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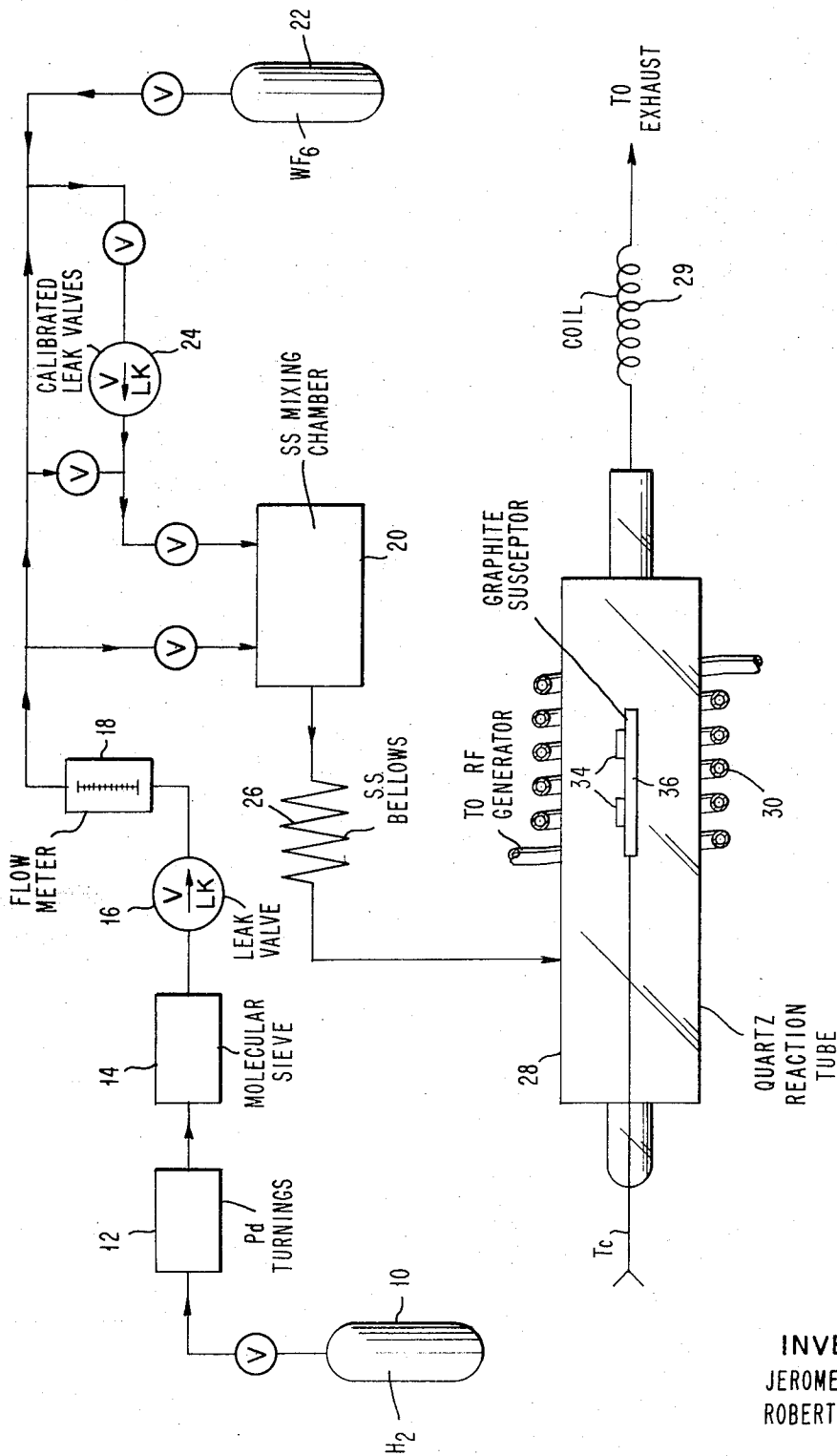
J. J. CUOMO ET AL

