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COPPER SUBSTRATE CLEANING AND VAPOR COATING METHOD

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ABSTRACT OF THE DISCLOSURE

The adhesion of vapor deposited chromium or aluminum overlaid with a layer of silicon monoxide to a copper substrate is improved by, after precleaning the copper substrate, subjecting the copper substrate to a glow discharge in the presence of an inert or reducing atmosphere, such as may be obtained by means of an argon and nitrogen or hydrogen atmosphere, respectively. After the glow discharge treatment of the copper substrate the metal to be vapor deposited thereon, chromium or aluminum, is vapor deposited thereon followed by the vapor deposition of silicon monoxide.

This invention relates to the cleaning and coating of substrates. More particularly, the invention relates to the cleaning of an easily oxidizable substrate and the depositing of an adherent coating on the cleaned substrate.

In the cleaning of a substrate prior to the deposition of a coating thereon, it has been the practice heretofore to employ a glow discharge in a normal atmosphere to remove contaminating substances from the surface of the substrate, such as hydrocarbons, water vapor and adsorbed gases. It has been found, however, that if the glow discharge cleaning operation is performed in the presence of an active gas, particularly oxygen or water vapor, and the substrate is easily oxidizable, then the cleaning operation results in the formation of an oxide film on the surface of the substrate. Materials deposited over the oxidized substrate surface have poor adhesion to the substrate. In particular, it has been found that if chromium or aluminum is deposited on the oxidized surface of a copper substrate and then overlayed with a silicon monoxide layer, the chromium or aluminum layer and the silicon monoxide layer will subsequently peel in a high humidity atmosphere.

Accordingly, it is an object of the present invention to achieve the cleaning of a substrate without oxidizing the surface of the substrate, so that coating material may be deposited on the cleaned substrate surface which will be strongly adherent to that surface.

It is a further object of the present invention to achieve the cleaning of a substrate by a glow discharge cleaning process in which oxidization of the substrate surface is prevented during the glow discharge, so that a strongly adherent layer of coating material may be subsequently deposited on the cleaned substrate.

These objects are achieved in the present invention by carrying out the cleaning of a substrate by glow discharge in an inert atmosphere, such as argon, or in a reducing atmosphere such as hydrogen. Briefly, the invention comprises precleaning a substrate, for example, through the use of solutions of ferric chloride, potassium cyanide and acetone. Next, the precleaned substrate is placed in a vacuum system which is evacuated to a low pressure to remove the major portions of contaminating gases, such as oxygen, water vapor and hydrocarbon fractions. Thereafter, the vacuum system is filled with dry gas, such as argon, nitrogen, or hydrogen, at a relatively high pressure (though below atmospheric pressure), which is thereafter exhausted to remove still further portions of the contaminating gases until a lower operating pressure is reached. A glow discharge is then maintained for a predetermined period of time in the inert or reducing atmosphere to clean the substrate. Next, the vacuum system is exhausted to a very low pressure, the glow discharge automatically extinguishing itself as the pressure is reduced. The vacuum system is maintained with inert or reducing gas at this low pressure, and one or more layers of coating material may be deposited on the cleaned substrate.

It has been found that the present invention is eminently suitable for the cleaning of copper substrates, for the subsequent deposition by evaporation of chromium and silicon monoxide layers. The following example more particularly describes the invention:

A piece of copper 1" x 2" x 0.050" was preliminarily cleaned by being dipped in a 40% solution of ferric chloride at 45° centigrade for 1 second, thereafter, rinsed under warm tap water and dried with filtered compressed air. This preliminary cleaning operation, involving dipping in ferric chloride, rinsing in water and drying with air, was repeated to provide a total of 3 preliminary cleanings.

The copper piece was next dipped in a ½% solution of potassium cyanide at room temperature for 10 seconds, thereafter rinsed under cold tap water, rinsed under room temperature demineralized water, and successively dipped in three successively cleaner acetone baths under a dust-free hood.

