is referred to as a **catalyst ligating group**.

Thus, an appropriate **ligating film** intervening between the substrate and the catalyst solution has at least *two groups*, the **catalyst ligating group** and the **substrate binding group.** The catalyst ligating group attaches the catalyst to the ligating film. The ligating film, in turn, is attached to the substrate via a bond formed between the substrate binding group (e.g. the Si of the organosilane) present within the ligating film precursor (e.g. the organosilane) and a **substrate surface reactive group** (e.g. a substrate surface -OH group) by the formation of an exemplary siloxy bond.

Sometimes, attachment of the catalyst is accomplished, for example, via adsorption, coordination binding and/or electrostatic attraction to the surface of a substrate. However, in a preferred embodiment, attachment of the catalyst to the surface of the substrate *generally* requires that the substrate have upon its surface a catalyst coordinating functionality. Either the substrate surface inherently has a catalyst coordination functionality upon its surface or the substrate surface is modified to contain a catalyst coordination functionality.

For example, polyvinylpyridine film intrinsically contains such catalyst ligating groups with the pendant pyridine serving as the catalyst ligating group. The pyridyl group has been found to be a particularly preferred catalyst ligating group for an exemplary palladium catalyst. Similarly, a substrate comprising aluminum oxide will bind an exemplary palladium catalyst by the AlO and AlOH groups of the exemplary alumina. Further, the catalyst ligating functionality need not be the sole component of the substrate. Thus, the catalyst ligating functionality may be physically blended as one of multiple components comprising the substrate surface to ligate to the catalyst.

A possible shortcoming of such a blending approach is that incorporation of large quantities of a second material may impair the film-forming or other properties of the bulk material. A potential solution to this problem is to incorporate a surfactant form of the catalyst ligating component into the bulk material by proper choice of the relative solubility/polarity characteristics of the catalyst ligating component and the surfactant. By incorporating a small percentage of the surfactant into the bulk, a high surface concentration of the catalyst ligating functionality could be produced.

Many substrates that do not inherently comprise suitable catalyst ligating groups may be readily modified to possess the necessary catalyst ligating groups. Substrate modification methods include, but are not limited to, thermolysis, reaction of the surface of the substrate with one or more chemical reagents, irradiation with photons or ions, vapor phase modification, graft polymerization, x-ray and nuclear radiation treatment or, more generally, any treatment that effects the desired conversion of the substrate to provide catalyst ligating groups upon the substrate. ***See*** **J.M. Calvert et. al., Patterned Electroless AMetallization of Ligand-AModified Surfaces, Materials Research Proceedings, 260,p. 905 (1992)**, incorporated herein by reference in its entirety and for all purposes. ***See*** **T.G. Vargo et al., Adhesive Electroless Metallization of Fluoropolymeric Substrates, Science, 262, p. 1711 (1993)**, incorporated herein by reference in its entirety and for all purposes.

Not all substrates inherently possess adequate **substrate surface reactive groups** to attach the ligating film precursors (such as the aforementioned organosilanes) to the substrate surface wherein the ligating film so formed has catalyst ligating groups upon its surface. For example, with substrates such as poly(ethylene), epoxy, poly(ethersulfone), fluoropolymers, polyimide, paralyne, polyesters, polyethers and diamond, which do not contain high concentrations of inherent substrate surface reactive groups such as surface hydroxyls, it is necessary to oxidize and/or hydrolyze the surface of these substrates wherein organosilane ligating film precursors are to be used. Oxidation and/or hydrolysis of these and similar substrates can be accomplished in several ways including plasma (e.g., radio frequency plasma generation, microwave plasma generation), thermal oxidation, acid treatment, base treatment and/or other chemical treatments (e.g. treatments with oxidizing agents such as permanganate, dichromate and/or ozone). Thus, with any substrate that inherently possesses, or can be modified to possess, sufficient substrate surface reactive groups such as reactive hydroxyl groups or similarly reactive moieties, the substrate can be functionalized with a ligating film.

In some cases, such as $SiO_2$, which contains surface -OH groups, a film can be directly deposited upon the $SiO_2$ substrate. Films of organosilanes can be formed upon the $SiO_2$ surface containing surface -OH groups. In the exemplary case of diamond vapor deposition, since diamond will deposit on carbon containing functional groups, it is possible to deposit diamond on a film such as a film of an organosilane without the use of a catalyst. Numerous organosilanes that contain carbon containing functional groups (which carbon containing functional groups act as nucleation sites for diamond vapor deposition--obviating the need to use an intervening catalyst layer) include methyl-, ethyl-, cyclohexyl-, octadecyl-, napthyl-, anthracenyl-, biphenyl-, and adamantyl- containing silanes. Ordered cyclic- or polycyclic hydrocarbon moieties mimic graphite edge plains, which nucleate diamond during the CVD of diamond. The exemplary adamantyl functionality is a polycyclic hydrocarbon analog of the diamond latice that may nucleate diamond growth when applied to a substrate as an adamantyl-containing silane UTF, other UTF, or film, respectively.

Exemplary organosilanes of the general form $R_nSiX_{4-n}$, where R is an organofunctional group and X is usually -Cl, $-OCH_3$, or $-OC_2H_5$, have been used to deposit films (e.g. catalyst ligating films) on various substrates. For instance, organosilanes of the general form $R_nSiX_{4-n}$, where R is an organofunctional group and X is usually -Cl, $-OCH_3$, or $-OC_2H_5$, react with exemplary substrate surface hydroxyl groups to form covalently bound -O-Si-R moieties wherein the R moiety contains a catalyst ligating group (n = 0,1, 2, or 3).

Exemplary organosilanes of this form include, but are not limited to, octenyldimethylchlorosilane, N-(2-aminoethyl-3-aminopropyl)trimethoxysilane, m,p-(aminoethylaminomethyl)phenethyltrimethoxysilane, 2-(trimethoxysilyl)ethyl-2-pyridine, 3-mercaptopropyltrimethoxysilane, 2-(diphenylphosphino)ethyltriethoxysilane and N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride.

