

Chapter 37

Coordination Compounds in New Materials and in Materials Processing

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Coordination compounds are found in new materials such as one-dimensional conductors and are also utilized as volatile precursors for the deposition of metal oxides in thin superconducting films or deposition of metal carbides or nitrides for refractory protective coatings and other applications. Coordination compounds have also proven to be useful precursors for the deposition under relatively mild conditions of high purity thin metal films for microelectronic applications. Historically, we consider $\text{Ni}(\text{CO})_4$ as the prototypical example discovered by Mond in 1898. Purely hydrocarbon complexes such as $(\eta^5\text{-C}_5\text{H}_5)\text{Pt}(\text{CH}_3)_3$ can be decomposed initially at around 120 °C. in an atmosphere of H_2 to give highly pure thin metal films of platinum metal. Deposition of electronically high-grade copper metal is achieved from precursors such as (hexafluoroacetylacetonate) $\text{Cu}(\text{cyclooctadiene})$ under vacuum conditions. The deposition of other metals is discussed including aluminum from the complex $(\text{Me}_3\text{N})_2\text{AlH}_3$ and mixed metal films such as PtGa_2 , PtGa , and CoGa from precursor coordination compounds.

Thin films with a large variety of uses such as conductors, semiconductors, and refractory materials have extensive importance in modern technology (1). The films can be deposited by using physical methods such as sputtering or evaporation. However, where conformal coverage is required for deposition into channels, chemical vapor deposition (CVD, including Vapor Phase Epitaxy, VPE) is the method of choice (2-4), in which volatile coordination compounds play a key role. CVD is carried out most simply by thermal decomposition of a metal complex that cleanly releases its ligands with negligible hetero-atom incorporation into the deposited thin metal film. Frequently, very clean deposition (less than 0.1 % impurities) is achieved in the presence of hydrogen gas. This article is largely an account of the work in our own laboratory with selected examples of other recent developments illustrating the role of coordination compounds in the deposition of thin films of metallic conductors.

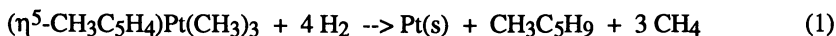
Platinum Group Metals

Historically, tetracarbonylnickel, $\text{Ni}(\text{CO})_4$, was the first organometallic complex to be used for metal deposition (5). The carbonyls usually decompose at relatively mild

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temperatures; however, they are known to contaminate the metal films with traces of carbon and oxygen, owing to the dissociative chemisorption of CO on freshly formed (and highly reactive) metal films (6). Hydrocarbon precursors, especially compounds with carbon-ring fragments that are more likely to be disengaged without leaving behind carbon fragments offer the purest films for metals on which adventitious surface carbon can be removed as CH₄ under a H₂ atmosphere. Where simple hydrocarbon derivatives are not available, chelating groups such as acetylacetonate and its fluorinated analogs have been used. These have appropriate volatility, but special safeguards must be undertaken to avoid hetero-atom incorporation into the films. Such safeguards are described in the sections which follow. The application of volatile transition metal precursors in MOCVD (or MOVPE as alternatively termed) has been recently reviewed (7, 8), and a monograph is in preparation (Kodas, T.; Hampden-Smith, M. *Chemical Aspects of Chemical Vapor Deposition for Metallization*; VCH: Deerfield Beach, FL, in preparation).

Hydrocarbon complexes were found to be ideal precursors for the deposition of platinum group metals (9-12). This is because they are volatile and also thermally decompose in the region of 100 to 300 °C. Adventitious traces of carbon arising from ligand decomposition are removed as methane (in the presence of hydrogen). This removal can be achieved only when the deposition temperatures are significantly below 450 °C, the temperature at which surface carbon will graphitize and cannot be removed by hydrogenolysis. The deposition of very clean platinum metal, for example, is achieved at 180 °C. from (η⁵-methylcyclopentadienyl)(tris-methyl)platinum, accompanied by the formation of methane and methylcyclopentane (equation 1) (9, 10):



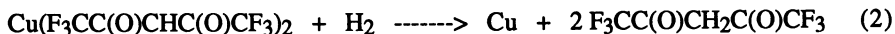
Kinetic studies show the existence of an induction period, which is found to be 80 minutes at 100 °C on Pyrex® glass. After induction the reaction becomes *autocatalytic* and proceeds without further external heating. An added trace of moisture in the gas stream will *shorten* the induction period, while the deposition of metal is *suppressed* by pretreatment of the glass with trimethylchlorosilane. This reagent converts surface hydroxyl groups to trimethylsiloxy groups. These results suggest that the principal initial reaction must be driven by an electrophilic interaction of the surface -OH groups (which are acidic) with the hydrocarbon metal complex. The initially attached platinum moieties, however, need to migrate together to form ensembles of some minimum size before a catalytically active deposit is achieved. There is much surface organometallic chemistry that needs to be explored to confirm such working hypotheses.

