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VAPOR DEPOSITION OF TANTALUM AND TANTALUM COMPOUNDS

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VAPOR DEPOSITION OF TANTALUM AND TANTALUM COMPOUNDS

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Abstract

Tantalum, and many of its compounds, can be deposited as coatings with techniques ranging from pure, thermal chemical vapor deposition to pure physical vapor deposition. This review concentrates on chemical vapor deposition techniques. The paper takes a historical approach. We review classical, metal halide-based techniques and current techniques for tantalum chemical vapor deposition. The advantages and limitations of the techniques will be compared. The need for new lower temperature processes and hence new precursor chemicals will be examined and explained. In the last section, we add some speculation as to possible new, low-temperature precursors for tantalum chemical vapor deposition.

Introduction

Tantalum is an industrially important element. It finds use in a wide variety areas; from thin-film oxide coatings for dynamic random access memory (DRAM), to wire for capacitors on printed circuit boards, to shape charge and explosively formed projectiles. This paper is a review of chemical vapor deposition (CVD) of tantalum and its compounds. We will focus our attention on the chemistries available for forming thin-film coatings of tantalum, and many of its compounds, by CVD. The actual deposition techniques will not be explored in detail, as that is another paper in itself. The paper takes a historical approach to the CVD of tantalum and its' compounds. For each historical "period", we will point out what was the motivation for the research, and the advantages and the disadvantages of the CVD processes. We conclude the paper with some speculation on new chemical precursors that might further the CVD of tantalum and its compounds.

Vapor Deposition Techniques

In the most general description, there are two major vapor deposition techniques. These are chemical vapor deposition (CVD) and physical vapor deposition (PVD). As we noted above, this

paper concerns itself with CVD. However, we would like to point out the difference in the two types of processing.

Physical vapor deposition, as the name implies, uses a physical method to produce a thin-film coating on the substrate. The two major classes of PVD are evaporation and sputtering. The evaporation techniques can be as simple as resistive heating of the source material. However, electron beam heating is much more common. The evaporative techniques are characterized by low pressures, $\sim 10^{-5}$ pascal, to prevent gas phase condensation of the evaporated material. The other major class of PVD is sputtering techniques. These include direct current (dc) glow discharge, radio-frequency (rf) glow discharge, and magnetron-based sputtering. The sputtering processes occur at higher pressures than the evaporative techniques. Magnetron-based sputtering gives about an order of magnitude higher rate deposition than dc glow discharge or rf glow discharge.

Chemical vapor deposition is a process where one or more volatile chemical precursors are transported in the vapor phase to a substrate. At the substrate, they undergo chemical reaction to produce, hopefully, a solid film along with the elimination of volatile byproduct. CVD is usually performed at reduced pressures to prevent undesired chemical reaction in the gas phase. The precursor can be inorganic, metal-organic or organometallic, as well as other reactive gases such as H₂, NH₃ and O₂. It is not unusual to use an inert gas, such as argon, to either dilute the mixture or aid in the transport of the precursor. The reaction at the substrate can be promoted in numerous ways. The most common method is to simply heat the substrate. However, plasma- and laser-assisted CVD are active areas of research, and there are many hybrid techniques that are combinations of the above.

If one were to distill PVD and CVD into the simplest picture possible, one would picture PVD as an evaporation followed by condensation. For CVD, the simple mental picture is surface chemistry. PVD is a line-of-sight coating process. Coating intricate shapes with PVD requires one to design complex systems to move the substrate. CVD is not a line-of-sight process. Complex shapes can be coated with relative ease. In addition, deposition rates are often an order of magnitude higher with CVD. Until recently, PVD was the dominate process in such industries as microelectronics. It offered the advantage of lower temperature processing. The advent of organometallic and metal-organic CVD processes, and corresponding lower temperature depositions, has led to explosive growth in industrial application of CVD. This is especially true in the microelectronics industry.

Tantalum CVD

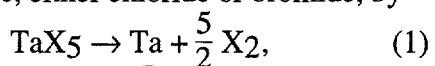
For simplicity, we have broken tantalum CVD into four historical periods. We have dubbed them early, transitional, current and future. The transitional period links the early tantalum CVD chemistries and motivation with what research and development is currently being performed. We will consider only the thin, solid films coating processes, This review will not address the gas phase reaction and nucleation processes for powder production.