3,697,343

METHOD OF SELECTIVE CHEMICAL VAPOR DEPOSITION

Filed Dec. 16, 1970

4 Sheets-Sheet 1



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FIG. 2

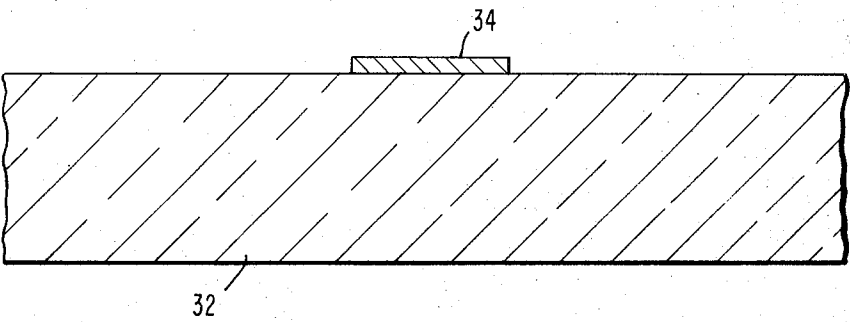


FIG. 3

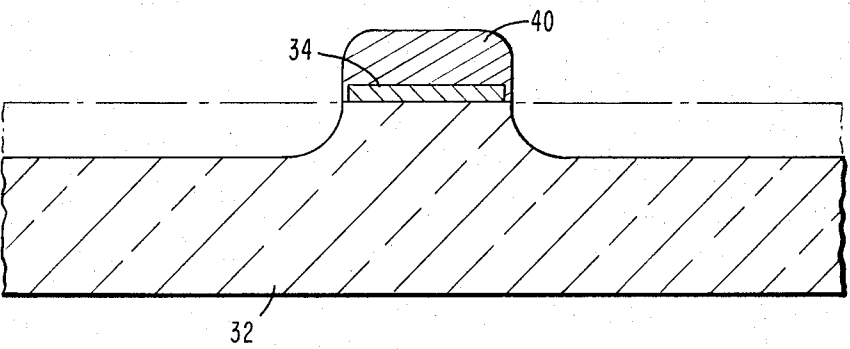


FIG. 4

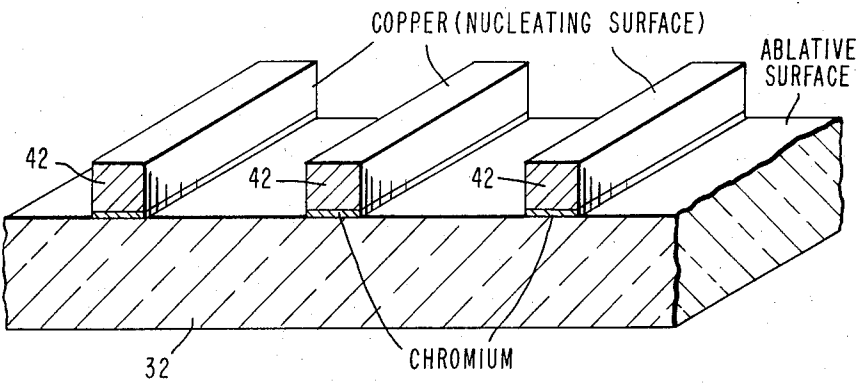
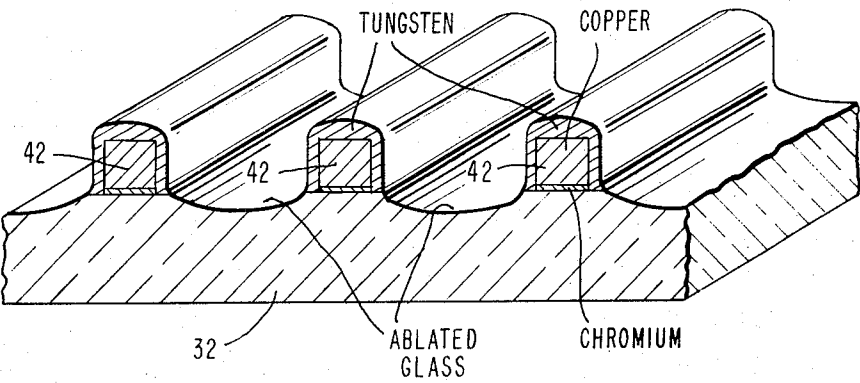


