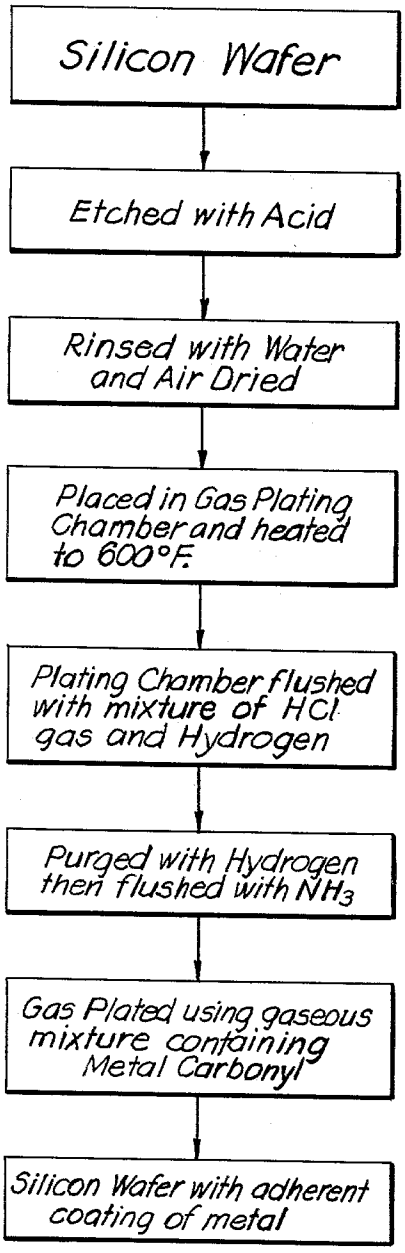
Nov. 23, 1965 W. C. JENKIN 3,219,482

METHOD OF GAS PLATING ADHERENT COATINGS ON SILICON

Filed June 25, 1962



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United States Patent Office

3,219,482
Patented Nov. 23, 1965

3,219,482

METHOD OF GAS PLATING ADHERENT COATINGS ON SILICON

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Filed June 25, 1962, Ser. No. 205,050
4 Claims. (Cl. 117—213)

This invention relates to a method of obtaining adherent plating deposits on oxidized substrate surfaces and materials which are difficult or impossible to plate satisfactorily by ordinary plating methods. The invention is more particularly concerned with a process of obtaining an adherent coating on such materials as deposited by thermal decomposition of a gaseous heat-decomposable compound, and commonly known as "gas plating."

It has been observed that merely cleaning of a material by conventional methods and then subjecting the thus cleaned material to heat in the presence of vaporized heat-decomposable compounds or mixtures of such compounds does not produce an adherent coating deposit. Many industrial materials and parts are required to be provided with an adherent coating and which has been difficult to achieve. For example, materials which readily oxidize in the presence of air or oxygen are very difficult or impossible to plate by ordinary methods, and especially materials which, after cleaning, rapidly form non-reducible oxides. Thus, in the manufacture of silicon rectifiers and diodes, a coating is required which is strongly adherent to withstand soldering or brazing of conductive metals thereto, and to remain adherent throughout the useful life of the product. Utilizing the method of this invention, an adherent, brazable metal deposit is obtained on these difficulty coatable materials.

Test results carried out in connection with the method of the present invention have indicated that there are two critical requirements that must be observed in order to obtain an adherent deposit of metal or metallic compound when gas plating such deposits on a substrate surface which readily acquires an oxide film. These requirements are:

(1) The material must be cleaned completely free of non-volatile salts, oxides, etc., even of a mono-molecular film, and kept free of contamination or reoxidation until the gas plating of the same is accomplished.

(2) The surface of the material thus cleaned must be treated with a gas that is sufficiently adsorbed to cause desorption of other and interfering gases. Such adsorbed gas, however, is one that is readily desorbed as gas plating and deposition of a coating is initiated, rather than at a later period when it tends to form a barrier to good adhesion.

In carrying out the process, the same can be made operable at ordinary atmospheric pressure conditions, or employing sub-atmospheric or even pressures above atmospheric. The pressure is thus not a critical limitation of the process of this invention.

In accordance with the present invention, materials that are difficult to plate because their surfaces immediately acquire a stable and difficult reducible oxide are first cleaned by etching the surface with acid or reagents that dissolve a portion of the material, including oxide or surface film. The operation must be done in the absence of oxygen to prevent reoxidation of the etched surface. Examples of materials which may be so cleaned and gas plated are silicon and titanium.