Early Tantalum CVD

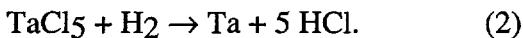
Early tantalum CVD was motivated by much different needs than today's. Protective coatings was a dominate theme in the early work in CVD. The applications could be wear, corrosion and oxidation resistance. In addition to protective coating, coatings for nuclear fuels application was also an active area of research and development. In the nuclear fuels applications, the coating could be for protection (mainly corrosion or barrier layer) or fission product retention. Unlike today, microelectronics and optical materials were much less important applications for these thin-film coatings. The other item that distinguishes early CVD from today is the temperature of the processing. Most applications for the coatings were at high temperature, thus the processing was performed at high temperatures. Logically, due to the high temperatures, refractory substrates were used in the research and development.

The chemistry used in early CVD matched the drivers. (1) The volatile source of tantalum was the pentahalide. The most common of these was $TaCl_5$. This was generated, usually, by flowing chlorine gas over the metal at 500 K to 600 K. Hydrogen gas or some hydrogen containing species provided the other reactant. Deposition temperatures were generally in the range of 1300 K to 2300 K. The advantages of these chemistries were films that were crystalline and were often high purity. One disadvantage was the high temperature severely limited ones choice of substrate material. In addition, the hard acid byproduct could incorporate in the film and restrict their application. Finally, with tantalum metal, the metal would be embrittled by the hydrogen if the deposition was performed in a certain temperature range.

There were two dominate chemistries used for depositing tantalum metal. The first was thermal decomposition of the pentahalide, either chloride or bromide, by

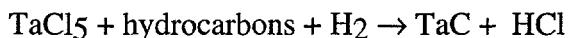


where X= Cl or Br. The process was usually carried out under argon at about 2300 K. The second, more common, process was hydrogen reduction of TaCl₅,

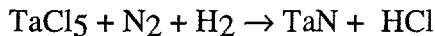


The process was performed with excess H₂ between 1000 K and 1500 K. Both process could produce high purity tantalum metal. Substrates included both refractory metals and oxides. Reaction (2), if performed at higher temperature, would give hydrogen embrittled material.

Refractory carbides and nitrides of tantalum were also investigated in this early work. Tantalum carbide coatings were produced by



Literally, every hydrocarbons one could imagine was used (ex. benzene) and hydrogen was used in excess. The reaction was typically performed near 2050 K, with some processing as high as 2800 K. At the lower temperatures, the phase Ta₂C was observed. The high temperature was necessary because one had to consider the competitive reaction (2). A second process for TaC thin-films by CVD was a two step process. First, reaction (1) or (2) was used to coat Ta metal on graphite. This coating was then taken to high temperature to convert the tantalum metal to tantalum carbide. Tantalum nitride coating were produced by two similar processes. The first was



at 2600 K to 2700K with hydrogen in excess. In some cases, ammonia was used in place of molecular nitrogen. Again, the high temperature was necessary because one had to consider the competitive reaction (2). The second process used reaction (1) or (2) to produce Ta metal, which was converted to nitride with either N₂ or NH₃. The nitriding process was performed at 2400 K to 2600 K, for reasons that are not entirely clear. Today, it is well known one can nitride clean tantalum metal at much lower temperatures.

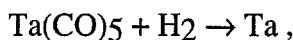
In all of the early CVD of tantalum, no reliable process for producing the boride was developed. In addition, no effort was expended on producing tantalum oxide thin-films by CVD.

Transitional Period in Tantalum CVD

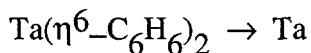
Following the early work in tantalum CVD, there occurred what we choose to call a transitional period. Little effort was expended in developing new chemistries for the deposition process. Lower temperature depositions were reported in the literature. But, these were at the expense of deposition rate. In addition, we see the advent of tantalum chemical vapor infiltration (CVI). (2,3) These CVI processes were based on the same chemistries as early tantalum CVD. During this period, progress was made in the area of tantalum boride coatings. (4) Reacting the pentachloride

with diborane gave TaB_2 coatings. If performed below 875 K, amorphous boron co-deposited with TaB_2 . Above 875 K no free boron was observed. At all temperatures the material was sub-stoichiometric. The most striking change we see during this period, and it hints to the current tantalum CVD motivation, is the advent organometallic-based CVD (OMCVD). In addition, we see the first experiments motivated by the needs of microelectronics industry. This is what we dubbed this the transitional period.