Films (e.g. catalyst ligating films) formed from such silanes attach to the underlying substrates via an exemplary siloxy bond and are further capable of attaching to an exemplary catalyst via a catalyst ligating group present within the exemplary silane. For example, 2-(trimethoxysilyl)ethyl-2-pyridine provides both catalyst ligating groups and substrate binding groups. The alkoxysilane group can chemically bind the compound to a substrate. For instance, the methoxy group of the trimethoxysilyl group reacts with exemplary surface hydroxyl (silanol) functionalities of an exemplary quartz substrate, displacing methanol to directly bond to the substrate. The thus bound pyridyl group of the silylpyridyl molecule serves as a catalyst ligating group for chelating with the exemplary metallization catalyst.

Additional materials and methods for the attachment (chemisorption) of ultrathin ligating film precursor materials (such as organosilanes or organotitanates) to substrates that either intrinsically possess, or are treated to have, polar surface groups such as hydroxyl functionalities have been described elsewhere. *See* **Calvert, J. M., *J. Vac. Sci. Tech. B* 11, 2155 (1993)**, incorporated herein by reference in its entirety and for all purposes. *See* **Dressick, W. J., and Calvert, J. M., *Jpn. J. Appl. Phys.* 32, 5829 (1993)**, incorporated herein by reference in its entirety and for all purposes. *See* **Vargo, T. G., Gardella, J. A., Calvert, J. M., and Chen, M. C., *Science* 262, 1711 (1993)**, incorporated herein by reference in its entirety and for all purposes. *See* **Calvert, J. M., Pehrsson, P. E., Dulcey, C. S., and Peckerar, M. C., (Mat. Res. Soc. Symp. Proc. 260, Pittsburgh, 1992), p. 905**, incorporated herein by reference in its entirety and for all purposes. *See* **Calvert, J. M., Pehrsson, P. E., and Peckerar, M., U.S. Patent Application 07/933,147**, incorporated herein by reference in its entirety and for all purposes. *See* **Schnur, *et. al.*, U.S. Patent 5,077,085**, incorporated herein by reference in its entirety and for all purposes. *See* **Schnur, *et. al.*, U.S. Patent 5,079,600**, incorporated herein by reference in its entirety and for all purposes. *See* **Calvert, *et. al.*, U.S. Patent 5,389,496**, incorporated herein by reference in its entirety and for all purposes. *See* **Calvert, *et. al.*, *Solid State***

*Technology* **34, 77 (1991)**, incorporated herein by reference in its entirety and for all purposes. *See* **Merrian, C. K. R., Perkins, F. K., Brandow, S. L., Koloski, T. S., Dobisz, E. A., and Calvert, J. M.,** ***Appl. Phys. Lett.*** **64, 1, (1994)**, incorporated herein by reference in its entirety and for all purposes. *See* **Perkins, F. K., Dobisz, E. A., Brandow, S. L., Koloski, T. S., Calvert, J. M., Rhee, K. W., Kosakowski, J. E., and Merrian, C. R. K.,** ***J. Vac. Sci. Tech. B*** **12, 3725 (1994)**, incorporated herein by reference in its entirety and for all purposes. However, this work had not been extended to gas-phase deposition processes prior to the present invention.

Rather than directly modifying the substrate, the substrate may be imparted with suitable catalyst ligating groups by indirect modification of the surface of the substrate. For example, a substrate may be coated with one or more film layers, at least one layer comprising one or more suitable ligating agents. The film layer preferably adheres well to the substrate, for example, by containing a substrate functional group that will chemically and/or physically adhere to the substrate.

The catalyst ligating function (e.g. via catalyst ligating group) and the substrate adhesion (e.g. via substrate binding group) may be performed by multiple chemical groups with bond formation or other linkage between the catalyst ligating group and the catalyst, as well as, the substrate binding group and the substrate, respectively. The linkage connecting the multiple functional groups may be of variable length and chemical composition. Examples include 3-(trimethoxysilyl) propylamine and quinoline-8-sulfonic acid chloride. The aminosilane is applied as the substrate adsorbent. The coated surface is then reacted with quinoline-8-sulfonic acid chloride, the -$SO_2Cl$ group coupling to the amine group of the aminosilane to form a sulfonamide linkage, and the quinolinic group serving as a catalyst ligating moiety.

Similarly, 3-(trimethoxysilyl) propylamine can be applied to a substrate and then reacted with the acid chloride group of 4,4'dicarbonyl chloride-2,2'-bipyridine to from an amide linkage. The pyridyl moieties of this complex serve as a catalyst ligating group.

Other silyl amines can be condensed in a similar manner, for example 3-(triethoxysilyl) propylamine. Another sequence provides condensing the hydroxyl groups of a chemically etched polyethylene substrate with a suitable substrate ligating film precursor, for example, 3-(trimethoxysilyl) propylamine, which after formation of the siloxy bond by methanol displacement, the amino group can condense with a suitable catalyst ligating compound such as nicotinoyl chloride.

Substrates successfully treated to form catalyst ligating films (e.g. of organosilanes such as octenyldimethylchlorosilane, N-(2-aminoethyl-3-aminopropyl)trimethoxysilane, m,p-(aminoethylaminomethyl)phenethyltrimethoxysilane, 2-(trimethoxysilyl)ethyl-2-pyridine, 3-mercaptopropyltrimethoxysilane, 2-(diphenylphosphino)ethyltriethoxysilane and N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride) include single-crystal silicon with native and thermal oxide surfaces, polycrystalline silicon, silicon nitride, quartz, alumina, platinum, tungsten, aluminum, poly(vinylphenol), poly(ethylene), epoxy, polyimide, polyesters, novolac, polyethers, poly(ethersulfone), fluoropolymers, and diamond. Other suitable substrates include Ag, Au, tin oxides, indium tin oxides and zinc oxides.

