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Why is coordination chemistry stretching the limits of micro-electronics technology?

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Abstract

As a result of its low resistivity and ability to reliably carry high-current densities, copper is a reasonable alternative to more commonly used contact materials, such as tungsten and aluminum in integrated circuits (ICs). Copper films can be deposited by different techniques: sputtering, electroless or electrolytic plating and CVD (chemical vapor deposition). We report here that CVD is the only conformal film growth method, and surface chemistry controls conformality which is critical for the next generation of integrated circuits (ICs) with interconnect dimensions of 0.18 μm. In the case of Cu CVD, the precursors used are volatile coordination compounds. In this paper, we develop mainly our own contribution to the study of volatile β-diketonate copper complexes that have been designed and synthesized to be used as precursors for Cu CVD. These complexes are volatile liquids under ambient conditions and decompose at temperatures between 130 and 240 °C to a clean copper film and volatile stable species through a disproportionation reaction. Besides the Cupra-select [(VTMS)Cu(hfac) from Schumacher where VTMS is vinyltrimethylsilane and hfac is hexafluoroacethylacetonate], which is by far the most widely used precursor for the deposition of blanket and selectively deposited copper films, several compounds such as (MHY)Cu(hfac) (where MHY is 2-methyl-1-hexen-3-yne) appear well suited for Cu CVD. We give here our latest results on the performances of these new stable precursors.

For interconnection dimension less than 0.1 μm, selective metallization by Cu CVD is an alternative to the Damascene process which is the envisaged process for the metallization of ICs by Cu CVD. In contrast to the Damascene process, selective metallization by CVD is a very simple process that can be performed on flat surfaces. The problem is to obtain on a surface growing and non-growing areas for Cu CVD. We report in this paper our results obtained on new processes using CVD precursors and self-assembled molecules (SAMs). We achieved selective metallization of surfaces using (VTMS)Cu(hfac) or (MHY)Cu(hfac) in a completely dry two-step process. Silica surfaces, Si_3N_4 and TiN were derivatized with mono- or trifunctional silanes by gas phase silylation. UV-exposure of the halogen terminated molecules employing a mask resulted in a controlled pattern of the surface affinity towards the copper complex and hence selective Cu CVD was achieved. Such ultrathin monolayers are potentially useful for very high resolution resists because the lateral resolution which is accessible, is on the order of molecular dimensions. Metallization of substrates at a nanometric scale using Cu CVD and hence copper coordination complexes is discussed.

Keywords: Volatile copper complexes; Copper CVD; Copper films; Metallization; SAMs; Surface derivatization; Selective copper deposition

1. Introduction

The microelectronics industry does not seem to admit physical limits. On one side, the size of the monocrystalline silicon wafers which are the universally used substrates, is increasing: 200, 300, 400 mm etc. On the other side, the critical feature sizes of the basic transistor and of the metallic interconnection (plugs and lines) are rapidly decreasing. Moreover, integrated circuit (IC) devices performance is continually increasing. One of the most significant challenges in IC manufacturing is the filling of very small openings that connect the interconnect "wiring" with the source, drain and gate of the CMOS transistor, and those that connect one level of wiring with the underlying or overlying level. The challenge is simply that these openings—commonly called "contacts" and "vias", respectively—are getting narrower and deeper, and harder to fill with metal. The narrowness of contacts and vias is mainly a result of transistor scaling and the need for high interconnect packing density. The reason for the continued increase in aspect ratios (height:width) is that height cannot be decreased along with width because the dielectric that separates the metal lines cannot be made much thinner without an unacceptable increase in capacitance.

It was recently demonstrated that the resistivity of the metal interconnects may limit device performance in these multi-level thin-film structures [1]. For the current generation of devices, the nearly universal choice for interconnects is Al-based metallurgy with tungsten plugs embedded in an oxide/nitride dielectric. More specifically for interconnects and via applications, Al-alloy reflow and chemically vapor deposited (CVD) tungsten, respectively, with various liners (Ti–W or Ti–TiN) are the standards of the industry (Fig. 1).

Cu holds promise as an alternative metallization material to Al alloy due to its low resistivity and ability to reliably carry high-current densities. Cu has a bulk resistivity of 1.68 μΩ cm, whereas Al has a bulk resistivity of 2.65 μΩ cm. The only metal with a resistivity lower than Cu is Ag (1.59 μm cm). Moreover, since Cu has a melting point and atomic weight both higher than Al, it is expected to have better resistance to electromigration and has been found that Cu exhibits a roughly 10 × improvement in electromigration characteristics . relative to Al alloys [2]. Nevertheless, some important problems concerning Cu metallization exist: a diffusion barrier between Si/SiO_2 and Cu is needed because Cu diffuses rapidly into Si and can form centers with deep energy levels in the Si bandgap (one possible diffusion barrier film is TiN [3]). Consequently, Cu will induce generation recombination leakage currents in p–n junctions and jeopardizes the performance of bipolar and MOS transistors. These problems have been overcome since recently IBM announced the production of a 0.25 μm generation microprocessors plated with copper.

One of the main issues is what is the best way to deposit copper: CVD, sputtering, electroless plating or electrolytic plating [4]. All have advantages and disadvantages, but most research now appears to be focused on CVD using Cu(I) complexes because CVD is a unique conformal deposition technique as we will discuss in this paper (see Section 1.1).

For CVD, the main problem is the chemical precursor: a CVD process will be developed if an appropriate source exists. A new field of investigation is wide open for synthetic chemists to design and to propose new CVD precursors with improved physical and chemical properties to be synthesized. We will give in the paper how to meet the requirements to obtain and synthesize new precursors for CVD (see

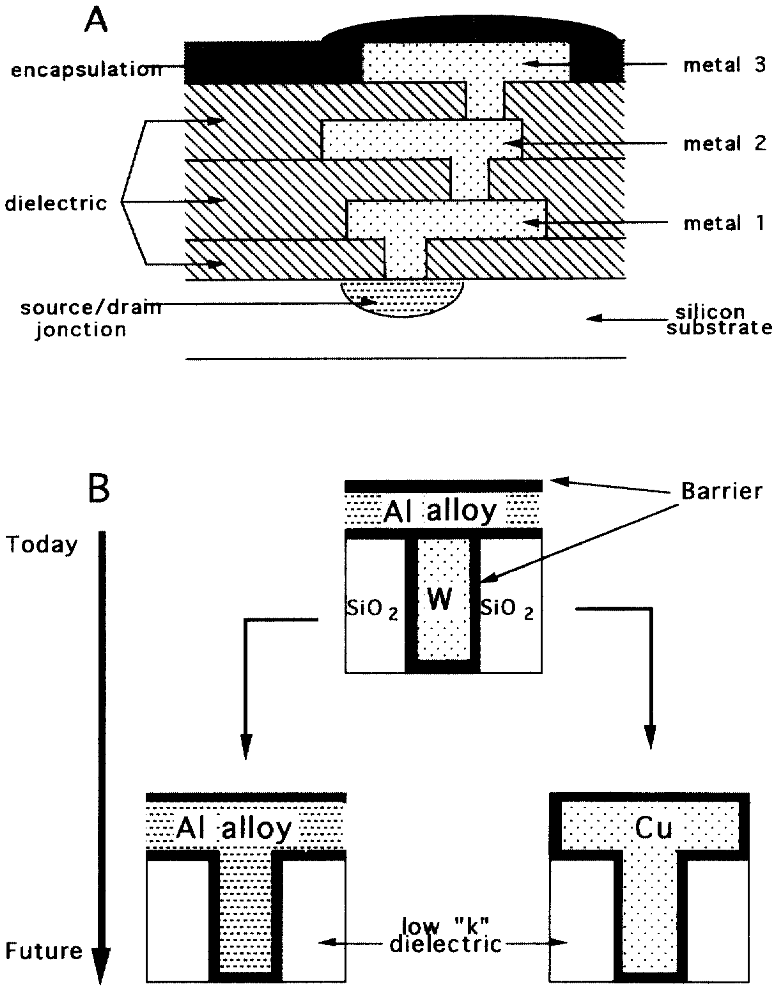


Fig. 1. (a) Schematic drawing of a multilevel metallization structure; (b) architectural trends for the metallization of ICs.

