Research Article

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Practical precursor aspects for electron beam induced deposition

Abstract: The purity of a structure made with electron beam induced deposition (EBID) is a the major concern when creating micro and nano-scale functionalities, for example for rapid prototyping. Substantial research focuses on the improvements of the purity using chemical vapor deposition (CVD) based precursors. However, from a practical point of view, many other aspects of a precursor are very relevant in the design of a process and the actual use of a tool for EBID. To a large extent, these precursor-related characteristics will determine whether or not a precursor can successfully be applied. Some of these characteristics include: vapor pressure range, transition behavior, chemical stability, pyrolitic thresholds, release of corrosive ligands during deposition, toxicity, commercial availability, compatibility with the instrument and operator safety. These characteristic are discussed in more detail here in order to understand what an ideal EBID precursor may be. Although some parameters such as toxicity or flammability seem less important, in practice they can be a road block for application unless the main instrument, such as a regular scanning electron microscope (SEM), is adapted accordingly.

Keywords: EBID, precursor, properties

1 Introduction

The basic mechanism of electron beam induced deposition (EBID) is simple and elegant: electron energy is locally transferred to a precursor molecule adhered to a surface and as a result this molecule decomposes into a solid and a gaseous component. Because of the excellent patterning control of the electron beam (position, size, dwell-time) the EBID method allows direct creation of three dimensional structures on virtually any substrate. A detailed description of this process is provided elsewhere [1]. The main application area is the creation of nano- and micro-scale structures for rapid prototyping. Local properties of interest are electrical conductivity and isolation (for contacting of nano-wires), ferro-magnetic behavior (for domain wall pinning, magnetic force microscopy), optical and plasmonic behavior (light transmission and field enhancement).

Currently, most EBID precursors that are used are listed in standard CVD and ALD chemistry books and cover a wide scope of elements and oxides that can be deposited. In general a CVD reaction can be described by one of the following mechanisms:

1) Pyrolytic reaction or thermal decomposition:

$$AX(g) \rightarrow A(s) + X(g)$$

EBID example:

$$W(CO)_6 + el \rightarrow W\,(s) + 6\,CO\,(g) + el$$
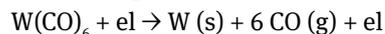
Similar reactions for $Pt(PF_3)_4$, $Fe_2(CO)_9$, $Fe(CO)_5$, $Co_2(CO)_8$, $Co(CO)_3NO$, $Au(CO)Cl$

2) Reduction / oxidation reaction to create a volatile component:

$$2AX(g) + H_2\,(g) \rightarrow 2A(s) + 2HX(g)$$
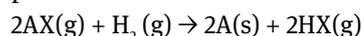
EBID example: $Si\,(C_2H_5O)_4 + 2\,H_2O + el \rightarrow SiO_2 + 4\,(C_2H_5OH) + el$

Or oxidizing reaction: $C_9PtH_{16} + 5\,O_2 + el \rightarrow Pt + 4CH_4 + 5\,CO_2 + el$

3) Displacement reaction. Create new compound that is volatile:

$$AX(g) + B(g) \rightarrow AB(s) + X(g)$$
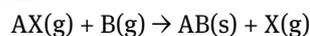
EBID example: None

The pyrolitic reaction is the most promising reaction owing to its inherent simplicity, while the reduction / oxidation reaction involves a second gas supply whose flux becomes a new, additional parameter. It should be stated that both reaction types can benefit from additional

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thermal enhancement such as using the substrate at elevated temperature.

A quick scan of the CVD precursors shows that the more complex precursors are less well-suited for EBID; this is because the larger organic groups seem to deposit rather than produce a volatile particle, hence, they contribute to the deposition and form a contamination, reducing the purity of the element of interest. The most promising precursors, from a purity point of view, seem to be based on short and simple ligands such as carbonyl groups, phosphine groups, and halogen groups and, to a lesser extent, the acetyl and acetyl acetonate groups with CH_3 or CF_3 functional groups.

2 Precursor properties and choices

When an EBID process is designed, one of the most important choices is the chemical composition of the actual precursor molecule; the main driver for the precursor choice is the element(s) of interest for the deposition. In practice, a precursor is often selected from a long list of CVD or ALD precursors. Many secondary parameters follow from the choice of the precursor molecule which include: vapor pressure as a function of temperature, chemical stability, sticking coefficient / residence time of the precursor molecules on the sample, system behavior and practical aspects such as toxicity issues and pump out of precursor molecules after use of EBID and possible contamination of the system. The most relevant parameters and their relation to the actual EBID process are discussed in the following section in more detail.