FIG. 5



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FIG. 6

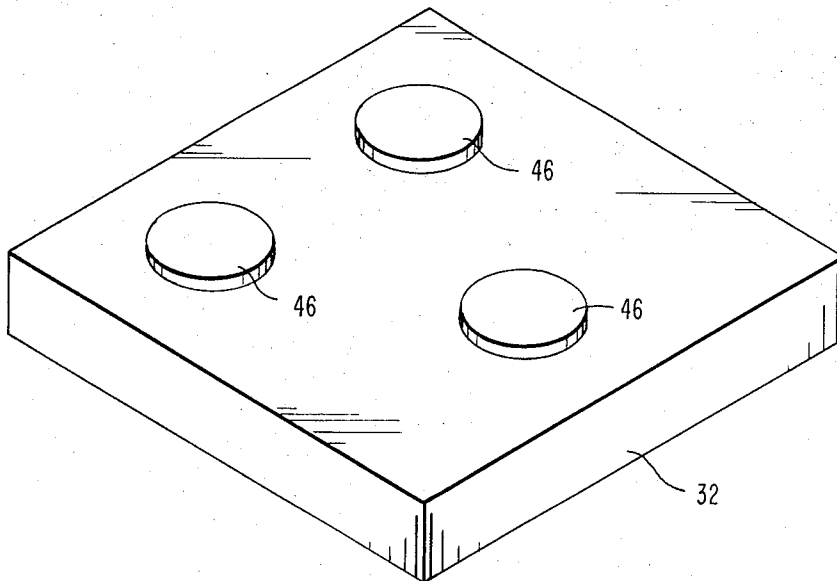
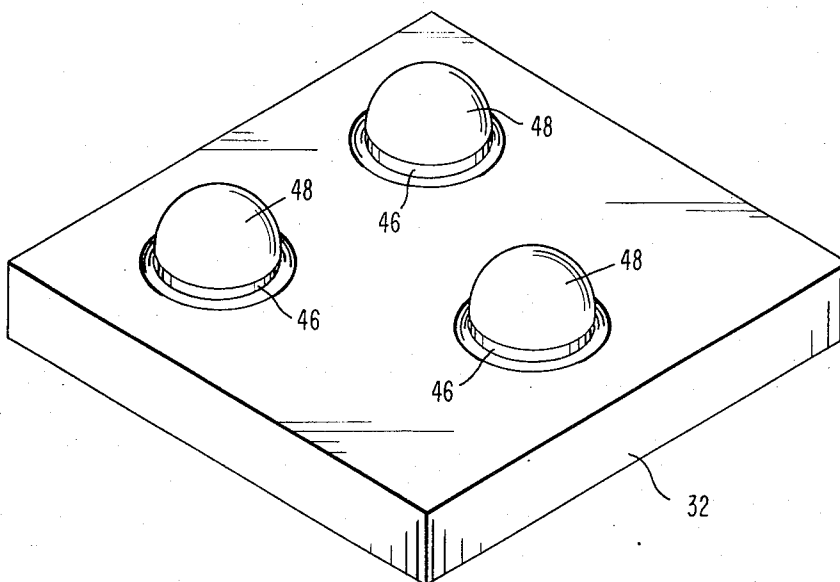


FIG. 7



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FIG. 8

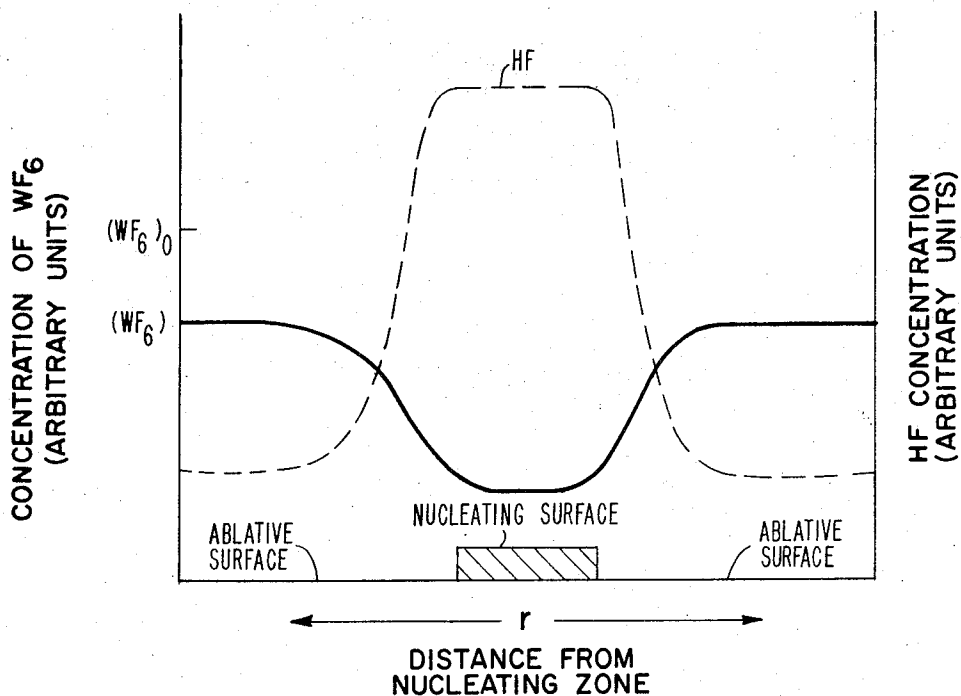
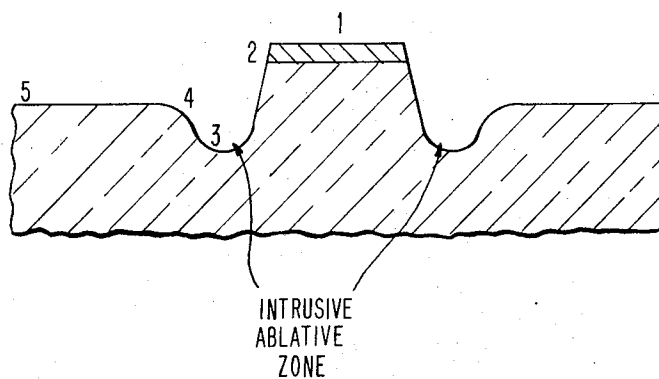