Section 2). In the case of Cu CVD, we will demonstrate that a number of Cu CVD precursors exist; among them, some have been studied or conceived by the author. The existence of these precursors which are coordination compounds push the CVD technology to be effectively used for ICs metallization (see Section 3) [5].

Furthermore, filling holes and trenches via Cu CVD also has physical limits (it is difficult to conformally fill holes under 0.1 μm even by CVD), which is not the case for selective Cu CVD deposition which can be performed on flat surfaces. In Section 4, we will report mainly our results obtained on new selective deposition processes using copper CVD precursors and self-assembled molecules (SAMs) [6].

1.1. CVD versus PVD: an irreversible technology shift [7]

Metallic film deposition can be realized by physical vapor deposition (PVD) processes that employ evaporation and sputtering of elemental sources. Since the 1960s, CVD using molecular precursors has been increasingly studied for deposition on integrated circuits. While PVD works well for depositing material on surfaces in line-of-sight of the source, conformal deposition of rough surfaces is a crucial issue. This issue becomes very critical for integrated circuits with feature sizes less than 0.5 μm because trenches with rather high aspect ratio (height:width) must be coated uniformly (conformally) and/or filled [8].

Compared with PVD, CVD processes are more complex because, by their very nature, chemical reaction mechanisms are involved. For CVD, often large and complex metal precursor is delivered onto an activated substrate, and then the precursor decomposes to give a solid film of metal, metal oxide or metal nitride on the surface in the presence or not of reactive gases. The surface can be activated in a variety of ways including by heat, plasma or a light source.

Often inert gases such as nitrogen, argon or helium are used as carrier gases in CVD reactors to facilitate the movement of the gaseous precursor toward the reaction chamber. In certain circumstances, gases such as hydrogen, oxygen and ammonia are used as a reactive material for oxidation or reduction reactions. CVD thin layer growth is considered to arise through several clear steps as illustrated below (Fig. 2). The precursor being in a bubbler is transported in the vapor phase with an inert gas or directly injected [9] into the reactor chamber to the substrate, at which stage it must overcome the boundary layer present at the surface in order to have sufficient proximity to be adsorbed. Once the precursor has been adsorbed, there are three possibilities as to what can happen next. The precursor can diffuse on the surface or immediately be desorbed from the surface or, alternatively, surface reactions take place and a film is formed along with various side products. These side products are desorbed and pass to the other side of the boundary layer from where they are removed from the apparatus and trapped. To get high growth rate and conformal covering (see the following paragraph), the different parameters must be tuned to obtain a process controlled by the mass transport of the precursor vapor in the reactor [10]. These parameters include source temperature, substrate temperature, pressure, flux...

Deposition of a thin film which uniformly coats all exposed parts of a three-dimensional structure is known as conformal film growth. The trench cut given in Fig. 3 is representative of the features found in a substrate that is conformally (part B) or non-conformally filled (part A). Without conformal growth, some important steps in current microelectronics fabrication would be impossible. Conformality is a common requirement for dielectric films. It is also useful in filling cylindrical holes with metal contact material. CVD is the only conformal film growth method, and surface chemistry controls confomality [7].

The main parameter for conformal growth is the reactive sticking probability, S_R. It is the fraction of incident flux of molecules (atoms) that stick on a specified surface. The maximum value of S_R is one and is achieved when every collision results in deposition: the non-uniform film thickness profile in Fig. 3(A) is obtained using

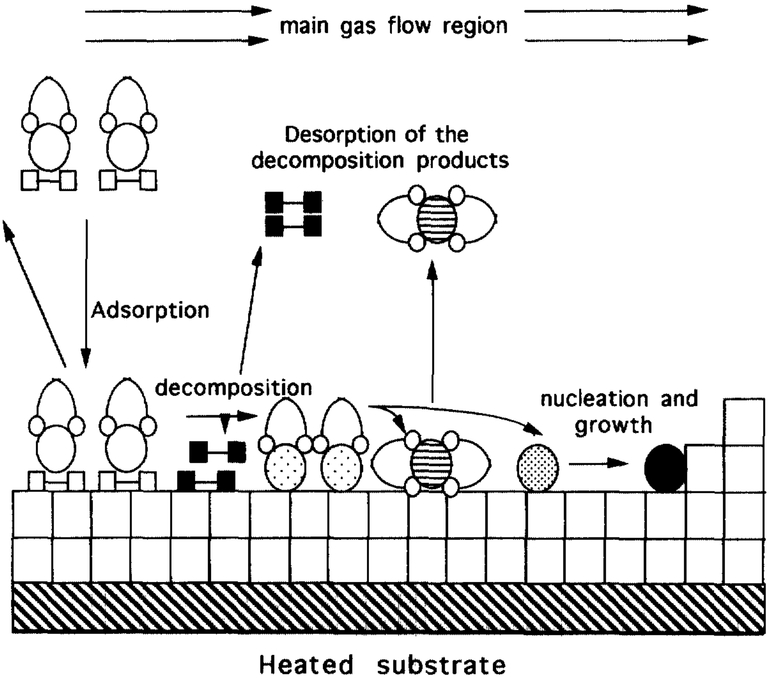


Fig. 2. Chemical pathway of the precursor on the substrate surface during CVD.

line-of-sight delivery of highly reactive precursors (atoms or radicals) with $S_R \sim 1$. This case is found in PVD; it is typical of film growth by evaporation or by sputtering, and can be produced in plasma-enhanced CVD (PECVD) under certain conditions. In that case, the growth species stick preferentially near the top of the side walls and on the bottom surface, depleting the flux incident on the side walls near the bottom. This result is confirmed by calculated film profiles: a unity S_R gave a result similar to Fig. 3(A), while $S_R = 0.05$ gave a profile similar to Fig. 3(B) (conformal) [11].

The shaded film in Fig. 3(B) illustrates "perfect step coverage", with equal film thickness on all exposed surfaces [12, 13]. As the figure implies, different mechanisms can yield such a conformal film: weakly adsorbed precursor (physisorbed) surface state, surface diffusion in this state, and finally chemisorption. "Surface diffusion" is most important for small feature size (< 1 μm) and is labeled as a fat arrow in Fig. 3(B). During diffusion, desorption of the adsorbed precursor competes with chemisorption. Multiple reflections before reactive sticking [left side of Fig. 3(B)] will tend to eliminate the flux gradient in the trench, also resulting in a conformal film.

New deposition techniques have been proposed [14–16], including collimated sputtering (in the case of TiN and Ti films) or reflow sputtering (in the case of aluminum) to improve the conformality of the films, but it is difficult to believe that such technique could be used for via under 0.18 μm and high aspect ratio holes (height:width > 3) filling.

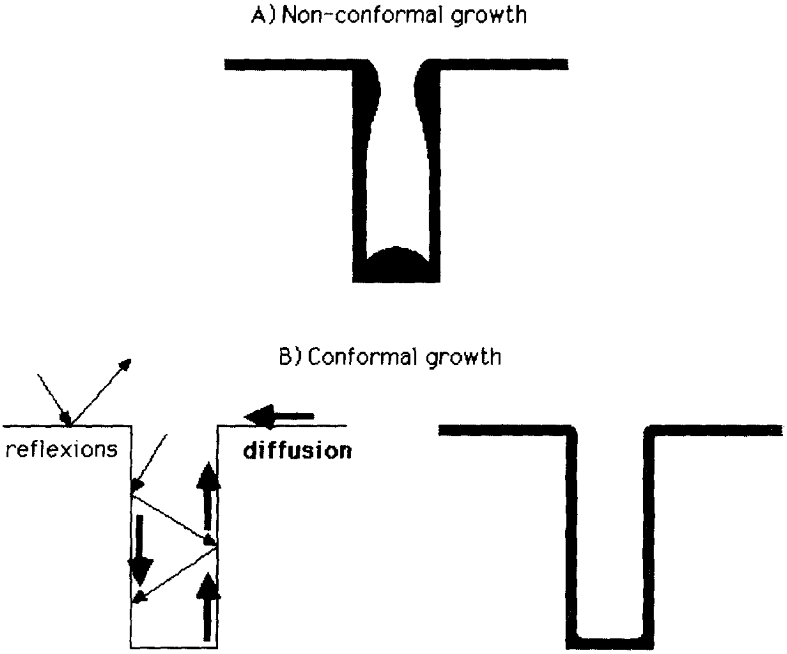


Fig. 3. Schematic cross-sections showing the thickness profile for a thin film deposited over a three-dimensional trench structure: deposition with a very reactive species, resulting in a non-uniform film thickness (non-conformal covering) over the sidewalls and bottom of the trench found for PVD or PECVD (B) A typical CVD film showing conformal covering.

