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[54] **GOLD POWDER**

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[58] **Field of Search** ..... 75/0.5 A, 118; 106/290

[56] **References Cited**

UNITED STATES PATENTS

2,086,384	7/1937	Lady	75/118
3,421,885	1/1969	Adler	75/118
3,473,921	10/1969	Schmuckler	75/118
3,539,114	11/1970	Short	106/290
3,542,540	11/1970	Heinen et al.	75/118
3,565,608	2/1971	Anspon et al.	75/118
3,576,620	4/1971	Wilson	75/118
3,558,288	1/1971	Burrows	75/118

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[57] **ABSTRACT**

Gold powder useful in the formation of thick film microelectronic circuitry is formed by dissolving a gold bearing material in aqua regia, thereafter adding to the solution so formed a sufficient amount of an emulsifying agent or a particle size inhibitor such that upon precipitation of the gold from the solution, the average particle size of the precipitate will be less than about 20 microns, and thereafter adding, in a rapid fashion, a precipitating agent to the solution in an amount sufficient to precipitate the gold from the solution. The freshly formed gold particles are encapsulated with the emulsifier and a powder formed. By using the described tenchinque, the powder so formed, after washing and drying, generally has a bulk density of greater than about 5.0 grams per cc. and each of the fine particles of gold have a coating of the emulsifying agent that acts as a lubricant when used with an organic binder in a thick film printing formulation.

16 Claims, No Drawings

GOLD POWDER

This invention relates to a process for producing powders of gold and gold powders produced therefrom. More particularly, this invention relates to techniques for forming gold powders having a high bulk density and a low average particle size which are useful in the production of thick film microelectronic circuits.

With the advent of computer technology, the demand for high quality microelectronic circuits increased manyfold. Many microelectronic circuits depended for their high quality and long lasting characteristics upon the formation of a strong, tenaciously bonded, high density, thick film of substantially pure gold. While gold powders have been known for hundreds of years in the art, especially in the art of dentistry, many of the processes for formulating gold powders from gold-bearing materials resulted in powders having low bulk density and relatively high particle size. Thus, the better known and more economically feasible processes for making gold powder are generally inadequate to produce a gold powder which has the requisite bulk density and small average particle size necessary for the production of high quality gold films useful in microelectronic circuitry. On the other hand, several techniques have been developed for producing gold powders which form generally acceptable, although in many instances not excellent, gold powders useful in microelectronic circuitry art. Generally speaking, however, these techniques form gold powders by relatively complex and expensive processing and/or produce powders which are in the lower range of acceptability relative to their bulk density and average particle size.

It is generally recognized in the industry that for a gold powder to be acceptable for the purposes of thick film printing of microelectronic circuitry from paste form, such powders must have a bulk density of between about 5.0 and 7.5 grams per cc. Preferably, the bulk density should be as high as possible, usually exceeding about 6.8 grams per cc. In addition to bulk density, the art has recognized that the average particle size of the powder plays a large role in insuring the production of the requisite film density. Particle sizes greater than about 20 microns usually result in a thick film having an unacceptably low film density. Preferably, the particle size of the gold is as low as possible, usually below about 5 microns and in some instances, preferably lower than 1 micron.

As alluded to hereinabove, the art has long known of techniques for producing powdered gold in relatively pure form. Such techniques usually comprise the dissolving of a gold-bearing material into solution and the precipitation of pure gold by the addition of a reducing agent or other type of precipitating agent added to the resulting solution. Examples of the usually preferred dissolving agents are the various cyanide compositions and aqua regia. Obviously, because of the toxicity and other factors involved in using cyanide, aqua regia is usually preferred. Examples of well-known precipitating agents include various organic compounds such as sugar and the like, as well as various inorganic compounds including the various sulfites, SO_2, and sulfurous acid.

As stated hereinbefore, while such processes do indeed form gold powders of a sort, they generally form powders of low bulk density. In addition, and in almost

every instance, flakes of gold are formed along with the powder which renders the powders, without further processing, inoperative for the purposes of forming pastes useful in printing gold microelectronic thick film circuits.