FIG. 9



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METHOD OF SELECTIVE CHEMICAL VAPOR DEPOSITION

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U.S. Cl. 156—13

8 Claims

ABSTRACT OF THE DISCLOSURE

Tungsten and other refractory metals such as molybdenum, tantalum, hafnium, zirconium, rhenium, etc. and metalloids such as silicon are caused to be deposited selectively by the hydrogen reduction of their fluorides and chlorides. The process is termed selective-chemical vapor deposition since the metal is deposited only on prepatterned areas of a substrate. The substrate is suitably a glass such as a borosilicate, boroalumino-silicate, phospho-alumino-silicate, phospho-silicate or a soda-lime glass. The selective chemical vapor deposition process occurs when two surfaces with different chemical reactivities are exposed to the chemical vapor deposition environment. The prepatterned areas provided one of these surfaces, such areas comprising a nucleating layer of a material such as chromium, tungsten, molybdenum, copper, aluminum, silicon, silicon dioxide, aluminum oxide, silicon nitride, and the like or of composite layers of chromium-copper, chromium-copper-chromium, and the like. The other surface is provided by the remainder of the surface, i.e. the exposed surface of the substrate. The surface provided by the prepatterned area acts as a metal nucleation site while the substrate, i.e., the glass surface chemically erodes (ablates) and the metal does not nucleate thereon. In considering the mechanism of the inventive process, the deposition reactions and simultaneous ablation reactions acting in close proximity are an essential element thereof.

BACKGROUND OF THE INVENTION

This invention relates to a method of selective chemical vapor deposition. More particularly it relates to a method for selectively chemically vapor depositing a metal, essentially of the refractory type, on a substrate.

In many situations, it is desired to have a metal in a given pattern deposited on a substrate. For example, in the manufacture of monolithic circuitry, it may be desired to have a deposited pattern of transmission lines of a particular refractory metal. Heretofore, to produce such refractory metal patterns, there have been required complicated techniques such as multiple step evaporating and subsequent subtractive etching utilizing photolithographic techniques. For example, the lines of large aspect ratios, i.e. height to width, cannot be provided by the known refractory metal pattern producing methods. Total covering of structures with a refractory metal also cannot be readily achieved by known methods.

Accordingly, it is an important object of this invention to provide an improved simple method for providing a refractory metal layer in a chosen pattern on a substrate. It is another object to provide an improved simple method for totally covering a structure with a refractory metal layer.

It is a further object to provide a method in accordance with the preceding objects for selectively chemically vapor depositing the refractory metal in the desired pattern or as the covering layer.

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SUMMARY OF THE INVENTION

Generally speaking and in accordance with the invention, there is provided a method for depositing a metal on the surface of a substrate body in a chosen pattern. The metal which is used is one which is capable of forming a gaseous or relatively high vapor pressure chemical compound which is reducible in a reducing atmosphere with the production of a by-product eroding material. The substrate material which is used is one which is capable of chemically reacting with the gaseous or high vapor pressure metal compound and the by-product material.