But even CVD can give poor conformality and the probability that a CVD precursor molecule reacts directly at the first point of contact with the growth surface is a factor influencing surface roughness (smoothness) and conformal coating of three-dimensional structures. If the precursor is very reactive, it dissociates (chemisorbs) at the point of impact, giving a high S_R value approaching unity. The value of S_R must then be controlled through precursor design. For example, at a given temperature, precursors with lower decomposition temperatures will have higher values of S_R.

Therefore, conformality can be improved by using precursors that are more thermally inert, but at the expense of lowering the deposition rate.

2. Molecular requirements for CVD precursors: the example of copper precursors

2.1. *Chemical precursors for CVD*

In order to be appropriate for the use within the CVD reactor, the chemical precursors must fulfill certain requirements defined by the operating conditions for the thin layer growth.

2.1.1. Volatility

As its name suggests, CVD thin layer growth requires a precursor that can be easily manipulated, i.e. a solid or a liquid, yet that is sufficiently volatile to vaporize at relatively low temperatures (below 200 °C).

2.1.2. Reactivity

A precursor is also required that will react at the substrate surface to give the desired thin film. Substrate surfaces are generally heated to a temperature of the order of several hundred °C. The precursor should be reactive at these temperatures.

However, one potential problem with CVD thin layer growth, is that the precursor could react in the vapor phase throughout the reactor, as opposed to reacting only on the substrate surface. This should be minimized due to the resulting diminished concentration of the chemical precursor in the reaction chamber and hence the diminished growth rate. Moreover, reactions in the gas phase generate particles that can pollute the film.

A precursor is sought which will react on the substrate surface, yet being not so reactive as to react in the vapor phase throughout the CVD machine. That is an important parameter since liquid injection systems that are more and more used for CVD, contain heated parts where the precursor may decompose leading eventually to a blockage of the flow. For the use of such system, the precursor must withstand elevated temperatures during short periods without decomposition.

2.1.3. Synthesis

In order to be valuable for the use in CVD thin layer growth, any precursor must be able to be synthesized in quantities of at least several grams, with as few synthetic steps as possible. The synthesis must be adaptable to larger scale production without major problems.

2.1.4. Purity

It is often demanded that the resulting thin films be extremely clean and free of contaminants. Obviously, in order to yield such results, all impurities must be strictly avoided within the CVD reactor and precursors must also be highly pure (electronic grade purity).

2.1.5. Environment and cost

As environmental issues grow increasingly important nowadays, it is advisable that new precursors be as non-toxic as possible and preferably recyclable. Because different deposition technique are available, the price of the CVD precursor must be as low as possible to offer a challenging cost-of-ownership.

2.2. Chemical vapor deposition and inorganic synthesis

Due to the strict property requirements for CVD precursors, one of the many challenges facing modern inorganic chemists is the synthesis of suitable complexes for CVD thin layer growth. These challenges lie in the continual moderation of previously made molecules to achieve a substance more and more ideal for the use as a CVD precursor. Frequently the property which requires the most attention is the volatility of the precursor, which can be affected in a variety of ways. When using liquid injectors, this parameter is less important but still, to ensure a high growth rate, the precursor must be very volatile.

2.3. Methods of controlling the volatility of a given molecule

2.3.1. Charge and polarity

Ionic molecules tend to be involatile because they must overcome their strong intermolecular electrostatic forces in order to vaporize. A similar principle is applied to dipolar molecules, which tend to be less volatile due to the presence of electrostatic forces. Therefore, when considering CVD precursor, a molecule is sought which is covalently bonded, and is not dipolar. This may dictate that the molecule be totally symmetric.

2.3.2. Molecular size

In general, the larger an atom or molecule is, the more polarizable and hence the less volatile it is. It would seem logical, therefore, that the smaller the ligands surrounding a metal center, the greater that complex's volatility will be. It is somewhat surprising therefore, that one common method for increasing a molecule's volatility is by the introduction of bulky groups. This can be explained by the fact that the larger groups minimize intermolecular interaction by steric hindrance. It is in this way that the incorporation of bulky groups into a molecule can increase its volatility. A compromise must be found between effectively isolating the metal center and avoiding ligands that are too large and, therefore, give rise to a more polarisable molecule.

2.3.3. CF_3 groups

The introduction of a CF_3 group into a given molecule can appreciably increase its volatility [17]. In general, the presence of these groups in a precursor will also have little or no adverse effect on the CVD results, unless the substrate temperature is so high that the C–F bonds are broken, at which point fluorine atoms may become a major contaminant of the thin films.

The effect of CF_3 groups on a molecule's volatility can be explained by the various properties of this chemical group. C–F bonds are very stable and extremely polar and the CF_3 group is not particularly bulky. This high bond polarity means that CF_3 groups often behave as self-repellent electron rich balls. It is important to differentiate between the positive effect of the CF_3 group's polarity and the undesirable effect of dipolarity within a molecule. The CF_3 group is an electronegative entity, "pulling" negative charge towards itself. The rest of the molecule is left with a slightly positive charge which is spread out among the entire molecule and extremely small in relation to the concentrated negative charge on the CF_3 group. Hence, the molecule contains a polar group, but no dipole and hence has an increased volatility.

3. CVD of copper films

3.1. The example of β-diketonate copper(I) complexes: precursor chemistry and molecular structure

Earlier research [18,19] has clearly demonstrated the potential of Lewis-base (L) stabilized copper(I) β-diketonate complexes as copper CVD precursors. The reactive copper(I) β-diketonate moiety may be ligated with phosphines or unsaturated organics, such as alkenes, dienes and alkynes, to obtain an assortment of precursors with different physicochemical properties. The deposition of pure copper films from the Cu(I) precursors results from a thermally induced disproportionation reaction, shown in Eq. (1):

$$2(\beta-\text{diketonate})\text{Cu}^{(I)}\text{L}\Rightarrow\text{Cu}^{(O)}+\text{Cu}^{(II)}(\beta-\text{diketonate})_2+2\text{L}. \qquad (1)$$

Although the mechanism of the heterogeneous decomposition is still under investigation [20], the proposed mechanism consists of the following steps [21–27]:

$$2\text{LCu}^{(I)}(\beta-\text{diketonate})(\text{g})\rightarrow 2\text{LCu}^{(I)}(\beta-\text{diketonate})(\text{s}). \qquad (2)$$

$$2\text{LCu}^{(I)}(\beta-\text{diketonate})(\text{s})\rightarrow 2\text{Cu}^{(I)}(\beta-\text{diketonate})(\text{s})+2\text{L}(\text{g}). \qquad (3)$$

$$2\text{Cu}^{(I)}(\beta-\text{diketonate})(\text{s})\rightarrow\text{Cu}^{(0)}(\text{S})+\text{CU}^{(II)}(\beta-\text{diketonate})_2(\text{g}). \qquad (4)$$

where (g) indicates gas phase and (s) is an absorbed species. Since the Lewis base ligand is weakly bound in the complex, the thermal decomposition of these complexes occurs at low temperatures (150 to 250 °C) and results in the formation of near-bulk copper films (see Fig. 2). Film resistivities down to 1.85 $\mu\Omega$ cm (as opposed to 1.7 $\mu\Omega$ cm for bulk copper) for a 99.99% copper content have been reported [9].