Various groups of ligating film precursors (serving as suitable catalyst ligating groups) include amino, phosphino, pyridyl, ammonium, alkylammonium, thiol, thiolate, sulfonate, thiocyanate, olefin, alkyne, titanium nitride, carbon nitride, silicon carbide, aluminum nitride, graphite, diamond like carbon, amorphous carbon, polyethers, polycrystalline diamond, single crystal diamond, bipyridyl, 2,2":6,2"-terpyridine, oxalate, ethylene diamine, 8-hydroxyquinoline, and 1,10-phenanthroline. Organophosphines, nitriles, carboxylates and thiols should also ligate catalysts well. For example, 3-mercaptopropyltriethoxysilane, 2-(diphenylphosphino)ethyltriethoxysilane and cyanomethylphenyltrimethoxysilane should serve as suitable ligating film precursors for use in accordance with the present invention.

A catalyst ligating group comprising a radiation sensitive chromophore can provide a convenient selective radiation patterning and metallization process where selective photolysis, radiation ablation, or radiation induced transformation modifies the chemical groups on the substrate or the film formed on the substrate to substantially reduce or eliminate the catalyst ligating ability in the selected film surface areas. Subsequent exposure to a catalyst solution and exemplary material deposition via vapor deposition provides a positive tone image of the photomask employed during photochemical patterning. For example, the pyridyl group of 2-(trimethoxysilyl)ethyl-2-pyridine serves as a chromophore for convenient patterning and subsequent selective exemplary metallization of the substrate surface via vapor deposition.

Analogously, a catalyst ligating film can be employed where selective photolysis transforms a catalyst non-ligating group within the film into a catalyst ligating group. For example, azoxybenzene derivatives photoisomerize from a weakly or catalytic non-ligating azoxybenzene group to the ligating 2-hydroxyazobenzene group. The exemplary chelating ability of 2-hydroxyazobenzene and 2-(2-pyridylazo)-1-napthol has been described elsewhere. See U.S. Patent No. 5,389,496. For example, polyacetoxystyrene can be irradiated with ultraviolet radiation to provide the ligating 2-hydroxyacetophenone moiety which moiety functions as a catalyst ligating group. Also, for example, a thiol silane can be converted to a sulfonate by photooxidation. ***See*** **S.K. Bhatia et al., Fabrication of Surfaces Resistant to Protein Adasorption and their Application to Two Dimensional Protein Patterning, Analytical Biochemistry, 208, p. 197 (1993)**, incorporated herein by reference in its entirety and for all purposes.

Depending on the nature of the radiation sensitive materials employed, such transformations may be accomplished with a variety of exposure sources and imaging tools. For example, UV or visible light will be suitable for certain transformations, while other transformations may require exposure sources such as electron beam, ion-beam or x-ray treatment. Such energy sources can be provided by image tools known to those in the art, for example, UV contact printers and projection steppers, electron beam writers, scanning tunnelling microscopy, atomic force microscopy, near field scanning optical microscopy, focused ion beam exposure and x-ray proximity printers. Such transformations can be accomplished by mechanical/physical means such as stamping, scraping and stylus writing.

For such patterning of a catalyst ligating film, the film preferably is an UTF, which is a film defined herein to mean a film with a thickness of about 1 - 10 molecular layers of the molecule (e.g. $R_nSiX_{4-n}$) of which the film is comprised. Such a film can be formed through dip coating or vapor phase deposition procedures which are known in the art.

The invention will be better understood by reference to the following examples. The following examples describe specific methods and materials for the promotion of selective copper chemical vapor deposition on diamond and other substrates. The process used for selective enhancement of CVD is shown schematically in Fig. 1. It is demonstrated in the examples below that the specific steps of substrate surface oxidation (Fig. 1, Scheme 1, step 1), ligand attachment (step 2), catalysis (step 3) and selective chemical vapor deposition (step 4) have been accomplished. It is shown that the uncatalyzed organosilane films does not promote Cu CVD, and appear to hinder Cu deposition. Selective Cu deposition was also achieved on Si and $SiO_2$ substrates. Selective patterned deposition of Cu (Figure 1, Scheme 2) was achieved by patterning the ligating silane film prior to catalyst attachment and Cu CVD.

## Example 1

### Oxidation of single-crystal diamond substrate using $O_2$ plasma treatment

Synthetic high-pressure, high-temperature (HPHT) single-crystal C(100) diamond substrates (Sumitomo Electric Carbide) were cleaned by sequential ultrasonication in acetone, 1,1,1-trichloroethane, and methanol, and then cleaned sequentially in boiling *aqua regia*, 6:4 $H_2SO_4$/ $HNO_3$, and then in 1:1:1 HF/$HNO_3$/Acetic acid. The water contact angle (measured using the sessile drop method and a Zisman-type Goniometer) for the solvent- and acid-cleaned diamond surface was approximately 60,° indicative of a partially oxidized diamond surface. The diamond substrates were then inserted into an Astex 1.5 kW microwave plasma reactor and subjected to a 600 W microwave plasma using 10 Torr and 400 sccm of $H_2$ at 1073 K for between 20 s and 120 min. The diamond substrates were highly hydrophobic after $H_2$-plasma treatment, and gave water contact angles of 85-90.° Such high contact angles are indicative of an H-terminated diamond surface. The diamond substrates were then inserted into a Branson Model IPC plasma etcher and subjected to an RF plasma using 1 torr and 250 sccm of $O_2$ for 2 to 4 min at 200 W. Diamond surfaces after $O_2$-plasma oxidation were highly wettable by water, and gave contact angles of $(20\pm10)$.° X-ray photoelectron spectroscopy (XPS, Surface Science Laboratories, SSX-100) of oxidized diamond shows development of a feature on the high binding energy side of the C1s peak that was absent on the unoxidized diamond. The binding energy and intensity of this feature are consistent with a surface layer of oxygen bonded to the diamond surface. The contact angle and XPS measurements demonstrate that the $O_2$ plasma treatment is very effective at converting the initial diamond surface into a polar, highly wettable surface. This observation is consistent with the formation of carbonyl or hydroxyl groups at the diamond surface, such as carbonyl, alcohol, lactone or carboxylic acid moieties, which have been identified on oxidized diamond using high-resolution electron energy loss spectroscopy (HREELS). *See* **Pehrsson et al., Proceedings of the 2nd NIRIM International Symposium on Advanced Materials (ISAM '95) Tsukuba, Japan, March 6-10, 1995 (Y. Bando, M. Kamo, H. Haneda and T. Aizawa, Editors) pp. 279-286 (1995).**

## Example 2

### Functionalization of an oxidized diamond surface with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane = (UTF-EDA or EDA)

This example demonstrates that surface of a diamond substrate produced by $O_2$-plasma etching provides the necessary functional groups for the attachment of an organo-silane UTF from aqueous solution.

