Current Trends in Patterning with Copper

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I. The Microelectronics Industry

A. Metal Interconnects for Integrated Circuits

The microelectronics industry is undergoing rapid expansion and miniaturization, producing semiconductor devices which are increasingly smaller, faster and of higher density.[1] Increasing the degree of integration on semiconductor devices is governed by the material and practical limits of the device features. These limits include properties of the semiconducting and insulating materials, the layout of the device, and the circuit configuration.[2] In real manufacturing terms the most severe limitation for chip fabrication is not the transistor or other complex features, but the metal interconnects performing signal communication and power distribution.[1] These conducting networks are currently impeding the development of chips with shorter response delays. This issue is presently circumnavigated by keeping the interconnects short.[2] To roll back the frontiers of interconnect technology, considerable efforts are directed toward more conductive interconnects which are easier to manufacture.

Ultra large-scale integration (ULSI) has led to metal interconnects on these devices being processed well below 0.25 μm.[3] On, for example, a 1 Gb dynamic random access memory (DRAM) wafer the via holes (vertical interconnects) measure only 0.2 μm across.[4] The logic speed of a device is determined by its RC time constant ($\alpha = \rho \cdot L^2$, where ρ is the resistivity and L is the total length of the interconnects). To produce faster and smaller devices it has become necessary to use a metal with lower resistivity.[4-6]

Traditionally aluminum has been widely used in the fabrication of metal interconnects.[4] Metallization with aluminum can be carried out by physical vapor deposition (PVD) techniques such as high-temperature sputtering for reflow, sputtering with a collimator, long distance sputtering, and chemical vapor deposition (CVD).[4,6] With all these techniques aluminum films can be produced with excellent conformity, though only a limited number of CVD precursors are available. Metallization with aluminum becomes unreliable below 0.5 μm due to its high tendency for electromigration (EM) and stress-induced migration (SM) which can lead to voiding.[2,7]

The next generation of faster integrated circuits (IC) will have higher device densities, faster operating frequencies, and larger die sizes, but it may be limited by metal interconnects.[8] There is an obvious need for new interconnect materials with lower resistivities, and that is true especially for longer global interconnects that run from one end of a chip to the other.[2] In recent years Cu has attracted increasing attention as a candidate to replace aluminum due to its low bulk resistivity, 1.7 $\mu\Omega$ cm^{-1} compared with 2.7 $\mu\Omega$ cm^{-1} for aluminum.[9-11] In fact, the only metal with a lower resistance is silver.[4] Cu is also less susceptible to EM, being 2 orders of magnitude more resistant than aluminum, possibly due to its higher melting point.[12] In addition, Cu has good thermal stability and a low-temperature coefficient of resistance.[2] There are however problems associated with using Cu; it diffuses substantially into Si/SiO_2 layers, which could cause electrical malfunctions, and TiN barrier layers are employed to reduce this.[13,14] So far no easy dry etching process has been developed to fine-pattern the blanket Cu films produced by CVD.[15,16] This issue can presumably be addressed by the use of selective deposition techniques. Until then the microelectronics industry will continue to employ traditional plating techniques, requiring external power sources or conducting seed layers to deposit and etch Cu films.[17]

B. Current and Future Trends in Cu Interconnect Fabrication

Since chip technology is such a lucrative industry, huge effort is being invested in improving device interconnect response time.[1] These efforts are aimed especially at improving current fabrication methods as well as devising new patterning processes. Current photolithographic methods of manufacturing Cu interconnects will be reviewed along with Cu deposition techniques used to prepare patterned films.

Conventional and slightly more unconventional plating techniques, widely used in ULSI circuits manufacturing, are examined with respect to their Cu film patterning capabilities. Chemical vapor deposition (CVD) is becoming important for depositing Cu as blanket and patterned films.[18] The development of CVD will be addressed with particular attention to precursor design. Recently attention has been deflected from photolithography and various Cu direct-write techniques have emerged. These are reviewed since they are expected to eventually supersede the older lithographic technologies.[19]

II. Photolithographic Film Patterning

A. Introducing Cu Patterning

Current trends in the fabrication of semiconductor devices show that metal interconnect production is the principal bottleneck in manufacturing.[20] Photolithography is still the sole industrially practiced technique for patterning aluminum and Cu interconnects.[1]

The example in Figure 1 demonstrates how inefficient photolithography is as a manufacturing process. Patterning a Cu-coated substrate via lithographic methods requires upward of nine manufacturing steps.

(1) Film Cleaning and Adhesion Promoter Deposition. Initially the Cu film is rigorously cleaned; this is followed by the application of an adhesion promoter film, which improves the adherence of the photoresist to the metal surface.[21,22] Adhesion promoters are

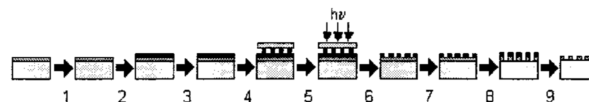


Figure 1. Multistep photolithographic process for Cu patterning.[173] Process: (1) film cleaning and adhesion promoter deposition; (2) photoresist deposition; (3) prebake; (4) mask alignment; (5) light exposure; (6) development; (7) postbake; (8) metal etch; (9) stripping.

generally silanes, and they are selected specifically for each photoresist.[23]

(2) Photoresist Deposition. The photoresist is the radiation-sensitive, polymeric material which undergoes a chemical or physical change when exposed to light.[24] The resist can be developed by treatment with solvents or with plasma.[25] After development the resist must have resistance, hence the name, to the etching of the manufacturing process. Positive resists are rendered soluble and negative resists become insoluble upon exposure to light.[26] The photoresist film is applied to the substrate surface via spin coating. A solution of the photoresist is poured onto the substrate, and the liquid is leveled by the centrifugal forces of spinning.[27] This process is very wasteful as the excess solution simply spins off the substrate.

(3) Prebake. The film is mildly baked to remove residual solvent from the spin coating processes.[28] In addition, it allows the resist film to set on the surface.[28]

(4) Mask Alignment. Fabrication of masks is primarily performed using electron-beam exposure to create opaque regions on films of diazonium polymers, germanium on glass, and europium oxide.[29] However, as wafer sizes increase and features become finer, masks become more complex, more difficult to coat, image, and process.[29] Currently masks can be used to create features below 0.2 μm, and they are unrivalled in patterning miniaturized Cu interconnects.[2,30]

(5) Light Exposure. The example given in Figure 1 involves a negative photoresist.[31] The substrate is exposed to light, and the regions of the photoresist not protected by the mask undergo, e.g., photochemical cross-linking. Radiation sources employed in photolithography range from ultraviolet, X-ray, or even ion beams depending on the sensitivities of the photoresist.[25] Exposure wavelengths range upward from $v = 800$ to 150 nm, and there have recently been moves toward shorter wavelengths to achieve higher image resolution.[32]

(6) Development. The negative resist in Figure 1 is treated with a solvent, which will remove the uncross-linked, unexposed regions, thereby developing the image. For a positive resist the solvent should remove only the exposed resist. The solvent used as the developer is chosen for its ability to selectively remove resist from the desired regions but leave the other regions untouched.[24,31]

(7) Postbake. Postbaking is performed principally to enhance the dimensional stability of the developed resist image during etching. Baking the substrate hardens the resist, drives off residual solvent trapped during development which improves adhesion to the substrate, and reduces the effects of plasticization.[33] In addition, there are certain cases where increases in cross-link density result in sharper solubility differences during development.[32]

(8) Metal etch. Exposed Cu is etched away with buffered nitric acid or by dry plasma etch methods, leaving resist-protected Cu intact, resulting in the Cu film being patterned.[16,34]

Table 1. Examples of Positive Photoresist Systems[32]

photosensitive polymers	photosensitive additive + polymer
PMMA	DQN
As_2S_3	sensitizer + PMMA
photoxidizable polymers	nitroaldehydes + PMMA
ablative exposure	onium salts + scission polymers

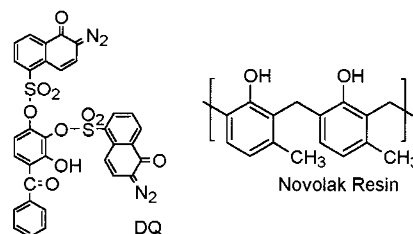


Figure 2. Chemical components of a DQN resist system.

(9) Stripping. The final step is to remove resist from the Cu surface. This is achieved with a stripper. This can be one of a variety of liquid compositions or a gas-phase process involving activated oxygen. The negative resist in Figure 1 would require oxidation by a liquid or by a plasma stripper.[35]

B. Photoresists

1. Positive Resists

Positive resists undergo photochemical reactions, which allow light-exposed regions to be developed by washing with a solvent. Photosensitivity is achieved by the incorporation of a small photosensitive additive, or the polymer itself can be photosensitive.[30]

The chemical transformation photochemically induced in a positive resist occurs in one of two ways. A photosensitive additive induces a solubility change in the polymer changing solvent preference from polar to nonpolar or vice versa. Or if the polymer itself is photosensitive, it reverts to small, monomeric components, thereby becoming soluble or even volatile.[26] From the examples in Table 1, diazoquinone-novolak (DQN) systems and the scissionable poly(carbonates) will be examined in further detail.

Diazaquinones (DQ) combined with novolak resins (N) as in Figure 2 have been used prior to 1940 for making blueprints and letterpress plates. They are now the most widely used positive resist; at least 12 companies currently manufacture DQN resists. DQN is not oxygen sensitive and absorbs light in the range of 300–500 nm which transforms it into a polar, base-soluble product.[25]

Figure 3 illustrates how a hydrophobic DQ undergoes photolysis generating a carbene via a Wolff rearrangement.[36] The carbene in turn rearranges into a ketene, which absorbs moisture from the resin to form a base-soluble indene acid.

There are distinct advantages of DQN resists. The phenolic component of novolak resins affords a plasma etch resistance that is better than all other conventional resists.[24] DQN can be thermally stabilized to 200 °C. The aqueous developers employed are nontoxic, and the DQN resists are reworkable and easily stripped. Finally, image reversal to a negative image is possible. However, there are problems such as there is a small process window in the developer

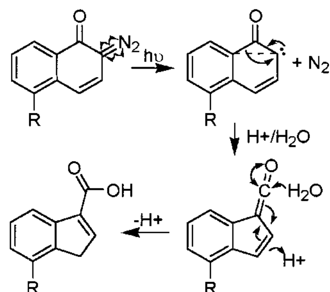


Figure 3. Wolff rearrangement development mechanism of DQ resists.

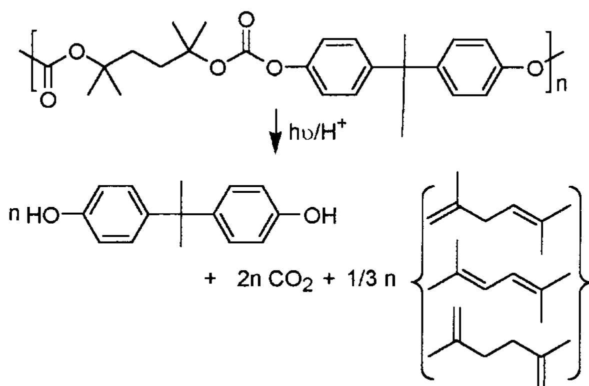


Figure 4. Acid-catalyzed poly(carbonate) backbone scission.[26]

at moderate to low doses. Only moderate contrast is attained plus a slow photospeed averaging only 75 mJ/cm^2.[32]

Poly(carbonate) resists are a relatively minor category of positive resists. However, they are a good example of photosensitive polymers. They are synthesized by condensation polymerization; the carbonate linkages in their backbones allow facile polymer degradation.[26] Backbone scission causes a reduction in molecular weight and forms new solubilizing groups allowing poly(carbonates) to act as positive resists. They can also be used to illustrate the concept of chemical amplification.[26,31] The term chemical amplification refers to photoinduced chain reaction mechanisms which can be triggered via generation of a photoacid or photobase in the polymer film on exposure to radiation. These species react catalytically with the polymer backbone, causing main chain cleavage or functional groups, resulting in a developable solubility change.

The polymer in Figure 4 is an alternating copoly(carbonate) based on bisphenol A and 2,5-dimethyl-2,5-hexanediol. When films of this polymer are used in combination with photoacid generator triphenylsulfonium hexafluoroantimonate (TSHA), they operate as chemically amplified positive resists.[26] Exposure of the resist to UV radiation (254 nm, 5 mJ/cm^2) does not effect the poly(carbonate), which retains its integrity; however, TSHA forms local concentrations of acid in the exposed areas and therefore a latent image. This image is developed by a 3 min postbake at 60 °C. The acid catalyst causes multiple main chain scissions and is not consumed in the overall process.[26] It may become further involved in the cleavage of neighboring chains, thus initiating chemical amplification. The mobility of the reactive catalytic species and other amplification-reducing side reactions limits the chemical amplification process. Byproducts of polymer main chain scission are volatile and evaporate off the substrate during the postbake. This poly(carbonate), therefore, does not require a washing step to remove developed resist; it effectively self-develops.[26,37]

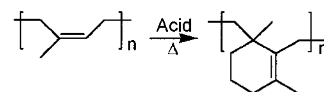


Figure 5. Cyclization product of poly(isoprene).

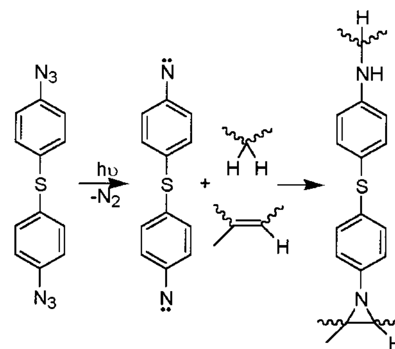


Figure 6. Photoinduced cross-linking of poly(isoprene) by a bisazide.