In carrying out the invention, there is provided in the aforesaid chosen pattern, a layer of a protective material which is substantially non-chemically reactive with the gaseous or high vapor pressure metal compound and the by-product material, the purpose of the protective material layer being to provide a nucleating surface upon which the metal deposits. The metal compound is reduced to the metal and the by-product in a reducing atmosphere in a container for the substrate body whereby the metal deposits on the surface of the protective material in the desired pattern. That portion of the surface of the substrate body which does not have the protective material layer thereon is ablated by its chemical reaction with the metal compound and the by-product. The metal may be a refractory metal which is capable of forming a gaseous compound or high vapor pressure compound at a temperature of from room temperature up to about 700° C. and is one such as is included in the group consisting of tungsten, molybdenum, tantalum, hafnium, zirconium and rhenium. The gaseous or high vapor pressure metal compounds are suitably the fluorides and chlorides of these metals. The substrate material is suitably a soda-lime, a borosilicate, a boroalumino-silicate, a phospho-alumino-silicate or a phospho-silicate glass. The protective material may be one selected from the group consisting of chromium, tungsten, molybdenum, copper, aluminum, silicon dioxide, silicon, aluminum oxide, silicon nitride and the like or a composite layer of copper-chromium, chromium-copper-chromium, and the like. The reducing atmosphere is suitably hydrogen.

The foregoing and other objects, features, and advantages of the invention will be apparent from the following more particular description of the preferred embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings,

FIG. 1 is a schematic depiction of apparatus for carrying out the process according to the invention;

FIG. 2 is a cross-sectional view of a substrate prior to selective chemical vapor deposition thereon;

FIG. 3 is a view similar to that of FIG. 2 but after selective chemical vapor deposition thereon;

FIG. 4 is a perspective view showing an arrangement to which the overcoating mode of the process is suitably applied prior to selective chemical vapor deposition;

FIG. 5 is a view similar to that of FIG. 4 but after selective chemical vapor deposition;

FIG. 6 is a perspective view showing an arrangement to which the growth mode of the process is suitably applied prior to selective chemical vapor deposition;

FIG. 7 is a view similar to that of FIG. 6 but after selective chemical vapor deposition;

FIG. 8 is a model of the vapor phase concentration surrounding a nucleating zone; and

FIG. 9 is a schematic of an electron microprobe tracking of a line on a substrate after selective chemical vapor deposition thereon.

DESCRIPTION OF A PREFERRED EMBODIMENT

In considering the invention, it is to be noted that the properties of tungsten such as its high melting point, high recrystallization temperature, low expansion coefficient, low electrical resistivity, barrier to noble metal diffusion and low thermal expansion coefficient have made it desirable as a fabrication material. The chemical vapor deposition of tungsten by the hydrogen reduction of tungsten hexafluoride has a number of advantages such as fast deposition rates, low operating temperatures, high purity deposits and the formation of only gaseous by-products. Tungsten, deposited by the hexafluoride process, has been successfully used in a number of applications such as, for example, in the fabrication of tungsten crucibles and the preparation of single crystals.

In accordance with the invention, in contrast to the chemical vapor deposition process for a metal such as tungsten in which deposition takes place on all areas that have exceeded the thermal activation energy, the selective chemical vapor deposition process deposits the metal, e.g., tungsten on discrete prepatterned areas. The prepatterned surfaces act as nucleating sites for tungsten whereas the unpatterned, i.e. exposed surface of the substrate does not nucleate tungsten but, instead, chemically erodes (ablates). The inventive process depends on the presence of surfaces with different chemical reactivities such that deposition takes place in one area and not in the other although the surfaces are in excess of the activation energy for the deposition process. It is believed that an explanation of the mechanism of the invention is that the ablative surface presents a different chemical reaction path for the reactants and nucleation of the metal does not occur whereas the metal reduction reaction path is followed on the nucleation surface.

In FIG. 1, there is shown a suitable apparatus for carrying out the inventive process. The apparatus is constructed essentially of stainless steel with the exception of the reaction chamber which is suitably made of quartz.

In this apparatus, a stainless steel container 10 containing prepurified hydrogen provides a source of the latter gas which continually flows through the system. The hydrogen gas flows over palladium turnings depicted by the block 12, through a molecular sieve 14, a leak valve 16, and a flow meter 18, and flows into a stainless steel mixing chamber 20.

A stainless steel container 22 contains tungsten hexafluoride gas. The latter gas flows from container 22 through calibrated leak valves 24 into mixing chamber 20.

The mixture of hydrogen and tungsten hexafluoride passes through bellows 26 into a quartz reaction tube 28 which is heated by an RF coil 30. The gases, after exiting reaction tube 28, are directed through several feet of coiled tubing 29 to help prevent the back diffusion of ambient gases before being exhausted into a high velocity fume hood (not shown). As a safety precaution, a differential pressure may be set in the exhaust hood so that, in the event of power failure or exhaust hood failure, the sensor activates a normally open valve which floods the vent and hood with nitrogen. The tungsten hexafluoride is of high purity and bottled in precleaned stainless steel containers which are hydrogen fired and helium leak checked.