Clean deposits of Co, Rh, Ir, Ni, or Pd have also been achieved from similar hydrocarbon metal precursors (11, 12). However, it would be more desirable to deposit a good conducting metal such as tungsten under these mild conditions. Tungsten is now deposited by reduction of the volatile hexafluoride, WF₆, in the presence of hydrogen. However, this is accompanied by production of the corrosive reaction product HF, whose presence cannot be tolerated by other components of delicate microelectronic circuits. The first attempts to deposit tungsten from the volatile hydrocarbon precursor

(η⁵-C₅H₅)₂WH₂ led to films with as much as 30% carbon incorporation (13). This type of impurity greatly increases the resistivity of the metal film, causing it to be useless for integrated circuits. Tungsten is not catalytically active in the methanation of surface carbon. It was thus reasoned that a catalytic amount of platinum codeposited from a hydrocarbon precursor along with the tungsten could help to lower the carbon content. Indeed, this is what was found. A film of tungsten codeposited with a small amount of platinum was shown to contain less than 5% carbon (13). The research groups are presently attempting to measure the rate of migration of carbon from tungsten onto the codeposited small platinum islands so that optimum carbon removal from the films can be achieved.

Copper

Deposition of high quality copper films with a resistivity of less than $2.0 \mu\Omega\text{cm}$ and deposition rates of 80-180 nm./min. is achieved at 250°C . using the hexafluoroacetylacetonate complex $\text{Cu}(\text{hfac})_2$ with H_2 at 760 torr as carrier gas and reducing agent (14):

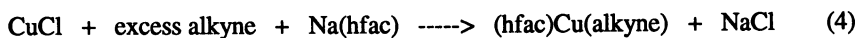


The β -diketonate copper(I) phosphine complexes have also been found to be good precursors to the deposition of copper, which occurs through a disproportionation reaction (15):



Since $\text{Cu}(\text{hfac})_2$ is more volatile and more stable than the copper (I) precursor, it volatilizes with both of the organic groups intact, leaving behind pure copper. The advantage of using the Cu(I) complexes is that deposition occurs at temperatures as low as 150°C ., and contamination of the films with impurities derived from the ligands is avoided. The films show a resistivity of $1.7\text{--}2.2 \mu\Omega\text{cm}$ with no detectable impurities. Another advantage of $(\text{hfac})\text{CuP}(\text{CH}_3)_3$ is that it is the only compound thus far known to deposit copper selectively on etched Teflon (Kodas, T; *et al. J. Electrochem. Soc.*, in press) (16); no copper deposits are found on the unetched Teflon. A simple three-step process of irradiation, chemical etching, and CVD of Cu is employed, replacing more involved processes for such selective deposition in various electronic devices.

Other Cu(I) precursors are the (β -diketonate)Cu(I) alkyne complexes (17). These are easy to synthesize (equation 4). The products are volatile and undergo the same disproportionation reaction depicted in equation 3 to produce highly pure copper films.



Aluminum

This metal with a melting point of 646°C . and a bulk resistivity of $2.74 \mu\Omega\text{-cm}$ is widely used in the fabrication of interconnects in electronic devices, lithographic patterns, highly reflective mirrors, and protective coatings of fibers and steel. Conventional precursors for CVD application are the pyrophoric aluminum alkyls such as $\text{Al}(\text{i-Bu})_3$, which is the most frequently used (18). It is a colorless, pyrophoric liquid. Pyrolytic deposition for very large-scale integration (VLSI) has been carried out in horizontal hot-wall CVD reactors. Typical conditions are furnace temperatures of $200\text{--}300^\circ\text{C}$. at up to 1 atmosphere pressure using H_2 as a carrier gas. A useful alternative to the pyrophoric trialkyl aluminum compounds are the alane amine adducts $(\text{R}_3\text{N})_2\text{AlH}_3$. Deposition of films is catalyzed by traces of titanium, applied by exposure of surfaces to TiCl_4 (19). Films are then deposited at rates an order of magnitude faster than with $\text{Al}(\text{i-Bu})_3$ and at lower lower temperatures ($100\text{--}200^\circ\text{C}$.), which is useful for deposition on temperature-sensitive substrates.

Transition Metal Gallides

Almost all pure metals deposited on compound semiconductors such as GaAs or InP are unstable with respect to chemical reaction forming MM' ($\text{M}' = \text{a group 13 element}$) or MM'' ($\text{M}'' = \text{a group 15 element}$) phases (20). Conductors which are thermodynamically stable (and lattice matched) are thus needed to form stable metal contacts to the compound semiconductors. Towards this end, intermetallic films of CoGa and PtGa_2 have been deposited from the precursors $(\text{CO})_4\text{CoGaCl}_2 \cdot \text{THF}$ (21, 22) and platinumbis-

(dimethylglyoximato)bis(dimethylgallium), $\text{Pt}(\text{dmga-GaMe}_2)_2$ (21), respectively. The nonstoichiometric intermetallic phase $\beta\text{-CoGa}$ becomes lattice matched to GaAs *only* when it is gallium-rich (*i.e.*, 64 atom% Ga). Thus separate precursors $\text{CpCo}(\text{CO})_2$ and GaEt_3 were employed in its deposition (23). The desired atom% of Ga is achieved using a 300-fold excess in the mole fraction $\text{GaEt}_3 : \text{CpCo}(\text{CO})_2$ in the carrier gas stream and at deposition temperatures in the range of 260 - 300 °C.

I hope the above selected survey has given a glimpse of how coordination compounds are useful in new materials and in materials processing.

Dedicated to Professor Ekkehard Lindner at the occasion of his 60th birthday.

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