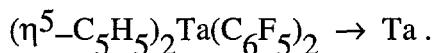
There were three OMCVD processes reported during this period. The carbonyl-based process,



produced coatings on copper between 725 K to 875 K. (5) The process produced thin-film coatings that were 90% metal, the balance being carbon. Two other processes (6), from the patent literature, were thermal decompositions

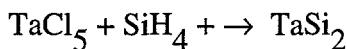


and



Low temperatures depositions were claimed, but details are sketchy and material purity was not addressed. We mention these for completeness.

The influence of microelectronics is seen from the flurry of activity in work on tantalum disilicide on silicon for barrier layer applications. Moderate temperature depositions from

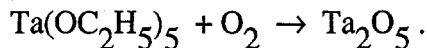


at 875 K to 975 K. (7,8) A variety of gas mixes, including Ar, HCl and H_2 , gave a sub-stoichiometric material. However, the material was very pure with total impurities less than 0.5% Annealing at 1200 K was used to correct the stoichiometry of the material. The same reaction, run at lower temperatures, produced a phase identified as Ta_5Si_3 . (9,10) Upon annealing at 1200 K, silicon would migrate from the substrate to form stoichiometric $TaSi_2$.

Current Tantalum CVD

Current work in CVD of tantalum and tantalum compounds is motivated by the needs of the microelectronics industry. Predominately, the material is the oxide and the application is high-density DRAM (hd-DRAM). To a much lesser extent, tantalum nitride is studied for barrier layer applications. There are a few reports of tantalum oxide CVD for oxidation and corrosion barrier applications.

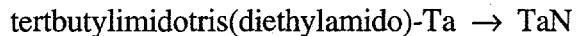
For the hd-DRAM arena, the CVD process is based on alkoxide precursors, predominately tantalum pentaethoxide reacted with oxygen,



This process is amazingly dominate in the research and development. Besides oxygen, processing with plasma activated O₂, ozone and nitrous oxide has also been studied. There are a few reports of similar work with the methoxide (11-13), one on Ta(dmpe)₂Cl, where dmpe = (CH₃)₂PCH₂CH₂P(CH₃)₂, (14) and one based on a homoleptic amide precursor.(15) A wealth of processing techniques have been tried. The literature reports plasma-assisted processes. (16,17) Thermal, low-pressure CVD near 745 K was performed that gave close to stoichiometric material.(18-22). Electron cyclotron resonance, plasma-assisted CVD was studied in a temperature range covering 300 K to 480 K. (23-26) Laser-assisted CVD was used to deposit tantalum oxide in the range of 300 K to 625 K, both with and without remote plasma excitation of the oxygen. (11-13) Finally, another report uses plasma-assisted CVD with liquid delivery of the precursor. (27) All of this effort is an attempt to lower the deposition temperature of the tantalum oxide. What they all have in common is: a) the material deposited is sub-stoichiometric. and b) all materials are subject to rapid thermal anneal to achieve the desired stoichiometry and crystallinity. The rapid thermal anneal, in turn, reduces leakage current.

Tantalum oxide coatings from the Ta(dmpe)₂Cl precursor and oxygen were deposited on quartz and Si(100). Fine (111)-oriented Ta₂O₅ films were obtained on both substrates at 900 K to 950 K. The tantalum oxide films deposited from homoleptic amide used Ta[N(CH₃)₂]₅ and oxygen in a low pressure CVD between 655 K and 795 K. Higher deposition rates were observed than with the ethoxide and good step coverage was maintained. The as deposited film was oxygen poor but annealing in an oxidizing ambient improves the stoichiometry.

Barrier layer material research and development centers on tantalum nitride. A series of reports based on



presents some very promising results. (28,29) At 725 K, the researchers were able to achieve 100% step coverage. Even though the material contained 10% carbon and oxygen, it performed well as a barrier in Al/TaN/Si up to 825 K.

