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PROCESS FOR THE CONTROLLED DEPOSITION OF SILICON DIHALIDE VAPORS ONTO SELECTED SURFACES

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This invention relates to a method of depositing an element onto a selected surface and, more particularly, relates to a method for the controlled deposition of an element onto a selected surface to form a crystallized layer of desired thickness thereon.

One of the known processes for coating an element onto a surface is by electroplating wherein the article whose surface is to be coated is placed in an electrolytic solution containing the coating element and the flow of current through the solution and article causes a thin coating of the element in solution to be deposited onto the surface of the article. Since the mass of any substance which is liberated at an electrode during electrolysis is proportional to the quantity of electricity which passes through the electrolytic cell, there may be a certain control over the quantity of the element deposited and, correspondingly, the thickness of the coating on the surface. Electroplating, however, has several obvious disadvantages. The primary disadvantage is that a surface which is non-conductive to electricity cannot be coated electrolytically. Surfaces of glass, resin, ceramics, certain plastic materials and the like, which are non-conductive, fall within this category. Another disadvantage in electroplating an article is the cost involved in depositing a layer of an element of desired thickness onto a metallic surface, since it takes 96,500 coulombs of electricity to liberate a gram-equivalent weight of any metal from a compound by electrolysis.

Another known process of coating the surface of an article is by dipping the article into a solution or bath of the coating material. Although articles having non-conducting surfaces may thus be coated, there can, of course, be no accurate control over the thickness of the coating on the surface of the article. The same holds true for spraying, brushing and other methods of coating surfaces of articles.

Therefore, an object of this invention is to obviate the above disadvantages which are present in existing coating processes.

Another object of this invention is to provide an improved method of coating an article with a well-crystallized layer of an element.

Still another object of this invention is to provide a method of depositing a coating of an element of desired thickness onto a selected surface.

A further object of this invention is to provide a method for depositing a thin crystallized layer of desired thickness of an element onto a selected surface by exothermically decomposing an unstable lower halide of the element onto the selected surface.

Still another object of this invention is to coat the surface of an article with a continuous crystallized layer of an element, which layer tenaciously adheres thereto.

In attaining the objects of this invention one feature resides in passing lower halide vapors of the element over the selected surface and decomposing these vapors over the surface so as to deposit a crystallized layer of the element thereon. Another feature resides in pass-

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ing the lower halide vapors over and in contact with the selected surface of a low flow rate so that the exothermic decomposition of the vapors causes a continuous crystallized layer of the element to be deposited thereon while simultaneously liberating higher halide vapors of the element.

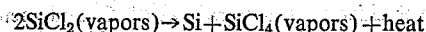
Still another feature resides in forming the lower halide vapors of the element at an elevated temperature wherein the vapors are stable and then cooling these lower halide vapors while simultaneously passing them over and in contact with a selected surface to decompose the vapors into the free element and higher halide vapors of the element which are stable at the lower temperature, and cause the free element to be deposited onto the surface.

Yet another feature resides in passing the heated, stable lower halide vapors of the element over and in contact with a selected surface of known area at a predetermined flow rate which is measured by the weight of the higher halide of the element which is reacted with the element per unit of time to form the lower halide vapors of the element which are then decomposed over and in contact with the surface to form a crystallized layer of the element of desired thickness thereon.

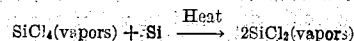
Other objects, features and advantages of this process will become more apparent from the following description of the invention.

Basically, the process includes the steps of decomposing normally unstable halide vapors of an element, such as lower halide vapors which are stable only at an elevated temperature, over and in contact with the surface of an article to be coated, thus depositing a fine, thin, crystallized layer of the element thereon when the lower halide vapors are cooled and thus decomposed.

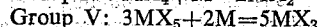
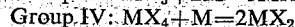
Using silicon as illustrative of an element which is to be coated onto a surface, it is believed that the following reaction occurs when silicon dichloride vapors which are stable only at elevated temperatures are cooled and decompose:



For every 2 molecules of SiCl_2 which are decomposed, an atom of silicon is deposited onto the selected surface, and a molecule of SiCl_4 vapor is formed. This latter compound, which is stable at room temperature, may be utilized in forming additional lower silicon halide vapors by reacting it with a silicon bearing material, or even silicon itself, at elevated temperatures. The reaction occurs as follows:

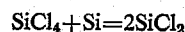


From the outermost electronic arrangements of groups III, IV and V elements, it may be predicted that lower halides of these elements can be produced at elevated temperatures as follows:



where M is the particular element and X is a halogen. Included among the elements whose lower halide vapors may be decomposed so as to deposit a layer of the element onto a surface are germanium, tin, boron, aluminum, gallium, indium, arsenic, antimony, bismuth, and the like.