2. Negative Resists

When a negative photoresist polymer is developed, the exposed areas are retained. Insolubilization can be induced in one of three ways. The polymer's molecular weight can be increased due to polymerization or cross-linking. The polarity of pendant functional groups can be altered, or the oxidation state of an ion or the permanent ionization of a charge-transfer complex can be changed. Only one negative photoresist is applied extensively in the microelectronics industry and that is cyclized poly(isoprene) (CPI) with a bisazide photoactive crosslinker. It can be used where high resolution is not required.[38]

Poly(isoprene) is cyclized under acid-catalyzed conditions, yielding a complex mixture of structures. Figure 5 shows an example of a possible structure.[38] Cyclized rubber has excellent substrate adhesion and provides ample reaction sites for the bisazide to attack, in particular allylic hydrogens and alkenes.[25]

Exposure of the bisazide to light results in the formation of nitrenes which in turn attack poly(isoprene), as shown in Figure 6.[38] Attack from both functionalities of the bisazide results in cross-linking and eventually to the formation of a cross-linked network. Bisazide-poly(isoprene) resists are imaged with wavelengths above 436 nm.[38]

The main drawback of negative resists occurs during image development. A good solvent is required to remove the unexposed, un-cross-linked areas of the resist. Unfortunately the solvent can also penetrate the image at the partially developed, partially cross-linked edges, swelling these regions.[38] For images with large spaces between features (>10 μm), postbaking returns the image to its original shape,

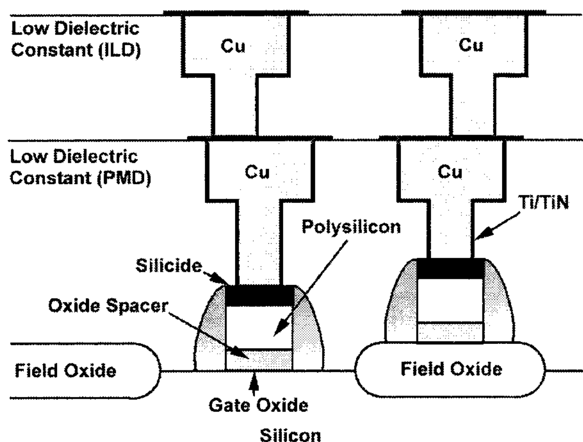


Figure 7. Example of a complex multilayer device (ILD = interlevel dielectric, PMD = polymetal dielectric).[2]

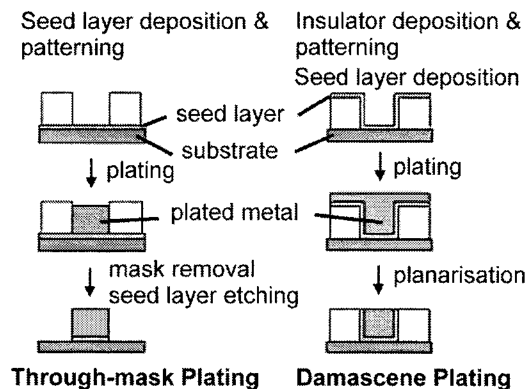


Figure 8. Patterning with Cu using plating techniques.[1]

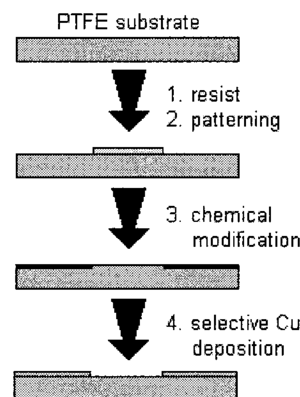


Figure 9. Selective Cu CVD.[2]

though there may be slight distortions at the image edges. Images with small separations (<3 μm) are more problematic; gaps can be bridged when neighboring images swell, touch, and finally coalesce.[38] In terms of an electronic circuit, this results in a short.[39] Other polymers are being investigated; for example, novolac resins reduce swelling during development and may therefore cure this problem.[32]

C. Lithographic Patterning of Cu Films

In section II.A the patterning of a Cu-coated substrate using photolithographic techniques was illustrated (Figure 1). This demonstrates how a photoresist may be used to pattern an underlying Cu film. The image was transferred to the Cu film by etching around the resist. There is however another way of achieving a similar result starting from the opposite direction. A substrate can be patterned using lithographic techniques followed by selective deposition of Cu. This method is of particular significance in the fabrication of multilayer devices.[40]

To achieve interconnections of the complexity shown in Figure 7, it is necessary to deposit Cu onto a surface. Manufacturing methods range from plating techniques such as electroplating, electroless plating to physical vapor deposition, sputtering, and finally chemical vapor deposition.[1,41,42] The practicalities of depositing Cu via PVD and sputtering will not be examined since these techniques require extreme conditions and are therefore limited in their usefulness. However, examples of Cu plating and CVD will be given.

Plating and CVD produce patterned Cu films via deposition of metal only on selected areas of lithographically prepatterned substrates. Plating deposits Cu on conducting regions such as seed layers; CVD precursors are selected for their ability to deposit on either conducting regions or insulating zones.[18,43,44]

Figure 8 demonstrates two different plating techniques.[1] In both cases the seed layer can be Cu which has been evaporated and deposited onto the substrate by PVD. This forms the electrode for plating to occur on.[41,43] Through-mask plating is performed across a resist mask, and Cu is deposited directly into a patterned seed layer. Removal of the mask leaves a Cu feature on the surface. Damascene plating was named after an ancient art of metal inlaying. Cu is plated onto the patterned substrate, filling holes and other features, and the excess material is removed in a process called chemical mechanical planarization.[1,45,46]

An example of selective deposition of Cu by CVD is given in Figure 9. A PTFE substrate surface was activated by chemical etching with a sodium naphthalenide solution.[44] The use of a photoresist allows a pattern to be etched onto the surface. After removal of the resist, selective CVD deposits Cu only on the activated regions generating a patterned Cu film.

D. Photolithography and Its Manufacturing Limits

The use of photolithographic masks allows devices to be patterned to less than 0.2 μm, and this method is currently unrivalled for manufacturing ULSI circuits.[47] However, photolithography proves to be a severe bottleneck in the fabrication of semiconductor devices, not just in the patterning of metal interconnects. Currently, no other process can rival its feature resolution and precision, but the multitude of manufacturing steps required to produce a complex device, for example, the one in Figure 7, is contributing to the high price of chip technology.

When considering alternatives for the patterning of Cu, four new direct-write methods have emerged over the past few years: (i) laser-induced metal–organic CVD (MOCVD), (ii) laser plating, (iii) jet plating, and (iv) inkjet printing.[48–50] These new techniques could eliminate the need for multistep lithographic procedures, masking, baking, exposure, development, etching, and stripping, but it must be

admitted that currently the feature size and definition accessible via these techniques does not come close to what can be achieved using lithography.[20] However, circuitry with resolution above 10 μm form a substantial part of the IC market, and as a result these new technologies may prove to be very lucrative.

III. Plating Patterned Cu Films

A. Cu Plating

The fabrication of Cu interconnects in circuit boards have been achieved principally via electrolytic and electroless metal deposition.[51] Electrolytic plating requires an external current source; electroless Cu deposition utilizes an external reducing agent to facilitate the heterogeneous reduction of metal ions without the need for the substrate to be conductive.[51,52]

B. Plating Patterned Films

Patterned Cu films are currently plated using both electrolytic and electroless techniques.[53] Traditionally, this involves the use of photoresists and all the manufacturing steps associated with photolithography.[17,54] The method is examined along with a variety of direct-write Cu plating techniques which have emerged over the last two decades.

1. Patterning via Lithographic Masks

How lithographic masks are patterned allowing patterned Cu films to be selectively formed via Damascene and through-mask plating was examined in section II. As illustrated in Figure 8, Cu patterns can be plated on a substrate with the photoresist applied and patterned either before or after the catalytic seed layer.[55,56]

The order of application of the seed layer and resist was investigated by Chiang et al.[53] They prepared patterned seed layers on epoxy-based substrates using a PVI-500 Taiyo Co dry film resist with the Pd catalyst seed layer. Their first method involved applying the photoresist to the substrate where it is patterned and subsequent selective adsorption of a Pd catalyst to the regions left unmasked. For the second method, they coated the substrate surface with a Pd catalyst and then applied and patterned the resist. Electroless plating of Cu was performed, resulting in the metallization of the Pd-seeded areas of the substrate. Their results indicated that the first method led to Cu deposition beyond the desired regions since Pd appeared to adhere unselectively over the entire substrate.[53] However, for the substrate where the Pd seed layer was applied before the surface was masked, Cu patterns were successfully deposited despite numerous processing steps being performed between activation and plating.[53]

Damascene plating, where the surface is activated after masking with the catalyst seed layer, involves removal of Cu, which has been plated on the masked regions.[34,57,58] Removal of the excess Cu film is performed via a technique called chemical mechanical polishing (CMP).[59] Excess Cu is polished off the surface, leaving conducting Cu patterns embedded in insulating material. The polishing tool normally operates using an alumina-based slurry with H_2O_2 as the oxidizing agent. Zeidler et al. developed a novel method for end-point detection, i.e., when the Cu top layer has been polished off the surface and the insulating material and inlayed Cu begin to be removed.[60] By measuring the potential of Cu^{2+} ions in solution against time they could observe a constant rate of removal of Cu followed by a decrease in the potential as the Cu removal rate decreases once insulating material began to be removed. This method allows precise end-point detection instead of simply relying on a calibrated polishing time since overpolishing reduces the planarity and thickness of the Cu line and insulator.[60]

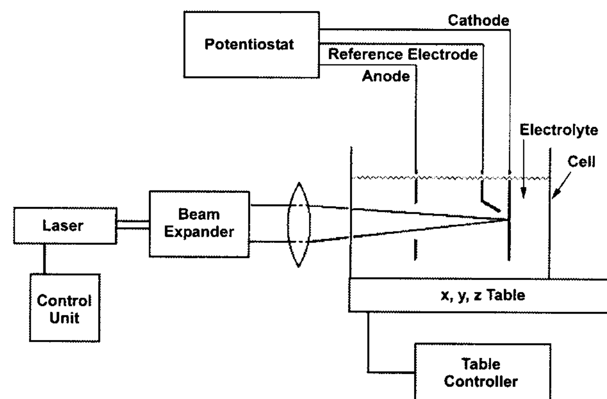


Figure 10. Setup for laser plating Cu. (Adapted from ref 67.)

2. Laser-Enhanced Plating

This process allows Cu to be written directly from a commercial plating solution by precisely heating the desired regions of a substrate with a laser. A schematic diagram of the apparatus used is given in Figure 10.[61] The laser induces a rise in substrate surface temperature, which in turn triggers Cu deposition.[62,63] This subject has been reviewed relatively recently by G. A. Shafeev. Here it will be summarized briefly taking into account recent developments.[64]

Laser-enhanced plating was originally developed by von Gutfeld et al., who observed that a laser beam targeted at a substrate could enhance deposition rates by several orders of magnitude.[61] They established that the enhancement mechanism is thermal rather than photolytic or photon-assisted and performed a series of experiments demonstrating that lasers could enhance plating rates with and without an external power source.[62,65] The initial work involved electroplating Cu from a two-electrode system with a platinum anode and the substrate as the cathode.[62] The substrates plated were dielectrics predeposited with a thin metallic film, which served as the cathode. These electrodes were immersed in acidic plating solutions containing $CuSO_4$, and an argon laser (514.5 nm) was directly incident to the substrate surface. The laser enabled the surface to be heated in a highly localized manner, and local plating rates were enhanced by up to a factor of 10^3.

Regions as small as 4 μm in diameter were achieved and could be defined in this way as well as line features.[62]

von Gutfeld et al. went on to examine laser enhancement in electroless plating systems, in particular exchange-plating systems of Cu ($CuSO_4$ in acidic solution) onto Ni, W, Cr, and Cu.[62] Heating of regions illuminated by the laser enabled these areas to act as cathodes producing a thermobattery effect. This resulted in oxidation and solvation of the less noble metal, with the reduction and deposition of the more noble metal (Cu) onto the surface. The Cu films formed were found to be pore-free, and von Gutfeld et al. proposed this technique for microelectronic circuit repairs.[62]

More recent work in this field centers around laser-enhanced electroless plating of Cu for the fabrication of maskless patterned substrates.[66,67] Electroless plating is an autocatalytic process, i.e., once metal deposition is initiated, it proceeds until the plating solution becomes depleted. Electroless plating solutions generally consist of a Cu(II) complex containing counterions such as tartrate, EDTA, and succinic acid plus an external reducing agent, for example, formaldehyde or hypophosphate.[66] For electroless plating to occur the reduction potential of the reducing agent must be less than that of the metal being deposited. In addition, to achieve anodic oxidation at a reasonable rate the metal must have sufficient catalytic activity. Electroless plating solutions are formulated so that reduction does not take place at ambient temperature. The use of a laser to heat localized regions of a substrate enables reduction of Cu(II) to occur locally without significant background plating.[66]

Chen et al. performed laser-enhanced plating experiments on Si substrates using aqueous $CuSO_4$ with D-glucose as the reducing agent and Cu formate in glycerol solution, where glycerol acts as the reducing agent and prevents oxidation of the growing metal film.[66] The features deposited from the aqueous $CuSO_4$ plating solution were found to have minimum resistivities of 3.6 $\mu\Omega\ cm^{-1}$ and those from the Cu formate glycerol solution 23 $\mu\Omega\ cm^{-1}$. Line widths achieved were in the range of 2−12 μm with thicknesses of 0.25−1.2 μm. In addition, the deposition rates of Cu from the aqueous $CuSO_4$ solution were approximately 5 orders of magnitude faster than those achieved via conventional electroless plating.[66]

Lasers have also been used to produce patterned Cu films from solid Cu formate films.[66,68] The formate ion can serve as a reducing agent, thermally depositing pure metallic Cu films while producing volatile byproducts such as water, CO, and CO_2. Decomposition occurs in the temperature range 190−210 °C. Müller developed an improved method of depositing Cu films via the use of a pulsed Nd:YAG-laser.[68] Previous problems surrounding precursor film preparation, Cu film morphology, feature resolution, and Cu film resistivity were addressed.[68] The primary advantages of this method are that the precursor is nontoxic, so that processing can be performed in air; fabrication becomes easy and inexpensive. High scanning speeds are possible, and low resistivity Cu films are formed.[68]

Laser writing in liquid solution is a newly coined term for laser-enhanced plating with the introduction of CAD (computer-aided design) to directly plate Cu. A solution containing a Cu(II) complex is poured onto a substrate, and a computer-controlled laser is directed at the areas to be autocatalytically electrolessly patterned with Cu.[69] Cu is deposited from the liquid solution by photothermal reduction of a Cu(II) complex. Residual solution is then washed off the substrate.[20,49] Initial reports stated that a thin conducting seed layer was required for metal deposition to occur. More recent papers describe processes that do not require a seed layer.[49,69]

A recent example of laser-induced Cu direct writing from a liquid electrolyte is that given by Kordas et al.[49] They patterned polyimide substrates (Kapton) with Cu using a CW Ar^+ laser beam. In basic solution, they reduced Cu(II) tartrate (T) photothermally with formaldehyde.[49]

The photothermal reaction shown in Figure 11 occurs in solution, and Cu deposits from the reaction mixture. The laser beam also has the effect of thermally breaking bonds at the polyimide surface. This provides further sites for Cu(II) reduction followed by metal deposition on the polymer surface.[49]

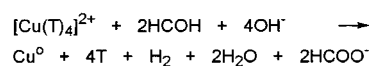

$$[Cu(T)_4]^{2+} + 2HCOH + 4OH^- \longrightarrow Cu^0 + 4T + H_2 + 2H_2O + 2HCOO^-$$

Figure 11. Photothermal reduction of Cu(II) tartrate in solution.

The films prepared adhered well and were conducting with high conformity and could be patterned to a resolution of 2 μm. The lines could be patterned from a width of 30−60 μm and a height of 2−20 μm.[49] Increasing the number of laser scans improved the conductivity of the film. Twenty four scans with a laser power of 10 mW and a scan speed of 25 μm/s produced a 1 mm-long Cu line with a resistance of 1.1 Ω.[49] However, it proved impossible to produce thick Cu patterns due to light scattering from hydrogen bubbles. Contamination of these films is likely to be due to Cu(II) oxide. The lines themselves were coated with oxide.[49] It would seem likely that within the limitations identified this process could be applied commercially for Cu direct write in the foreseeable future.