2.1 Inherent purity

For actual application of the EBID process in methods such as in rapid prototyping, the purity of the deposition is very important. It is generally known, that purity levels of most EBID processes are quite low [2], with some positive exceptions [3,4]. The very widely used Pt precursor $MeCpPtMe_3$ produces only 16 at% Pt while the remainder is carbon, most likely from the cyclopentadienyl ring. The generally high carbon content results from either the partial decomposition, such as for $W(CO)_6$, or because the decomposition is simply not pyrolitic and hence the precursor cannot split into pure volatile and non-volatile groups, such as for $MeCpPtMe_3$ or TEOS. Many techniques are being developed to understand the surface reactions of the decomposition process [5], to improve the purity of the deposition by adding some form of additional energy (annealing) [6] or adding additional particles such as

water vapor for TEOS. Good results have been obtained by carbonyl precursors [4] such as $Co_2(CO)_8$, $Fe_2(CO)_9$ in a standard vacuum environment and $Fe(CO)_5$ in a UHV environment [7]. It should be noted that the addition of thermal energy may also lead to enhanced (catalytic) growth of high purity material [8]. Most recently, progress has been made to improve the deposition purity by tuning of the deposition parameters and by adding additional particles for example to remove the carbon rich matrix from the deposition by the creation of CO and CO_2 and / or CH_4. An example of a pure Pt deposition using the standard $MeCpPtMe_3$ precursor in combination with in-situ O_2 post-irradiation is given in [10].

A pyrolitic reaction can be driven to higher purity by adding some energy in the form of an elevated temperature of the substrate during deposition (Figure 1). Of course the temperature should be well below the spontaneous decomposition temperature in order to avoid thin film growth.

2.2 Vapor pressure and chemical precursor changes

As EBID uses gas molecules that adhere to a substrate, the molecules have to be delivered into the main system such as a scanning electron microscope (SEM). Typically, this is achieved by using the vapor of the molecules, present above the liquid or solid precursor material. This method assumes that the gas molecules have the same chemical structure as the solid or liquid precursor *i.e.* that the Causius-Clapeyron relation describes how the vapor pressure relates to the applied temperature. For many precursors this indeed is the case, however in some cases the phase change from solid to vapor also induces a chemical change. An example of this is shown in Figure 2; here, a silver precursor (Vinyltriethylsilane hexafluoro acetyl acetonate silver I,
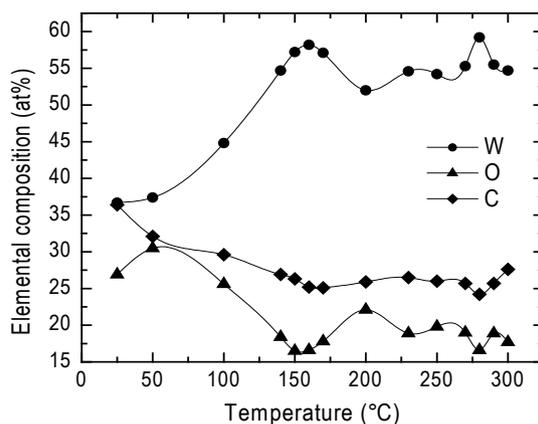
Figure 1: Composition of 5keV deposition using the W(CO)6 precursor as a function of substrate temperature [9]
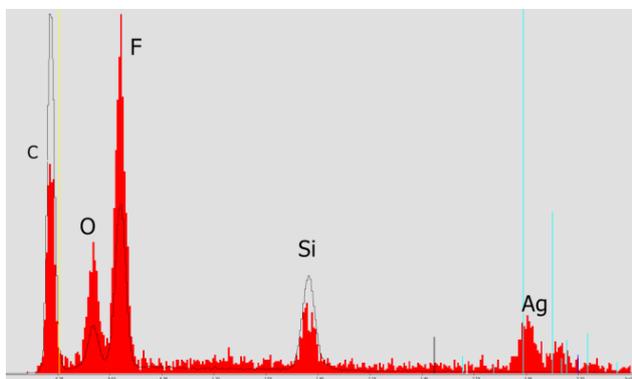
Figure 2: EDX spectra of vinyltriethylsilane hexafluoro acetyl aceto-nate silver I (red) and of its frozen vapor (black) showing the vapor no longer contains silver in-line with the missing silver in an actual EBID structure.