As the heated lower halide vapors of the element pass over and come in direct contact with the cooler selected surface at a controlled low flow rate, a continuous crystallized layer of the element is deposited thereon due to the decomposition of the lower halide at the cooler temperature. By using silicon as an example of the element to be deposited onto a surface and since the equilibrium equation



begins at 800° C., this temperature would be the minimum temperature of the gaseous mixture striking the selected surface. Thus, articles or materials having melting points in excess of this temperature may readily be used as receptors for the deposited element. Those materials or surfaces having a much lower melting point than the minimum equilibrium equation temperature cannot be coated by this process. Materials having melting points slightly lower than the temperature of the gaseous mixture can be coated if the materials are in massive form or if they are placed on a good conductor so that the surface temperature of the material is not too high. In some instances, surface fusion of the deposited element to the selected surface occurs and may be desirable.

The thickness of the layer of the element deposited onto a given surface is very accurately controlled by either setting the residence time, or by controlling the weight of lower halide per unit time passing over a selected surface of specific area. An inert carrier gas, such as helium, nitrogen and the like, is used to vary the percent or weight of lower halide for a given flow rate of the gaseous mixture. The flow rate of the lower halide vapors may be determined by reacting a known weight of the higher halide of the element with the element per unit of time, thus forming the lower halide vapors of the particular element. If the flow rate of lower halide vapors is too slow or too fast, the quantity of higher halide of the element which is to react with the element is correspondingly increased or decreased. If the flow rate of the lower halide vapors is too high, a powdery layer of the element is formed on the selected surface rather than the desired continuous crystallized layer obtained by a low flow rate.

The following examples of coating a surface by depositing thereon a layer of an element formed by the decomposition of unstable lower halide vapors of the element are merely illustrative of the process and are not to be considered as limiting the scope of the invention.

Example 1

A mixture of lower silicon dichloride vapors and helium was formed by passing the helium at a controlled low flow rate over silicon tetrachloride at 0° C. and then passing the mixture over impure silicon at 1220° C. The free silicon in the latter reacted with the silicon tetrachloride to form silicon dichloride vapors. A tantalum surface which was to be coated with silicon was placed adjacent this high temperature reaction zone and the mixture of silicon dichloride and helium was passed over and in contact with the cooler tantalum surface at a low flow rate. Decomposition of the unstable silicon dichloride resulted in a continuous adherent crystallized layer of pure silicon being deposited upon the tantalum surface. The resulting silicon tetrachloride which was formed by the decomposition of the silicon dichloride vapors was removed and collected in a condenser.

Example 2

Helium was passed over silicon tetrachloride at 25° C. to form a gaseous mixture containing 31% by volume of silicon tetrachloride and this mixture was passed over and in contact with commercial silicon at 1200° C. to form silicon dichloride vapors. A tantalum cylinder was placed immediately adjacent this high temperature zone and the exothermic decomposition of the silicon dichloride vapors caused the deposition of a well-crystallized diamond cubic silicon layer on the inner surface of the tantalum cylinder. The flow rate was in excess of one gram of liquid silicon tetrachloride per hour, and a layer of silicon one millimeter in thickness was deposited in 72 hours at a rate of 0.1 to 0.2 gram per hour.

Example 3

A gaseous mixture of 18% SiF₄ and 82% He by vol-

ume was passed over commercial silicon at 1190° C. to form silicon difluoride vapors which were passed through and in contact with the inner walls of a tantalum cylinder placed adjacent the high temperature zone. Decomposition of the silicon difluoride vapors resulted in a thin layer of silicon being deposited on the inner walls of the cylinder. The resulting SiF₄ vapors were recovered.

Example 4

A gaseous mixture of SiBr₄ and N₂ was passed over and in contact with commercial silicon at 900° C. to form SiBr₂ vapors which were then passed through a silica tube placed adjacent the high temperature zone. The deposited silicon resulting from the decomposition of SiBr₂ formed a continuous mirror on the inner walls of the silica tube. SiBr₄ vapors and N₂ were removed and the SiBr₄ was condensed.

While it is preferred to coat a selected surface with an element which is unlike the surface (for example, a glass surface being coated with a metal), it is also possible to coat a surface with an element similar to that of the surface (for example, a silicon surface can be coated with a layer of silicon). Sillimanite surfaces have been successfully coated with extremely adherent coats of silicon up to approximately 3 mm. in thickness. An important consideration in the selection of the surface material is its reactivity with the depositing element at the decomposition temperature. For example, silicon reacts only slightly with tantalum at high temperatures and, therefore, a layer of silicon may be deposited on a tantalum surface. However, if reactivity between the element and the surface were not desirable, then it is only necessary to select the materials with care so that such a reaction does not occur. In some cases, a reaction layer of demarcation might be desirable on the surface.