The substrates, in the form of flat glass slides, are made of a borosilicate, soda-lime or other similar glasses onto which nucleating protective material patterns 34 are deposited or prepared by photoresist techniques. The substrates prior to patterning, are ultrasonically cleaned in detergent and then in hot sulfuric-dichromic acid solution. They are rinsed in deionized water, alcohol, and, finally, in Freon vapor. Patterned nucleating coatings 34 on the glass are prepared by electron beam evaporation or RF sputtering. The prepared substrates are placed upon a tungsten coated graphite susceptor 36 which may be on a quartz sled (not shown). The system is allowed to be

purged with hydrogen for one hour at a flow of 15 liters of hydrogen per minute. The susceptor is inductively heated to 440° C. and the temperature is sensed by a thermocouple (not shown) in a well embedded in the susceptor. After about ten minutes at the 400° C. temperature, tungsten hexafluoride is metered into the system.

As has been mentioned above, patterned nucleating coatings 34 may comprise chromium, molybdenum, tungsten, copper aluminum, silicon, silicon dioxide, silicon nitride, aluminum oxide, or a composite layer of copper-chromium or chromium-copper-chromium. Under the foregoing operating conditions, tungsten deposits only on the patterned areas and the exposed glass areas are somewhat ablated away.

FIG. 2 shows the substrate 32 having the nucleating surface material 34 thereon. FIG. 3 shows the situation which obtains after deposition. It is seen therein that the metal accumulates on the nucleating area and some glass ablates in the non-nucleating area.

Two modes of selective chemical vapor deposition can be achieved by the inventive process, viz "overcoating" and "growth" modes.

In the overcoating mode, selective chemical vapor deposition occurs when the nucleating layer has essentially a three-dimensional form. Thus, as shown in FIG. 4, the nucleating surface is provided by a copper-chromium transmission line 42 on a borosilicate glass substrate, FIG. 4 showing the situation which obtains prior to selective chemical vapor deposition. In FIG. 5 there is shown the results which ensue after the application of the selective chemical vapor deposition process using tungsten hexafluoride. Tungsten totally covers the transmission lines 42 and there is no deposition on the non-nucleating areas of exposed glass between the lines, which are chemically eroded away.

The selective chemical vapor deposition growth mode is distinguished from the overcoating mode in that the nucleating surface has essentially a two-dimensional shape which is developed into a three-dimensional structure. For example, three-dimensional metal structures such as tungsten can be selectively grown on thin films of nucleating material patterned on a non-nucleating surface. Thus, in FIG. 6 there is shown a deposited nucleating material pattern 46 on a substrate glass. FIG. 7 shows the situation which obtains after selective chemical vapor deposition. The deposited metal has grown on the nucleating surfaces. A thin film, of the order of a few hundred angstroms thickness, can be grown into a structure of many microns thickness while maintaining its shape, i.e. with little lateral growth.

In Table I, there are shown some results of overcoating electrical transmission lines. The samples used during these experiments consisted of 10 micron thick chromium-copper or chromium-copper-chromium patterned lines on 1 mil thick 7070 (Corning) borosilicate glass which is fired on alumina substrate. It is to be noted that the total thickness change after tungsten deposition includes the tungsten accumulation on the line and the chemical ablation of the adjacent exposed glass surface.

TABLE I

Sample number	Micrometers			Substrate temp., °C.	Time, min.	Approx. rate of deposition, Å/sec.
	Starting thickness	Final thickness	Total change			
1.-----	10.5	16.5	6.0	400	3	200
2.-----	10.5	24.4	16.9	405	5	200
3.-----	10.5	19.6	9.1	400	1	200-400
4.-----	10.5	15.3	4.8	390	2	150
5.-----	10.5	19.9	8.4	398	4	160
6.-----	(1)	24.7	24.7	420	12	50

¹ 1,000 angstrom.

In carrying out the invention, the reaction temperature may suitably be from about room temperature to 700°. A suitable range of flow rate ratios of tungsten hexafluoride to hydrogen is from 0.0001 to 0.1, typically about 0.2. Thus, a suitable flow rate into the reaction chamber

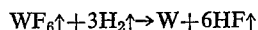
is about 0.3 liter/minute of tungsten hexafluoride with a concurrent flow of about 15 liters/minute of hydrogen.

