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PLASMA CVD USING ORGANOMETALLIC COMPOUNDS


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Abstract
About 50 organometallic compounds have been tested as precursors in the plasma-enhanced chemical vapour deposition (PECVD) of metallic and oxidic films. The classes of compounds which are best suited for the deposition are described. Experimental techniques and problems are discussed. This paper besides briefly reviewing some of our earlier work, focusses on recent, unpublished.

1 - Introduction
The "plasma-enhanced chemical vapour deposition" (PECVD) has recently become an important technique for the preparation of thin films since it has certain advantages over other methods. As compared to thermal CVD, PECVD requires considerably lower substrate temperatures and can thus be applied to the coating of more sensitive materials, as e.g. polymers. Furthermore, films prepared by PECVD show very good adhesion and coherence; they are pinhole-free and do not exhibit any shadows /1/.

2 - Experimental techniques
PECVD depositions are usually carried out in parallel-plate reactors. Tunnel reactors, which have formerly been used in plasma polymerizations, have meanwhile been more or less abandoned because they do not lead to uniform films. Important parameters for
the deposition which can be easily controlled are the total pressure, power density, bias, and substrate temperature. Typical values used in this laboratory are pressures of 10–100 Pa and power densities of 0.1–0.5 W/cm² electrode surface. The substrate temperature ranges from 25°C to 400°C. Either the self-bias caused by the rf discharge or an additional bias are being used.

**Precursors for the film formation**
The most elementary precondition for all CVD experiments is the availability of volatile starting materials. The oldest PECVD technique, the plasma polymerization, can make use of a multitude of adequately volatile precursors. Suitable volatile materials for the preparation of films containing other elements are far less abundant. Some elements form volatile halides and hydrides, as for example BCl₃, SiCl₄, TiCl₄, SnCl₄, WF₆, SiH₄, AsH₃, and PH₃ which have been used in PECVD and other CVD experiments. The majority of elements, however, form neither volatile hydrides nor halides. On the other hand, organometallic compounds are known of almost all elements, some of which possess a sufficient volatility, as e.g. (C₂H₅)₄Pb or Ni(CO)₄. Unfortunately, questions of volatility, thermal and photostability have seldom been addressed in organometallic literature. Adequate data which might help to predict the suitability of possible PECVD precursors are available only for a few compounds. In most cases, it is thus necessary to check this by experiments.

The demand for new films with specific compositions and properties caused an intensive search for suitable starting materials in the field of organometallic compounds. The possibility of using organometallics in PECVD has been studied for many years in the plasma chemistry group in Tübingen /2/. The main goals were to find out which classes of compounds would prove to be especially suited for such experiments, to synthesize new compounds, and to prepare films of certain metals or metal compounds.

**Organometallic compounds suitable for PECVD**
For PECVD experiments, the precursor should have a vapour pressure of several Pa at room temperature or at temperatures below its decomposition temperature. Of course, heating requires an additional experimental effort, since all connecting tubes and reactor walls have to be kept at a temperature high enough to prevent condensation. In PECVD, the organometallic compounds are hardly ever used without dilution. If their partial pressure is too high, gas
phase reactions might occur resulting in powdery depositions. The dilution can be achieved by inert gases like argon or reactive gases like H₂, N₂, or O₂ which are commonly used in a tenfold excess.

In recent years we have tested about 50 different organometallic compounds as starting materials for PECVD. The formation of films of Rh, Pd, Pt, Cu, Ag, Au, Sn, films of alloys, BaO, Y₂O₃, Eu₂O₃, Tb₂O₃, CuO, Au₂O₃, PdO₂ and PtO₂ has either been published or is in press. A detailed description of 6 further metallic and 17 oxidic films is in preparation. Since the space available does not permit to elaborate on individual data, the following paragraphs will summarize our experience as to which structural features make a molecule a good precursor for a PECVD process. Some groups proved to be especially suitable:

**Metal alkyl compounds**

Tetramethylditin ((CH₃)₄Sn) is an almost ideal compound for PECVD experiments because it is commercially available and has a high thermal stability as well as a high vapour pressure. Consequently it has been studied by several authors. It easily forms films which show a metallic lustre even with 30% of carbon impurities. By careful adjustment of the experimental parameters, pure metallic thin films with conductivities similar to those of the bulk material are available /3/. The analogous alkyl compounds (CH₃)₄Ge, (CH₃)₃In, and (CH₃)₂Zn also have a sufficient volatility and thermal stability and are good precursors for PECVD. (CH₃)₃Ga and some aluminium trialkyls are being used in thermal CVD experiments by several laboratories. The lower aluminium alkyl compounds are very sensitive to air and moisture and require extreme experimental precautions in PECVD experiments. Normally traces of water or oxygen present in the equipment cause the formation of oxidic rather than metallic films. Recently, neopentyl derivatives have been proposed due to their volatility /4/. (C₅H₁₁)₄Ti, (C₅H₁₁)₄Zr and (C₅H₁₁)₄Hf have a sufficient stability and good vapour pressures. They have been tested as precursors for thermal CVD by Girolami and for PECVD in our group. They transform into carbidic films by both techniques. Their disadvantages are the limited shelf live and the difficult synthesis.