CAS[177279-28-6]) was used to make an EBID deposition that indeed contained all of the elements present in the precursor, apart from the silver that was aimed for. To investigate what happened the precursor material was analyzed with EDX quickly after pump down (red spectrum in Figure 2). Additionally, the vapor as delivered by the gas supply system was frozen onto the stage at − 50 °C and also analyzed (black line in Figure 2). As expected, C, O, F and Si are present, while the Ag is missing in the frozen vapor. Furthermore, the ratios are slightly changed and hence it is concluded that the precursor itself has a different composition than the vapor phase above it.

One possible solution, to meet this challenge, would be to use a carrier gas and a much higher temperature of the precursor to improve the dragging of molecules into the vacuum. This will however immediately increase the gas load of the vacuum system such that high vacuum conditions are difficult to maintain.

Indeed, if a precursor has a gas phase equal to the solid phase, then it is possible that other reactions occur than a simple evaporation process. Most carbonyl precursors are not extremely stable and the CO groups are sometimes slowly released at room temperature. An example of a chemical system with low stability is the Au(CO)Cl precursor, that produces very high purity gold in a single deposition step. However, the stability of the chemical is low; upon release of the gas into the chamber, the main component is CO. This implies a release of the CO group in the precursor reservoir and hence a "deposition" of Au / $AuCl_2$ in the crucible, which has been observed here. To this end, the transfer from solid to gas phase and successive pump out is the first loss of precursor material, while the spontaneous release of CO induces a second process. In this way the life time of the precursor is short (~10 hrs for 0.5 grams).

Another example of a transfer reaction is polymerization which is known to occur for the $Co_2(CO)_8$ precursor, following the equation

$$2\,Co_2(CO)_8 \rightarrow Co_4(CO)_{12} + 4\,CO$$
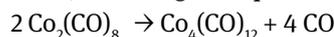
This reaction induces pressure build up in the reservoir and upon opening of the reservoir, the CO escapes; that is, a part of the precursor has changed chemically and this introduces precursor loss. As a result, it is observed that when the deposition process with Co no longer works, the crucible is not empty but the material has polymerized to a higher Co chain as indicated above.

Often the vapor pressure is too high in a precursor that is a liquid at room temperature and a restrictor (e.g. an orifice, a needle valve or mass flow controller) is required to reduce the actual flux delivered to the sample. For a good delivery of the vapor to the sample it should be noted that the temperature along the supply line should have a positive gradient towards the output, to prevent any condensation of precursor on other parts than the reservoir. Of course the maximum temperature of the total supply system should be well below the spontaneous deposition temperature of the precursor, to prevent coating of the inside of the supply system.

2.3 Etching

Many precursors are synthesized organo-metallic compounds, and as such they often contain many carbon atoms per precursor molecule. For this reason many depositions are not very pure, with carbon being the main component. In the search for higher purity depositions, sometimes carbon free precursors are used. For example, $Pt(PF_3)_4$ may be used to replace $MeCpPtMe_3$, which produces around 16 at% Pt and 84 at% C. Although the $Pt(PF_3)_4$ produces a higher Pt content of greater than 45 at%, the release of F atoms during the deposition is not always desirable owing to the strong etching capability of this element. Similarly precursors containing Cl, such as Au(CO)Cl will have an etching component on the mostly Si based substrate (Figure 3). Of course the etching speed largely depends on the release rate of the halogen involved as well as the composition of the substrate.

The etching process induced by the release of halogen containing ligands is a competing process with the deposition process. Hence the complexity of the system increases and this, in turn, sets a limit to the choice of sample substrates. This implies that the deposition process window is reduced and that the actual shape of the deposition is easily affected. Additionally, this corrosive behavior should also be compatible with the main system so brass or copper based materials must be avoided.
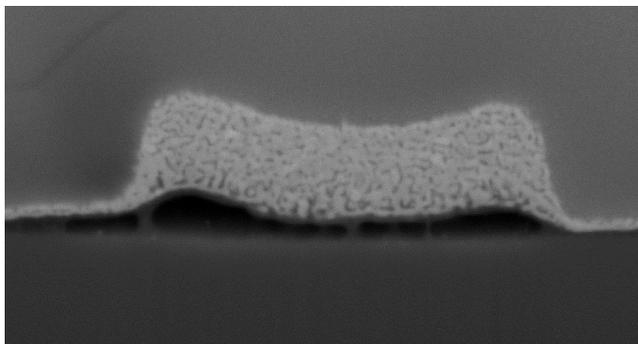
Figure 3: Cross-sectional view of a deposition of 1 x 1 μm made with Au(CO)Cl. The deposited material is pure Au, but the release of Cl induces etching effects on the Si substrate, likely in the form of sub-surface gas production that partially lift the structure at the side.