In the inventive selective chemical vapor deposition process, tungsten structures have been grown on very thin films prepared by photolithography. Arrays of dots and conductor-line patterns as thin as 50 Å have been found to act as nucleating sites for tungsten growth. Table II which follows hereinbelow shows the nucleating materials that have been used. The thickness d of tungsten grown on these surfaces range to $0.1 < d < 50$ micrometers. 10

TABLE II

Nucleating material	Film thickness, Å	Method of deposition	Thickness of tungsten growth, microns
Cr.....	50	{E-gun evaporation.....}	4
		{RF sputtered.....}	
Al.....	2,000	Evaporation.....	4
Mo.....	1,000	RF sputtered.....	4
W.....	50	{E-gun evaporation.....}	3-6
		{RF sputtered.....}	
Al ₂ O ₃	750	RF sputtered.....	2-4
SiO ₂	1,500	do.....	1.5
Cr-Cu.....	1,500	E-gun evaporation.....	2-10

In considering the mechanism of the inventive process, the deposition reactions and simultaneous ablation reactions acting in close proximity are an essential element thereof. In this connection, the nucleating surface can be considered a protective layer relative to the hydrogen fluoride and metal fluoride compound attack, the hydrogen fluoride resulting from the following reaction using tungsten hexafluoride for example. 15



The protective materials which are suitable for providing nucleating surfaces are either unaffected by hydrogen fluoride and the metal compound or the rate of hydrogen fluoride attack is sufficiently slow whereby sufficient tungsten can accumulate on the nucleating surface. The characteristic feature of the ablative surface, i.e., the exposed surface of the glass substrate, is that it tends to be more easily attacked by hydrogen fluoride and the metal compound. 20

The general composition of examples of ablative materials are shown in Table III under the heading of soft glass and hard glass. Soft glass, also known as soda-lime glass is composed mainly of SiO₂ and Na₂O. Hard glass of the borosilicate type is generally composed of SiO₂ and B₂O₃. Both aluminum and barium are often chemically significant species in determining properties of these glasses. The SiO₂ in both types is approximately 50 to 70 percent by weight. A mechanism for the rapid rate of SiO₂ removal in the ablative materials might be modeled upon the solution corrosion mechanism for glass. The reaction with or the leaching of the more reactive species in the glass, would expose an open network of SiO₂ of high specific surface. The reaction rate of such an active surface far exceeds that of a coherent planar surface as is present in fused quartz. 25

TABLE III.—APPROXIMATE CONSTITUENT OXIDES (WEIGHT PERCENT)

Class	Type	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	B ₂ O ₃	Al ₂ O ₃	BaO	Li ₂ O
Soft glass.....	Soda-lime.....	70.1	16.8	0.3	5.4	3.6	0.8	2.58	-----	-----
		65.5	4.3	3.1	1.0	-----	16.0	5.5	2.5	-----
Hard glass.....	Borosilicate.....	70.0	-----	0.5	0.1	0.2	28.0	1.1	-----	-----
		50.2	-----	-----	-----	-----	13.8	10.7	-----	25.0

The shape of the metal's growth, for example, tungsten is affected by the environment, i.e. hydrogen flow rate, tungsten deposition rate, substrate temperature and other factors. FIG. 8 shows a model thereof. It is seen in FIG. 8 that in tracking an arbitrary phase concentration of tungsten hexafluoride along the surface of a substrate, a sharp depletion occurs as the insulating surface is approached since tungsten is depositing here. Simultaneously, upon examination of the hydrogen fluoride, it is seen that a 30

sharp increase in its concentration occurs since this is a by-product of the reduction action. The intensive erosion area immediately surrounding the nucleating areas results from the presence of excessive amounts of hydrogen fluoride. FIG. 9 is a schematic of an electron microprobe tracking of a line on borosilicate glass after selective chemical vapor deposition of tungsten. The position numbers thereon are from the following tabulation. Position 3 represents the intensive ablative zone. 35

Position number	X-ray intensity ×1,000		
	Si	W	F
1.....	0.3	128.0	0.3
2.....	1.3	128.0	0.3
3.....	40.3	1.0	0.6
4.....	11.0	15.0	13.0
5.....	35.0	4.5	4.5

In considering the foregoing, it is to be realized that the criteria for selectivity for the selective chemical vapor deposition process is the sharp line of demarcation which forms between the ablative zone where chemical erosion takes place and the nucleating zone where the chemical reduction of tungsten hexafluoride occurs. The following are some of the many applications where in the inventive process can be availed of, either in the overcoating or growth work. 40