**π-Complexes**

Some metal π-complexes whose ligands contain only carbon and hydrogen have a sufficient volatility for CVD experiments, for
example the sandwich-type molecules ferrocene, nickelocene, and dibenzene chromium. The plasma treatment of these complexes leads to films with a fairly high carbon content. A compound which has been studied more extensively is allylcyclopentadieny1 palladium 15. It can be converted either into pure metallic films or films with a defined carbon content depending on the experimental conditions.

**Metal carbonyl compounds**
Several metal carbonyls have a high volatility and good thermal stability and are thus interesting precursors for CVD processes. Ni(CO), for example, has been used in thermal CVD processes for a long time past. Fe(CO), Co(CO)₈, Ni(CO), Cr(CO), Mo(CO), W(CO), and Mn₂(CO)₁₀ have been tested in Tübingen for PECVD. The films prepared from these compounds often contain carbon and/or oxygen (Mo, W). Only by careful adjustment of the parameters and the use of Ar/H₂ as carrier gas, pure metallic films can be deposited (Co, Ni). The impurities are probably caused by plasma reactions of the CO ligand which may dissociate into carbon dioxide and carbon, the latter being incorporated into the growing film. Cr(CO), and Mn₂(CO)₁₀ led to oxide films even in the presence of excess hydrogen. The PF₃ ligand is isoelectronic with CO. Several PF₃ complexes have a good stability and volatility. A complex of the type CpCuPF₂R has been tested and could be converted into a pure metallic film.

**Chelates**
Certain metal chelates show a reasonable volatility and might be used in CVD experiments. The simple acetylacetonates are less suited but their trifluoro- or hexafluoro- derivatives are often good precursors for PECVD. The tetramethyl-3,5-heptandione complexes have also been tested. By using the Cu(hfa)₂ complex, pure copper films have been prepared 16. The close vicinity between the metal atom and oxygen in these complexes might cause problems. If the central atom has a high affinity to oxygen, the plasma reaction leads only to oxide films (e.g. Ba, Al). The chelates of Fe, Co, and Ni result in films with high metal contents but also with considerable carbon and oxygen contaminations. The chelates of Y and several rare earth elements have only been treated in Ar/O₂-plasmas 17. Under these conditions they form the oxide films which are of special interest for high Tc-superconductors.
A few preliminary experiments have been carried out using alkoxy compounds. In the case of Ti(OR)$_4$ and Zr(OR)$_4$, these have been converted into films of TiO$_2$ and ZrO$_2$, respectively. The plasma treatment of Ti(NR)$_2$$_4$ (R = CH$_3$, C$_2$H$_5$) at temperatures ≤ 400°C seems not lead to TiN but rather to a carbonitride.

There is a variety of volatile organometallic compounds which contain different types of ligands, some of which have been tested for PECVD, as for example compounds with a combination of alkyl groups and chelate-forming groups (e.g. (CH$_3$)$_2$Au(AcAc)/8/). A combination of alkyl groups and π-substituents has been realized in (CH$_3$)$_3$Pt(π-C$_5$H$_5$), whereas organometallics with carbonyl groups and π-donors have been used for the deposition of metallic (Nb), carbidic or oxidic films (Ti, V) films, depending on reaction conditions.

A number of metallic films have been prepared by PECVD using organometallics in an argon atmosphere or a mixture of argon and hydrogen. Particularly good results are achieved if organometallic compounds of Rh, Pd, Pt, Cu, Ag, and Au are used. In all cases, bright shiny films are being formed. The degree of contamination depends on the experimental conditions. To prepare high purity films it is necessary to remove all organic ligands. There is an obvious dependence of film purity on substrate temperature, bias, and rate of formation.

With increasing temperature the rate of deposition decreases; however, the films become more and more metallic. For each system there is a temperature above which no deposition is possible. Under optimal conditions the electrical resistivities of the films approach those of the pure bulk material. An increase in the bias has approximately the same effect as an increase in temperature. An increase in the deposition rate often increases the amount of contamination.

The organometallic compounds of Nb, Mo, W, Fe, Co, Ni, Zn, In, and Sn lead to films with considerable contamination both by carbon and oxygen. Only a careful adjustment of the experimental conditions and the use of hydrogen or hydrogen/argon as carrier gas allows the deposition of pure metallic films.
Films of metal alloys
PECVD techniques to prepare metallic films have to compete with sputtering and evaporation. In large areas, PECVD techniques have substituted these methods because they offer certain advantages. For a long time it has, however, been argued that alloyed films will remain a domain of sputtering since CVD techniques would have to overcome the difficulties caused by different volatilities and different rates of decomposition when mixtures of starting materials are being used. Recently, however, alloys of Fe/Co and Au/Pt/Pd have been prepared by PECVD 9/.

