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VAPOR DEPOSITION FROM PERFLUORO-ORGANOMETALLIC COMPOUNDS

Christ Tamborski, Dayton, Ohio, assignor to the United States of America as represented by the Secretary of the Air Force

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ABSTRACT OF THE DISCLOSURE

A method of depositing transition metals on selected surfaces by vaporizing perfluoroorganometallic compounds and bringing the resulting vapor into contact with a surface which is at a temperature above the decomposition temperature of the perfluoroorganometallic compound. Metals deposited are preferably group IV metals such as titanium or zirconium but may be any transition element of groups III, IV or V.

The invention described herein may be manufactured and used by or for the United States Government for governmental purposes without the payment to me of any royalty thereon.

The invention deals with the deposition of a metal from a vapor of an organometallic compound and is particularly directed to the deposition of certain transition elements capable of forming a cyclopentadiene derivative.

It is known in the art that certain organometallic compounds can be heated to their decomposition temperatures to effect a separation of the metal in relatively pure form. Advantage has been taken of this fact to provide for the plating or deposition of a selected metal on a solid surface. Such deposition, generally referred to as "vapor deposition," may be carried out in order to provide a solid surface with a heat-resistant or corrosion-resistant coating, or such deposition may be carried out as a step in the purification of the metal.

The availability of suitable organometallic compounds has been limited by the low volatility and the low stability toward oxygen of many of the organometallic compounds which might otherwise be useful. This is especially true of organic compounds of trivalent, tetravalent, and pentavalent transition elements of the periodic table of the elements. There are metals in group IV; for example, titanium and zirconium; which workers in the art are particularly desirous of plating or depositing but which have proved particularly susceptible to reaction with oxygen not only in their elemental form but in their form as organometallic compounds.

Many organometallic compounds decompose at relatively low temperatures and at temperatures which are very near their vaporization temperatures. Such compounds are difficult to handle in vapor deposition processes because of their tendency to deposit metal in the vapor generating apparatus or on surfaces other than the one selected for coating.

OBJECTS

It is an object of this invention to provide an improved method for the deposition of trivalent, tetravalent, and pentavalent transition elements.

It is a further object to provide a method for the deposition of such an element by vapor deposition.

It is a further object to provide a method of vapor deposition of a metal from a compound wherein the difference between the vaporization temperature and decomposition temperature of said compound is quite substantial.

It is a specific object of the invention to deposit titanium, zirconium, tantalum or like metal by an improved vapor deposition process involving the decomposition of a highly volatile, relatively oxygen-stable organometallic compound.

I have now found that the foregoing and related objects can be attained in a method of vapor deposition of a transition element selected from the transition elements of groups III, IV, and V; said method comprising:

(a) Vaporizing a compound of the formula:

$$(C_5H_5)_2M(C_6F_5)_{n-2}$$

wherein M is said element and n is the valence of said element in said compound;

(b) Heating the resulting vapor of said compound above its decomposition temperature; and

(c) Effecting the deposition of said element on a surface.

The invention includes also effecting the contact of the vapor of the compound with a surface heated to a temperature above the decomposition temperature of the compound to effect the deposition of said element on the surface.

The metal to be deposited is preferably a group IV metal such as titanium or zirconium but may be any transition element of groups III, IV, or V; tantalum, for example.

Other metals of particular interest are indium and columbium (niobium). Some of these metals; for example, indium with a melting point of 155° C.; deposit as liquids from most of the organometallic compounds of interest while metals such as titanium, zirconium, columbium, and tantalum deposit as solids. It will be apparent to workers in the art that various combinations of these metals may be deposited as codeposits, alloys, sequential metal layers, or other combinations which may be desired. Similarly the invention provides for the "deposition" of a metal even though the deposited metal may immediately lose its identity as an element; for example, the deposition of titanium on a molten aluminum surface to form a solution of titanium in aluminum or to form a titanium-aluminum alloy. Similarly, the surface upon which the metal is deposited may be a liquid surface as might occur in alloy formation or in metal purification processes.