3. Jet Plating Cu

Jet plating is a direct-write technique for electroplating Cu on conducting substrates. The experimental setup involves an anode being located within or as part of a jet nozzle and an electric current passing through an electrolyte jet stream to the cathode surface.[67] The substrate forms the cathode with electrodeposition occurring only in the regions reached by the jet.[70] Maskless patterning is achieved by moving the sample with respect to the jet stream.[67]

von Gutfeld et al. developed methods to enhance jet-plated Cu film deposits via the use of laser and ultrasound beams.[71,72] Their use of argon ion lasers resulted in Cu films being formed at very high plating rates and with improved film morphologies using the

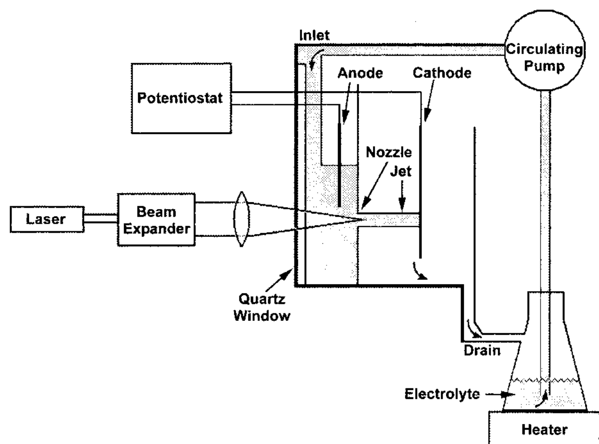


Figure 12. Setup for laser jet plating Cu. (Adapted from ref 67).

experimental setup shown in Figure 12.[71] The electrolyte $CuSO_4$ acidified with H_2SO_4 was jetted onto Ni or Be−Cu substrates. The laser was directed through the jet stream, allowing the jet to act as an optical fiber.[71] The laser did not have any effect on plating rates which were already high since the Cu(II) system plates very efficiently; however, the surface and internal morphologies of the films were found to improve. von Gutfeld et al. theorized and modeled that nucleation rates and metal grain growth were increased thermally with increasing laser power. Lines of Cu with near bulk resistivities have been fabricated with laser-jet plating with deposition rates as high as 50 $\mu m\ s^{-1}$ and plating efficiencies as high as 60% as opposed to 20% for conventional jet plating.[71] von Gutfeld et al. also used 7.5 MHz sound fields directed through the jet stream to plate Cu patterns with similar results to those found for laser-jet plating.[72] Enhancements in the morphology of the Cu films were observed but no increase in plating rate. The improvement in film morphology was attributed to the ability of the acoustic field to lower the diffusion density thickness via microstirring, thereby increasing the limiting current density, particularly effective for films grown at higher current densities. In addition, the reduction in electrical resistivity observed led von Gutfeld et al. to believe that sonic agitation causes closer atom packing in the growing film, resulting in fewer defects.[72]

Jet plating allows Cu lines and individual spots to be directly written onto metallic substrates; it is therefore limited in its usefulness with respect to microelectronic circuit repair and prototyping, since the range of viable substrates is limited. It is however an efficient method of Cu deposition since the plating efficiency can be up to 60%; deposition is fast because of the high current densities possible, and it does not suffer from film contamination problems.[71]

IV. Chemical Vapor Deposition of Cu

A. Depositing Cu Films by CVD

Chemical vapor deposition is a process in which Cu films can be deposited on a substrate, as mentioned in section II.C. A volatile metal−organic precursor is heated until it evaporates and is transported in the vapor phase under high vacuum, sometimes in the presence of a carrier gas, into a reaction chamber to the surface of a heated substrate. The Cu-containing precursor decomposes on the surface of the substrate, resulting in deposition of a metallic Cu film and the formation of volatile organic byproducts.[18,73]

CVD is emerging as an important new technique for Cu deposition in semiconductor device fabrication since it can be performed at lower temperatures than PVD and does not require a seed layer as in electroplating techniques.[2] In addition, selective CVD allows Cu to be deposited preferentially on lithographically patterned regions of substrates, for example, on metal and not on semiconductor surfaces. The advantage of this is that Cu can be deposited directly onto a substrate without the need for a resist mask and all the steps associated with the patterning of Cu films. CVD is also being developed as a Cu direct-write application, in the form of laser-assisted CVD.[48] Since technology is increasingly shifting toward Cu film deposition via CVD, the precursors involved will be reviewed and the associated deposition techniques summarized. For reference, ligand abbreviations are included in section VII.

B. Industrial Requirements

Cu has been cited as the replacement for aluminum in areas of device interconnect.[9] Better electromigration resistance, an improved thermal expansion coefficient, lower resistivity, and a lower tendency to form hillocks are among the main reasons why this change is desired.[4] Manufacturing devices with Cu interconnects instead of aluminum would increase the device operating frequency and allow the use of higher current densities.[9]

Cu has only been considered relatively recently due to some rather fundamental manufacturing problems. Rapid diffusion of Cu into SiO_2 and Si layers poisons the active device area, forming deep acceptor level traps in the forbidden gap.[14] The result of this is a reduction in minority carrier lifetime. A major problem with respect to device manufacture is the lack of a suitable anisotropic, low-temperature, rapid Cu etch process.[14,15] CVD of Cu using precursors containing ligands such as hfac often result in films contaminated with carbon and fluorine. This can considerably reduce the conductivity of the film. Finally, Cu oxide has a lower heat of formation than SiO_2, which results in low thermal stability during annealing, planarization, and etch back processes.

To facilitate the introduction of Cu MOCVD into the microelectronics industry, efforts have been made to address these problems. The development of diffusion barrier layers such as TiN and new dielectric materials will resist Cu diffusion into SiO_2.[1,74] Cu precursors with lower decomposition temperatures and greater ligand stability will minimize film contamination.[5] Selective CVD will circumnavigate etching issues.[15,18] As for the final problem, design of multilevel circuits can incorporate different metals more compatible with silicon for junctions requiring metal−silicon contacts.[75]

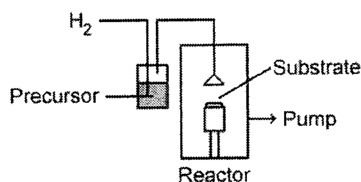


Figure 13. Standard setup for a CVD reactor.

C. Cu MOCVD Techniques

A range of techniques have been developed for MOCVD of Cu; since these have been reviewed previously, they are only outlined here.[2] Thermally induced CVD is by far the most extensively practiced form of CVD. The basic components of a CVD reactor are illustrated in Figure 13. A gaseous precursor is passed over a heated substrate; contact with the hot surface induces precursor decomposition, resulting in Cu film formation. Thermally induced CVD is used to produce blanket and selectively deposited films of good purity and conformity from a wide range of precursors.[18,76] Plasma-assisted CVD may be of use for applications requiring blanket growth at low temperatures with high film growth rates.[77] However, nonselective deposition and poor film conformity are the disadvantages of plasma-assisted CVD.[78] Also, the plasma can cause damage to the underlying substrate.[79] Laser-assisted CVD is potentially useful for direct-write applications; a laser is used to heat a substrate, inducing pyrolysis of the Cu precursor.[48] This technique will be discussed in more detail in section IV.G. Photochemical laser-assisted CVD employs a laser to induce a specific excitation in the Cu precursor, which activates the molecule for subsequent reaction.[80] Aerosol-assisted CVD delivers the precursor into the reaction chamber as a fine spray.[81] Once in the reaction chamber the drop in pressure causes the precursor to evaporate and deposition occurs in the usual way on a heated substrate.

D. CVD Precursor Design Criteria

Forming a Cu film via CVD relies on a Cu complex being delivered to the substrate as a vapor, and the precursor must react with the surface to deposit Cu. Historically, few volatile Cu compounds have been recorded; therefore, to impart volatility in a Cu complex, it is necessary to modify the complex at a molecular level.[82] When designing a Cu CVD precursor, two major criteria have to be considered. The precursor compound must have a high enough vapor pressure to achieve a reasonable rate of mass transport into the reactor.[83] Second, the precursor must be thermally stable at least to its vaporization temperature and should decompose cleanly at its decomposition temperature.[84]

1. Precursor Volatility

The rate-limiting step in the CVD process is frequently the precursor mass transport into the reactor. Film growth will be restricted if the concentration of vaporized precursor is not sufficiently high.[85] To achieve an industrially workable feed rate, the Cu precursor must be a reasonably volatile solid or liquid. General guidelines for selecting a good precursor would be to have a vaporization temperature below 150−200 °C. In recent years precursors have been developed with decomposition temperatures below 200 °C. Vaporization temperatures have also dropped well below 200 °C in order to prevent premature precursor deposition.[85] In addition to facile precursor handling, a lower precursor vaporization temperature allows CVD to be performed on polymeric substrates.[3,86] Previously CVD of Cu could not be performed on polymers due to their relatively low thermal stability. CVD has now been performed on polymers such as poly(imides) and Teflon, both of which are thermally stable above 300 °C. With the aid of CVD, more gentle techniques such as laser-assisted CVD could be used to deposit Cu films on other less thermally stable polymers.

2. Incorporating Volatility into Cu Precursors

For a Cu complex to be volatile it must fulfill three criteria. The first is the molecule should possess little ionic character, i.e., a very small dipole moment is advantageous. The second factor is molecular size, with smaller precursor complexes typically being better in terms of volatility. The final factor is incorporation of functional groups (such as the ubiquitous CF_3) which reduce intermolecular forces and thus increase volatility even further.

Molecules containing strongly ionic bonds and molecules with large dipole moments require vaporization at high temperatures to overcome strong associative intermolecular electrostatic forces.[87] Precursors such as Cu halides have very high vaporization temperatures, the lowest being 350 °C at reduced pressure.[88,89] The first Cu(I) precursors were Cu alkoxides, and these too suffered from volatility problems. Cu(I) *tert*-butoxide can be vaporized at 160 °C but only at a pressure of 10^{-4} Torr.[11] A consequence of high vaporization temperature and subsequent high deposition temperature is that films suffer from a higher incidence of contamination. The answer to this is to use less ionic, less polar organic ligands such as β-diketonates and cyclopentadienes. These ligands not only lower complex vaporization temperatures but also improve complex decomposition and Cu film deposition.[18,73]

Ligands with intrinsically large dipole moments are also to be avoided. Ligands with a single strongly electronegative substituent possess asymmetric electron density distributions, which cause a large dipole moment.[90] This results in strong intermolecular interactions and again increases the vaporization temperature. The most obvious example of this is the introduction of the CF_3 groups to acac. $Cu(acac)_2$ has a vaporization temperature of about 180−200 °C.[80] By introducing one CF_3 group to acac, i.e., $Cu(tfac)_2$, the vaporization temperature is reduced to 135−160 °C.[88] The addition of a further CF_3 group gives hfac; $Cu(hfac)_2$ has an even lower vaporization temperature of 97−120 °C.[82] The addition of a single CF_3 group causes a small increase in the volatility of the precursor. The volatility of the Cu precursor does not dramatically increase until two CF_3 groups are used.

Another clear example of the importance of symmetry within ligands is that of (hfac)Cu(hexyne).

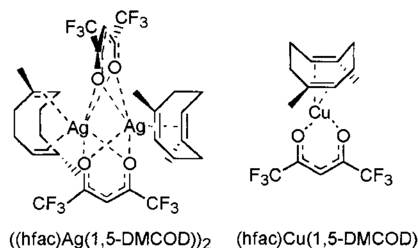


Figure 14. Hydrophobic cage effect caused by 1,5-DM-COD.

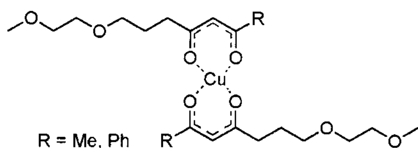


Figure 15. Cu(II) oligoether complexes.

3-Hexyne is symmetrical, and the corresponding precursor has a melting point of −10 °C; however, the precursor with the asymmetric 2-hexyne isomer has a melting point of 35 °C.[91] Asymmetry causes dipole moments in the transition-metal complex, which leads to stronger intermolecular interactions.[91]

Molecular size obviously also affects the volatility of a complex. Small unpolarized ligands with low boiling points are favorable for the formation of volatile complexes.[83] Larger molecules are more prone to internal polarization, but despite this, bulky substituents are frequently introduced into ligands. Intermolecular interactions can result in dimerization or oligomerization of complexes; this also contributes to a reduction in volatility.[11] The use of bulky substituents can prevent aggregation from occurring and thereby counteracts the decrease in volatility. Take (hfac)Cu(COD) as an example, which is an air-stable solid with a melting point of 100−105 °C. By substituting two methyl groups onto cyclooctadiene into the 1 and 5 positions, Doppelt et al. found that (hfac)Cu(1,5-DMCOD) was a organometallic liquid with a melting point of −25 °C.[92] They concluded that this effect could be explained by X-ray crystallographic data they acquired while studying ((hfac)-Ag(1,5-DMCOD))$_2$.[92] As illustrated in Figure 14, the four methyl groups orientate themselves toward the center of the molecule, forming a hydrophobic cage around the metal center. (hfac)Cu(1,5-DMCOD) appears to experience a similar metal isolation effect which minimizes dimerization.[92]

Another attempt to avoid precursor oligomerization is employed in barium CVD complexes. Barium can expand its coordination sphere up to decacoordination while retaining its valence of two. As a result, barium complexes are very hard to volatilize. In an attempt to get around this, Nash et al. used precursors such as bis(8,11-dioxadodecane-2,4-dionato)barium(II), shown in Figure 15.[93,94] The ligand is composed of a β-diketonate and an extended poly(ether) side chain. The side chain was intended to envelop itself around the metal center, thus preventing other ligands entering the coordination sphere of the metal.[95] Unfortunately for the Ba(II) and Cu(II) complexes studied, the poly(ether) chain was found to favor binding another metal rather than chelating its own metal center. These complexes were found to be involatile and decomposed well below their sublimation temperatures.[96]

The introduction of groups such as *tert*-butyl and CF_3 can also improve precursor volatility by reducing van der Waals interactions between molecules.[75,97] Cu(acac)$_2$ has a boiling point of 180−200 °C.[80] Substitution of two *tert*-butyl groups for the two methyl groups, as in Cu(thmd)$_2$ decreases the vaporization temperature to 100 °C (10^{-2} Torr).[98] The change from CH_3 to CF_3 groups as in Cu(hfac)$_2$ reduces the vaporization temperature further to 97 °C.[82] Heavily fluorinated ligands in particular significantly increase complex volatility. CF_3 is a highly electronegative but not a particularly bulky group and effectively acts as a negative point charge. Ligand such as hfac can draw electron density from the d orbitals of Cu, which effects the complex in two specific ways. First, the metal−ligand bond is stabilized by increased metal to ligand back-bonding. Second, the symmetry of hfac allows the positive charges generated through the presence of the electronegative CF_3 to be distributed over the whole ligand. The resulting dipole moment causes the entire molecule to be encapsulated in a positive shield and will therefore repel other precursor molecules and undergo facile vaporization.