Figure 4: Mass spectrum (Zmax = 100) recorded with Co2(CO)8 precursor released in the chamber. Precursor components are CO at 28 and Cobalt at 59.The main multiplet components around 44, 58 and 72 are groups related to C6H14 (hexane) that serves as a stabilizer.

2.4 Possible tool contamination

The precursor will be released in the specimen chamber and hence all chamber and vacuum parts are exposed to it. Assuming the chemical reactivity of the precursor with the materials of the chamber and vacuum system can be neglected, it is still possible that the precursor induces damage or contamination to the system. The main reason is that the basic behavior of the precursor is that of a CVD chemical and hence designed to decompose on any hot surface. The decomposition is generally assumed to occur only above a certain temperature threshold, but for the various precursors this is quite different: $Co_2(CO)_8$ will start to decompose at 55 °C while MeCpPtMe$_3$ has a threshold above 350 °C

Although the chamber wall is at room temperature, other components are operated at higher temperatures such as a heated aperture in the column and possible Pirani gauges in the system. Additionally, a Penning gauge is operated at high voltage and when the precursor gets into the active area it may be ionized and accelerated and hence deposit a thin film in the Penning gauge. Thus, it is good to add a baffle to the Penning to avoid direct line of sight. In the end, the Penning will contaminate slowly but the speed is related to the amount and type of precursor used. It is good practice to document the vacuum readout after an overnight pump and monitor this over time. A contaminated Penning will produce a read-out better than the actual vacuum level. It is good practice to replace or clean the Penning gauge every 6 months on average.

An example of a precursor that is easily decomposed is $Co_2(CO)_8$. To test this, a mass spectrometer (residual gas analyzer – RGA) was attached to the system. This device is not a standard option for the main instrument. When
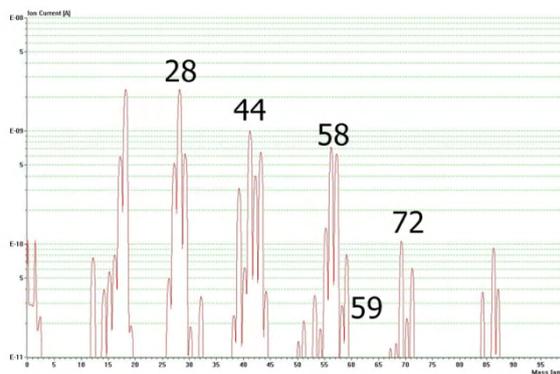
the precursor valve was opened the individual gaseous components could be measured.

Of course water at 18 is clearly visible as it forms the main component in any high vacuum system. Surprisingly hexane was still released from the reservoir. This hexane is used by the supplier of the $Co_2(CO)_8$ as a stabilizer compound and although the far majority is lost in the first few minutes of operation, some hexane still seems to be present, after 10 hours of operation. It may even be that it plays a role in the actual deposition process in the form of assisted catalytic growth of Co by combined deposition of C, which is known to act as a catalyst: this is shown by a predefined carbon EBID pattern that shows strong growth enhancement of Co [8].

The time to record the mass spectrum (Figure 4) was around 3 minutes and within that time the RGA completely lost its functionality and turned out to be coated on the inside with Co, forming an internal short circuit. The example shows that the cobalt precursor starts to decompose on the warm surfaces of the RGA which are far above its spontaneous decomposition threshold of 55 °C. Similar experience with the MeCpPtMe$_3$ precursor shows that this precursor is less capable of coating the RGA and measurements can be made over a longer period of time. This is because the Pt precursor decomposes at much higher temperatures. However, in general an RGA in combination with precursor molecules should be used very carefully.

2.5 Precursor pump out

The total time an amount of precursor can be used is driven by the applied temperature setting of the supply system as this dictates the vapor pressure of

the precursor. Together with the pump speed and the flow resistance the throughput, Q (mbarL/s), of the precursor is defined. Taking into account, the size of the reservoir the total pump out time can then be calculated. In practice, Q is around 10^{-3} mbar.L/s, the precursor amount is between 1 and 5 grams and hence precursor is pumped out in a typical time period of 80 – 400 hours, for the various precursors used. Ideally the precursor is completely pumped out over time so at the end of the process the reservoir is empty. It should be noted that some precursors degrade over time for example by contamination (back streaming) of water vapor or polymerization or chemical reaction with oxygen.