In view of the above, it is apparent that there exists a need in the art for a process of forming a gold powder having a high bulk density and a low average particle size which is both economic, and which produces gold powders capable of forming high quality thick films of gold useful in microelectronic circuitry. It is a purpose of this invention to fulfill this need in the art. Other purposes of this invention will become apparent from an analysis of the following description.

Generally speaking, this invention contemplates a method for forming a gold powder having a bulk density greater than about 5.0 grams per c.. and having an average particle size of less than about 20 microns which comprises:

A. dissolving a gold-bearing material in an acid comprised of HCl and HNO_3;

B. adding to the solution of (A) a sufficient amount of particle-size inhibitor such that upon precipitation of the gold from said solution, the average particle size of said precipitate will be less than about 20 microns; and

C. precipitating the gold from said solution.

After the gold is precipitated from solution, it is usually thoroughly washed and dried. The resulting powder so formed has a bulk density greater than about 5.0 grams per cc. and, in most instances, a bulk density on the order of about 6.8 – 7.5 grams per cc.

Any conventional and well-known gold-bearing material can be used for the purposes of this invention. Such materials include gold-bearing natural materials, pure gold in its many forms, and reclaimed gold such as gold chips or pieces of used microelectronic circuitry. Preferred for the purposes of this invention and because it is usually required that the gold powder so formed be of extremely high purity for use in a microelectronic circuit, are the many forms of substantially pure gold as well as reclaimed gold from microelectronic circuits which may contain small portions of glass bonded thereto. Examples of commercially available, substantially pure gold in its refined form, include sponge gold, gold bars, gold granules, and previously prepared gold powder of low bulk density and relatively high particle size.

As stated hereinbefore, the gold-bearing material is dissolved in acid comprised of HCl and HNO_3. Generally speaking the HCl must be in an amount sufficient to form gold chloride ($HAuCl_4$) with at least a portion, and preferably all, of the gold present in solution. Thus, the HCl is presented in order to form a salt of the gold, which salt is soluble in the acidic medium in which it is dissolved. On the other hand, the HNO_3 is used to actually dissolve the salt in the solution. Thus, a sufficient amount of HNO_3 must be present in order to insure that at least a portion of the salt so formed by the HCl will be dissolved in solution. Obviously, and preferably, a sufficient amount of HNO_3 is presented in order to insure the dissolution of all of the gold chloride salt into solution.

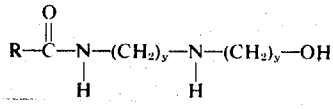
The actual weight ratios of HCl:HNO_3 and the combined acid to the amount of the bold-bearing material will vary as different conditions are sought to be met, especially with respect to the use of different starting materials. Generally speaking, however, the larger the

particle size of the starting material, the greater the amount of HNO_3 which must be employed to insure dissolution of substantially all of the gold presented in the gold-bearing material into solution. On the other hand, it is desirous in the most preferred form of this invention to drive off all nitrogen compounds from the solution prior to precipitating the gold therefrom. Thus, as little HNO_3 as possible should be used so as to speed the process of eliminating nitrogen compounds from the solution. An example of a particularly preferred weight ratio of HCl to HNO_3 is from about 1:1 – 4:1 and preferably about 2:1. Such acids are generally known as aqua regia.

In accordance with the present invention, the particle size inhibitor or emulsifying agent such as butyl stearate is added to the acid solution of the gold chloride salt apparently to envelop and coat the newly formed gold particles to prevent coalescing and cold welding. The addition of the emulsifying agent that is preferably a liquid at the reaction temperature insures that the particle size of the resulting precipitate powder will be of a small size and will be utilized for a high quality microelectronic gold powder paste. The emulsifying agent that is used to coat the newly formed gold particles and later act as a lubricant in the gold powder paste includes organic compounds known as lubricants, dispersants and emulsifiers. The preferred emulsifying agent is an ester of fatty acid such as an alkyl stearate with the best results being obtained with a butyl stearate. The alkyl esters of fatty acids are those in which the alkyl group is about one to eight carbon atoms and preferably about three to five carbon atoms and a fatty acid generally represented by the formula $C_nH_{2_{n+1}}COOH$ in which n is generally greater than 10 and preferably greater than 17 up to about 24. Examples of the suitable fatty acid component of the alkyl ester of fatty acid is lauric acid, palmitic acid, and stearic acid. Hence, the suitable fatty acids are those in which n is 11 such as lauric acid, where n is 13 such as myristic acid, where n is 15 such as palmitic acid, and where n is 17 such as stearic acid. Also suitable are unsaturated aliphatic acids such as oleic (having 18 carbon atoms including the carboxyl group), erucic acid (having 22 carbon atoms), linoleic acid (having 18 carbon atoms) and linolenic acid (having 18 carbon atoms).