3. Precursor Reactivity

Precursor reactivity and ability to deposit high-quality Cu films is determined by the strength of the metal−ligand bond. This bond must be strong enough to survive vaporization yet labile to cleavage at the surface of the heated substrate. Reactivity of the precursor is dictated by the activation energy of decomposition at the substrate surface. For high rates of film growth this activation energy barrier is overcome by heating the substrate surface.[99] Three factors dictate the rate and quality of Cu film growth as the precursor reacts with the surface.[18,85] First, the ability of the precursor to react with the surface. Second, contamination of the growing Cu film through byproducts of precursor ligand decomposition or by diffusion of Cu into the substrate itself.[13,18,100] Finally, by control of the reactivity of the precursor to allow conformant film growth.[100]

When considering the choice of substrate for Cu CVD, it is obviously important to know whether the precursor will actually react with the surface. In this context, precursor selectivity has become an increasingly important avenue of research in recent years. Some precursors will selectively deposit Cu on conductive surfaces such as metals but not on dielectric surfaces, for example, SiO_2.[18] Examples of this are (hfac)Cu(COD), which deposits indiscriminately on both tungsten and SiO_2 surfaces, whereas (hfac)Cu-(VTMS) can selectively deposit on tungsten in the temperature range 120−420 °C.[18,101] Selectivity is clearly determined by the nature of the ligands which surround the metal, and it can also be achieved by exploiting the fact that dielectric surfaces require a higher deposition temperature than conductive materials.[18,79] Therefore, by carefully controlling the substrate temperature, Cu can be deposited selectively on conducting materials.[102]

The purity and resistivity of the deposited film can be adversely affected by two problems: (i) thermal decomposition of ligands such as hfac at the heated substrate surface can leave residual CF_3 in the film, which in turn decomposes to carbon and fluorine, and (ii) high temperatures can also promote the diffusion of Cu into substrates and TiN barrier layers, which is aided by fluorine contamination.[75,100,103−105] These issues provide further incentives to develop Cu precursors with lower decomposition temperatures.

Ideally the precursor also should decompose cleanly in a wide temperature range above its vaporization temperature.[85] Having a broad temperature window for deposition allows greater flexibility in the control of film growth. This is of particular significance for very reactive precursors. Nonconformal film growth can result if a reactive precursor molecule chemisorbs directly with the first point of contact.[106] The precursor is unable to diffuse and reacts evenly over features on the substrate. To achieve higher film conformity it is therefore necessary to lower the deposition rate by either lowering the substrate temperature or designing more thermally inert precursors.[83] The precursor should not react with the walls of the CVD reaction chamber, with deposition occurring only on the surface of the heated substrate. Only the decomposition activation energy barrier and substrate selectivity restricts precursor decomposition at low temperatures. A major problem with precursors such as (hfac)Cu(ATMS) is decomposition below the vaporization temperature.[84,106] Premature decomposition limits the usage of such precursors as it can cause blockages in feed lines, particularly in aerosol-assisted CVD.[84]

4. Controlling Precursor Reactivity

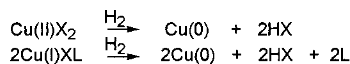
Precursor reactivity is determined by the nature of the Cu complex, in particular the oxidation state of Cu and the ligands used to chelate the metal center. The effect the metal species has in the reactivity of Cu CVD precursors will be examined first followed by the role of the ligands.

Cu has three common oxidation states 0, +1, and +2, but only Cu(I) and Cu(II) complexes are used as CVD precursors. CVD is unlikely to be performed with the few known Cu(0) complexes. Such complexes very extremely unstable and decompose at very low temperatures.[107] Cu(0) carbonyls, for example, Cu-$(CO)_n$ (where $n = 1, 2, 3$), have been prepared at very low temperatures and were found to photochemically decompose at 20 K.[107]

The mechanism of the decomposition reaction plays an important part in designing Cu(I) or Cu(II) precursors in terms of decomposition temperature and reactivity. The precursor can be reduced from Cu(I) or Cu(II), in the presence of a carrier gas such as hydrogen, to metallic Cu. Complexes whose decomposition follows this pathway are generally less reactive as precursors and require higher decomposition temperature.[108,109] Some more labile Cu(I) complexes, however, can decompose via another pathway, namely, disproportionation.[110]

In Figure 16 X represents a singly negatively charged ligand such as hfac and L is a Lewis base ligand. Disproportionation allows facile deposition of Cu because Cu(I) precursors are kinetically trapped but are thermodynamically unstable. The Lewis base ligand aids complex stabilization by donating electron density into the d^{10} of Cu(I).[111]

Copper deposition via the reduction mechanism:



Copper deposition via disproportionation:

Figure 16. Deposition mechanisms of Cu(II) and Cu(I) CVD precursors.

The choice of ligands in CVD is of critical importance for the effectiveness of the complex as a precursor. The most important, the most common, and the most promising novel precursor ligands will be examined in more detail in section IV.E.

E. Review of Cu Precursor Ligands

The precursors, and their ligands, surveyed are divided into two sections, those with a Cu(II) metal center and those with Cu(I) centers. The synthesis of these ligands is not discussed; instead, their performance as Cu precursors i.e., their volatilities and decomposition properties, are analyzed.

1. Cu(II) Precursors

Cu(II) CVD precursors have been extensively researched since Van Hemert et al. first reported them in 1965.[82] Despite being superseded by Cu(I) complexes in recent years, Cu(II) precursors remain a viable option for the deposition of Cu films.[77,112] The various Cu(II) precursor complexes will be discussed in terms of the ligands employed to chelate the metal center.

Cu(II) Bis(β-diketonate) Precursors. The most commonly used ligands in Cu(II) precursors are β-diketonates, in particular, the commercially available β-diketonates with heavily fluorinated substituents or bulky *tert*-butyl groups. The Cu precursors of these ligands generally evaporate below 200 °C and under optimized reaction conditions decompose without ligand decomposition.

The complexes illustrated in Figure 17 have simple four-coordinate square-planar geometries.[82] In some cases these complexes can exist in hydrated forms, when the metal center is not surrounded with bulky substituents. A water molecule can bind to an available coordination site to form pentacoordinated Cu. For example, $Cu(hfac)_2{\cdot}H_2O$ and $Cu(hfac)_2$ are colored differently (purple vs green) and possess different melting points (95−98 °C vs 133−136 °C).[82] In terms of the CVD of these complexes, they exhibit differences in deposition rates and substrate selectivities.[11]

By far the most important Cu CVD ligand for both Cu(I) and Cu(II) precursors is 1,1,1,5,5,5-hexafluoroacetylacetone. CVD with $Cu(hfac)_2{\cdot}H_2O$ was first reported along with $Cu(tfac)_2$ by van Hemert et al.[82] $Cu(hfac)_2$ has low toxicity, is soluble in organic solvents, and has a relatively high vapor pressure of 10^{-2} Torr at 300 K.[113] The hfac ligand imparts

Table 2. Studies of Cu CVD Using $Cu(hfac)_2$ and $Cu(hfac)_2 \cdot H_2O$[82]

precursor	evaporation temp (°C)	deposition rate (nm/min)	carrier gas	reactor pressure (Torr)	deposition temp (°C)	film resistivity ($\mu\Omega$ cm^{-1})
$Cu(hfac)_2$	120	4	Ar	760	340−390	3−6
$Cu(hfac)_2 \cdot H_2O$	30−60	10	H_2	10^{-3}−760	250−350	1.9−2.8

Table 3. Studies of Common Cu(II) Bis(β-diketonate) and Cu(II) (β-Ketoiminate) CVD Precursors[75,82,88,98,117,178,179]

precursor	evaporation temp (°C)	deposition temp (°C)	carrier gas	reactor pressure (Torr)
$Cu(hfac)_2$	120	340−390	Ar	760
$Cu(tfac)_2$	135−160	250−300	H_2	760
$Cu(acac)_2$	180−200	225−250	H_2/Ar	760
$Cu(thmd)_2$	100	400	None	$< 10^{-2}$
$Cu(ppm)_2$	100	400	None	<0.3
$Cu(fod)_2$	-	300−400	H_2	10^{-3}−760
$Cu(acim)_2$	287	400	H_2	730
Cu(acen)	204	450	H_2	730
$Cu(nona\text{-}F)_2$	85−105	270−350	H_2	10−70

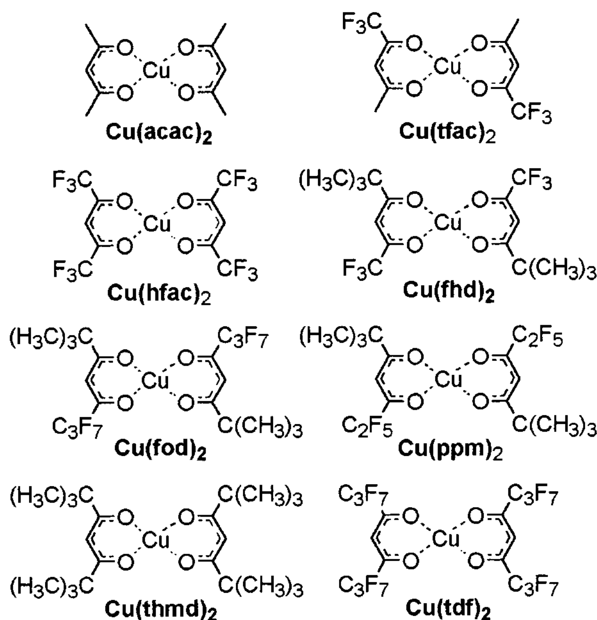


Figure 17. Selection of common Cu(II) bis(β-diketonate) precursors.

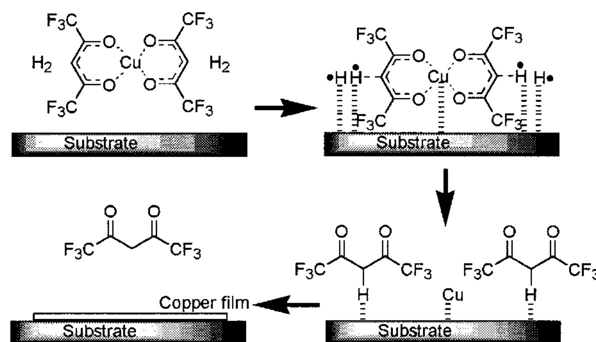


Figure 18. Cu deposition by a Cu(II) CVD precursor.

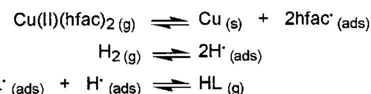


Figure 19. Detected surface intermediates in Cu(II) CVD.

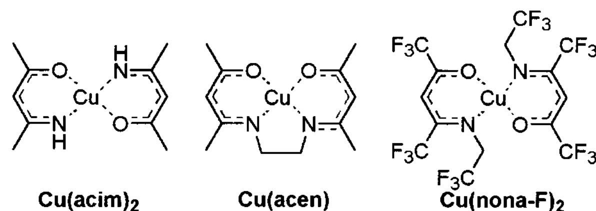


Figure 20. Cu(II) bis(β-ketoiminate) CVD precursors.

extraordinary volatility to $Cu(hfac)_2$ by shielding the metal center from intermolecular interactions.[113] The hfac ligand stabilizes the complex and allows facile thermal reduction of Cu(II) by, for example, hydrogen gas; CVD studies involving $Cu(hfac)_2$ are included in Table 2.[82,113]

In terms of deposition mechanism $Cu(hfac)_2$, like all Cu(II) precursors, deposits Cu films via reduction of Cu(II) followed by ligand dissociation.[114] Figure 18 illustrates a possible reaction mechanism of Cu deposition. It is only a schematic representation, and the ligands around the metal center are, more probably, perpendicular to the surface. Further research into the decomposition mechanism of Cu(II) CVD precursors is required to clarify surface-bound intermediate species.

Experimental data from kinetic studies would indicate the surface intermediates and reaction steps in Figure 19 are involved in Cu(II) CVD.[114,115] CVD experiments involving other β-diketonate Cu(II) precursors are presented in Table 3.

Schiff's Base Cu(II) Precursors. Figure 20 illustrates the first two reported β-ketoiminate Cu(II) CVD precursors and $Cu(nona\text{-}F)_2$. $Cu(nona\text{-}F)_2$ is the only Schiff's base precursor of real practical use in Cu CVD. $Cu(acim)_2$ and Cu(acen) can be reduced with hydrogen carrier gas but require very high decomposition temperatures.[116] $Cu(nona\text{-}F)_2$, first reported by Fine et al., and can deposit Cu on substrates in a more viable temperature range.[117] At reduced pressure it displays a reasonable vapor pressure and evaporation temperature. Cu films deposited by $Cu(nona\text{-}F)_2$ have been found to possess very low resistivities (2.1 $\mu\Omega$ cm^{-1}).[117] CVD experimental data involving these precursors are presented in Table 3.

Cu(II) Bis(β-ketoesterate) Precursors. Two variations of the β-ketoesterate ligand theme have been prepared for use as Cu(II) CVD ligands, as shown in Figure 21. Hwang et al. (1996) prepared a range of Cu(II) bis(β-ketoesterate) complexes by varying the substituent on the esterate functionality.[118,119] Guillon et al. prepared $Cu(mpa)_2$ with a *tert*-

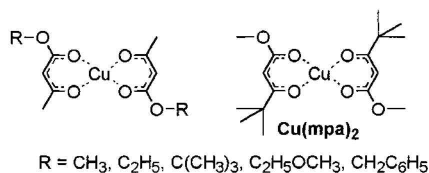


Figure 21. Cu(II) bis(β-ketoesterate) CVD precursors.

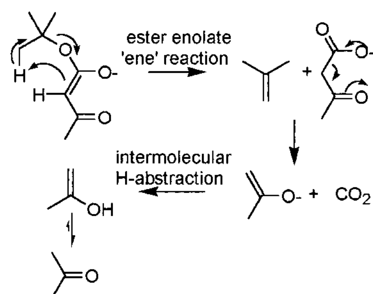


Figure 22. Proposed pyrolysis mechanism of btac during Cu CVD.[122]

butyl group on the ketonate functionality.[120] They used this precursor to deposit Cu oxide films instead of Cu films, as contamination occurs due to partial decomposition of the ligands. The TGA data acquired for $Cu(mpa)_2$ indicated a weight loss of 62% in the interval between 150 and 255 °C followed by a further 15% weight loss at 255–340 °C.[120] Guillon et al. concluded that this was due to clean loss of the first ligand and subsequent partial decomposition of the second.[120,121] Devi et al. (1998) researched the decomposition mechanism of $Cu(tbac)_2$ (R = $C(CH_3)_3$).[122,123] They proposed that pyrolysis at low temperature takes place via a thermal "ene"-type reaction in a concerted pathway that deposited Cu and produced volatile organic byproducts.