The total overcoating of metal lines has many applications in the processing of electronic devices. For example, it can be used in the prevention of electromigration in metals, in reducing corrosion problems in metals, in matching thermal expansion coefficients, in matching hardnesses, for improving adhesion, and as a chemical or diffusion barrier layer. 45

The growth of metal lines from essentially two-dimensional films is effective to selectively increase conductivities in specific areas and in the growth of pins and conduction lines. 50

Typical examples of applications are as follows:

(1) Tungsten on patterned protective material on 7070 borosilicate glass:

- (a) Glass on aluminum oxide.
- (b) Silicon dioxide, aluminum oxide, silicon, silicon nitride or other suitable protective material (as detailed hereinabove) patterned on the glass.
- (c) Tungsten deposited selectively on the protective material pattern and not on the exposed glass areas from the reduction of tungsten hexafluoride by hydrogen. 55

(2) Encapsulation of metal lines.

- (a) Borosilicate 7070 glass on aluminum oxide.
- (b) Layer of chromium-copper or other protective material on glass surface.
- (c) Patterned photoresist on protective layer.
- (d) Electroform copper or other suitable substitute.
- (e) Strip photoresist and exposed layer.
- (f) Selectively deposit tungsten on the electroformed ma-

terial by the hydrogen reduction of tungsten hexafluoride. The material is thereby encapsulated.

(3) The same as (2) except that the copper lines are produced by etching rather than by electroforming.

(4) The use of partially fired borosilicate glass as a chemical ablative coating.

(a) Same as in (1), (2) and (3).

(b) Refill with glass and partially fire. 75

- (c) Pattern a protective coating on or in holes in partially fired glass.
- (d) Selectively chemically vapor deposit tungsten.
- (e) Remove uneroded glass refill and fire at glassing temperature.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A method for depositing a metal in a chosen pattern on the surface of a substrate body comprising the steps of:

providing as said metal, a metal which is capable of forming a gaseous or relatively high vapor pressure compound, said compound being reducible to said metal in a reducing atmosphere with the production of a by-product material;

providing as said substrate body, a material which is substantially chemical reactive with said metal compound and said by-product material the substrate material selected from the group consisting of soda-lime, borosilicate, boroaluminosilicate, phosphoaluminosilicate and phosphosilicate glasses;

providing on the surface of said substrate body in said chosen pattern, a layer of protective material which is substantially unreactive with said metal compound and said by-product; and

reducing said metal compound to said metal and forming said by-product in a reducing atmosphere in a container containing said substrate body having said chosen pattern protective material layer thereon, the surface of said layer forming a nucleating surface upon which said metal deposits, the exposed portion of the surface of said substrate body not having said protective material layer thereon being concurrently ablated during said reduction of said metal deposition.

2. A method as defined in claim 1 wherein said metal is a metal which is capable of forming a gaseous or relatively high vapor pressure compound at a temperature of from room temperature up to 700° C.

3. A method as defined in claim 2 wherein said metal is selected from the group consisting of tungsten, molybdenum, tantalum, hafnium, zirconium, rhenium and silicon.

4. A method as defined in claim 2 wherein the gaseous

and vapor pressure metal compounds of said metal are selected from the group consisting of fluorides and chlorides of said metals.

5. A method as defined in claim 2 wherein said protective material is selected from the group consisting of chromium, tungsten, molybdenum, copper, aluminum, silicon dioxide, silicon, aluminum oxide and silicon nitride and composite layers of copper-chromium and chromium-copper-chromium.

6. A method as defined in claim 2 wherein said reducing atmosphere is a hydrogen atmosphere.

7. A method of providing a tungsten deposit of a chosen pattern on a surface of a glass body comprising, placing in said pattern on a surface of a body comprising a glass selected from the group consisting of soda-lime, borosilicate, boroaluminosilicate, phosphoaluminosilicate, and phosphosilicate glasses, a layer of a protective material selected from the group consisting of chromium, tungsten, molybdenum, copper, aluminum, silicon dioxide, silicon, aluminum, and silicon nitride and composite layers of copper-chromium and chromium-copper-chromium; and

reducing tungsten hexafluoride in a hydrogen atmosphere in a vessel containing said glass body having said protective material on its surface whereby the metal resulting from said reduction deposits on the surface of said protective material on said deposit while concurrently said tungsten hexafluoride and the hydrogen fluoride resulting from said reduction causes that portion of said glass body not having said protective material deposited thereon to be ablated.

8. A method as defined in claim 7 wherein said glass is borosilicate glass.

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U.S. Cl. X.R.

117—107.2 R, 212, 217; 156—11, 15, 24