In general, CVD copper processes have utilized vinyltrimethylsilane (VTMS) Cu(hfac) [21] (where hfac is hexafluoroacethylacetonate), which is a commercial, thermally labile material. In our continuing search [18] for novel CVD copper precursors, we synthesized a series of alkene, diene or alkyne stabilized complexes, as well as several new mixed metal precursors for depositing copper alloys [28,29]. Other groups have reported compounds of the same family [30–33].

In this family of complexes, the physical properties are easily varied by chemical substitution and structural modifications. CF_3 groups which are strong electronic withdrawing groups, decrease the electronic density on the electron rich d^{10} Cu(I) and strengthen the Cu–L bond: in the series (COD)Cu(β-diketonate) (where COD is 1,5-cyclooctadiene), the stability of the complex (and by consequence the Cu–L bond) increases with the number of CF_3 present in the structure. The second effect of the introduction of CF_3 group in an organometallic compound is to increase the volatility as demonstrated for copper(II)(β-diketonate)$_2$ [17]. When a single CF_3 group is present, the volatility may be limited, because of the presence of a dipole moment. Such effects may be provoked by change in the structure of the Lewis base as well: 3-hexyne is a symmetrical molecule and the corresponding precursor, (3-hexyne)Cu(hfac) is a liquid at room temperature (m.p. −10 °C), whereas

2-hexyne is asymmetrical and (2hexyne)Cu(hfac) has a melting point of 35 °C and a decreased partial pressure [34].

Subtle chemical changes may have dramatic effects upon these physical properties. Changing the Lewis base in the copper(I) complex can directly alter the physical state (liquid or solid), the partial pressure, the decomposition temperature and the long-term stability of the copper precursor. (COD)Cu(hfac) has been described for the deposition of copper films [35]. This CVD source is an air stable solid with a moderate vapor pressure. Substitution of two methyl groups, namely dimethyl-1,5-cyclooctadiene (DMCOD)Cu(hfac), affords a moderately volatile liquid source for Cu CVD. Both the 1,5-dimethyl (80%) and 1,6-dimethyl (20%) isomers are present in commercially available DMCOD. Recently, we have successfully isolated the (1,5-DMCOD)Cu(hfac) complex by isomeric separation with a Ag(I)hfac complex; its liquid physical state is a result of methyl groups substitution and not a result of isomeric impurities [36]. In the X-ray structure of the Ag(I)(hfac) compound, the four methyl groups of the two 1,5-DMCOD ligands are oriented toward the center of the molecule. The carbon atoms are located only 3.2–3.6 Å away from the two silver atoms, thereby forming a methylated, hydrophobic cage around the silver centers. This structural information can be extended to (1,5-DMCOD)Cu(hfac). Since the latter complex is a liquid below −25 °C, no X-ray crystallographic data are available. Assuming an identical conformation of the 1,5-DMCOD ligand in (1,5-DMCOD)Cu(hfac), the hydrophobic cage may be the origin of the enhanced volatility observed in (1,5-DMCOD)Cu(hfac) by elimination of the intermolecular interactions detected in (COD)Cu(hfac) [37].

During recent CVD experiments using (η^2-alkyne)Cu(hfac) precursors, a less volatile compound was formed in the bubbler along with copper metal. When the alkyne was 3-hexyne, the liquid precursor [38] was transformed into a yellow solid residue with time. The FTIR spectrum of this solid displayed a well-defined band at 1722 cm^{-1} that was absent in the IR spectrum of the starting compound. Isolation of the new compound was attempted, but rapid decomposition occurred in solution even at low temperatures. This unstable compound was thought to be a dinuclear complex, in which the alkynes bridge two copper(I) centers in a "butterfly" geometry. To positively prove this hypothesis, bis(trimethylsilyl)acetylene (BTMSA), an alkyne ligand bearing strong donating groups on the alkyne bond ($C{\equiv}C$) was used to synthesize a dinuclear copper(I) β-diketonate. Using BTMSA, we successfully isolated a dinuclear analogue by direct synthesis. For a 4:1 Cu to alkyne ratio, a mixture of the mononuclear and of the dinuclear species was obtained, their separation was realized by a difference in volatility. The potential of using a volatile, dinuclear copper precursor for CVD was of interest towards facilitating the disproportionation of two copper(I) centers on a heated surface and depositing a very non-selective copper film. However, attempts to utilize this approach have met with limited success as a result of the decreased volatility and the decreased thermal stability of the dinuclear complex. Indeed, the solid dinuclear complex is stable, at −25 °C for weeks but in solution, it is stable only for several hours at −25 °C, but rapidly decomposes at room temperature. Decomposition leads to the mononuclear complex, metallic copper and Cu(II)$(hfac)_2$ (Eq. (1)), as expected for a copper(I) disproportionation reaction:

$$2((\text{hfac})\text{Cu}^{(\text{I})})_2(\mu-\eta^2-\text{BTMSA})\rightarrow\text{Cu}^{(0)}+\text{Cu}^{(\text{II})}(\text{hfac})_2$$
$$+2(\eta^2-\text{BTMSA})\text{Cu}^{(\text{I})}(\text{hfac}). \qquad (5)$$

An attractive way to avoid dimer formation while keeping the precursor potential, is to deactivate the C≡C bond with electron withdrawing groups such as a conjugated double bond, -OCH_3 or CF_3 groups (P. Doppelt et al., unpublished results) [39,40]. The different tested alkynes are given in Fig. 4. The complexes have been

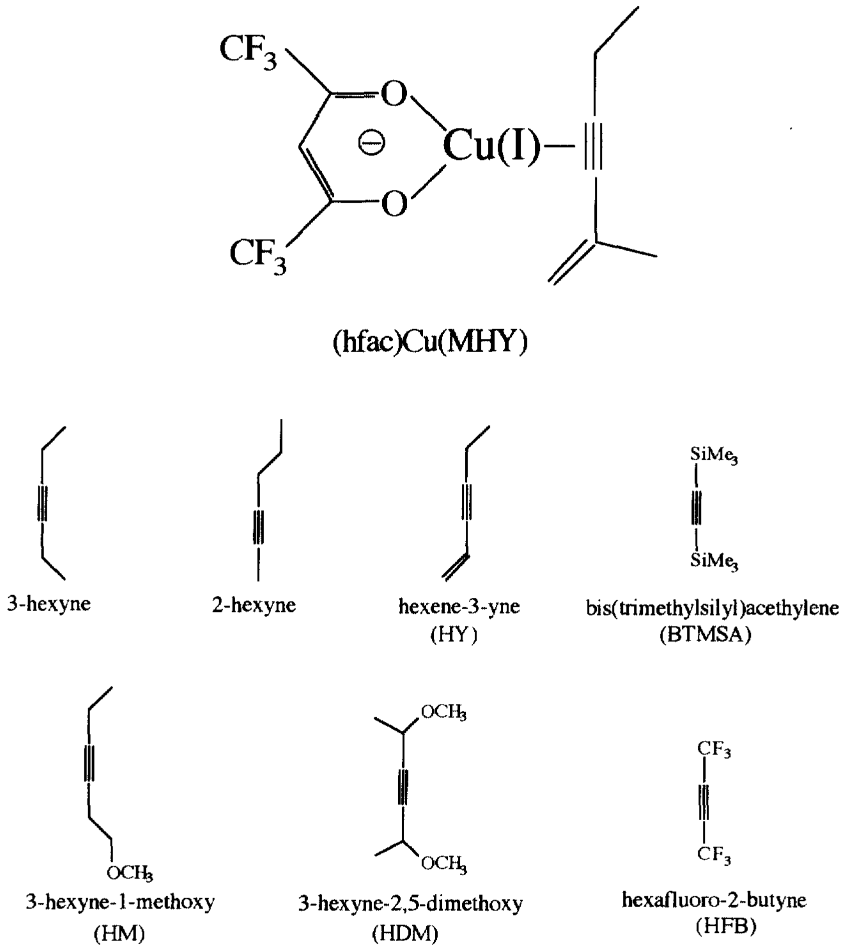


Fig. 4. Copper(I)(hfac) Chemistries developed in this study. MHY can be substituted by VTMS (vinyltrimethylsilane), COD(cyclooctadiene), DMCOD (dimethyl-1,5-cyclooctadiene) or any alcyne present in the list except HFB (see text).

synthesized using the reaction pathway given in Eq. (6):

$$Cu_2O + 2H(hfac) + 2L \rightarrow 2LCu(hfac) + H_2O. \tag{6}$$

The liquid products are purified by column chromatography. This method is particularly useful for the large scale production of pure liquid copper precursors.