Some effort has been devoted to studying CVD of Ta₂O₅ as an oxidation and corrosion barrier. Thin-film coatings, from methoxide chemistry, were produced on Si₃N₄ and SiC. These showed good oxygen protection to 1275 K. (30,31) In another study, CVD of tantalum oxide as well as

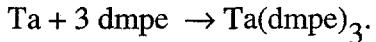
tantalum oxide, chromium oxide and aluminum oxide multilayers were studied as a corrosion barrier for steel. (32) Films for all three metals were from ethoxide precursors at 473-623 K at atmospheric pressure and low pressure. Films of tantalum oxide as thin as 80 nm showed good corrosion resistance in 3% NaCl. The multilayer films display higher corrosion resistance than the single layer film in 3% NaCl solution and 1 M H₂SO₄.

Future of Tantalum CVD

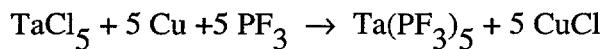
As we have seen from current tantalum CVD, coatings based on the alkoxide precursors, especially ethoxide precursor, have been studied extensively. In this, the speculative, section of this paper, we discuss some possibilities that might lead us out of the “ethoxide rut.” As we noted above, there were reports of oxide growth from both homoleptic amide and dmpe precursors that showed great promise. A look in the literature indicates there may already be some other promising organometallic compounds for tantalum CVD studies. However, although the OMCVD routes are the ones that produce low-temperature chemistries, let us first discuss their disadvantages.

Perhaps the most compelling reason not to look towards OMCVD is the precursors themselves. They could be viewed as “designer” precursors and not everyone has the luxury of having an organometallic chemist on-hand. This is, basically, a staffing decision. Second, the air sensitivity of OMCVD precursors is a potential problem. These precursors require special handling that may not be compatible with ones processing. Careful design of the oricessing will certainly address this. Lastly, if one decides to purchase the organometallic precursor, there is always the question of “what is in the bottle?” The exact composition, and many other properties, is highly dependent on the synthetic route used to prepare the compound. A change by the supplier, in synthetic route, could affect many months or years of effort. This, in-turn, effects bringing the product to market. Given that we can tolerate these disadvantages, let us explore what the future of OMCVD of tantalum and its compounds has to offer.

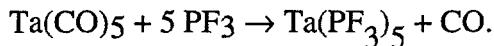
Perhaps, the most interesting potential area of tantalum CVD stems from the zero valent organometallics. Geoffery et.al. (33), developed the co-condensation reaction



Extensive x-ray analysis were performed and the compound is stable at room temperature. Preparation of the dmpe complex suggests that extension of the work of Kruck et.al.(34), or Head et.al.(35) to tantalum should be possible. Using Krucks' method the fluorphosphine complex could be prepared by

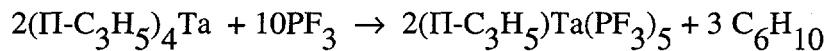


or by Heads' method



Both $\text{Ta}(\text{dmpe})_3$ and $\text{Ta}(\text{PF}_3)_5$ should have good vapor pressures. Analogous fluorophosphine compounds have measured melting points ~ 470 K, vapor pressures of ~ 250 pascal at 295 K and decompose ~ 575 K. Therefore, decomposition $\text{Ta}(\text{dmpe})_3$ or $\text{Ta}(\text{PF}_3)_5$ by successive loss of dmpe or PF_3 ligands appears a promising route to low temperature tantalum metal coatings.

Another interesting class of compounds has been prepared by Kruck and Hempel. (36) They use the reaction



run at 295 K and under 20 atmospheres of PF_3 . The compound sublimes at room temperature.

The compound decomposes by successive loss of PF_3 ligands. It is quite common for the π -allyl ligand to split off a C_2 group at moderate temperature. The net result being an OMCVD route to TaC coating.

Lastly, at Los Alamos we have developed three classes of OMCVD precursors that appear very general and should be applicable to tantalum deposition. (37-41) These are homoleptic amide, silicon amido and β -diketonate complexes. The homoleptic amides when reacted with an oxidizer are a promising route to low temperature oxide coatings. When reacted with ammonia, these produce low temperature nitride coatings. Like the homoleptic amides, the β -diketonate complexes are a good starting point for oxide coatings. Also, reaction with H_2S gives the sulfide. The least effort has been expended in the silicon amido complexes. Reaction with oxidizer can give either oxide or silicate. Little has been done with tantalum for all three classes of these complexes. These would all be interesting starting points for further exploration of low temperature OMCVD of tantalum compounds.

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