It should be noted that at some point the reservoir needs to be re-filled and hence a transfer from the storage ampule or bottle to the reservoir is necessary. Because many precursors are either sensitive to water vapor or oxygen or both it is always recommended to load the reservoir in a secure and inert environment, such as a glove box filled with Ar or N_2, which is often available in chemistry departments.

Overall, the EBID process is not very efficient. For example, for a carbon deposition rate at 1 nA beam current of 10^{-3} $\mu m^3/s$ is roughly equivalent to 5.10^7 carbon atoms per second. These are converted from 2.10^{14} precursor molecules/s delivered to the sample surface at a typical chamber pressure increase of 10^{-5} mbar upon opening of the precursor supply line. Hence the efficiency of the process is only around 2.10^{-7}. Precursor usage can be reduced by using smaller needles for the gas delivery system.

2.6 Toxicity

All precursors are chemically synthesized materials and almost by definition toxic to some extent. These precursors may also be flammable (alkanes), corrosive (XeF2) or carcinogenic (naphthalene). As human safety is a major concern it should be clearly taken care of. The carbonyls may easily release CO; this can be a major component of the toxicity. However in some cases it is not the CO but the active metal group that is heavily toxic, such as for $Ni(CO)_4$ (which is far more toxic then for example $Fe_2(CO)_9$). The toxicity is described in a materials safety data sheet (MSDS), however, for relatively new precursors many data sheets are missing. It should be noted that the exhaust of a system used for EBID has to have an external line, which is directly attached to the outside of the building for further dilution. Some precursor materials may pile up and / or decompose in the vacuum pump (scroll pump) and whenever vacuum components are taken apart, this

should be done in a fume hood with active flow to remove (particle) residues. For the best results the system should be equipped with an active filter.

2.7 Post delivery

In most precursor supply systems, the valve separating the vapor from the chamber vacuum is not at the very end of the supply line (usually a needle). The precursor is also attached to the chamber walls and sample surface. Hence, when closing the valve to stop the precursor delivery, the systems supply lines will still be pumped out. This implies that the EBID process is not immediately stopped, but deposition for example when making an image, is still occurring. Although the deposition rate is decreasing with time, it is very good practice to wait a few minutes between the creation of a nano structure and taking an image of it. To study the decay of the deposition process, tests have been done using the standard $MeCpPtMe_3$ precursor. After closing the valve, point depositions were made at successive time intervals. The pillars grown as a function of time were all equally large to prevent the influence of growth kinetics (long or short pillars) on the volume to be measured. To achieve this, the deposition time was adapted. A result is shown in Figure 5, for two (low) beam currents and 5 kV beam energy.

It should be noted that this behavior is dependent on the precursor, the substrate, the temperature and the distance between supply system and substrate. The fit in Figure 5 is for a single exponential decay and for both currents the behavior is in the current- limited regime. Withdrawal of the supply system (GIS retract) reduces the actual yield, but the trend remains the same, within the measurement accuracy.
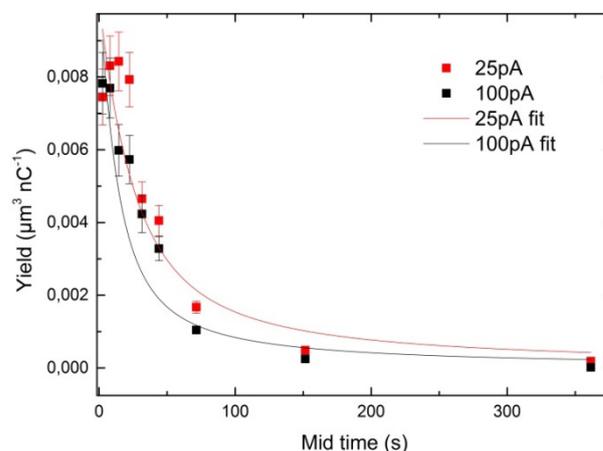
Figure 5: EBID yield of MeCpPtMe3 as a function of time after closure of the precursor supply system. Even after 3 minutes, deposition still occurs though at a yield which is around 20 times smaller.

3 Conclusion and summary

Based on the discussion above the following properties of an "ideal" precursor for EBID are proposed. The precursor should:

1. Contain the element of interest
2. Split into non-volatile element of interest and volatile components
3. Have small ligand groups
4. Not release halogens
5. Have sufficient vapor pressure – roughly in the range 0.01 – 50 mbar
6. Have gaseous precursor molecules that are the same as in the solid or liquid phase
7. Be stable when stored in the reservoir (preferably at room temperature)
8. Have a short pump out time
9. Have low toxicity and be safe to use without many system modifications
10. Be available commercially at reasonable price

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