An organometallic compound of the invention is usually vaporized in a vapor generator. It is preferred that the vapor generator be not only a vessel in which the compound can be heated but one through which a nonoxidizing gas, preferably hydrogen, can be passed to entrain the vapor. The gas stream (nonoxidizing gas and entrained vapor) is then brought into contact with a surface heated to a temperature above the decomposition temperature of the organometallic vapor. Upon contact of the vapor with the hot surface, the organometallic compound decomposes and leaves a deposit of elemental metal on the hot surface.

The vaporization temperatures of the various organometallic compounds of the invention are different but, generally speaking, it will be found that the vapor generator can be maintained at a temperature substantially above the vaporization temperature without fear of effecting decomposition in the generator. Regardless of the temperature required it is of course necessary that the compound be vaporized.

Similarly, the decomposition temperatures of the various compounds of the invention are different but, generally speaking, it will be found advantageous to maintain the temperature of the surface receiving the elemental deposit substantially above the decomposition temperature. Such temperatures are recommended for the reason that some of the compounds of interest decompose in stages and

the pure elemental metal does not always separate out completely in the first stage of decomposition.

EXAMPLE

A sample of bis(pentafluorophenyl)bis(cyclopentadienyl)titanium, having the formula $(C_5H_5)_2Ti(C_6F_5)_2$, was vaporized in a vapor generator at a reduced pressure in the substantial absence of oxygen and at a temperature above the vaporization temperature of the sample. The resulting vapor was entrained in hydrogen. The gas mixture of hydrogen and bis(pentafluorophenyl)bis(cyclopentadienyl)titanium was brought into contact with a copper surface which was at a temperature substantially above the decomposition temperature of the titanium compound. Elemental titanium was deposited on the copper surface. In addition to the titanium compound of the example; the compounds $(C_5H_5)_2Ta(C_6F_5)_3$ and $(C_5H_5)Zr(C_6F_5)_2$, from which tantalum and zirconium are deposited, respectively, are of particular value.

The compounds of interest herein are solids which are readily soluble in many organic solvents and therefore can be used in solution vapor plating as well as being entrained in a carrier gas.

The perfluoroorganometallic compounds used for vapor deposition in this specification may be formed by the method disclosed by P. M. Treichel, M. A. Chaudhari and F. G. A. Stone, Journal of Organometallic Chemistry, 1 (1963), p. 98; 2 (1964), p. 206, or by M. A. Chaudhari and F. G. A. Stone, Journal of the Chemical Society (1966), p. 838.

I claim:

1. A method of vapor deposition of a transition element selected from the transition elements of the group consisting of indium, columbium, titanium, zirconium and tantalum; said method comprising

(a) vaporizing at a reduced pressure a compound of the formula:

$$(C_5H_5)_2M(C_6F_5)_{n-2}$$

wherein M is said transition element and n is the valence of said transition element in said compound;

(b) heating the resulting vapor of said compound above its decomposition temperature; and

(c) effecting the deposition of said transition element on a surface.

2. The method according to claim **1** wherein said surface is at a temperature above the decomposition temperature of said compound.

3. The method according to claim **1** wherein said vapor is entrained with a nonoxidizing gas.

4. The method according to claim **1** wherein said vapor is entrained with hydrogen.

5. The method according to claim **1** wherein said compound is

$$(C_5H_5)_2Ti(C_6F_5)_2$$

6. The method according to claim **1** wherein said compound is

$$(C_5H_5)_2Ta(C_6F_5)_3$$

7. The method according to claim **1** wherein said compound is

$$(C_5H_5)_2Zr(C_6F_5)_2$$

8. The method according to claim **1** wherein said surface is a metal surface.

9. The method according to claim **1** wherein said vapor is entrained in a nonoxidizing gas and said element is deposited on a solid surface at a temperature above the decomposition temperature of said compound.

10. The method according to claim **9** wherein said element is titanium.

11. The method according to claim **9** wherein said element is tantalum.

12. The method according to claim **9** wherein said element is zirconium.

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ALFRED L. LEAVITT, *Primary Examiner.*

A. GOLIAN, *Assistant Examiner.*

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