Facile ligand decomposition is caused by differences in strengths of the Cu–carbonyl ligand bonds. The esterate bond is weaker than the ketonate bond. The *tert*-butyl esterate triggers decomposition via the mechanism shown in Figure 22. This concerted mechanism is driven by the formation of small volatile organic species; in particular, the ketonate–Cu bond is labile to cleavage as this process yields acetone.[122]

Hwang et al. (1996) investigated plasma-enhanced CVD using $Cu(etac)_2$ (where R = Et, from Figure 21).[4] Cu films of high purity (resistivity = 2 $\mu\Omega$ cm^{-1}) were deposited on substrates such as TiW and SiO_2.[124] Optimum processing conditions were in the range of substrate temperature at 220 °C, precursor temperature at 140 °C, plasma power of 17 W, and reactor pressure at 0.8 Torr.[4] TGA analysis of $Cu(etac)_2$ revealed only two transition temperatures, at approximately 200 and 300 °C. The first was assigned to the melting point of the sample; the second was due to exothermic ligand dissociation.[4,125] Ligand decomposition was not reported.[4,125] Hwang et al. (1996) also carried out CVD with a range of other Cu(II) bis(β-ketoesterate) complexes, some of whose properties are shown in Table 4.[118]

Ethanolamine Derivatives of $Cu(hfac)_2$. Film growth rates have been known to increase, particularly at higher temperatures, when CVD was performed in the presence of water and gas-phase alcohols.[126] Two reasons have been proposed to explain this phenomenon. First, more volatile $Cu(hfac)_2$·alcohol complexes will enhance the rate of precursor transport into the reactor. Second, alcohols may serve as reducing agents for $Cu(hfac)_2$. Attempts were made to synthesize alcohol adducts of $Cu(hfac)_2$; however, these precursors were found to be unstable at reduced pressure.[126] Subsequently attention was focused toward the development of $Cu(hfac)_2$ ethanolamine derivatives, some are illustrated in Figure 23. The hfac ligand would impart volatility to the complex, and the alcohol-containing substituent would facilitate reduction without the need for a reducing carrier gas. Ammonia adducts were found to be relatively stable to CVD conditions. Therefore, by using ethanolamine-based ligands, the amino functionality stabilizes the complex and the alcohol acts as a reductant.[126]

Table 4. Physical Properties of Cu(II) Bis(β-ketoesterate) Precursors[118]

precursor	melting point (°C)	vaporization temp (°C/0.16 Torr)
$Cu(mtac)_2$	194	112
$Cu(etac)_2$	192	108
$Cu(meta)_2$	117	97
$Cu(btac)_2$	92	88
$Cu(beac)_2$	125	108

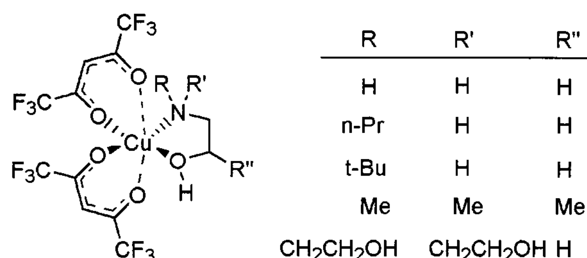


Figure 23. Some ethanolamine derivatives of $Cu(hfac)_2$.[126]

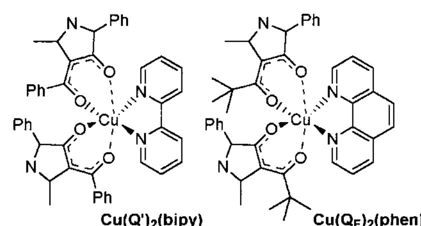


Figure 24. Cu(II) bis(heterocyclic β-diketonates) precursors.

Of the ethanolamine ligands explored by Pinkas et al., the most promising precursor was found to be $Cu(hfac)_2{\cdot}N(CH_3)_2CH_2CHOHCH_3$ (R = R′ = R″ = Me, Figure 23) containing a secondary alcohol functionality. This precursor deposits Cu at 300 °C without the need for the presence of a carrier gas.[126]

Cu(II) Bis(heterocyclic β-diketonates) Precursors. These novel precursors synthesized by Drozdov et al. are based around 4-acylpyrazolones ligands, illustrated in Figure 24.[127,128] These precursors are of interest because they possess an additional donor center. Nitrogen atoms can become involved in secondary bonding interactions, which can induce quite different reactivities to conventional β-diketonates.

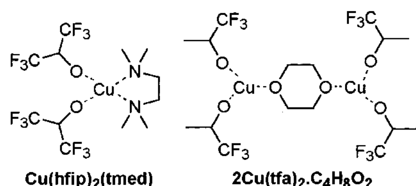


Figure 25. Fluoroalkoxide Cu(II) precursors.

Despite their claims that these precursors are volatile, volatilization did not occur below 190−225 °C at 10^{-2} Torr as reported. Decomposition temperatures were not reported in this publication.[127] Complexes of this nature could be further investigated with, for example, fluorinated substituents to reduce molecular size and improve volatility.

Cu(II) Fluoroalkoxide Precursors. Several precursors of this nature have been synthesized. The two shown in Figure 25 are the only ones which show promise as CVD precursors.[11,129]

Both of these precursors are stable at room temperature in water and in a range of organic solvents. $Cu(hfip)_2(tmed)$ possesses reasonable volatility; it melts at 105−108 °C and sublimes at 75 °C (10^{-5} Torr). The dimeric 1,4-dioxan adduct of $Cu(tfa)_2$ was reported by Krupoder et al.[130] No extensive investigation of CVD with this precursor has been reported; however, vaporization occurs below 100 °C and thermal decomposition at 230 °C.

In conclusion, although Cu CVD has moved away from the use of Cu(II) precursors, complexes such as $Cu(hfac)_2$ have retained their importance in Cu film deposition. $Cu(hfac)_2$ has proved so effective and is so well-understood as a precursor that investigations continue to this day to further optimize its film-forming ability. $Cu(hfac)_2$ is in fact a byproduct of the disproportionation mechanism of Cu(I)(hfac)(L) precursors.[18] Therefore, understanding reactivity and decomposition at substrate surfaces continues to be vital in the development of Cu(I) precursor CVD.

2. Cu(I) Precursors

Cu(I) metal centers are significantly softer (more weakly acidic) than Cu(II) centers. Consequently, Cu(I) is more likely to form stronger bonds with softer ligands (large, easily polarizable with low electronegativity). Ligands containing basic functionalities such as phosphorus, sulfur, alkenes, and alkynes are particularly favored in terms of Cu(I) CVD.[2] Cu(I) has a complete 3d subshell and is therefore considered analogous to a monovalent main-group cation. The occupancy and hybridization of s and p orbitals dictate ligand coordination geometry.

Cu(I) CVD precursors can be divided into two classes, CuX and $XCuL_n$, where X is a singly charged anionic ligand and L is a neutral Lewis base electron pair donor ligand. The Cu(I) complexes examined in this section have all been used in and are effective as Cu(I) CVD precursors.

CuX_n Precursors. Cu(I) precursors of the form CuX generally suffer from low vapor pressures due to extensive oligomerization at the singly coordinated metal center, as shown in Figure 26.

$[Cu(O\text{-}t\text{-}Bu)]_4$ is known to exist as a tetramer. Blocking a coordination site can reduce oligomerization, for example, $[(O\text{-}t\text{-}Bu)CuPPh_3]_2$ exists in the solid state as a dimer.[11] $[Cu(OSi\text{-}t\text{-}Bu_3)]_4$ vaporizes at 160 °C (10^{-2} Torr), and thermal homolytic Cu−O bond cleavage yields Cu and tri-*tert*-butylsilyloxide radicals which later convert to stable silyl alcohols.[131] Precursors of this type are more commonly used in the formation of Cu oxide films.[87] This is due to the high incidence of film contamination with oxygen, caused by the homolysis of C−O or Si−O bonds.

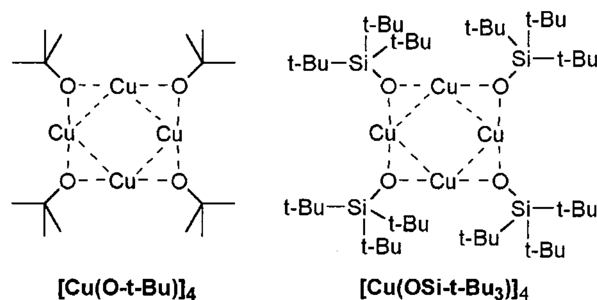


Figure 26. Cu(I) alkoxide and siloxide CVD precursors.

$XCuL_n$ Precursors. These can be further divided into six sections, (β-diketonate)CuL, (cyclopentadienyl)CuL, (β-ketoiminate)CuL, $[(RO)CuL]_n$, (β-diketonate)CuL_2, and (halide)CuL_2. The principal $XCuL_n$ precursors from each category of ligands are listed in Figure 27. Selected examples of $XCuL_n$ precursors will be discussed later.

Figure 27 illustrates the wide range of ligands available for designing Cu(I) CVD complexes. The role of cyclopentadienyl ligands will be examined in this section. In addition, (β-diketonate)CuL_n, (β-ketoiminate)CuL, and (β-ketoesterate)CuL precursors will be discussed. The stabilizing ability of Lewis base in Cu(I) precursors will be examined using the (hfac)CuL complexes as examples.

Cyclopentadienyl Cu(I)L Precursors. The cyclopentadienyl anion was investigated as a possible solution to the detrimental tendency of oligomerization and oxygen and fluorine contamination problems experienced with Cu(I) alkoxide precursors.[109,132] The cyclopentadienyl anion is a bulky group which can occupy three coordination sites around the metal center resulting in these precursors being monomeric. The η^5 metal−ligand bond is a relatively strong bond, which makes these precursors more thermally stable.[5,11] As a result of this and because of their low volatilities, these precursors cannot compete with precursors such as (hfac)Cu(VTMS). For example, the conditions required for CVD with $(\eta^5\text{-}C_5H_5)Cu[P(CH_3)_3]$ in a hot wall reactor are at 1 mTorr, vaporization at 60 °C, substrate temperature 400 °C (Pt, SiO_2).[133] Cu is deposited on the surface via thermally induced reduction of Cu(I) by its ligand or a carrier gas. Many Cu(I) precursors deposit Cu in this way. More recently deposition through this mechanism is being avoided in favor of the disproportionation mechanism. The mechanism of decomposition for cyclopentadienyl Cu(I) precursors is illustrated below as an example of thermal decomposition.

The electron-rich nature of the cyclopentadienyl ring allows facile electron transfer to the Cu(I) center; therefore, no reductant carrier gas is required. By

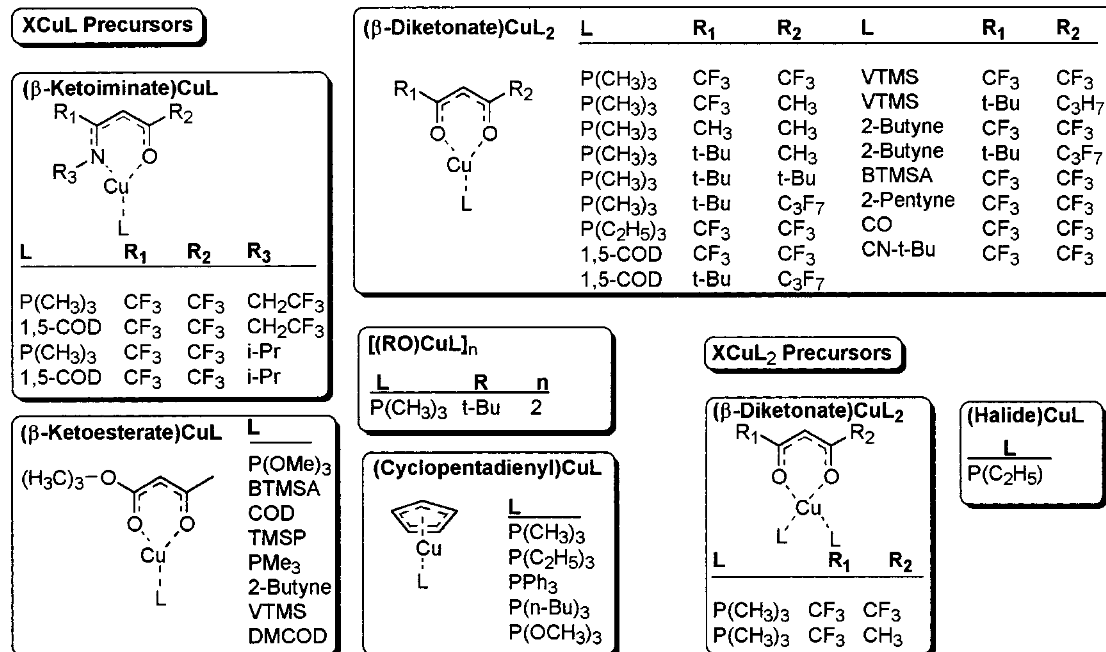


Figure 27. Selection of Cu(I) precursors.[2]

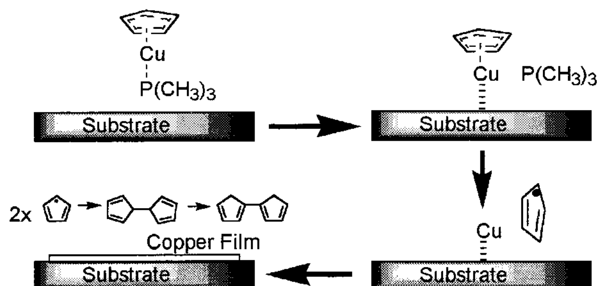


Figure 28. Proposed mechanism of Cu deposition from (Cp)Cu(P(Me)$_3$).

isolating the reaction byproducts the mechanism was derived, see Figure 28. Cyclopentadiene, 9,10-dihydrofulvalene, trimethyl phosphene, and trimethyl phosphenous oxide were isolated.[133−135] 9,10-Dihydrofulvalene is unlikely to be the kinetic product, C_5H_5. 9,10-Dihydrofulvalene is probably formed via radical combination of two $C_5H_5^{\bullet}$ reacting to give 1,5-dihydrofulvalene with subsequently rearranges.[136] Metal bond homolysis frequently leads to film contamination with carbon.[133] Despite this, cyclopentadienyl Cu(I) precursors were originally favored as nonfluorinated complexes, eliminating the problem of fluorine contamination.[11,137]

***β*-Diketonate Cu(I)L$_n$ Precursors.** *β*-Diketonates have been used as widely in the preparation of Cu(I) precursors as they have in Cu(II) precursors. Many of the anionic *β*-diketonate ligands illustrated in Figure 17 have been used in conjunction with Lewis bases for Cu(I) precursors. To examine the effect of both types of ligands, *β*-diketonate Cu(I) L$_n$ precursors will be used to illustrate the effects observed as one ligand is varied while the other is kept the same. To examine the CVD performances of *β*-diketonate ligands, (*β*-diketonate)Cu(PMe$_3$) precursors will be assessed. The CVD of (hfac)Cu(Lewis base) precursors will be used as an example of the trends observed as Lewis base ligands are varied. In

Table 5. Cu Film Deposition Data for (*β*-Diketonate)Cu(PMe)$_3$ Precursors[138,151]

precursor	evaporation temp (°C)	pressure (Torr)	deposition temp (°C)
(hfac)Cu(PMe$_3$)	30	6×10^{-2}	150−300
(tfac)Cu(PMe$_3$)	50	10	100−150
(acac)Cu(PMe$_3$)	23	10^{-4}	<80
(fod)Cu(PMe$_3$)	40	10^{-2}	150−300

surveying the wide range of Lewis base ligands used in Cu(I) CVD precursors, we have divided them into three sections depending on their Lewis base functionality. The classification of ligands used here is olefins, alkynes, and miscellaneous.