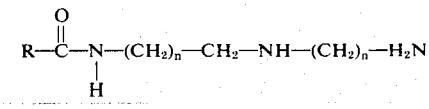
Thus, suitable emulsifiers that later act as lubricants in the gold powder paste are fatty acids, fatty acid alcohols and fatty acid amines that preferably are liquids at the reaction temperature, say, from room temperature to 70° to 80° C. or more and preferably from ambient temperature to about 30° to 40° C. Useful acid alcohols are well known liquid primary, straight chain alcohols generally having from four to 10 or 12 carbon atoms such as n-butyl alcohol, iso-butyl alcohol, n-octyl alcohol, n-decyl alcohol and even dodecyl alcohol.

Suitable fatty acid amines include fatty amidomonoamines derived from fatty monocarboxylic acids having as low as two, four or six up to 12, 14, 16 or 18 carbon atoms having the general formula:



where y is generally one to eight and preferably two to three, and where R is preferably an alkyl group.

Also suitable are fatty amidodiamines derived from fatty monocarboxylic acids and polyamines and having the general formula as follows:



wherein n is generally one to eight and preferably two to four and where R preferably is an alkyl group of two to eight carbon atoms.

Also suitable emulsifiers are polyalkanol polyamines such as monohydroxyethyldipropylenetriamine, tetrahydroxyethylenediamine and monohydroxyethyltrihydroxypropyl-ethylenediamine.

Excellent emulsifying agents are those classified as non-ionic surface active agents including alkylphenolpolyglycolethers. Such non-ionic surface agents include reaction products of alkylphenylpolyglycol ethers with ethylene oxide, the product having some 4 to 15 moles of ethylene oxide and include specific alkylphenolpolyglycol ethers containing 6 moles of polyethylene oxide, 9 moles of ethylene oxide, 11 moles ethylene oxide and 15 moles ethylene oxide. These products are liquid and act to encapsulate the freshly formed gold particles and thereafter act as lubricants in the gold paste formulation. The non-ionic emulsifiers also include reaction products of low molecular weight polyethylene glycol such as those having molecular weight of 250 to 600 and preferably 300 to 500 with a fatty acid such as soybean fatty acid, stearic acid, coconut fatty acid and oleic acid. Also reaction products of diethanolamine and lauric acid and palmitic acid provide suitable liquid non-ionic emulsifying agents. Specific non-ionic emulsifying agents are a reaction product of a polyethylene glycol having a molecular weight of about 600 plus soybean fatty acids. Another reaction product is that of a methoxy polyethylene glycol having a molecular weight of about 550 with coconut fatty acids. Another reaction product is that of oleic acid and a polyethylene glycol having a molecular weight of about 300. As previously indicated, it is highly preferred that the emulsifying agent be liquid and wet and envelop the surface of the freshly formed gold particles to prevent coalescing thereof. In the resultant gold paste formulation, the emulsifying agent acts as a lubricant to prevent the cold welding of the particles.

In accordance with the present invention, the emulsifying agent is generally used in amounts of about as low as 0.01 part by weight per 100 parts by weight of gold starting material. It is preferred that there be at least 0.1 part by weight of the emulsifying agent per 100 parts by weight of gold starting material and generally up to 10 or more parts can be used. Although more than 10 parts can be used, it is generally wasteful inasmuch as apparently no further benefits are gained from the use of a great excess of an emulsifying agent and in some cases there can be too many oily particles therein for further processing. It is preferred generally that there be around 4 to 8 parts emulsifier per 100 parts by weight starting gold material and optimally about 6 to 7.5.