An $O_2$-plasma-oxidized diamond was prepared as described in Example 1, using an RF power of 200W for 4 min. The diamond was then treated with a 1% (v/v) aqueous solution of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (Huls America, Piscataway, NJ), UTF-EDA, 0.001 M in acetic acid, at room temperature. The diamond was removed from the solution and rinsed twice in filtered, deionized (DI) water. The diamond was then baked for 5 min. at 393 K on the surface of a hotplate. XPS analysis of the UTF-EDA modified surface shows signals for Si and N, both constituents of the UTF layer that are not present on the unmodified diamond surface.

## Example 3

### Functionalization of an oxidized diamond surface with UTF-PEDA

This example illustrates the generality of the procedure for modification of oxidized diamond surfaces with chemisorbed films.

A plasma oxidized diamond film was prepared as described in Example 1. The substrate was then treated with a 1% (v/v) solution of m,p-(aminoethylaminomethyl)-phenethyltrimethoxysilane (Huls America), UTF-PEDA, in 95:4 (v:v) methanol:water with 0.001 M acetic acid at room temperature for 20 min. The diamond substrate was removed from the solution, rinsed twice in fresh methanol, and was baked for 5 min. at 393 K on the surface of a hotplate. XPS analysis of the UTF-PEDA modified surface shows signals for Si and N, both constituents of the UTF layer that are not present on the unmodified diamond surface.

## Example 4

### Selective copper chemical vapor deposition on functionalized diamond surfaces at 444 K

This example demonstrates that the UTF process can used to selectively produce adhesive, conductive copper deposits at low temperature (e.g. less than 450K) on an insulating diamond substrate.

Three separate diamond substrates similar to those described in Example 2 were prepared in the following manner: Substrates 4.1, 4.2, and 4.3, were subjected to a $H_2$-plasma for 60 s, as described in Example 1. Substrates 4.2 and 4.3 were then subjected to an RF $O_2$-plasma, as described in Example 1, and coated with UTF-EDA, as described in Example 2. Substrate 4.3 was then exposed to an aqueous palladium-based catalyst solution (designated Ac3; the exact composition and preparation method for the Ac3 solution is given in **Dressick, W. J., Dulcey, C. S., Georger, J. H., Calabrese, G. S., and Calvert, J. M., J. Electrochem. Soc. 141, 210 (1994)**, incorporated herein by reference in its entirety and for all purposes, in which **Ac3** is designated as **solution IV, Method B**) for 120 min, rinsed with DI water, and dried in a stream of filtered $N_2$ at room temperature. All three substrates were then mounted in the center of a 0.010-mm thick, 1x1-$cm^2$ silicon wafer using a Ag-based colloidal adhesive.

The Si wafer with the attached substrates was then mounted in a copper chemical vapor deposition chamber on a Pt foil that was heated resistively. The cool-wall, low-pressure CVD chamber (*See* **Hsu, D.S.Y., Tenth micrometer trench fabrication by aperture narrowing of 0.6 μm starting mask structures using chemical-beam deposition and ion-beam redeposition, J. Vac. Sci. Technol., B 12(5), 3048-3053 (Sept/Oct 1994)**, incorporated herein by reference in its entirety and for all purposes; ***See*** **Hsu, D. S. Y., Turner, N. H., Pierson, K. W., and Shamamian, V. A., *J. Vac. Sci. Tech. B* 10, 2251 (1992)**, incorporated herein by reference in its entirety and for all purposes; ***See*** **Hsu, D.**

**S. Y., and Gray, H. F.,** ***Appl. Phys. Lett.*** **63, 159 (1993),** incorporated herein by reference in its entirety and for all purposes; ***See*** **U.S. Patent No. 5,110,760**-- incorporated herein by reference in its entirety and for all purposes) was pumped with a 15-cm, liquid-nitrogen-trapped diffusion pump (base pressure = $4x10^{-6}$ Pa). Sample temperature was monitored with a Pt-Pt(10% Rh) thermocouple spot welded to the Pt foil. A 12-mm glass doser tube was used to direct the flow of gases onto the sample during Cu deposition. The metallorganic copper precursor hexafluoroacetylacetonatocopper-trimethylvinylsilane (CupraSelect, Schumacher Co.), hfac-Cu-tmvs, was purified with several freeze/pump/thaw cycles and then warmed to approximately 320 K. Immediately prior to Cu deposition, the sample was heated in vacuum to 444 K in about 10 min. With the doser pointed away from the sample, $H_2$ was flowed through the doser at approximately 1 sccm and $4x10^{-3}$ Pa. The sample temperature and $H_2$ pressure were stabilized in approximately 10 min, and then the precursor was metered into the $H_2$ stream until the total chamber pressure increased to $8x10^{-3}$ Pa. The doser tube was then rotated to a position 3 mm in front of and normal to the substrate. After 24 min, the precursor flow was stopped and the sample temperature was maintained in $H_2$ flow for approximately 5 min. The sample was then cooled at approximately 10 K/min to 350 K and maintained at this temperature for 30 min to allow any unreacted precursor to desorb. Then the $H_2$ flow and sample heating were turned off. After the sample had cooled to near room temperature, the chamber was vented to atmospheric pressure with nitrogen, and the samples were removed.