The copper piece was next immediately placd in a holder in a vacuum system, and the vacuum system was evacuated to roughly 0.02 micron pressure. This exhausing of the vacuum system removed major portions of contaminating gases, such as oxygen, water vapor and hydrocarbon fractions. Following this, dry argon gas was applied to the vacuum system until the system pressure reached roughly 1,000 microns. Next, the vacuum system was evacuated to roughly 50 microns pressure to remove most of the inert dry argon gas and still further portions of the contaminating gases.

Following this, the argon gas was increased in pressure to roughly 200 microns in the vacuum system and maintained at this pressure through an adjustable bleed valve in the argon gas line while a roughing pump continued to exhaust the system. A glow discharge was maintained for roughly 5 minutes within the vacuum system at approximately 15,000 volts A.C. The glow discharge electrode consisted of a ring having a gap positioned roughly 2 inches below the copper piece. Following the five minute glow dischage cleaning operation, the supply of argon to the vacuum system was stopped, and the system was evacuated. The glow discharge continued during the evacuation of the system until a system pressure of roughly 10 microns was reached, at which time the glow discharge automatically extinguished itself because of lack of pressure in the system. The exhausting of the vacuum system continued until a pressure of roughly 0.02 micron was reached. Evaporation of chromium is preferably deposited in a range of 0.02 to 0.1 micron.

At a system pressure of roughly 0.1 micron, approximately 200 Angstroms of chromium were evaporated onto the cleaned copper piece. The chromium was evaporated from a tungsten boat positioned roughly 6 inches below the copper piece and containing 0.013 gram of chromium at a temperature between 1,300° and 1,400° centigrade. Next, a layer of silicon monoxide of a thickness varying from 1,000 Angstroms to 100,000 Angstroms was deposited over the chromium layer at zero stress. The silicon monoxide was evaporated from a Drumheller type of evaporation source positioned roughly 7 inches below the copper piece. The evaporation rate was roughly 150 to 200 Angstroms per second.

It was found that, for the copper piece cleaned as described above by glow discharge in the argon atmosphere and subsequently coated with layers of chromium and silicon monoxide, the layers of chromium and silicon monoxide were strongly adherent, even when exposed to a 100% humidity atmosphere for several weeks. It was found that, for copper samples cleaned in the same manner as above by glow discharge, not in an inert atmosphere such as argon but in an atmosphere of air, or oxygen, the coatings had poor adhesion qualities. The coatings peeled from the substrates when exposed to normal atmosphere for more than a few hours.

It will be noted that the invention provides for the cleaning of a substrate in a glow discharge maintained in an inert or reducing atmosphere which prevents the oxidation of the surface of the substrate during the cleaning operation, thereby improving the adhesion of a coating on the cleaned substrate which is subsequently deposited thereon. The invention is most suitable for the cleaning of substrates which are easily oxidizable, such as copper. The invention, of course, is applicable also to other substrates. Accordingly, the invention should be taken to be defined not in terms of the specific example given above but in terms of the claims, which are set forth as follows.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The method which comprises precleaning a copper substrate by immersing said copper substrate in sequence in an aqueous solution of ferric chloride, in an aqueous solution of potassium cyanide and in acetone, subjecting the resulting copper substrate to glow discharge in the presence of an inert or reducing gas selected from the group consisting of argon, nitrogen and hydrogen to additionally clean the copper substrate, reducing the pressure during the glow discharge treatment operation to a low pressure sufficient to extinguish the glow discharge, vapor depositing on the resulting treated copper substrate a layer of a metal selected from the group consisting of chromium and aluminum and subsequently vapor depositing thereon an overlaying layer of silicon monoxide.

2. The method in accordance with claim **1** wherein said precleaning operation includes immersing the copper

substrate in a 40% solution of ferric chloride at about 45° C. for about one second followed by rinsing with warm tap water and drying with filtered compressed air, thereafter immersing the copper substrate in a .5% solution of potassium cyanide at room temperature for about 10 seconds followed by rinsing with cold tap water and then demineralized at about room temperature and then by immersion in an acetone bath.

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