The preferred method of cleaning consists in placing the material in an airtight chamber, then purging the air therefrom with a non-oxidizing or non-reactive gas, such as hydrogen or helium. Thereafter the material is heated to 400° to 1000° F., preferably about 600° F., while retained in the gas plating chamber, and the heated material subjected to a gaseous mixture of the purging gas and the vapor of a gas that chemically attacks the material and forms a volatile compound as a by-product. Gases which are useful for this purpose are the halides of hydrogen, gaseous hydrogen chloride being the most economical and easiest to handle.

The process of the present invention is illustrated by the flow sheet on the drawing. No vacuum or elaborate equipment is required, as aforementioned, although use may be made of a blower or sub-atmospheric or pressure creating means to cause the gaseous substances to flow or circulate in direct contact with the material being gas plated.

Etching of the material with hydrogen chloride is effective employing a treatment of one or two minutes and which removes a thin layer of the material whereby a fresh and chemically clean substrate surface is produced. The etching gas is then purged from the plating chamber with hydrogen or helium or other non-reactive gaseous mixture that is readily desorbable during the initial gas plating operation.

Further treatment of the surface preparatory to depositing a coating, consists in exposing the material to a gas that becomes adsorbed and displaces other gases that may be present, but is readily desorbed as plating is initiated. For this purpose, ammonia gas is a very effective gas, particularly in gas plating adherent coating on silicon. In practice, the purging gas hydrogen is discontinued, and ammonia admitted until the chamber is flushed. The material being gas plated may be allowed to cool temporarily, but preferably it is kept hot. The material is brought to plating temperature, if this is different from the vapor etching temperature, and a small amount of the vapors of the plating compound admitted to the gas plating chamber. To prevent premature decomposition of the plating compound, a small percentage amount of one of the gaseous products of decomposition of the plating compound is injected simultaneously into the gas plating mixture. Such addition preferably amounts to about 5% by volume of the desorbing gas, e.g., fresh carbon monoxide.

An example of a suitable plating compound is nickel carbonyl, and in which preferably is introduced 0.1% by volume of ammonia. Into this plating gas mixture is bled approximately 10% by volume of carbon monoxide, to suppress premature decomposition of the nickel carbonyl.

Once a thin "flash" coating of metal is deposited, the introduction of ammonia or equivalent desorbing gas is discontinued and inert carrier gas or gases introduced in place thereof, together with increased amounts of the vapors of the plating compound. The temperature of the gas plating is also lowered about two hundred degrees after the initial flash coating and the plating continued.

The strength of the adhesive bond of coatings deposited in accordance with this process where they are solderable or brazable, are readily determined by soldering or brazing a stud on directly opposing surfaces of a plated piece. These are then gripped in a tensile test machine and pulled until a break occurs.

Tests carried out with silicon wafers gas plated in accordance with the method of the present invention have been found to adhere to the silicon surface so tenaceously that bits of silicon continue to stick to the coating deposit gas plated thereon. Thus, the bond between the silicon wafer and the deposite film approaches the strength of the silicon or base material.

The following examples are exemplary of several embodiments of the invention, but are not limitative thereof.

Example 1

A thin disc or wafer of silicon is etched free of oxides by immersing the wafer in an aqueous solution of hydrofluoric acid (10%). The wafer is removed from the solution, rinsed with water and then suspended in an airtight chamber. Heat is applied to the wafer by an infra-red heat source focused thereon which passes through transparent walls. The chamber is purged with hydrogen and then flushed with hydrogen containing 10% by volume of dry hydrogen chloride gas and the silicon wafer heated to 600° F. for two minutes. Thereafter the chamber is purged with hydrogen until free of hydrogen chloride, then flushed with ammonia. While the wafer is still heated to 600° F., a gaseous mixture, by volume, of 5% carbon monoxide, 0.1% nickel carbonyl vapor, and the balance ammonia, is injected into the plating chamber for one minute. Then a mixture of carbon monoxide only, and containing 0.2% nickel carbonyl, is circulated and in contact with the heated wafer for three minutes. Following the "flash" coating deposit produced, the temperature of the wafer is decreased to 400° F., or thereabout, and the amount of nickel carbonyl introduced raised to increase the rate of deposition. The deposited nickel tenaceously adheres to the silicon surface.

Example 2

In this example, an aluminum alloy sheet or panel (3 x 6") is etched in an acid solution comprising a mixture of nitric and hydrofluoric acids (8:1 by volume). After immersing the alloy sheet in this acid solution for three minutes it is removed and rinsed in clean water, then heated and subjected to gas plating as described in Example 1. Using the nickel carbonyl plating gas mixture, the deposited nickel is sufficiently adherent to withstand a bend test of 180° around a diameter equal to approximately twice the thickness of the plated panel.