Preferential chemical vapor deposition of copper on substrate 4.3 was demonstrated with XPS and scanning electron microscopy (SEM, Hitachi) images of the three substrates. SEM showed formation of a continuous copper film on substrate 4.3. Only isolated particles were detected on substrates 4.1 and 4.2. By estimating particle density on each substrate from SEM images, substrate 4.3 contained 1,000-10,000 times the copper particle density of substrates 4.1 or 4.2. The film on substrate 4.3 was 58±15 nm thick, as measured with profilometry (Trench Alphastep Co.). A surface resistivity test on substrate 4.3 using a four-point probe method yielded a bulk resistivity of 10.3 $\mu\Omega$-cm for the Cu film. Though this resistivity is higher than that for bulk copper (1.67 $\mu\Omega$-cm--***See*** **Weast, Ed.,** <u>**Handbook of Chemistry and Physics**</u>**, 65th ed., (CRC Press, Boca Raton, FL, 1984), p. F-120**, incorporated herein by reference in its entirety and for all purposes), the value compares well with those reported by other practitioners of copper CVD. ***See*** **Cohen, S. L., Liehr, M., and Kasi, S.,** ***Appl Phys. Lett.*** **60, 1585 (1992)**, incorporated herein by reference in its entirety and for all purposes; ***See*** **Gross, M. E., and Donnelly, V. M., in** <u>**Advanced Metallization for ULSI Applications**</u>**, edited by V. V. S. Rana, R. V. Joshi, and I. Ohdomari, (Materials Research Society, Pittsburgh, 1992), p. 375**, incorporated herein by reference in its entirety and for all purposes. An ASTM-tape peel adhesion test and a 3M Scotch tape adhesion test on this copper film yielded no detectable removal of copper.

## Example 5

### Selective copper CVD on functionalized Si substrates at 447 K

This example demonstrates that the modification and catalysis process for enhancing selective chemical vapor deposition is applicable to Si and $SiO_2$ in addition to diamond substrates, that the UTF-OTS film can reduce copper deposition on Si, and that the enhancement in copper deposition due to the modification techniques described here is dramatic, as evidenced by the composition depth profiles.

Four Si pieces (approximately $2x3x0.1\text{-mm}^3$) that were cleaved from a 2-inch diameter Si-native oxide wafer, and one $SiO_2$ piece, were cleaned with sequential ultrasonic agitation in toluene and methanol, immersed for 30 min in 1:1 $HCl/CH_3OH$, rinsed in filtered, deionized (DI) $H_2O$, immersed for 30 min in $H_2SO_4$, rinsed with DI $H_2O$, and then immersed for 5 min in DI $H_2O$ at 353-363 K. One Si piece (5.1) was removed from the hot DI $H_2O$, dried in a stream of filtered $N_2$, and received no further treatments. Two Si pieces (5.2 and 5.4) and the $SiO_2$ piece were coated with the UTF-EDA organosilane film as described in Example 2. One Si piece (5.4) and the $SiO_2$ piece were then immersed in the Ac3 catalyst solution for 120 min, rinsed in DI water, and dried in a filtered stream of nitrogen. Another Si piece (5.3) was immersed in a 1% (v/v) solution of octadecyltrichlorosilane (Huls America), UTF-OTS, in anhydrous toluene for 7 min at 295 K under a dry argon atmosphere. The UTF-OTS film has a long straight-chain alkyl functionality and is similar to octadecylmercaptan, which can form ultrathin films on Au and Ag surfaces. ***See*** **Ulman, A., <u>An Introduction to Ultrathin Organic Films,</u> (Academic Press, New York, 1991).Moazed, K. L., Zeidler, J. R., and Taylor, M. J., J. Appl. Phys. 68, 2246 (1990),** incorporated herein by reference in its entirety and for all purposes. Octadecylmercaptan films have been used to exclude copper deposition from a gold surface. ***See*** **Schoer, J. K., Ross, C. B., Crooks, R. M., Corbitt, T. S., and Hampden-Smith, M. J.,** *Langmuir* **10**, 615 (1994), incorporated herein by reference in its entirety and for all purposes. Octadecylmercaptan, however, can not be applied directly to Si surfaces. The four Si pieces and the $SiO_2$ piece were then mounted in the copper CVD chamber and copper deposition was performed as described in Example 4 at a substrate temperature of 447 K.

After copper CVD, sample surfaces were analyzed with SEM, and sputter depth profiles were obtained using XPS and $Ar^+$ ion sputtering (Surface Science Laboratories, Inc., SSX-100) for samples 5.1, 5.3, and 5.4. A Cu film was visible with the unassisted eye on Si piece 5.4 and the $SiO_2$ piece, and SEM revealed that these surface consisted of continuous copper films. Copper films were not evident in SEM images of samples 5.1, 5.2, and 5.3. **Figure 2** shows composition depth profiles of samples 5.1, 5.3, and 5.4 in **plots labelled (a), (b) and (c)**, respectively, obtained using alternating cycles of $Ar^+$ ion sputtering and XPS surface analysis. **Figures 2, plot (a)** shows that less than 11 atomic % Cu deposited on the Si native oxide surface, and that most of the Cu was quickly removed from the surface with 50 s of sputtering. Figure 2, plot (b) shows that the

OTS-coated Si piece contained approximately 4 atomic% Cu, and that most of the Cu was quickly removed from the surface with less than 50 s of sputtering. In contrast, the surface of Si sample 5.4 (**Figure 2, plot (c)**) contained a thick Cu film, such that Si was not detected by XPS after copper CVD, Si was still not detected after 35 s of sputtering, and Cu was the dominant element during the first 200 s of sputtering. Since the sputtering rate for Cu was estimated to be between 0.1 and 0.2 nm/s, the Cu film on sample 5.4 was approximately 25-50 nm thick.

## Example 6

### Selective copper CVD on functionalized diamond and Si substrates at 424 K

This example shows that the process of this invention can be successfully applied for selective Cu CVD at temperatures at least as low as 424 K and for times at least as long as 45 min.