The above-described preferred emulsifier materials, which include the fatty acids, fatty acid alcohols, fatty acid esters and fatty acid amines, are preferred for the purposes of this invention because they are found to be compatible with the other ingredients used to formulate microelectronic circuitry pastes. Thus, such mate-

rials are burned off during the conventional firing of the paste to thick film form and therefore need not be washed from the gold powder prior to firing from the system. That is to say, the gold powder formed from a solution in which these fatty acids are present, need not be washed free thereof in order for them to be useful in microelectronic circuitry production. In those instances where washing is desired, however, these inhibitors are readily removed by washing with a simple organic solvent such as acetone or the like.

The amount of particle size inhibitor necessary to provide the requisite particle size in the ultimate powder resulting from precipitation, will, of course, vary over a wide range depending upon the type of emulsifying agent or inhibitor used, the type of starting material employed, and the other parameters of the system. In a preferred technique, such as where gold sponge is used and the preferred, above-described aqua regia solution is used, a fatty acid such as butyl stearate is effective to produce a particle size of less than about 5 microns in the ultimate powder formed by precipitation, if it is employed in amounts of about 1 part by volume inhibitor to 200 parts by volume solution. Functionally speaking, the emulsifier is added in amounts sufficient to prevent flaking in the ultimate powder formed and maintain particle sizes less than about 20 microns, preferably less than 5 microns, and even more preferably sub-micron in size. On the other hand, the amount of emulsifier should not exceed practical limitations of the system so as to result in tackiness, undue viscosity, and the like. Generally speaking, and for most systems contemplated by this invention, the particle size inhibitor may be employed in amounts of about 1 part per volume inhibitor to 50 parts by solution to 1 part by volume inhibitor to 500 parts by volume solution, especially when fatty acids as hereinabove described are employed as the emulsifying agent.

The exact mechanism by which the above-described emulsifying agents or particle size inhibitors contemplated by this invention operate to inhibit particle size of the ultimate precipitate, is not known. However, it is believed that this particle size inhibitor acts by coating the minute particles of precipitate upon their formation and that such a coating thereby acts to prevent what is known in the art as "cold welding" of the particles being precipitated. By another name, the inhibitors are thought to prevent "agglomerated bonding" of the particles, particularly when used in a gold paste formulation. Thus, in this respect, the particle size inhibitor is thought to act as a type of coating and isolating agent, by substantially simultaneously precipitating and coating the gold particles.

Another important parameter in controlling the ultimate particle size and bulk density of the precipitated powder, is the adjustment of the concentration of the solution prior to precipitation either before or after the addition of the emulsifying agent thereto. The adjustment of the concentration of gold in the solution may be effected by any conventional technique. Preferably, however, the concentration is adjusted by the addition of HCl and/or the addition of distilled water thereto.

While the exact concentration employed will, of course, vary over a wide range depending upon the particular system employed, generally speaking the concentration should be adjusted prior to precipitation such that there is about 1 part by weight of gold (Au) to 2.5 parts by volume solution to about 1 part by weight gold (Au) to about 100 parts by volume solution. Most preferably, the concentration of gold should be about 1 part by weight to about 20 parts by volume of the solution. In a preferred technique, distilled water is added just prior to precipitation in order to adjust the concentration to the desired degree.

The above-described, adjusted concentrations may, of course, vary in unusual situations, outside of the above-described ranges. However, it has been found that, for most situations, the gold is present in an amount greater than about 1 part by weight to 2.5 parts by volume solution, the particle sizes formed, regardless of the addition of emulsifying agent, will be too large for the purposes of gold powder useful in microelectronic circuitry. On the other hand, there is theoretically no lower limit to the dilution of the gold in the solution. However, it is usually found that if dilutions greater than about 1 part by weight Au:100 parts by volume solution are employed, practical and economic considerations enter in such that insufficient yield is obtained for the bulk of material that must be handled.

The precipitation of the gold from solution, may generally be affected in accordance with any conventional technique. However, it has been found that bulk density may be optimized by the rapid addition under vigorous agitating conditions, of a precipitating agent to the solution. Generally speaking, the precipitating agents, examples of which have been described hereinabove, should be added as rapidly as possible since such rapid addition usually provides a particle size and bulk density which is optimized. In those instances, where the addition of the precipitating agent is substantially instantaneous, e.g., about 500 parts by volume/-sec., vigorous agitation is relied upon to effect dispersion of the precipitating agent throughout the solution so as to substantially homogeneously effect the precipitation of the gold from the solution. While substantially instantaneous rates of the precipitating agent are preferred, slower rates may, of course, be employed. Generally speaking, however, the rate of addition should not be lower than about 1 part by volume/sec.