Effect of *β*-Diketonate Ligand on Precursor Performance. (*β*-Diketonate)Cu(PMe)$_3$ precursors were among the first Cu(I) precursors investigated for CVD. A variety of *β*-diketonates were employed to synthesize a range of precursors providing insight into the effect of the *β*-diketonate ligand.

In Table 5 are the results of CVD studies into (*β*-diketonate)Cu(PMe$_3$) precursors. These results indicate that *β*-diketones as ligands for Cu(I) CVD are very effective. When compared to cyclopentadienyl and alkoxide ligands, evaporation temperatures are very low and film deposition is possible at temperatures well below 300 °C.[138] However, of the various Cu(I) precursors prepared to date, one ligand stands far above the rest in terms of precursor stability, volatility, and CVD film-forming ability. 1,1,1,5,5,5-Hexafluoroacetylacetone is by far the most widely employed ligand for both Cu(I) and Cu(II) precursors. Investigations into other *β*-diketonate ligands have been limited since ligands such as tfac, acac, and fod do not yield Cu(I) precursors with sufficient thermal stability for reliable CVD. (acac)Cu(COD), for example, is not stable in solution above −30 °C.[90]

Olefins as Lewis Base Ligands. Olefins are very soft electron donor ligands; the Cu(I)−olefin bond is quite labile as a result of this.[139−141] Precursors

Table 6. CVD Studies of Cu(I) Precursors[18,83,91,100,151,152,155,161,162,166,180]

precursor	evaporation temp (°C)	deposition temp (°C)	reactor pressure (Torr)
(hfac)Cu(VTMS)	50	75−420	0.1
(hfac)Cu(ATMS)	40	50−70	1−3
(hfac)Cu(VCH)	45	150−200	0.3
(hfac)Cu(MP)	35	150−200	0.3
(hfac)Cu(DMB)	45	150−200	0.3
(hfac)Cu(COD)	62	150−250	0.007
(hfac)Cu(1,3-butadiene)	a	30−40	760
(hfac)Cu(DMCOD)	62	150−250	0.135
(hfac)Cu(MHY)	45	120−220	0.1
(hfac)Cu(BTMSA)	60	130−225	0.3
(hfac)Cu(2-butyne)	60	150−225	0.3
(hfac)Cu(TF-TMSP)	45	100−400	0.05
(btac)Cu[P(OMe)$_3$]	33	120	0.1
(btac)Cu(BTMSA)	58	95	b
(btac)Cu(COD)	77	130	0.05
(btac)Cu(TMSP)	b	75	b
(btac)Cu(P(Me)$_3$)	b	63	b
(btac)Cu(2-butyne)	50	70	0.1
(btac)Cu(VTMS)	52	55	0.1
(btac)Cu(DMCOD)	b	60	b
(iihfac)Cu(PMe$_3$)	45	150−250	10^{-2}
(nona-F)Cu(PMe$_3$)	35	150−250	10^{-2}

[a] Could not be measured due to decompostion of the precursor, [b] No data quota.

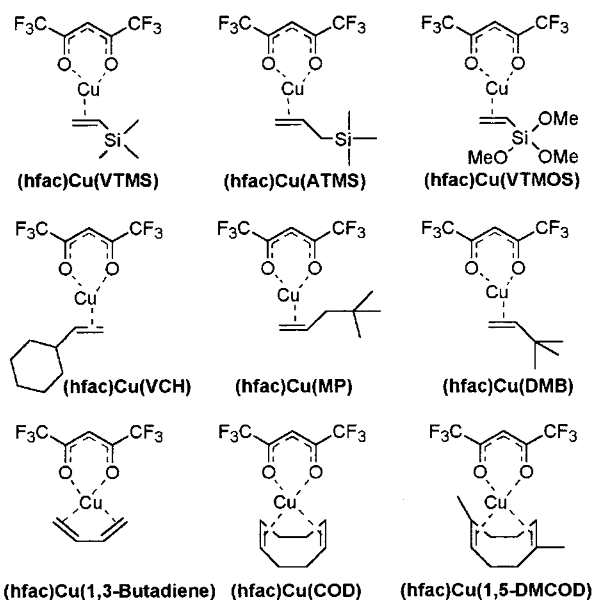


Figure 29. Lewis base ligands used in combination with (hfac)Cu.

stabilized by an olefin Lewis base exhibit high reactivity at substrate surfaces. With an appropriate counterion ligand these precursors can undergo Cu deposition via disproportionation.[83,142−145] The most successful olefin CVD ligands reported so far are VTMS, ATMS, VTMOS, VCH, MP, DMB, 1,3-butadiene, COD, and DMCOD, as show in Figure 29. All of the (hfac)CuL precursors included in Table 6 undergo atmospheric pressure vaporization at very low temperatures and deposit Cu of high purity below 200 °C.

Vinyl functionality accompanied by bulky yet volatile substituents yields precursors with high volatility and very low decomposition temperatures.[18] All the precursors shown in Table 6 are liquids, with the exception of (hfac)Cu(COD). These precursors readily decompose via disproportionation. This mechanism is illustrated in Figure 30 on the example of (hfac)-Cu(VTMS).

(hfac)Cu(VTMS) is by far the most important Cu(I) precursor developed to date. It is a distillable liquid, stable at ambient temperature, but is very moisture and air sensitive.[18] The weak η^2-olefin−metal bond undergoes facile cleavage at the surface, releasing vinyltrimethylsilane (bp = 55 °C) as illustrated schematically in Figure 30. Disproportionation occurs between two neighboring (hfac)Cu moieties resulting in the deposition of Cu(0) and formation of volatile Cu(hfac)$_2$.[7] Heating the substrate drives off Cu(hfac)$_2$ without decomposition.[8]

Contamination of films formed by (hfac)Cu(VTMS) (temperature range 75−175 °C) was found to be due to carbon, fluorine, and oxygen impurities. These result from hfac ligand decomposition in the growing Cu film.[84] Ar^+ sputtering was found to remove these impurities, so film contamination is of a superficial nature.[13,103] Auger depth profiling of contamination depth reveals that contamination was indeed restricted to the top layer. Film resistivities were found to be as low as 1.68 $\mu\Omega$ cm^{-1}, which approaches that of bulk Cu.[8] Analysis of film morphology was achieved by SEM, AES, and AFM techniques. The low film resistivities were explained by the smooth, closely connected film grain structure; both small and fine crystals were observed. Film growth was believed to follow 3D-island growth (Volmer−Weber growth) rather than layer by layer growth.[103,104] This is due to slow diffusion of the precursor; with increased temperature grains become larger, rougher, and coalescence can occur.[84] The effect that postannealing has on the effectiveness of TiN barrier layers has also been investigated. Annealing at 500 °C improves film morphology and electronic characteristics; above this temperature rapid degradation of the barrier layer occurs.[105]

(hfac)Cu(ATMS) was synthesized to lower the precursor vaporization and decomposition temperatures even further.[84] Films with resistivities as low

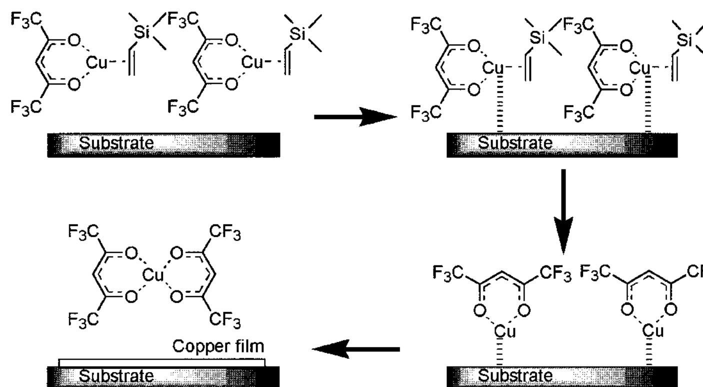


Figure 30. Possible mechanism of Cu(I) precursor disproportionation.

as 1.7−1.9 $\mu\Omega$ cm^{-1} have been grown by CVD of (hfac)Cu(ATMS).[84,106] However, decomposition can occur at temperatures as low as 40 °C; therefore, this is an exceptionally difficult precursor to work with, and feed lines are at constant risk of becoming blocked. Attempts at CVD of this precursor at higher temperatures have resulted in the formation of rough, poorly conducting films. This is caused by the high rate of the surface reaction. Higher rates of mass transfer result in less controlled film growth.[106]

Precursors such as (hfac)Cu(MP) and (hfac)Cu(DMB) offer Cu deposition rates that are between 4 and 7 times faster than those of (hfac)Cu(VTMS).[83,146] They also possess low vaporization temperatures and deposit excellent quality films in the temperature range 150−200 °C (2.0−2.2 $\mu\Omega$ cm^{-1}).[147]

Of the precursors mentioned in Table 6, (hfac)Cu(COD) is the most practical to be handled in a laboratory.[90,148,149] This compound is a solid, can be purified by recrystallization, is only moderately air sensitive, and has a reasonable shelf life. Workable (hfac)Cu(COD) vapor pressures can be achieved at temperatures as low as 70 °C.[150] Deposition can be performed on substrates at 120−250 °C (3 mTorr) producing films with resistivities of 1.9−2.2 $\mu\Omega$ cm^{-1}.[99,101,151,152]

Alkynes as Lewis Base Ligands. Alkynes are very effective electron donor ligands. They have the ability to stabilize Cu(I) metal centers via η^2-metal ligand bonding.[153] Being more electron rich than olefins, they bond more strongly to Cu(I) and are therefore more stable. X-ray crystallography revealed that these complexes are essentially planar, with a slight alkyl distortion, bending the substituents away from the metal center.[153] There is strong electron donation from π-electrons of the alkyne but minimal back-donation from metal d-orbitals to the ligand. All of these complexes undergo Cu deposition via the disproportionation mechanism.[154] A large range of alkynes has been investigated as Lewis base ligands, and CVD studies of precursors involving alkynes are listed in Table 6. The substituents on the triple bond range from alkyl groups ((hfac)Cu(2-butyne)) to trimethyl silyl groups ((hfac)Cu(BTMSA)), CF_3 groups ((hfac)Cu(TF-TMSP), phenyl groups ((hfac)Cu(B-PhA)), and even alkenes ((hfac)Cu(MHY)). Some of these are illustrated in Figure 31.[153,155]

(hfac)Cu(HFB) cannot be isolated because the C−C triple bond is deactivated to the extent that it can

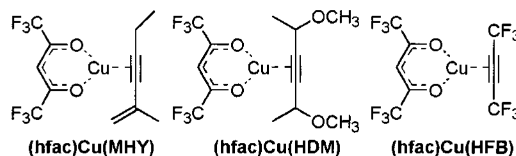


Figure 31. Cu(I) alkyne complexes.

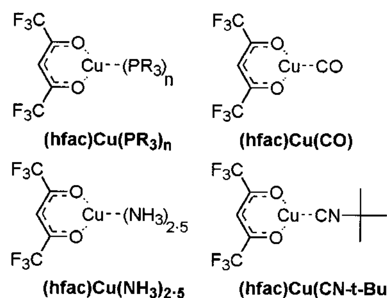


Figure 32. Other Lewis base ligands used in Cu(I) CVD.

no longer stabilize the Cu(I) β-diketonate complex.[111] (hfac)Cu(MHY) is another promising liquid precursor candidate for low-temperature CVD, in particular in photo-MOCVD.[155]

Miscellaneous Lewis Base Ligands. Three other types of (hfac)CuL_n precursor are worth mentioning, those with L = trialkyl phosphenes, carbonyl, and ammonia; some are shown in Figure 32. These precursors also undergo thermally induced disproportionation to form high-quality Cu films.[156] (hfac)Cu(CO), (hfac)Cu(CN-*t*-Bu), and (hfac)Cu(NH_3)$_{2.5}$ have not been investigated in detail to explore their potential as CVD precursors.[90,137,157,158]

A wide range of trialkyl and trialkoxyl phosphenes was synthesized, particularly in the early 1990s.[110,157] In recent years these precursors have become less attractive compared with new low-temperature precursors such as (hfac)Cu(VTMS). Nonetheless, (hfac)Cu(P(CH_3)$_3$) can deposit high-purity Cu films on substrates at 150−400 °C with a reactor pressure at 1 mTorr and with precursor evaporation at 45−50 °C.[159]

(hfac)Cu(CN-*t*-Bu) was incorporated into a chemical dry etch process described by Kruck et al.[16] This process involves first the removal of Cu from a substrate, oxidation of Cu to Cu_2O using O_2, and following this reaction with Hhfac and CN-*t*-Bu to give the Cu(I) species (hfac)Cu(CN-*t*-Bu). (hfac)Cu(CN-*t*-Bu) is robust enough to be stable to 170 °C, and it is stable toward oxygen.[16]

Etching studies performed at 200 mbar in a cold wall CVD reactor at 150 °C showed that Cu could be cleanly etched from the substrate surface at rates of more than 4.5 mg/cm^2 h via the reaction shown in Figure 33.[16] This process was performed in the temperature range 90−160 °C. Chemical etch processes of this nature could improve on dry etching of Cu via the use of reversed CVD reactions, illustrated in Figure 34. Using BTMSA as the neutral ligand, Farkas et al. etched Cu films at 390 K with etch rates of 50 nm min^{-1}.[160]

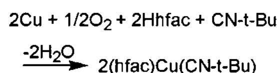


Figure 33. Chemical etching of Cu via formation of (hfac)-Cu(CN-*t*-Bu).

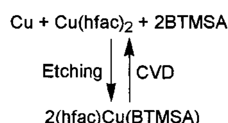


Figure 34. Dry etching of Cu.

Higher temperature Cu(I) CVD precursors incorporating Lewis base ligands such as phosphenes and isonitriles continue to be investigated for Cu etching. Their higher decomposition temperatures and greater stability make them ideal for surface etching processes.

(β-Ketoesterate) Cu(I)L Precursors. Choi et al. recently reported a series of (β-ketoesterate)Cu(I)L precursors of the form illustrated in Figure 35.[161] In contrast to the hfac ligand, which has been the backbone of Cu(I) CVD, ligands such as *tert*-butyl 3-oxobutanoate are nonfluorinated and impart high stability and, at the same time, volatility to Cu(I) complexes. Choi et al. synthesized (*tert*-butyl 3-oxobutanoate)Cu(L) complexes, where L = $P(OCH_3)_3$, BTMSA, COD, TMSP, PCH_3, 2-butyne, VTMS, and DMCOD. They reported that all of these complexes undergo disproportionation to form Cu films. CVD conditions are given in Table 6.[161] (btac)Cu($P(OCH_3)_3$), (btac)Cu(COD), and (btac)Cu(BTMSA) were the most stable complexes, even in air. This makes them far more easy to handle than (hfac)Cu(VTMS). Indeed, even the least stable of these complexes, (btac)Cu-(2-butyne), (btac)Cu(DMCOD), and (btac)Cu(VTMS), were more stable than their (hfac)Cu analogues. Films produced by selective growth with (hfac)Cu-(VTMS) do not give satisfactory reproducibility. A more stable liquid precursor would be desirable for CVD of Cu, and these β-ketoesterate seem to be interesting candidates.[161]

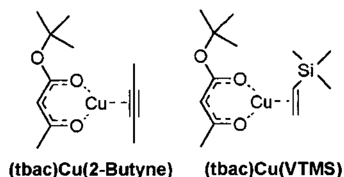


Figure 35. Two examples of Cu(I) β-ketoesterate precursors.