A C(100) diamond substrate was cleaned and treated in a $H_2$-plasma as described in Example 1 for 60 min. A second C(100) sample was processed as described in Example 4 for sample 4.3. That is, a diamond sample was oxidized, coated with an EDA film, and treated with the Ac3 catalyst solution for 120 min. Two Si pieces with native oxide surfaces were cleaned as described in Example 5; one of these pieces was then processed using the same techniques as those described in Example 5 for **sample 5.4.**

**This same Si piece** was coated with the EDA film and treated with the Ac3 catalyst solution for 120 min. These four samples were then mounted in the CVD chamber and Cu CVD was performed as described in Example 4, except that the substrate temperature was maintained at 424 K and the deposition was performed for 45 min.

After copper CVD, the samples were removed from the chamber and analyzed with SEM and XPS. Copper-colored coatings were visible to the unassisted eye on the Si and diamond samples that were treated with EDA and Ac3, and SEM images showed uniform granular films on these surfaces. The Cu film thickness was measured to be approximately 60 nm thick by profilometry. XPS showed that the films on these surfaces were primarily composed of Cu. In contrast, copper films were not visible and only isolated particles were detected with SEM on the $H_2$-plasma treated diamond and the clean Si native oxide surface.

## Example 7

### Selective copper CVD on functionalized diamond, Si, and $SiO_2$ substrates at 463 K

This example shows that the process of this invention can be successfully applied in Cu CVD at temperatures at least as high as than 463 K.

Two diamond and two Si pieces were prepared as described in Example 6, except that the diamond and Si samples that were treated with the Ac3 solution were immersed for 180 min. In addition, a $SiO_2$ piece was also coated with EDA and treated with the Ac3 catalyst solution for 180 min. We expect there are no significant differences between surfaces immersed in the Ac3 solution for 120 min and those immersed for 180 min. These five samples were mounted in the CVD chamber and Cu CVD was performed as described in Example 4 at a substrate temperature of 463 K for 12 min.

After copper CVD, the samples were removed from the chamber and analyzed with XPS and SEM. As in example 6, SEM showed distinct granular films on the C(100), Si and $SiO_2$ surfaces that were treated with EDA and Ac3 prior to Cu CVD. Composition depth profiles acquired using the method described in Example 5 showed that most of the Cu present on the hydrogenated C(100) and Si native oxide surfaces was sputtered from the surface in less than 30 s. In contrast, copper was the dominant component detected by XPS during the first 100 sec of sputtering on each of the three surface treated with EDA and Ac3. Thus, treatment of C(100), Si, and $SiO_2$ with EDA and the Ac3 catalyst promoted Cu deposition.

## Example 8

### Patterned CVD metallization of a UTF-PEDA functionalized diamond surface

This example demonstrates that lithographic techniques can be used to define areas of selectively-enhanced copper deposition during copper CVD and generate micron-sized copper features on an insulating substrate.

A diamond substrate was treated with UTF-PEDA as described in Example 3. The diamond substrate was placed in mechanical contact with a chrome-on-quartz lithographic mask that had arrays of line-and-space test structures with features to 1-$\mu$m linewidth.

The film was then exposed through the mask to 1.1 J/cm$^2$ of 193-nm radiation from a ArF (Cymer Model CX2) excimer laser. The exposed film was treated with Ac3 catalyst for 110 min, rinsed with DI water and dried in a stream of filtered nitrogen. The diamond substrate was then mounted in the copper CVD chamber and copper deposition was performed as described in Example 4. Optical micrographs and SEM images showed copper lines deposited with minimum feature sizes of 1 $\mu$m (the smallest features on the mask) in a positive-tone image.

## Example 9

### Selective copper CVD on functionalized diamond using alternate Pd-containing catalyst

This example shows that alternate Pd-containing catalyst formulations are active for enhancing copper CVD in the process of this invention.

Three C(100) diamond substrates were cleaned and treated in a $H_2$-plasma for 20 min as described in Example 1. One of these samples (sample 8.1) received no further treatment prior to Cu CVD. Two C(100) samples were oxidized and coated with an EDA film, as described in Example 2. One of these samples (sample 8.2) was treated with the Ac3 catalyst solution for 120 min as described in Example 4 for sample 4.3. One of these samples (sample 8.3) was treated with a catalyst solution designated AcJ2 for 4 min, after which the sample was rinsed two times with DI $H_2O$ and dried in a stream of filtered $N_2$. The AcJ2 catalyst solution was made in three stages. First a stock solution was made by diluting 0.90 gm $Na_2PdCl_4$ with enough 0.03 wt% aqueous HCl folution to generate 100 gm of solution. Then, a working solution was made by mixing 9.89 gm of the stock solution with 23.24 gm DI $H_2O$ and 64.44 gm 0.005 wt% aqueous NaOH. This working solution was allowed to ripen for 2 hours and then 2.43 gm 0.3 wt% aqueous HCl was added to stabilize the working solution. The final AcJ2 catalyst solution was formed by mixing 3 parts of the working solution with 1 part 1.0 M aqueous NaCl, and filtering this mixture through a 0.2 micron PTFE filter (Gelman acrodisc CR).

The three diamond substrates were then mounted in the copper CVD chamber and copper deposition was performed for 24 min at 444 K as described in Example 4. SEM images of samples 8.1, 8.2, and 8.3 revealed that continuous granular Cu films deposited on both of the Pd catalyst treated samples (8.2 and 8.3), but that only isolated Cu particles deposited on sample 8.1. The Cu films the formed on samples 8.2 and 8.3 appeared to be essentially identical in the SEM images.

## Example 10

### Selective W CVD on functionalized diamond using a Pd-containing catalyst

This prophetic example displays how a dielectric surface modified with a Pd-containing catalyst is used in the process of this invention to selectivly promote W CVD.

Clean three C(100) diamond substrates and treat them in a $H_2$-plasma for 20 min as described in Example 1. Provide no additonal treatment to one of these samples (sample 10.1) prior to W CVD. Oxidize one C(100) sample (sample 10.2) and coat it with an EDA film, as described in Example 2. Treat one sample (sample 10.3) with UTF-PEDA, as described in Example 3. PAttern the UTF-PEDA film on sample 10.3, as described in Example 8. Treat samples 10.2 and 10.3 with the Ac3 catalyst, as described in example 4, or with the AcJ2 catalyst, as described in example 9, and then rinse these samples with DI water and dry them in a stream of filtered nitrogen.