The amount of precipitating agent actually employed will vary depending upon the various parameters of the system. Generally speaking, it is desirable to precipitate as much gold from the system as possible. Therefore, the precipitate is usually added in amounts slightly in excess of the stoichiometric amount necessary to precipitate substantially 100% of the gold from the system. Examples of precipitates added slightly in excess of the stoichiometric amount necessary to precipitate all of the gold, useful for the purposes of this invention, include the various conventional precipitating agents hereinabove referred to, such as Na_2SO_3, $NaHSO_3$, SO_2, H_2SO_3, hydroquinone, and the various organics such as sugar and the like. Of the above, the preferred precipitating agent for the purposes of this invention is Na_2SO_3. Preferably, these precipitating agents are added by way of an aqueous solution or dispersion, since such optimizes dispersion of the agent in the gold chloride solution.

When Na_2SO_3 is employed, the reaction proceeds by the following reaction formula:

$$2HAuCl_4 + 3Na_2SO_3 + 3H_2O \rightleftharpoons 2Au + 3Na_2SO_4 + 8HCl$$

As can be seen from this formula, if substantially all of the gold is to be precipitated from the system, slight excess above 3 moles of Na_2SO_3 should be employed for every 2 moles of gold chloride salt.

As stated hereinabove, vigorous agitation is generally contemplated during precipitation so as to disperse in a substantially homogeneous fashion, not only the particle size inhibitor and thereby insure its effectiveness, but also to substantially homogeneously distribute the precipitating agent throughout the solution and thereby insure a speedy formation of precipitate in an amount close to theoretical yield. By vigorous agitation is meant agitation to the extent that the system will become turbulent and preferably highly turbulent. In substantially no instance should the agitation be so low as to present a laminar flow within the closed system. As stated hereinabove, vigorous agitation and the resulting homogeneous dispersion of the various ingredients, result in high density which, of course, is desired for the purposes of this invention.

After the precipitate is formed, and agitation has ceased, the precipitate, which is substantially pure gold, may be recovered by any well-known technique. In a preferred embodiment of this invention, the precipitate is recovered by simple filtration or decantation followed by washing and drying of the material so as to obtain a substantially dry powder. Washing is usually effected with distilled water so as to introduce no contaminates into the system at this point.

DETAILED DESCRIPTION OF PROCESS FOR FORMING GOLD POWDER

A particularly preferred process for carrying out the above-described technique contemplated by this invention generally comprises dissolving a gold-bearing material, preferably in the form of a gold sponge, in a concentration of aqua regia. For example, 20 grams of a commercial gold sponge (substantially pure refined gold) is added to a mixture of 30 ml. HNO_3 (concentrated) and 100 ml. HCl (concentrated). The solution is then heated to below its boiling point in order to dissolve the sponge in the acid more rapidly. Thus, heating is effected for a sufficient period of time at a temperature below the boiling point of the solution, until a solution is formed (i.e., until the sponge is totally dissolved in the acid medium).

It is both desirable and economical, to remove all nitrogen compounds at this time from the system. This is because nitrogen compounds, for example, present a nuisance in the form of off gases. Thus, these gases may be conveniently removed at this point rather than having them removed at a point where the off gases may not be so easily handled. In addition, it is advantageous to remove any nitric acid from the solution at this point so as to facilitate precipitation.

Removal of the nitrogen compounds, particularly the nitrates and nitric acid, formed upon dissolution of the gold sponge into solution, is effected most conveniently by heating the solution to above its boiling point and continuing to heat the solution until no further brown vapors come off. The brown vapors are, of course, the various nitrogen oxide gases which, when eliminated, indicate that no further nitrogen compounds exist. Such a removal step may be effected merely by boiling the solution or by boiling the solution with the further addition thereto of HCl, either once or numerous times, until substantially no brown gases come off from the system. Another technique effecting the same results without further addition of HCl is to reflux the system allowing the distillate gases of nitrogen to be driven off.