When the alkyne bears the too strong withdrawing CF_3 groups, no complex can be isolated since the deactivated alkyne is not able to stabilize the copper(I) β-diketonate complex.

The most promising compound is when the Lewis base is an alkyne deactivated by a conjugated double bond (P. Doppelt et al., unpublished results) [39,40]. Different alkynes have been tested (see Fig. 4); the best results were obtained when the commercially available 2-methyl-1-hexene-3-yne (MHY) was used. The 1:1 stoichiometry has been checked by ^{1}H nmr. By ^{13}C nmr, we could verify that the ligand is bound to the metal center via the triple bond while the double bond stays free. The X-ray structure of the complex displayed in Fig. 5 confirms this result. The compound is a liquid at RT (m.p. = 15–17 °C) with an enhanced stability as we will discuss later.

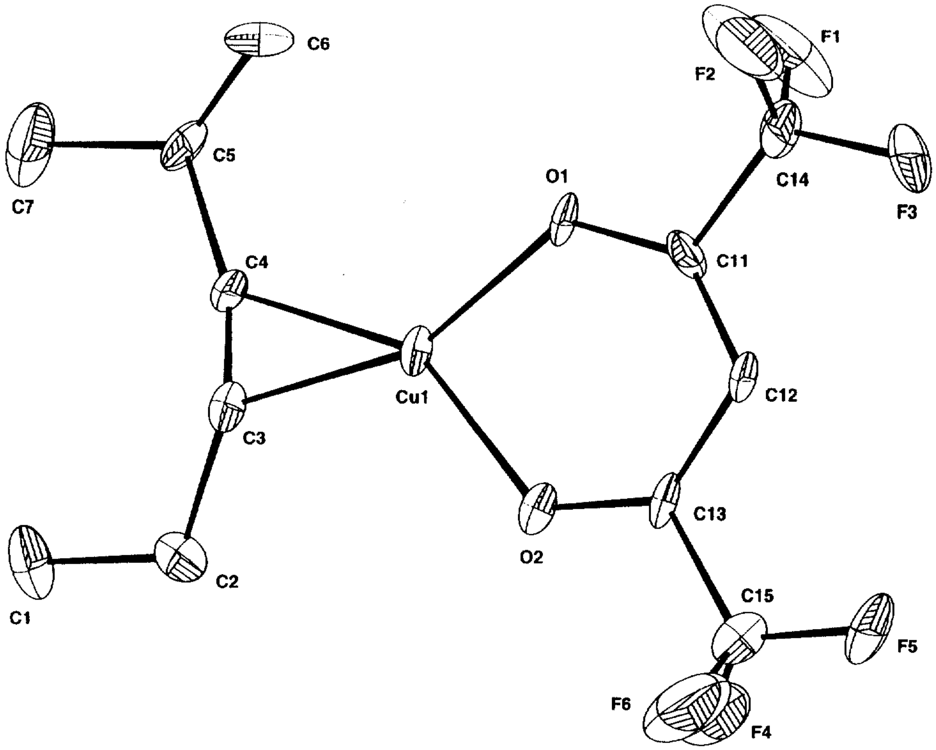


Fig. 5. ORTEP plot of (MHY)Cu(hfac) obtained by X-ray crystallographic analysis of a single crystal (J. Vaissermann et al., unpublished results).

3.2. Deposition conditions and film properties

The envisioned process for the metallization of ICs using copper CVD is the Damascene process. In the Damascene process, an insulator (usually silicon dioxide or a low «k» dielectric) is dry-etched to form trenches conforming to the wiring pattern. A thin diffusion barrier film, such as TiN, must be first deposited to prevent diffusion of Cu into the surrounding insulator. The trenches are then plugged with copper deposited by CVD. An alternative method is to use Cu CVD as a seed layer for further electroplating Cu. Then, application of the chemical–mechanical polishing of the copper (Cu CMP) down to the insulator surface yields copper interconnects surrounded by the insulator [41]. Of course, the top surface of the Cu interconnect must be protected by some other method.

3.2.1. (VTMS) Cu(hfac)

(VTMS)Cu(hfac) is by far the most widely used precursor for the deposition of blanket and selectively deposited copper films. This material is a low melting point (< -20 °C), yellow liquid possessing a vapor pressure of 0.3 Torr at 40 °C. Deposition rates as high as 200 nm min^{-1} are obtained at substrate temperatures of only 150 °C. Catalytic amounts of water have been used with TiN as a substrate to shorten the nucleation period [42,43] or all along during copper deposition [44] to enhance copper growth rate and improve adhesion. An alternative was the addition of H(hfac) dihydrate to the liquid precursor [5,45,46]. Excellent results were obtained with a novel direct liquid coinjection technique that enhanced deposition rates and allowed higher precursor throughput into the reactor at higher vaporization temperatures [9]. This coinjection technique involved the mixing of VTMS, with the (VTMS)Cu(hfac) prior to injection into the vaporizer and thereby limited precursor disproportionation. It has been shown that direct liquid coinjection is an effective method for enhancing deposition rates and producing high quality CVD copper films for microelectronic applications using Cu(I) precursors. Nevertheless, the liquid injection vaporization temperature is high and determines the flow of the precursor. For example, at a vaporization temperature of 65 °C which is the temperature used for the (VTMS)Cu(hfac)–VTMS mixture, the flow is limited to 0.4 ml min^{-1}. Even at this temperature, over time, copper deposition can occur in the evaporator causing a loss of the precursor and ultimately leading to a blockage of flow. The use of more stable precursor is indeed a critical issue because it could permit one to operate at higher temperatures with a higher precursor flow (at 90 °C, the flow can be doubled or tripled) without the problem of precursor decomposition in the evaporator.

3.2.2. The isomeric mixture (DMCOD) Cu(hfac)

The isomeric mixture (DMCOD)Cu(hfac) is a more thermally stable source than (VTMS)Cu(hfac) and Cu CVD from (DMCOD)Cu(hfac), provides an alternative process for Cu CVD [18]. Using (DMCOD)Cu(hfac), high-purity copper films were grown on a variety of substrates with temperatures between 150 and 250 °C. The complex displays a vapor pressure of 0.135 Torr at 62 °C. The deposition rate increases up to a $T_{sub}=200$ °C and then levels off due to mass-transport limited growth. The activation energy for film growth is ~25 kcal mol^{-1} (as opposed to ~10 kcal mol^{-1} obtained for (VTMS)Cu(hfac) [47]) based upon an Arrhenius plot of growth rate versus $1/T$. The purity of the deposited copper films was examined by Auger and XPS analysis; high-purity copper films with resistivities as low as 1.9 μΩ cm have been deposited. The process is highly reproducible and an electrical deviation of 1.9% over 5 in diameter wafers was achieved in a warm-walled reactor. Filling of 0.5 μm wide, 3:1 aspect ratio features was achieved at 190 °C with deposition rates of 35 nm min^{-1}. Higher deposition rates can be achieved, but lower growth rates provide optimal via filling. An example of via filling was previously reported [18]. Selective copper deposition was also observed on metal surfaces when compared with insulators (i.e. SiO_2 and polyimide). A surface chemical pre-treatment can enhance the observed surface selectivity, as reported for other copper CVD precursors [48].