Mount the three diamond substrates in a CVD chamber as described in Example 4. If necessary, modify the pumping capabilites of the CVD chamber to allow gas flowrates on the order of 100 sccm and chamber pressures on the order of 100 mTorr prior to mounting the samples. Attach a bulb containing high-purity liquid $WF_6$ to the chamber to allow metering of the vapor above the $WF_6$ liquid into the chamber via gas introduction lines and a sample doser, as described in Example 4. If necessary, cool the $WF_6$ bulb to reduce the vapor pressure above the liquid to allow easier conrol of the $WF_6$ flowrate into the chamber. If necessary, attach mass-flow controllers to the $H_2$ and $WF_6$ gas supply lines, and/or a variable-position valve on the exit of the reactor to allow control of the gas inlet flowrates and the total pressure in the chamber.

Prior to heating the sample, flow high-purity $H_2$ at approximately 50 sccm throught the doser and into the chamber, as described in example 4. Stabliize the chamber pressure at approximately 10 mTorr. Heat the sample to approximately 600 K in flowing hydrogen in approximately 20 min. The Pd-containing catalysts described will become substantially reduced to Pd metal by after exposure to $H_2$ at 50 sccm, 10 mTorr, at 600 K, and the reduced Pd will act as a catalyst to effect facile reduction of $WF_6$ to W on the Pd-catalysed film-coated diamond surfaces of samples 10.2 and 10.3. To begin W deposition, meter $WF_6$ vapor into the $H_2$ stream at approximately 5 sccm. Maintain the sample temperature at about 600 K for about 10 minutes in the flowing $H_2/WF_6$ gas mixture. Then, stop the $WF_6$ flow. Cool the sample in flowing $H_2$ as described in Example 4, and when the sample is cool, remove it from the chamber.

It is expected that sample 10.1 is not active for W deposition from $WF_6$ under the conditions outlined above, and this surface is expected to have only isolated particles or islands of W on the surface. In contrast, sample 10.2 is expected to contain a significant amount of W. Sample 10.3 is expected to possess lines of W, similar to the lines of Cu described in example 8.

## Example 11

### Enhanced diamond CVD on a film-coated silicon substrate

This prophetic example describes how the process of this invention can be used to effect enhanced CVD of diamond.

Clean two Si-native oxide wafer pieces with toluene, methanol, HCl/methanol, sulfuric acid, and DI water as described in example 5. Coat one of these Si pieces with UTF-adamantyl by immersing the Si piece in a 1% (v/v) solution of adamantylethyltrichlorosilane (Huls America) in toluene with 0.001 M acetic acid at room temperature under an inert He or Ar atmosphere for 20 min. The adamantyl functionality of the UTF-adamantyl provides a diamond CVD nucleation site with similar structure to the diamond lattice. Perform diamond CVD on both the UTF-adamantyl-coated and the uncoated Si pieces by placing each into a standard filament-assisted diamond CVD reactor. Perform diamond CVD using 1% $CH_4$ in $H_2$ at total pressure of approximately 10 Torr and substrate temperature of approximately 900 K for approximately 60 min. After diamond CVD, the sample treated with UTF-adamantylsilane is expected to display enhanced diamond nucleation relative to the uncoated Si piece.

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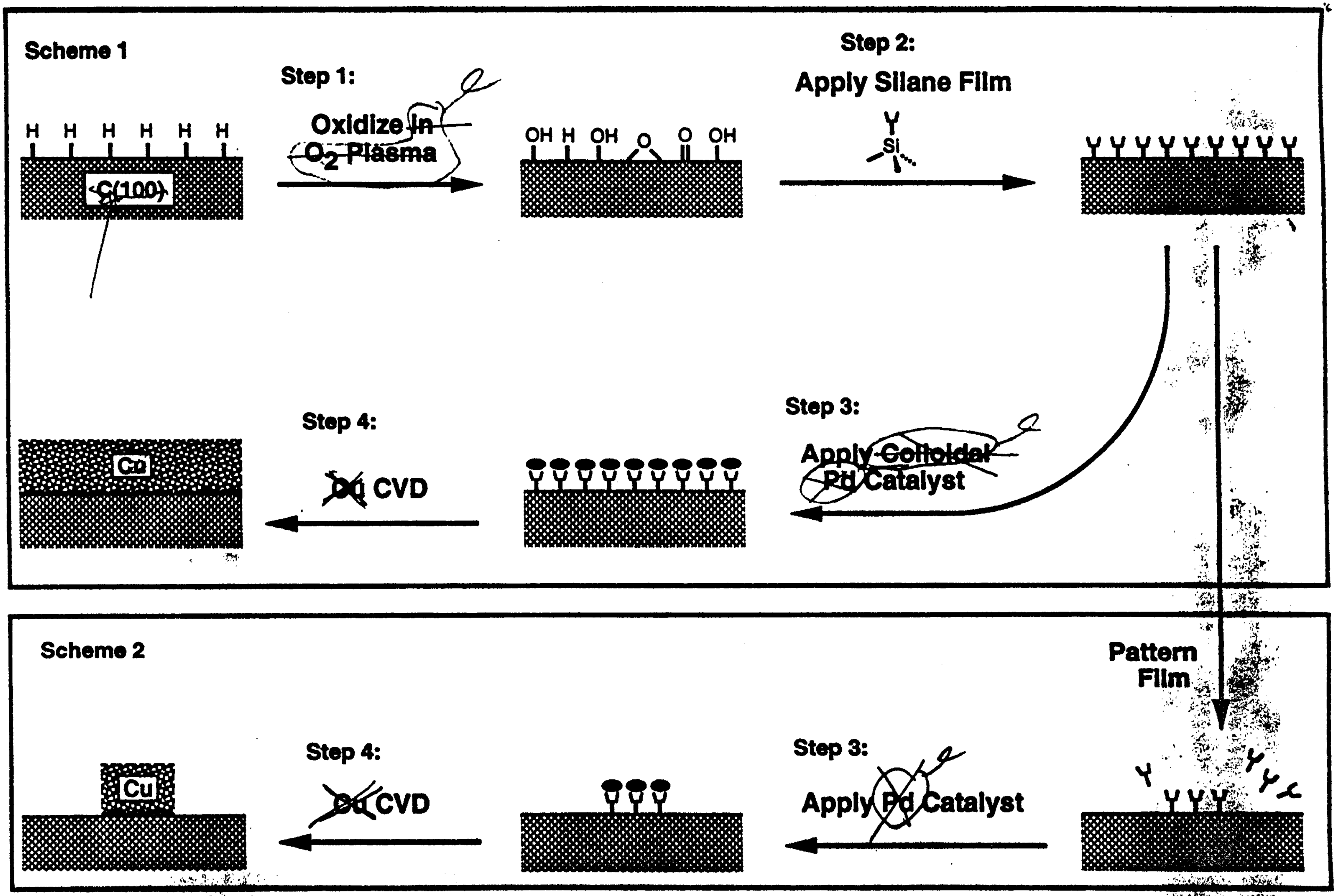
# ABSTRACT