Composite materials
For certain applications metal-polymer combinations are being required. As mentioned above, most organometallic precursors lead to films with a considerable carbon contamination if low substrate temperatures, low bias or excessive deposition rates do not allow the complete elimination of the organic ligands. Some applications need a deposit with a far lower metal content. This can be achieved by increasing the size of the ligand. For example, when we used \((\text{C}_4\text{H}_9)_3\text{SnO-CO-C(CH}_3\text{)=CH}_2\) with a C/\text{Sn} = 16 instead of \((\text{CH}_3)_4\text{Sn}\) with a ratio C/\text{Sn} = 4, films with considerably higher carbon contaminations resulted. Alternatively, films with higher carbon contents can be obtained by using mixtures of organometallics and alkenes. Various composite films with metal contents of 0 - 100% have been prepared using organometallic compounds of Au, Pd, Ni, etc. together with propene or acrylonitrile 10/. Metal-polymer combinations have been prepared previously by a combination of metal sputtering and plasma polymerization. Films prepared this way show a jump in conductivity by several orders of magnitude when the metal content reaches approximately 50 atomic percent. Films prepared by PECVD of organometallics and alkenes do not show such a coalescence point, and the conductivity shows an almost linear relationship with composition over many orders of magnitude.

Oxide films
Thin films of oxides have recently become of great importance. They find application as optical filters, transparent electrodes, as phosphorescent materials or high \(T_c\)-superconductors. Transparent conducting films of \(\text{SnO}_2\) and \(\text{In}_2\text{O}_3\) and films of \(\text{GeO}_2\) have been prepared using the alkyl compounds as starting materials. Films of \(\text{TiO}_2\), and \(\text{ZrO}_2\) have been deposited from the alkoxy compounds and complexes with \(\pi\)-ligands
and carbonyl groups. The preparation of \( \text{Y}_2\text{O}_3 \) or the rare earth oxides requires additional experimental effort since the only available precursors, the thd complexes, have but a low vapour pressure. For their use, special heating and transfer systems have to be applied. Organometallic compounds of Cu, Pd, Pt or Au which form metallic films when they are exposed to an argon plasma can also be used to prepare oxide films if the plasma gas is oxygen or an Ar/O\(_2\)-mixture. Thin films of CuO are now of special interest in superconductivity research.

**Other compounds**

The formation of films of carbides, nitrides, silicides, borides or sulfides is possible if the organometallic compounds are plasma-treated in the presence of suitable reagents (e.g. sulfide films can be prepared by addition of \( \text{H}_2\text{S} \) to the carrier gas). So far little has been done in this direction. Titanium nitride, TiN, which has great practical importance as hard coating is commercially still mainly prepared starting from TiCl\(_4\) and NH\(_3\). PECVD of organic Ti compounds usually leads to films consisting of carbide or a carbonitride even in the presence of NH\(_3\).

**3 - Conclusion**

The use of organometallics as precursors in PECVD experiments has several advantages. Most important is the good adhesion of the PECVD films. Metallic films on a variety of substrates (glass, ceramics, quartz, metals and polymers) show in general an adhesion which is far superior to that achieved by sputtering or evaporation. Peel tests of metallic films on organic polymers often cause breakage of the organic bulk material rather than of the interface /11/.

A number of the organometallics mentioned above have also been tested for thermal CVD and laser CVD in this group and in other laboratories. Often the same metallic or oxidic films have been obtained. Probably many of the compounds which are suitable for PECVD can also be used for the other CVD techniques. The choice of the CVD technique will mainly be influenced by the thermal requirements and the structure of the substrate.

Practically all PECVD experiments with organometallics have been carried out in research laboratories. Before the introduction of such processes into industry, several problems should be discussed. Only few of the materials used in this study are commercially available; most of them have been synthesized in Tübingen or have
been supplied by other groups. However, in discussions with chemical companies we have been assured that such compounds would be commercially available as soon as the market demands it.

Another question are the costs of organometallics. If a high conversion of the organometallics is achieved - which is possible - 1 cm³ of the precursor is sufficient to coat an area of 1 - 100 m² depending on the required film thickness. For substrates of considerable value, the cost of the coating would be negligible.

A further problem in dealing with organometallics is their health hazard and the required decontamination. Many organometallics decompose on exposure to air or moisture. Other compounds or their decomposition products may be poisonous or cancerogenic. For this reason, organometallics should be handled in closed systems. Reactors should be carefully flushed with inert gases and unreacted organometallics should be collected in cool traps and decomposed by treatment with an acid or an oxidizing agent.

References