The rate of deposition for the formation of a continuous layer of an element on a selected surface is quite low and, in fact, several hours are required to build up a thin layer of silicon. This rate increases, however, as the temperature of the equilibrium mixture increases and the temperature of the collecting surface decreases.

A silicon surface can be readily and rapidly coated with silicon because of its high melting point. At a temperature of 1400° C. for the equilibrium mixture, a high deposition rate of silicon upon silicon is produced even at the low flow rate required for this particular process.

Among the uses for this process is the coating of sensitive electrical components such as n-p-n junction transistors. Also controlled coating of glass with metals and non-metals or the controlled coating of crystals is possible by this process. Glass and ceramics may be coated for absolute inertness to hydrofluoric acid. Surfaces may also be coated with a thin layer of silicon in order to make them inert to acids such as HCl, H₂SO₄ and the like. The above processes are particularly adapted for coating the inner surfaces of cylinders. Metals and other materials may also be coated with a photosensitive layer of silicon for use as solar batteries.

While only several specific embodiments of this invention have been described and only several specific elements have been listed, these examples are merely illustrative of the invention and are not to be considered as a limitation thereon. It is intended in the appended claims to include all such processes which fall within the scope of this invention.

Having described fully the invention, what is claimed is:

1. The process of coating a thin well-crystallized continuous layer of silicon onto a surface capable of withstanding without physical change thereto a temperature which is at least as high as the minimum equilibrium temperature of silicon dihalide vapors comprising the step of passing heated silicon dihalide vapors over and in contact with said surface at a predetermined flow rate, the temperature of said surface being relatively cooler

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than the temperature of said vapors and causing exothermic decomposition of said silicon dihalide vapors into free silicon and silicon tetrahalide vapors, said free silicon being deposited onto said surface.

2. The process of coating a thin well-crystallized continuous layer of silicon onto a surface capable of withstanding without physical change thereto a temperature which is at least as high as the equilibrium temperature of silicon dichloride vapors comprising the step of passing heated silicon dichloride vapors over and in contact with said surface at a predetermined flow rate, the temperature of said surface being relatively cooler than the temperature of said vapors so as to exothermically decompose the silicon dichloride vapors into free silicon and silicon tetrachloride vapors, the latter vapors being removed from said surface while the free silicon is deposited onto said surface.

3. The process of adhering a thin well-crystallized layer of silicon onto a surface capable of withstanding without physical change thereto a temperature which is at least as high as the minimum equilibrium temperature of silicon dihalide vapors comprising the steps of reacting silicon tetrahalide with silicon at an elevated temperature to form silicon dihalide vapors, and passing said vapors over and in contact with said surface at a predetermined flow rate while simultaneously cooling said vapors, the resulting exothermic decomposition of said silicon dihalide vapors forming free silicon and silicon tetrahalide vapors, said free silicon adhering to said surface.

4. The process of adhering a thin well-crystallized layer of silicon onto a surface capable of withstanding without physical change thereto a temperature which is at least as high as the equilibrium temperature of silicon dichloride vapors comprising reacting silicon tetrachloride with silicon at an elevated temperature to form silicon dichloride vapors, and passing said vapors over and in contact with the surface at a predetermined flow rate, said surface being relatively cooler than said vapors whereby said

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silicon dichloride vapors exothermically decompose into free silicon and silicon tetrachloride vapors, said free silicon being deposited onto said surface while said latter vapors are removed therefrom.

5. The process of coating a surface of known area with a crystallized layer of silicon of predetermined thickness, said surface being capable of withstanding without physical change thereto a temperature which is at least as high as the minimum equilibrium temperature of silicon dihalide vapors, comprising the steps of reacting a known weight of silicon tetrahalide with silicon at an elevated temperature to form silicon dihalide vapors which are stable only at said elevated temperature, passing said silicon dihalide vapors over and in contact with said surface at a predetermined flow rate, said flow rate determined by the known weight of silicon tetrahalide undergoing reaction per unit of time, and cooling said silicon dihalide vapors to cause exothermic decomposition thereof as free silicon crystals and silicon tetrahalide vapors, said crystals adhering to said surface.

6. The process of fusing a layer of silicon onto a selected surface having a melting point just below the minimum equilibrium temperature of silicon dihalide vapors comprising heating said surface to just below its melting point temperature and passing silicon dihalide vapors over and in contact with said surface at a predetermined flow rate while simultaneously cooling and exothermically decomposing said vapors to form the free element and silicon tetrahalide vapors, said element being deposited onto and fusing with said heated surface.

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