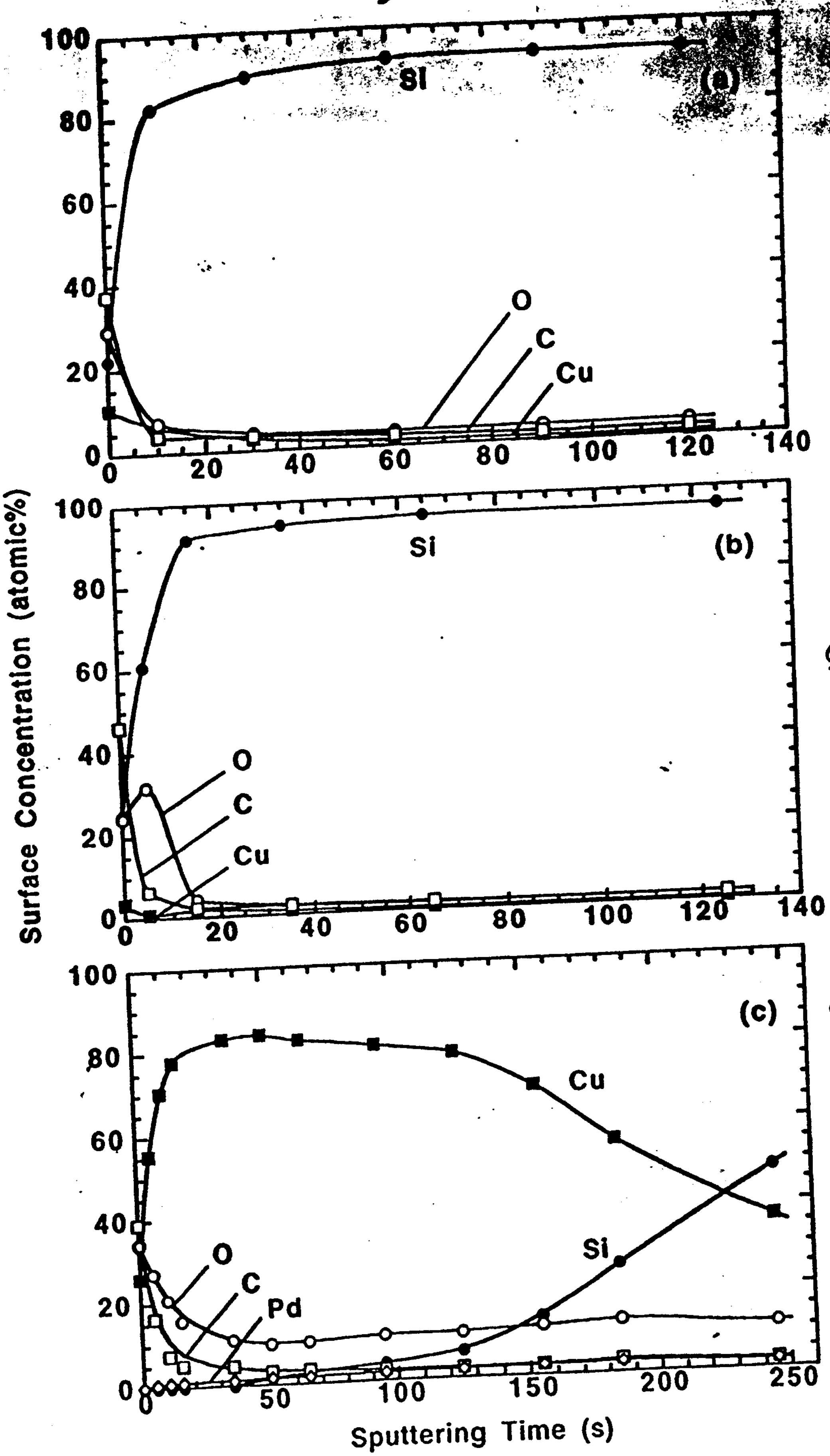
The present invention is directed to the selective and non-selective vapor deposition of materials upon substrates. Vapor deposition is accomplished by providing a substrate having one or more chemical groups on its surface, the chemical groups being capable of bonding to a deposition catalyst, contacting a deposition catalyst to the chemical groups of the substrate and vapor depositing a material upon the catalyst via vapor deposition. The vapor deposition may also be selective vapor deposition.

# Figure 1


Scheme 1
Step 1:
Oxidize ~~in O₂ Plasma~~
Step 2:
Apply Silane Film
Si
H H H H H H
~~C(100)~~
OH H OH O O OH
Step 3:
Apply ~~Colloidal Pd~~ Catalyst
Step 4:
~~Cu~~ CVD
Cu
Scheme 2
Pattern Film
Step 3:
Apply ~~Pd~~ Catalyst
Step 4:
~~Cu~~ CVD
Cu

Example 5.

Figure 2



~~SiO2-EDA~~

Si-

(NATIVE OXIDE)

Si-OTS

5.3

Si-EDA/Pd

5.4

Cu