3.2.3. (MHY)Cu(hfac)

Less data are available on the Cu CVD films using (MHY)Cu(hfac) because it is a more recently developed source (P. Doppelt et al., unpublished results) [39,40,49]. The complex displays a partial pressure of 0.7 Torr at 65 °C. The new liquid complex displays a partial pressure of approximately 700 mTorr at 65 °C and was used with 2% of pure MHY as a stabilizing agent. Using a direct liquid injection and vaporizer system, pure copper films were deposited on 4 inch diameter silicon wafers covered with a 20 nm thick CVD TiN film as a barrier (obtained with DTMAT as a precursor) in a cold wall LPCVD system with hydrogen as carrier gas. The copper films were deposited at precursor vaporization temperature of 70–80 °C and deposition temperature of 180–220 °C. The deposition rate increases up to 195 °C, at 200–250 nm/min and level-off due to the mass control growth. Shiny adhesive copper films with thickness range 500–1000 nm had resistivity of 2.5–3.2 μΩ cm. Semi-quantitive secondary ion mass spectroscopy (SIMS) analysis of the Cu layers indicated that the C contamination was very low whereas the oxygen contamination was non negligeable. Contamination by oxygen which is responsible for the rather high resistivity values obtained, can be attributed to a small leak in the set-up during copper deposition. (R. Madar et al., unpublished results). The critical parameters for this new compound, beside the volatility, are the stability and the viscosity because these compounds are supposed to be used pure or stabilized with a low percentage of free Lewis base. Both properties are essential for the use of the source in an injection system. The viscosity is comparable to that which is found for (VTMS)Cu(hfac) and is much lower than that of (DMCOD)Cu(hfac). Hence, concerning the viscosity, the order is (MHY)Cu(hfac) ~ (VTMS)Cu(hfac) < (DMCOD)Cu(hfac). Interestingly the thermal stability which is required for transport follows the reverse order (DMCOD)Cu(hfac) > (MHY)Cu(hfac) > (VTMS)Cu(hfac). For each compound, an excess of Lewis base was found to enhance thermal stability both at room temperature and at elevated temperature. As an example, a mixture of 4% MHY in

(MHY)Cu(hfac) can stand without decomposing for more than 1 h at 95 °C or more than 7 days at 65 °C (P. Doppelt et al., unpublished results) [39,40,50].

4. Below 100 nm?

4.1. Selective deposition of copper using SAMs and copper CVD

Selective deposition using copper CVD is an alternative to the metallization with Cu CVD plus Cu CMP. Furthermore, filling holes and trenches even via Cu CVD have physical limits (down to 0.1 μm), which is not the case for selective deposition which can be performed on flat surfaces. Although sub-10 nm structures have been obtained with electron beam resists, we will focus our approach to selective copper CVD on recent processes which use self-assembled molecules (SAMs) [6].

Self-assembled monolayers (SAMs) are very thin organic layers that are formed by the attachment of single organic chains in an ordered arrangement to a variety of surfaces by chemical bonding. The size of the molecule determines the layer thickness and can be carefully controlled to produce layers of uniform coverage typically ~1–3 nm thick. These materials are candidates for very high resolution resists not only because they are very thin but also the important lateral dimension of the films is a molecular diameter (<2 nm for these materials).

The problem of selective deposition is that film growth occurs only on one surface in the presence of others. These two different areas must be simultaneously present on the substrate during the film growth. The mechanism of selective Cu deposition has been extensively studied from the surface science point of view (Fig. 2) [51]. The first step in the deposition process is the chemisorption of precursors onto the surface (Eq. (2)). Depending on the substrate, the precursor dissociates into $Cu^{(I)}$(hfac) and L species (Eq. (3)) or desorbs intact from the surface. For selectivity, both are desired. In dissociative adsorption, L is usually more volatile and quickly desorbs, leaving $Cu^{(I)}$(hfac) species on the surface. Next two $Cu^{(I)}$(hfac) species react to form Cu metal and volatile $Cu^{(II)}(hfac)_2$ which is desorbed from the surface without decomposition at temperature below 250 °C (Eq. (4)). According to this mechanism, once the precursor has chemisorbed, there are two competing reactions: intact desorption and dissociation into L and $Cu^{(I)}$(hfac). This competition is largely determined by the relative strengths of the chemisorption bond and the Cu–L bond. In order to suppress the deposition of Cu on, for example, SiO_2 and promote deposition only on the metallic surface, the hydroxyl groups have been identified as the SiO_2 chemisorption sites. The selectivity was lost if the surface was exposed to water or ethanol which produces adsorbed hydroxyl groups before the adsorption of the precursor. This phenomenon has been largely exploited to enhance the nucleation step of copper CVD for blanket deposition. Clearly, intact desorption is the key issue for selective deposition [42–44]. Therefore, if the surface hydroxyl group is removed or passivated with a self assembled layer (SAMs) of hydrophobic trimethylsilane groups, the selectivity can be recovered. The selectivity is also precursor and substrate temperature dependant [26,27].

A way to enhance selectivity is to encourage the desorption of the precursor on the non-growing area while activating the reactivity of the growing surfaces. Therefore, the use of functionalized silane derivatives to modulate the chemical affinity of the surface towards the ligand of the metal–organic precursor or the copper itself has been proposed [52,53]. The functional residues attached to the surface by silylation has been previously used either to prevent Cu deposition on certain parts of the substrate [48] or to provide complexation sites for an oligomeric palladium-based catalyst which in turn enhances selective Cu deposition by CVD [52]. In that latest example, a five step process has been developed for achieving selective Cu CVD on diamond and SiO_2 substrates using ligating aminosilane self-assembled films and a Pd-based catalyst. The process involves five steps: (1) surface oxidation; (2) aminosilane film attachment; (3) film patterning; (4) Pd catalyst application; (5) Cu CVD. Substrate oxidation generates reactive surface species, such as hydroxyl groups, that allow covalent attachment of organosilane films. A ligating aminosilane film provides complexation sites for an oligomeric Pd-based catalyst. In subsequent copper CVD, copper deposits readily from (VTMS)Cu(hfac) on aminosilane-coated surfaces treated with the oligomeric Pd. Copper does not deposit readily on hydrogenated or aminosilane-coated surfaces. To create a pattern of surface reactivity for selective Cu CVD, the aminosilane film can be patterned with lithographic techniques prior to Pd catalyst application and Cu CVD.

4.2. Metallization of SiO_2 based substrates using Cu CVD by a two-step dry process (Fig. 6)

4.2.1. Gas phase silylation

In our attempt to create surfaces with enhanced or reduced affinity towards Cu(I) β-diketonate precursors [53,54], (VTMS)Cu(hfac) and (MHY)Cu(hfac), we investigated a variety of monofunctional and also some trifunctional silylating agents which are shown in Fig. 7.

The silylation procedure described above resulted in the formation of monolayers of silane molecules which were covalently bound to the silica surface via siloxane bonds as was confirmed by UV–Vis spectroscopy on quartz slides and imaging ellipsometry on silicon–silica samples [55]. Repeated rinsing in organic solvents resulted in the removal of a small amount (5–20%) of silylating agent during the first rinsing step only. No further decrease of UV-absorption was observed upon additional rinsing steps. The degree of loss clearly depended on the duration of the desorption step in the reactor after silylation (which consists of a heating at 200 °C under 1 mbar) thus providing further proof for the covalent attachment of the first monolayer.