Example 3

A titanium alloy bolt is etched free of oxides in an acid mixture of nitric acid and hydrofluoric acid as described in Example 2. After rinsing and drying the same, the etched bolt is suspended in a gas plating chamber and plated as described. In this instance, the chamber is purged with helium, and then flushed with helium containing 5% by volume of hydrogen bromide, and the bolt heated to 600° F. for two minutes. The chamber is thereafter purged with helium, while holding the bolt heated to 600° F., and a gaseous mixture of helium containing 1% by volume of tri-isobutyl aluminum introduced into the chamber and circulated in contact with the heated pretreated bolt.

After approximately ten minutes gas plating treatment, a thin adherent "flash" coating of aluminum is deposited on the bolt surface. The gas plating rate is then increased by increasing the concentration of tri-isobutyl present in the helium tri-isobutyl aluminum plating gas and lowering of the temperature to approximately 500° F.

Having described my process and given preferred embodiments thereof, what is claimed is:

1. A method of gas plating adherent coatings on silicon by thermal decomposition of gaseous compounds, and which comprises the steps of etching the surface of the silicon with acid to present a clean surface, subjecting the resultant silicon surface while in the absence of oxygen to a gaseous atmosphere containing hydrogen halide gas while heating said silicon, withdrawing the gaseous atmosphere while maintaining the silicon free of oxidation, thereafter treating the surface by exposing the same to a gaseous medium containing gas which is adsorbed but readily desorbed during initiation of said gas plating, and exposing the said surface of the heated silicon to a gaseous mixture containing less than 10% by volume of a gaseous heat-decomposable compound and wherein the temperature of said silicon surface is maintained high enough to cause said heat-decomposable compound to decompose and deposit a coating onto said silicon surface, and wherein said desorbable gas is ammonia.

2. A method of gas plating adherent coatings on silicon by thermal decomposition of gaseous compounds, and which comprises the steps of etching the surface of the silicon with acid to present a clean surface, subjecting the resultant silicon surface while in the absence of oxygen to a gaseous atmosphere containing hydrogen halide gas while heating said silicon, withdrawing the gaseous atmosphere while maintaining the silicon free of oxidation, thereafter treating the surface by exposing the same to a gaseous medium containing gas which is adsorbed but readily desorbed during initiation of said gas plating, and exposing the said surface of the heated silicon to a gaseous mixture containing less than 10% by volume of a gaseous heat-decomposable compound and wherein the temperature of said silicon surface is maintained high enough to cause said heat-decomposable compound to decompose and deposit a coating onto said silicon surface, and wherein said desorbable gas as ammonia, and said decomposable gaseous metal compound is nickel carbonyl, whereby nickel metal is deposited.

3. A method of gas plating adherent coatings on silicon by thermal decomposition of gaseous compounds, and which comprises the steps of etching the surface of the silicon with acid to present a clean surface, subjecting the resultant silicon surface in the absence of oxygen to a gaseous atmosphere containing hydrogen halide gas while heating said silicon, withdrawing the gaseous atmosphere while maintaining the silicon free of oxidation, thereafter treating the surface by exposing the same to a gaseous medium containing gas which is adsorbed but readily desorbed during initiation of said gas plating, exposing said silicon surface while heated to a mixture of gases containing less than 10% by volume of a gaseous heat-decomposable compound together with less than 25% by volume of a volatile product of decomposition of said gaseous mixture, said silicon surface being heated to a temperature high enough to cause thermal decomposition of the heat-decomposable compound and deposition of a coating on said silicon, and wherein said desorbable gas is ammonia.

4. A method of gas plating adherent coatings on silicon by thermal decomposition of gaseous compounds, and which comprises the steps of etching the surface of the silicon with acid to present a clean surface, subjecting the resultant silicon surface in the absence of oxygen to a gaseous atmosphere containing hydrogen halide gas while heating said silicon, withdrawing the gaseous atmosphere while maintaining the silicon material free of oxidation, thereafter treating the surface by exposing the same to a gaseous medium containing gas which is adsorbed but readily desorbed during initiation of said gas plating, exposing said silicon surface while heated to a mixture of gases containing less than 10% by volume of a gaseous heat-decomposable compound together with less than 25% by volume of a gaseous heat-decomposable compound together with less than 25% by volume of a volatile product of decomposition of said gaseous mixture, said silicon surface being heated to a temperature high enough to cause thermal decomposition of the heat-decomposable compound and deposition of a coat-

ing on said silicon, and wherein said desorbable gas is ammonia, and said decomposable gaseous metal compound is nickel carbonyl, whereby nickel metal is deposited.

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