(β-Ketoiminato) Cu(I)L Precursors. Studies into the use of (β-ketoiminato) Cu(I) precursors are scarce. Shin et al. synthesized and performed CVD experiments using (nona-F)Cu(PMe_3) and (iihfac)Cu-(PMe_3), shown in Figure 36.[162] Both were found to be volatile, oxygen-sensitive materials which deposited Cu via disproportionation under the CVD conditions listed in Table 6.

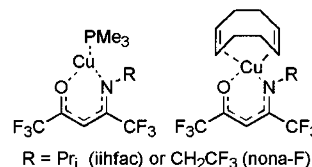


Figure 36. β-Ketoiminato Cu(I) L CVD precursors.

Additional Stabilization. Two methods have been developed to improve the solution stability of Cu(I) precursors. The first involves introducing an additional weaker group to the Lewis base ligand to feed more electron density into the metal center.[163] The second relates to the use of Lewis base donor solvents to stabilize highly reactive precursors in solution.

Complexes of (hfac)Cu with norbornadiene were reported by Doyle et al. as stable solids that can be handled in air for short periods of time without decomposition. Chi et al. attempted to improve the thermal stability of these precursors by preparing (hfac)Cu(7-Ac−NBD), illustrated in Figure 37. The coordinative effect of the lone pairs of the alkoxy oxygen was proven for the solid state via X-ray crystallography.[164] The coordination geometry of the complex was described as a highly distorted tetrahedron with the acetate -O- occupying the fourth coordination site, interacting weakly with Cu. They discovered that one olefin bond was longer than the other, 1.396 vs 1.285 Å, providing evidence for π-back-bonding.[164] This precursor sublimed at 70 °C (10 Pa) and deposited Cu on Si substrates (170−260 °C); films deposited at 140 °C were found to contain significant proportions of impurities.[164]

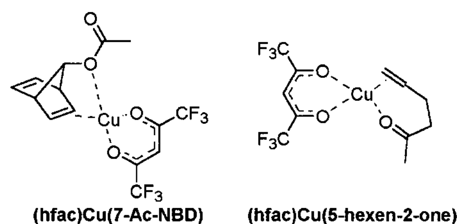


Figure 37. Using additional donor stabilization.

Xu et al. used the bidentate Lewis base ene−one ligand 5-hexen-2-one to improve the thermal stability of highly reactive olefin−Cu precursors.[163] This precursor sublimed at 75 °C and deposited copper on substrates in the temperature range 100−170 °C at 0.1−20 Torr. The decomposition temperature was found to be sufficiently high to minimize precursor decomposition during transport while maintaining the reactivity of the precursor. X-ray analysis of (hfac)Cu(5-hexen-2-one) displayed a nearest neighbor interaction, with the ketone of one mononuclear complex weakly interacting with the Cu(I) center of a neighboring second complex.[163] The structure illustrated in Figure 37 is the structure proposed for the monomer in solution.

Xu et al. went on to use weakly coordinating solvents such as cyclohexene and 1-hexene to prepare stable solutions of (hfac)Cu(5-hexen-2-one). For example, dissolving (hfac)Cu(5-hexen-2-one) in 1-hexene (1:1) yielded a solution which was stable for over 10 weeks.[163] In contrast, liquid precursor (hfac)Cu-(MHY) is stable neat for at least 6 months, whereas in a 50% ether solution it only lasts a few days at room temperature.[163] The use of donor solvents was originally proposed by Shin et al., who investigated the effect of excess Lewis base ligand on the stability of precursors such as (hfac)Cu(1-pentene) and (hfac)-Cu(VTMOS). They found that solutions of the precursor containing upward of 20 wt % solvent (i.e., 1-pentene or VTMOS) displayed outstanding thermal stabilities and could be processed in a liquid precursor vaporizer.[165]

Binuclear Cu(I) Precursors. Interest in the possibility that two Cu(I) centers could be incorporated into a precursor arose from the idea of a unimolecular disproportionation mechanism.[151] Particularly in high-vacuum CVD there would be a considerable advantage in being able to deliver two Cu(I) metal centers together onto a substrate because this would increase the probability of two Cu(I) species colliding and therefore disproportionating.[166] Some examples of binuclear Cu(I) complexes are given in Figure 38, of these, only the (β-diketonate)-Cu(DMDVS) has been shown to effectively deposit Cu.[163,167]

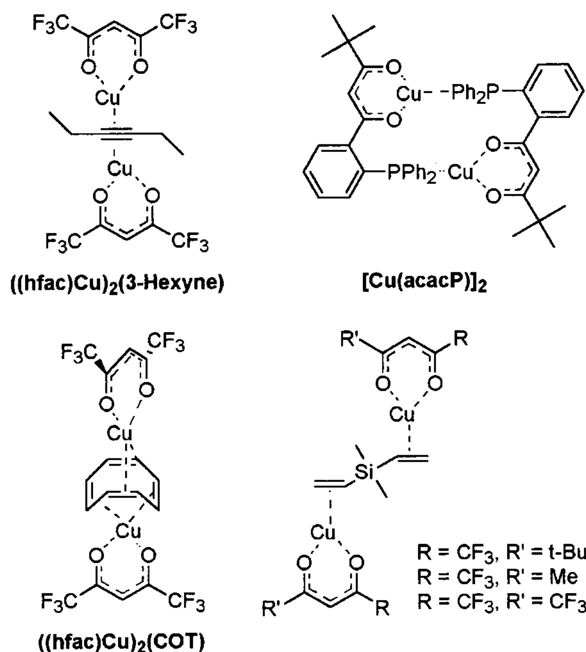


Figure 38. Examples of binuclear Cu(I) complexes.

Cyclooctatetraene was the first Lewis base ligand to be examined for binuclear Cu(I) precursors which could facilitate unimolecular disproportionation.[139,151] As a CVD precursor, ((hfac)Cu)$_2$COT was unremarkable in that it proved to be fairly involatile and its rate of deposition was reasonable when heated to around 100 °C, producing highly pure Cu films.[151] Analysis of the volatile byproducts suggested that Cu deposition was occurring through a reduction mechanism (H_2 was used as the carrier gas) rather than via disproportionation, since Cu(hfac)$_2$ was not produced, disproving unimolecular disproportionation.[151]

During CVD studies of (hfac)Cu(η^2-alkyne) precursors, Doppelt et al. observed a yellow solid forming in the precursor evaporation chamber when the alkyne was 3-hexyne.[111] This new compound was found to be extremely unstable in solution even at low temperatures and could not therefore be isolated. Doppelt et al. concluded that this could have been the dinuclear complex ((hfac)Cu)$_2$(3-hexyne) and went on to investigate this theory by preparing the dinuclear complex [(hfac)Cu]$_2$(BTMSA).[166]

Crystallographic data indicates that the complex illustrated in Figure 39 adopts a 'butterfly geometry', with the intramolecular distance between the two Cu centers being 2.8 Å.[166] The angle between the metal centers and the alkyne is about 105°; metal d−d repulsions are thought to explain why the metal centers are pushed further apart than 90°. Through this the Lewis base interactions of the alkyne are reduced, destabilizing the complex to the extent that it is unstable in solution above −25 °C. It was also insufficiently volatile for CVD, decomposing to the mononuclear complex, metallic Cu, and Cu(hfac)$_2$.[166] To avoid formation of such binuclear species and preserve the effectiveness of (hfac)Cu(alkyne) precursors, electron-withdrawing substituents can be introduced. Conjugated double bonds, $-OCH_3$, and $-CF_3$ have been shown to be effective at deactivating the triple bond.[111]

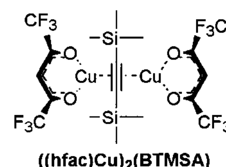


Figure 39. Dinuclear Cu(I) alkyne complex.

Rauchfuss et al. synthesized a binuclear Cu(I) complex using the bifunctional ligand [*o*-(diphenylphosphino)benzoyl]pinacolone illustrated in Figure 38.[168] This species was not investigated as a CVD precursor. The acacP ligand is original in that it incorporates an anionic diketonate functionality and a phosphene Lewis base to provide both components necessary for a Cu(I) precursor.

Schmidt et al. synthesized the range of binuclear complexes illustrated in Figure 40 with the aim of using them as CVD precursors.[169] It is known that when CVD is preformed under higher vacuum conditions, the growing film becomes increasingly contaminated. At lower concentrations it becomes less likely that a Cu(I) unit encounter another Cu(I) to effect disproportionation; this causes film contamination. To increase the odds of two Cu(I) metal centers reacting, Schmidt et al. prepared binuclear precursors which should deposit two Cu(β-diketonate) in close proximity on the surface.[169] The mononuclear sulfone precursor illustrated in Figure 40 was synthesized in order to determine whether a complex carrying only one Cu would be too stable. This was of concern because in the case of the dinuclear precursor reaction with a surface should result in chemisorption of both Cu centers. However, if deposi-

Table 7. CVD with (hfac)Cu(MHY) at Different Deposition Temperatures[155]

substrate	UV	120 °C	150 °C	220 °C
Ag/SiO_2	off	selectivity	selectivity	poor selectivity
Ag/SiO_2	on	blanket deposition	blanket deposition	blanket deposition
Si/SiO_2	off	selectivity	poor selectivity	poor selectivity
Si/SiO_2	on	blanket deposition	poor selectivity	poor selectivity

tion of one Cu center resulted in the remaining mononuclear precursor being too stable, then binuclear complexes would not be able to prevent film contamination issue. Fortunately, the sulfone complex demonstrated that the Cu−alkyne bond was not significantly deactivated.[169] So far these complexes have not been tested as CVD precursors; however, their complex stability was assessed. It was found that the use of electron-withdrawing R substituents lead to decreased complex stability.

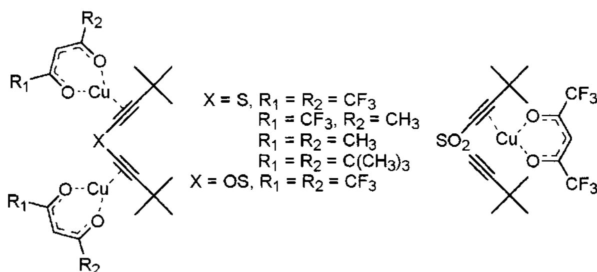


Figure 40. Hetroatom-bridged bisalkyne Lewis bases as potential CVD precursors.

F. Selective Deposition of Cu

One reason CVD has become increasingly important as a Cu deposition technique is that in recent years it has been shown that CVD can be performed selectively. CVD allows the selective deposition of Cu on photolithographically prepatterned substrates.[18,170] Precursor selectivity arises under certain reactor conditions (temperature, pressure, deposition time, etc.); it depends also on the nature of the precursor, the surfaces, and the chemical nature of the surfaces. Since selective CVD is now possible at low temperatures, on both conducting and insulating substrates it could begin to rival the plating techniques currently used in the microelectronics industry.[160]

Selective CVD has been extensively investigated in recent years utilizing the wide range of precursors developed for conventional CVD. A comprehensive analysis of selective CVD would have to be treated as a review in its own right. Here, a few selected examples have been chosen to illustrate the main features and mechanism in substrate-selective Cu CVD.

The first example involves the chemical modification of a surface to improve the surface selectivity of a precursor. Kim et al. studied the deposition of (hfac)Cu(VTMS) onto TiN surfaces in the presence of borophosphate glass (BPSG).[79] Surface hydroxyl groups of silicon dioxide have been investigated as the favored sites for Cu chemisorption. As a result, Cu deposits indiscriminately on TiN and on untreated BPSG at 170 °C. Kim et al. used nitrogen plasma treatment to modify the surface, resulting in the suppression of Cu nucleation on BPSG. By increasing the plasma treatment temperature to 200 °C, the greatest precursor selectivity for TiN was observed.[79] These conditions resulted in a Cu film with nuclei density of 5 nuclei/μm^2 with an average size of 80 nm. AFM was used to analyze the effect of the plasma treatment on the Cu film and the substrate surfaces. The Cu film, TiN, and BPSG were not significantly damaged by the plasma treatment, and Kim et al. concluded that removal of surface hydroxyl groups from BPSG considerably improves the selectivity of (hfac)Cu(VTMS) for TiN.[79]

Photo-MOCVD has also been investigated as a means of achieving selectivity through surface modifications. Vidal et al. performed CVD experiments using the precursor (hfac)Cu(MHY) between 120 and 220 °C.[155] Without UV irradiation, Cu is deposited nonselectively on both silicon and silver substrates. The growth was thermally activated, and the growth rate increased as the substrate temperature increased. Growth rates of up to 700 nm/min were observed for Cu films on (100)Si at 220 °C.[155] UV irradiation was found to significantly reduce growth rate on the SiO_2 surfaces, therefore enhancing selective growth on the (semi)conducting surfaces. This is thought to indicate that the reactive species Cu(hfac) favors desorption from the insulating SiO_2 surface under these conditions, as shown in Table 7.[155] The thermal activation energy was estimated at about 59 kJ/mol.

CVD has been cited as the future of Cu film deposition, and great efforts are being made to improve precursor selectivities for different substrate surfaces.[2] In order for CVD to achieve these high goals, it will be necessary to synthesize precursors which are even more selective for a variety of substrates and which have higher growth rates. Plating technologies and selective CVD are not patterning techniques in themselves; they require the surface to be patterned first using photoresists. Plating and selective CVD seem destined to be used in concert with lithographic patterning to produce more dense and finer microelectronic device features.

G. Laser-Assisted MOCVD

Cu direct write was first reported in 1985 using laser-assisted CVD. Originally the uses cited for direct write were mask repair, circuitization, and localized doping.[49] In recent years the applications of this technique have become more ambitious and the fabrication of Cu−metal interconnect lines is now possible.[48]

Laser-assisted CVD like conventional CVD relies on a volatile Cu precursor being delivered to the substrate in the gas phase.[171,172] Selective Cu deposition is achieved by heating the areas where Cu deposition is required with a laser, using the apparatus illustrated in Figure 41. This induces pyrolysis of the precursor and subsequent Cu film

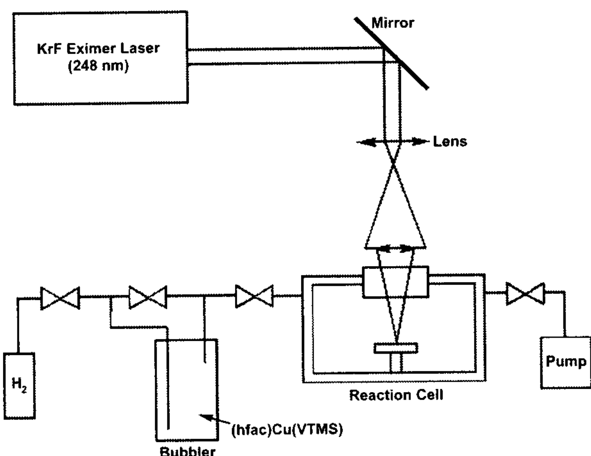


Figure 41. Experimental setup For laser-assisted Cu CVD.[48]

deposition.[48] The laser source can be any wavelength that is absorbed by both the substrate and the growing film.[97]

This process has the added advantage over other CVD processes that substrates such as polymers can be patterned. These substrates cannot be heated to the temperatures required for Cu deposition in conventional CVD. Popovici et al. (1998) describe laser-assisted CVD of Cu on Teflon AF 1600 using (hfac)Cu(VTMS) as the precursor.[48] Analysis of the Cu/Teflon AF 1600 interfacial interactions was performed using XPS. It was determined that the spectra of nonirradiated and irradiated samples were identical. Therefore, the polymer was not degraded by the laser during the relatively harsh conditions of the experiments.[48] The authors, however, point out that their experiments were extremely inefficient in terms of precursor conversion into Cu metal film. The films were also highly contaminated, with up to 45% fluorine and carbon.[48] Film conductivity measurements were not quoted. However, despite major concerns over film purity, Cu films with resistivities as low as 3.6 $\mu\Omega$ cm^{-1} have been produced by this method. Further development and optimization of this process is required before it can be commercialized.