Two effects of the UV illumination on 1-(dimethylchlorosilyl)-2-(*p*,*m*-chloromethylphenyl)ethane (DMCSE) treated SiO_2 surfaces can be deduced from FTIR spectroscopy results:

(1) Short term exposure leads to photochemical conversion of the functional $-CH_2Cl$ residue to aldehyde or carboxylic acid depending on the content of O_2 and H_2O in the ambient atmosphere as is evident from the broad band

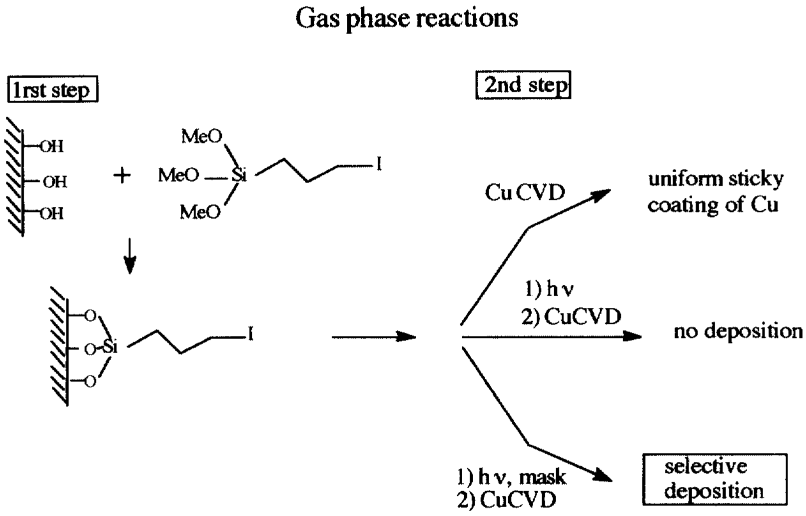


Fig. 6. Schematic diagram showing a surface reaction with IPTMS followed by different treatments.

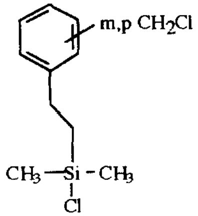
around 1725 cm^{-1} which can be assigned to the C=O stretching mode. As will be discussed below, this renders a surface with low affinity towards Cu CVD.

(2) After prolonged of exposure to UV light the intensity of the C=C stretching vibrations (from the aromatic ring, several bands between 1600 and 1500 cm^{-1}) and of the CH_3 stretching vibrations at 2850–2960 cm^{-1} decrease which indicates the damage to the molecular structure as for example C–C or Si–C bonds cleavages.

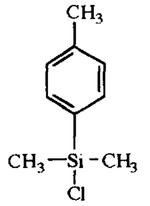
4.2.2. Copper CVD on silylated surfaces.

As expected for substrates temperature around 220 °C, very poor deposition or no deposition at all occurred on bare SiO_2 surfaces as well as on slides treated with p-tolyldimethylchlorosilane [48] (TDMCS). When the surface treatment was performed with DMCSE or iodopropyltrimethoxysilane (IPTMS) on silica or Pyrex slides, growth of a Cu film was formed by CVD. The copper film growth rate was comparable to that which is found using a metallic substrate (with our set-up typically 40 nm min^{-1} is obtained on gold film substrates when (MHY)Cu(hfac) is used as a precursor). A scotch tape test removed almost completely the Cu film from DMCSE treated slides. In contrast, copper film deposited via the same CVD procedure on IPTMS treated surfaces exhibited enhanced film adhesion. Surfaces derivatized with IPTMS and exposed to UV exhibit low affinity towards copper precursors comparable to TDMCS treated surfaces, i.e. one finds only very thin irregular copper deposition after prolonged CVD treatment. The iodide function has been transformed by UV irradiation in an inactive functional group versus CVD.

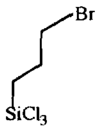
In order to determine selectivity of deposition on: (1) IPTMS; and (2) 3-mercaptopropyltrimethoxysilane (MPTMS), we used masks to form surfaces with



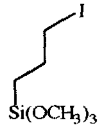
1-(dimethylchlorosilyl)-2-(p,m-chloromethylphenyl) ethane (DMCSE)



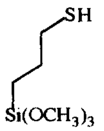
p-tolyldimethylchlorosilane (TDMCS)



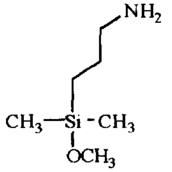
3-bromopropyltrichlorosilane (BPTCS)



3-iodopropyltrimethoxysilane (IPTMS)



3-Mercaptopropyltrimethoxysilane (MPTMS)



amino-propyl-dimethyl-monoethoxysilane (APDMES)

Fig. 7. List of silanes (and their abbreviations) used in this study.

an affinity pattern by UV irradiation. As the precursor, we chose (MHY)Cu(hfac) for these experiments because its lower growth rate made the process more controllable. In the case of IPTMS derivatized surfaces copper deposition occurred on non-irradiated surfaces and to a lesser degree on irradiated surfaces (positive image). There is a real contrast between the two areas: some local nucleation of copper is observed on the irradiated area, but a real continuous film is obtained on the non-irradiated area. Furthermore, the adhesion of the copper film (islands) is very different: the film is very adhesive on irradiated areas whereas the copper islands are very poorly bound to the derivatized irradiated SiO_2 surface.

The nature of the mechanism involved in the nucleation process [53] is still under investigation. We have observed that the functional group -CH_2Cl and even more so -CH_2I enhance the deposition of copper by CVD. In contrast CH_3-terminated surfaces (treated with TDMCS) yield a non-uniformly deposited Cu film of very low thickness. Furthermore, FTIR measurements show that UV exposure results in the photochemical conversion of the -CH_2Cl group to carboxylic acid or aldehyde. Based on these findings we proposed a very simple and selective mechanism: we assume that the functional group -CH_2I reacts with the ligand hfac which is bonded to a $Cu^{(I)}$-atom. In a subsequent reaction step $Cu^{(I)}$-atoms disproportionate to form metallic Cu and $Cu^{(II)}$ complexes. The substrate surface with the attached ligands hfac that are bonded to the $Cu^{(II)}$ may contain metallic copper that may serve as nucleation sites and thus promote further deposition of a copper film. A similar mechanism has been reported in the context of the reaction of alkyl bromide with $Cu^{(II)}$ or $Co^{(II)}$ β-diketonate in non-polar solvents [56,57]. It has been found that $Cu^{(II)}$ β-diketonate complexes although quite inert under standard ionic conditions, react through radical initiated reactions at the intercarbonyl position. This mechanism involves the formation of radicals and can be related to the present case of activated surfaces. We therefore assume that any chemical function capable of forming radical intermediates may be a candidate to serve as an activated group towards organic copper precursors as used in this study [49,58].

When the surface was treated with MPTMS, irradiated under argon as previously described and treated with Cu CVD using (MHY)Cu(hfac), a negative image of the mask was obtained (P. Doppelt et al., unpublished results) [39,40,53]. Apparently UV irradiation of MPTMS derivatized samples generates a surface with high affinity towards the copper precursor (negative image) that we suppose to be disulfide species. However, special care must be taken during UV irradiation of MPTMS derivatized surfaces: when the experiment was carried out in H_2O saturated O_2 atmosphere, the copper deposition was much less selective. We suppose that in such experimental conditions sulfonic acid groups are formed as reported for thiol self monolayers on gold [59]. To confirm our hypothesis, we formed chemically the disulfide of some MPTMS derivatized samples by oxidation in a basic solution with molecular oxygen. These surfaces display an enhanced affinity towards (MHY)Cu(hfac) comparable to irradiated MPTMS derivatized samples. After irradiation of these samples in an H_2O–O_2 atmosphere and after copper CVD, these samples display a positive image of the mask.

4.3. *Metallization of other surfaces using SAMs and copper CVD [54]*

4.3.1. *Other tested surfaces.*

As said earlier, a diffusion barrier is needed to prevent Cu diffusion into Si or SiO_2 so we report here on experiments to extend our metallization process to non-oxide materials such as TiN. We have also tested Si_3N_4 which is another material extensively used in microelectronics.

The chemical surface composition of TiN and Si_3N_4 films is less well known than SiO_2 surfaces. In particular, it is unclear if silane compounds may covalently bind to the surface and thus allow for deposition of defect free and thermally stable organic monolayer films as has been achieved on SiO_2. Since these monolayer films are the basic prerequisite for our monolayer lithography and selective metallization scheme, the goal of this study was to find optimum conditions for monolayer deposition using silane compounds. The primary goal of this study was to identify those pre-treatment procedures that would lead to maximum coverage with silane. ESCA was employed to probe silicon and iodide atoms on TiN surfaces treated with IPTMS which has previously been identified as particularly well-suited to monolayer-mediated selective metallization. In case of Si_3N_4, the silicon would not have been a good label to measure the coverage with silane. Therefore, a different procedure was used in order to assess the monolayer quality on Si_3N_4.

4.3.2. *ESCA results of modified TiN surfaces*

TiN (400 nm on 10 nm of Ti) was deposited on Pyrex slides by reactive sputtering. TiN contains oxygen atoms on the surface as soon as the substrate is exposed to air. To react with a functionalized silane, the surface must have OH groups that are formed by a pre-treatment of the surface. The surface pre-treatments included strong acidic bath, dilute HCl, dilute KOH, and O_2 plasma treatment. The best treatments were, however, diluted HCl or KOH solutions followed by a silylation reaction with IPTMS. ESCA analyses (%) gave the relative amount of the elements present at the surface (without consideration of hydrogen): I (0.8), Si (4.6) O (37) Ti (19). In all samples, the surface of the TiN thin films after deposition consists of about 50% of TiO_2. We consider the silicon signal as a good indicator for the coverage with IPTMS. The low concentration of iodine is puzzling. This may be due to partial decomposition of the chemically labile iodine compound. This question will be investigated by using different and more chemically stable silanes in future experiments.

4.3.3. *Results from visible absorbance measurements on modified Si_3N_4-samples*

The 300 nm thick Si_3N_4 films were obtained on Pyrex slides at 230 °C by PECVD. In the case of Si_3N_4. the silicon is not a good label to measure the coverage with silane. Therefore a different procedure was used in order to assess the monolayer quality on Si_3N_4. Amino-propyl-dimethyl-monoethoxysilane (APDMES) was deposited on substrates after the pre-treatment. The aminogroups of the silane were derivatized with a dye (Rhodamine isothiocyanide). Unreacted dye, i.e. merely physically adsorbed molecules, were removed by sonication in water and isopropylalkohol. The absorbance maximum of the dye is observed at 550 nm (Si_3N_4 is transparent at this wavelength) and is a measure for the coverage of the sample. The best results with respect to surface coverage of Si_3N_4 with APDMES are obtained after pre-treatment with plasma O_2 treatment followed by either dilute HCl or KOH solutions treatments [54]. Further experiments are necessary to clarify this and also to compare influence of pre-treatment on results obtained by selective metallization.

4.3.4. *Selective Cu CVD on modified Si_3N_4 and TiN surfaces*

Selective metallization experiments were run as previously described. The surfaces were first treated to obtain a high concentration of surface OH groups. Then, a silylation reaction was performed with IPTMS with silane being applied in the vapor. After irradiation through a mask, we estimated the efficiency of the pre-treatment by the quality of the selectively deposited copper films. Two different precursors, (VTMS)Cu(hfac) and (MHY)Cu(hfac) were tested. As expected, no deposition or very poor deposition occurred on native surfaces or pre-treated surfaces.

In the case of TiN and Si_3N_4 surfaces treated with IPTMS and irradiated through a mask, selective copper deposition was obtained and a positive image of the mask was created. On both, TiN and Si_3N_4 surfaces, a good contrast between irradiated area and non-irradiated area was obtained. Some nucleation of copper is also observed on the irradiated area, but a continuous film is obtained on non-irradiated areas (Fig. 8). Depending on the precursor used, a layer thickness of 300–500 nm was achieved within 10 min. Interestingly, while the film adheres very well on irradiated surface areas the copper islands are very poorly bound to the derivatized irradiated surface and may be removed with Scotch tape.

We have demonstrated the extension of the single-step Cu CVD process (see Fig. 9) based on monolayer lithography using silane compounds to technologically

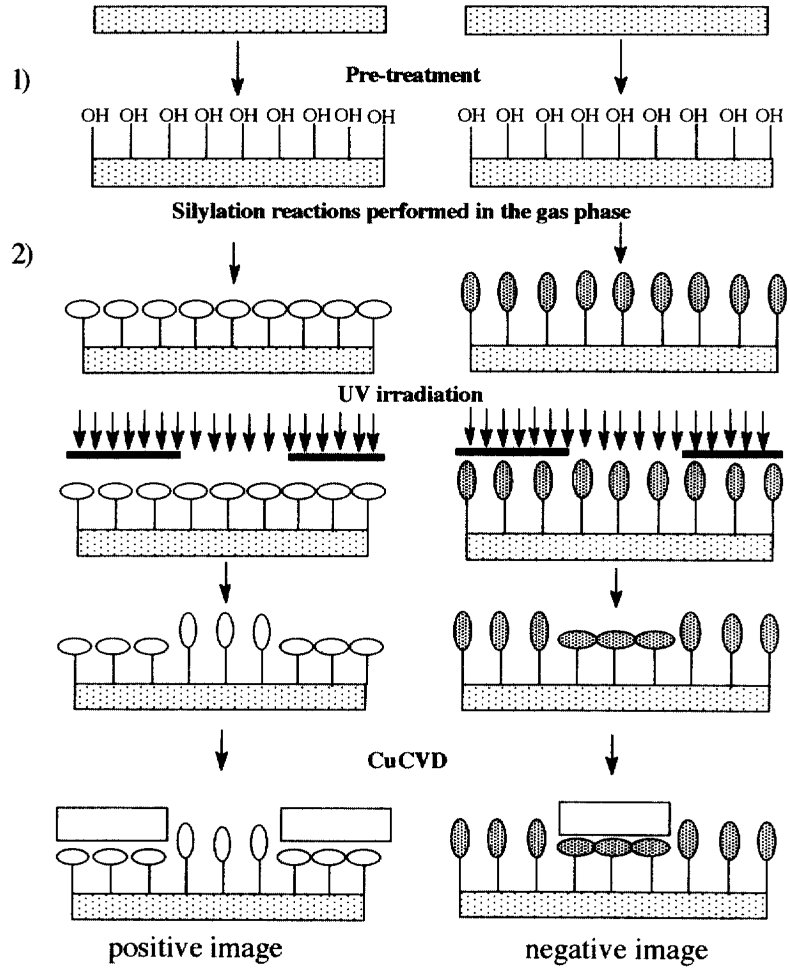


Fig. 8. Schematic of the processes (positive and negative behavior) for patterned, selective copper CVD on derivatized SiO_2, TiN or Si_3N_4.

Fig. 9. Selective Cu CVD (using (MHY)Cu(hfac)) on Si_3N_4 film treated with IPTMS and UV irradiated through a mask. The copper film is ~400 mm thick.

important TiN and Si_3N_4 surfaces. Optimum substrate pre-treatment procedures could be identified by analyzing the substrates with respect to maximum monolayer coverage. The results obtained by Cu CVD correlate well with the monolayer analysis. The study will be extended to other surfaces, silane compounds and will also investigate the influence of surface roughness produced as a result of plasma pre-treatment.

We demonstrated selective Cu CVD on Pyrex and SiO_2 glass, TiN and Si_3N_4 surfaces functionalized with silanes (Fig. 9). Such ultrathin monolayers are potentially useful for very high resolution resists because the lateral resolution may be of the order of molecular dimensions. Hence, attempts of metallization of such substrates at a nanometric scale have been undertaken (D. Tonneau et al., unpublished results).

5. Conclusion

Cu CVD is a mature technology because a number of CVD precursors exist. (VTMS)Cu(hfac) is the precursor most utilized but there exists a challenger which is the stable (MHY)Cu(hfac). The use of these coordination compounds have made possible the development of new technologies that are demanded to fulfill the requirements of the micro-electronic industry for 0.18 μm or less generation microprocessors and memories. Moreover, the use of these labile precursors on surfaces opens a new area of investigation for metallization of different supports such as SiO_2, TiN or Si_3N_4 at a nanometric scale. Thus, coordination chemistry is stretching the limits of micro-electronics technology.

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