V. Inkjet-Printed Cu

A. Cu Direct Write

The ability to directly write Cu pattern onto a substrate has become increasingly sought after in recent years. A technique superior to lithography must be found soon to speed up semiconductor device production, but it must provide comparable patterning resolution. Ideally, Cu would be written directly onto the substrate, yielding the metal interconnect pattern and eliminating multistep lithographic processes.[48] Realistically, direct-write techniques are unlikely to compete with lithographic patterning for sub-10 μm circuitry; however, for devices which do not require this level of integration, direct write provides fast and efficient Cu feature preparation.

The application of inkjet printing and computer-aided design (CAD) to Cu patterning is a recent

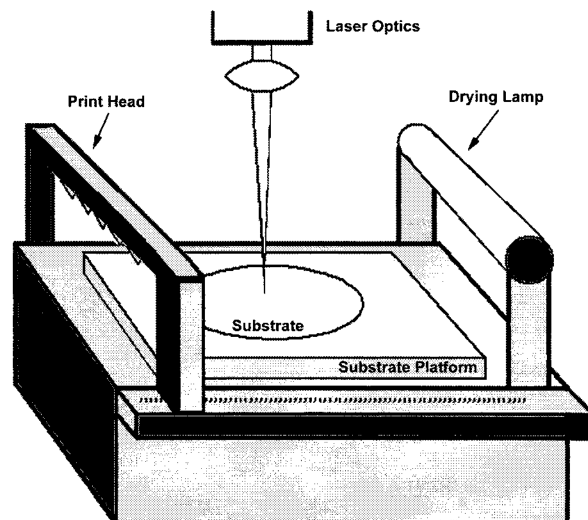


Figure 42. Schematic representation of a Cu precursor inkjet printer.[50]

innovation. Cu is delivered in the form of an ink to a heated substrate. The print head nozzle can control ink drop size, delivery speed, and drop frequency. Coupling this with CAD allows precise control of where on the substrate the drop is delivered. Complex metal interconnect circuits can be designed using CAD software and automatically printed onto a substrate. CVD converts only 5% of the precursor under the best conditions. In the case of inkjetting, the precursor is delivered in precise amounts, offering the opportunity of minimal waste.[173]

B. Inkjetting Cu from Colloidal Suspensions

Drummond et al. patented a process for direct writing of materials onto substrates using the printer set up shown in Figure 42.[50] Metals or dielectrics were deposited by an inkjet print head in the form of a colloidal suspension. The deposited material is resolved into the desired pattern via a laser or thermal annealing step, followed by a cleaning step to remove excess material. Using this system, features as small as 10−50 μm were obtained. It is also claimed that features smaller than 1 μm and as large as 400 μm are possible.[50] Cu colloids are among the materials claimed in their patent.

C. Cu Deposition from an Inkjetted Cu(II) Precursor

Hong et al. successfully inkjetted a Cu pattern onto hydrogenated amorphous silicon substrates.[19] They intended to use this process in the fabrication of amorphous thin film transistors. The precursor used was the Cu hexanoate $Cu_2(H_2O)_2(O_2C(CH_2)_4CH_3)_4$ in 2-propanol. Inkjetting this precursor onto the substrate followed by heating to 200 °C and exposure to UV radiation results in reductive Cu deposition on the substrate surface. The principal contaminants in these films were carbon (16%) and oxygen (7%) with film resistivities of around 10 $\mu\Omega$ cm^{-1} compared to 1.7 $\mu\Omega$ cm^{-1} for bulk Cu.[19] The Epson Stylus 400 piezoelectric inkjet office printer used in this study yielded a typical dot spread of approximately 90 μm.[19] This process is therefore a long way from achieving

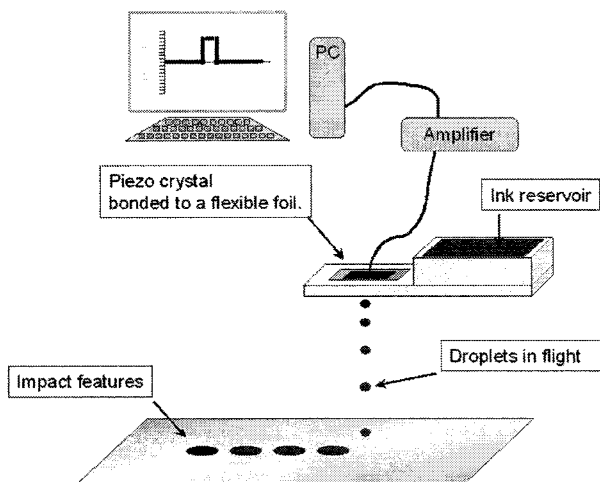


Figure 43. Drop on demand printing of Cu CVD precursors.[173]

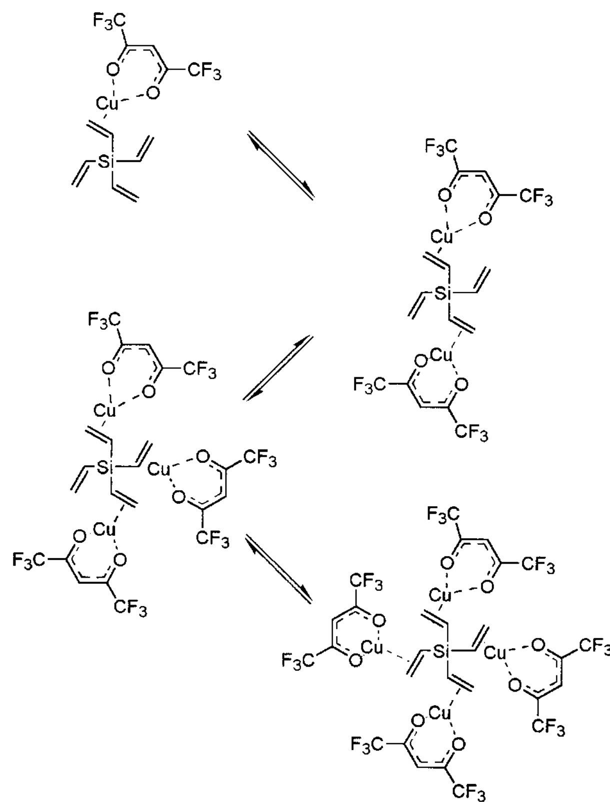


Figure 44. Solution-state exchange of tetramer to monomer in solution.

patterned Cu on par with the features processed routinely in today's semiconductor devices. Despite this, a lot of devices can be made which do not require high resolution, and inkjet technology will continue to progress further.

D. Drop Casting Cu from Cu(I) CVD Precursors

Homma et al. demonstrated that Cu(I) CVD precursor, (hfac)Cu(VTMS), can deposit Cu in the liquid phase.[174] (hfac)Cu(VTMS) was dissolved in *n*-heptadecane and applied to a heated substrate (100−250 °C) dropwise. The substrate was rinsed to remove residual precursor and other reaction byproducts and then annealed to improve film morphology. In contrast with previous publications, this study observed that (hfac)Cu(VTMS) disproportionated in solution as distinct from disproportionation on the substrate surface. Contamination levels of O, C, and F in these Cu films were as high as 10%, which was mostly attributed to the presence of $Cu(hfac)_2$ that had not been thoroughly removed by rinsing.[174] No efforts appear to have been made to produce patterned substrates using this procedure. By delivering the precursor in solution, the weight of precursor per volume of ink is reduced, and when the proposed reaction pathway is considered, only one-half of the weight of Cu is deposited as Cu(0), assuming 100% conversion. Confining a volatile Cu(I) CVD precursor in a high boiling point solvent on a heated substrate surface prevented precursor evaporation and uncontrolled gaseous phase deposition. However it also led to high levels of film contamination and poor film morphology, which required annealing.

E. Inkjetted Cu from Cu(I) CVD Precursors

Rozenberg et al. developed a technique for inkjet printing conducting Cu tracks onto a wide variety of substrates using Cu(I) CVD precursors as inks.[173] In addition, modified Cu(I) precursors were prepared, with properties tailored to the requirements of inkjet printing as apposed to CVD. Rozenberg et al. used a custom-built PZT piezoelectric ceramic unimorph research printhead as illustrated in Figure 43. Cu(I) CVD precursors such as (hfac)Cu(COD), (hfac)Cu(VTMS), and (hfac)Cu(ATMS) were delivered as inks (either neat or in solution) on a “drop on demand” basis to a heated substrate.[173] The precursor droplet undergoes thermally induced disproportionation resulting in metallic Cu being deposited on the substrate and evaporation of the volatile Cu(II) byproducts.[175]

Sheet resistance values of ~200 $\Omega\ \square^{-1}$ were obtained for films converted from (hfac)Cu(VTMS) using a 4-point probe. Film thickness was dependent on conversion temperatures and drop volumes but was on average 200−500 nm. The precursor was jetting through a 300 μm diameter nozzle which gave ~500 μm droplets, which in turn gave 550 μm diameter deposits.

The novel precursor materials designed and synthesized for this inkjet printing application utilized the Lewis base ligands tetravinylsilane and tetraallylsilane.[176] These ligands allowed multinuclear precursors to be prepared such as those illustrated in Figure 44. These precursors are better suited to inkjet printing than conventional CVD precursors because they are considerably less volatile while displaying comparable levels of reactivity.[173,176] High precursor volatility decreased the level of precision with which the substrate was patterned, since material was lost through evaporation. The majority of precursor evaporated and deposited Cu as vapor plume rather than from the ink droplet.[173]

$[(hfac)Cu]_4(TVS)$ is a crystalline solid with excellent stability to moisture and air and was therefore ideal for precursor purification and storage. It was found that by adding more Lewis base ligand, $[(hfac)Cu]_4$(TVS) exchanges rapidly in solution to give the

trinuclear precursor followed by the binuclear precursor and finally the mononuclear precursor, as illustrated in Figure 44.[173] The dinuclear precursor $[(hfac)Cu]_2(TVS)$ has a reduced Cu content compared to the tetrameric precursor; however, it is a liquid at 60 °C with a viscosity low enough to flow freely through the printhead.[176,177] The Cu film tracks inkjetted using these precursors were relatively smooth, again with resistivities in the 200 $\Omega\ \square^{-1}$ range.[177]

VI. Conclusions

The microelectronics industry will continue to rely on UV photolithography as the principal patterning method for the fabrication of patterned Cu films on a sub-200 nm scale. Lithographic patterning is currently entering the realm of electron beams and X-rays in order to overcome the resolution limits associated with UV radiation. A reduction of the number of manufacturing stages required in the patterning of films with lithographic masks is not on the horizon. As a result, the patterning of films above 10 μm is expected to be performed using direct-write techniques soon.

Considerable interest continues to fuel the development of plating techniques, Damascene plating in particular, which is used in the manufacturing of Cu interconnects in microprocessors. As well as optimization of the plating process, a variety of novel and potentially useful Cu direct-write methods are emerging, such as laser plating.

Despite the level of attention Cu CVD has attracted over the past two decades, CVD is only beginning to be used in the microelectronics industry. In particular, selective CVD is being rapidly developed as a viable alternative to plating. With the continued absence of a low-temperature dry etch process, the importance of being able to deposit Cu in selected regions of a substrate is becoming crucial. CVD precursors continue to be developed to deposit Cu at lower temperatures with faster deposition rates and onto a variety of substrates.

Cu “direct-write” processes are showing promise as potential candidates for the replacement of lithographic patterning at lower resolutions, possibly down to (or even below) 10 μm feature sizes. This will include device repairs, rapid prototyping of circuits, and simple feature fabrication. By producing low-resistivity patterned Cu films, all four reported Cu direct-write applications have the potential to rival conventional technology.

VII. Abbreviations

acac	acetylacetonate
acacP	[*o*-(diphenylphosphino)benzoyl]pinacolone
acen	4,4′-(1,2-ethanediyldinitrilo)bis(2-pentanonate)
acim	4-imino-2-pentanonate
beac	benzyl-3-oxobutanoate
bpy	bipyridine
etac	ethyl-3-oxobutanoate
fhd	1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionate
fod	6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate
hfac	1,1,1,5,5,5-hexafluoroacetylacetonate
hfip	hexafluoroisopropyl alcohol
iihfac	4-(isopropyl)imino-1,1,1,5,5,5-hexafluoropentan-2-one
meta	methoxyethyl-3-butanote
mpa	methylpivolyl acetate
mtac	methyl-3-oxobutanoate
nona-F	1,1,1,5,5,5-hexafluoro-4-[(2,2,2-trifluoroethyl)imino]-2-pentanonate
phen	phenanthrolone
ppm	6,6,7,7,7-pentafluoro-2,2-dimethyl-3,5-heptanedionate
Q′	1-phenyl-3-methyl-4-benzoylpyrazol-5-onate
Q_F	1-phenyl-3-methyl-4-trifluoro-acetylpyrazol-5-onate
tbac	*tert*-butyl-3-oxobutanoate
tdf	1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4,6-nonanedionate
tfa	1,1,1-trifluoroacetone
tfac	1,1,1-trifluoroacetylacetonate
thmd	2,2,6,6,-tetramethyl-3,5-heptanedionate
tmed	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
ATMS	allyltrimethylsilane
BPhA	bisphenylacetylene
BTMAS	bistrimethylsilylacetylene
CO	carbonyl
COD	1,5-cyclooctadiene
COT	1,3,5,7-cyclooctatetrene
DMB	3,3-dimethyl-1-butene
DMCOD	1,5/1,6-dimethyl-1,5-cyclooctadiene
DMDVS	dimethyldivinylsilane
FT-TMSP	1,1,1-trifluoro-3-trimethylsilyl-2-propyne
HDM	2,5-dimethoxy-3-hexyne
HFB	1,1,1,4,4,4-hexafluoro-2-butyne
MHY	2-methyl-1-hexene-3-yne
MP	4-methyl-1-pentene
NBD	norbornadiene
TMSP	1-trimethylsilyl-3-propyne
VCH	vinylcyclohexane
VTMOS	vinyltrimethoxysilane
VTMS	vinyltrimethylsilane

VIII. Acknowledgments

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