During this boiling step, various crystals or flakes of impurities as well as some gold chloride crystals may form in the solution. Therefore, preferably and before further proceeding with the solution, the solution is filtered to remove any solids therefrom. In those instances where the starting material is a reclaimed gold bearing material such as a gold glass chip, glass will be removed by this filtration step.

After filtering any solid materials from the solution, the solution is charged to the main reactor and the concentration is adjusted, as hereinbefore described, preferably by the addition thereto of distilled water or other inert liquid medium. After the concentration is so adjusted, the above-described emulsifying agitator particle-size inhibitor is added with agitation and the solution is continuously agitated for a period of time such as about 1 to 2 minutes to insure that the emulsifying agent has been distributed throughout the system.

Agitation is thereafter usually increased so as to insure high turbulence within the system and the precipitating agent, in the requisite amount, is added to the system preferably as fast as possible, the agitation being despositive of the speed of distribution throughout the system. After the addition of the precipitating agent, the precipitating reaction occurs very rapidly and agitation is continued for a short period of time such as about 1 to 3 minutes to insure that a complete reaction has been effected.

The temperature at which precipitation takes place is not critical to the operativeness of this invention. However, the precipitation reaction is generally exothermic and it has been found that bulk density is decreased if the temperature is maintained as low as possible during precipitation. Therefore, while in many instances, for economic reasons, it may be desirable to start the precipitation reaction at room temperature and allow it to proceed without further temperature controls, in certain instances, it may be more desirable to cool the system during the precipitation reaction. In this respect, cooling may take place so that the temperature during precipitation of the system does not exceed about 0°–50° C., thus insuring that the requisite bulk density will be achieved.

After the precipitate is so formed by the above-described technique, it is filtered using ordinary filtering techniques or decanted and then usually thoroughly washed to remove any impurities therefrom. Numerous washings are usually effected, generally with water and thereafter acetone, to insure that water is removed from the system. It is important to remove as much water as possible by solvent extraction and washing and thereafter by finally drying the powder so as to prevent aglomeration from taking place in the powder during storage or at any time prior to its use in the formation of a gold powder paste. Depending upon the washed solution used, drying is usually effected at a temperature greater than the boiling point of the washed solution so as to insure that a dry, substantially pure powder will result. In those instances, however, where an organic wash solution is used, the drying temperatures should not be so high as to decompose the organic sol-

vent thereby leaving behind a carbon residue in the gold powder. Washing, in some instances, is not necessary since small impurities are tolerable, the drying step removing any water present.

FORMATION OF A THICK FILM PRINTING PASTE

The gold powder formulated in accordance with this invention has a bulk density greater than about 5.0 grams per cc., usually a bulk density greater than about 6.8 grams/cc., and most usually a bulk density in the order of about 6.8 – 7.5 grams/cc., the latter being a highly preferred range. In addition, the gold powder of this invention generally has an average particle size of less than about 20 microns, usually less than about 5 microns with substantially no particles greater than about 5 microns. It is preferred for many applications that the average particle size be less than about 1 micron or at least a majority of the particles have a size less than 1 micron and the balance not greater than about 5 microns. Such powders are also of relatively high purity where the starting materials were judiciously chosen for their high purity quality, and the above-described steps were carried out to prevent undue contamination. Such powders so formed are uniquely useful for the production of thick films of gold useful in printed microelectronic circuitry.

Such films are generally formed by conventional thick film printing techniques which usually provide for the formation of a paste from the gold powder. Such a paste is usually formulated by admixing the gold with a glass binder such as that of the borosilicate glass type and an organic vehicle such as ethyl cellulose which will burn off during firing of the printed paste. The amount of material employed to form the paste is regulated in accordance with the needs of the printing system so that the viscosity, flow and the like are controlled. Conventional techniques for forming the paste well-known in the art are contemplated by this invention.

After the paste is formed, it is printed through conventional devices such as a screen or mask in a desired pattern upon a substrate such as a microelectronic circuitry board. The paste is then fired at the requisite firing temperature, usually on the order of about 500–1,000° C. for sufficient period of time to drive off the organic vehicle and coalesce the glass binder and the gold into a tightly bonded thick film of the requisite size, shape and electronic characteristics. Because of the high bulk density and low particle size of the powders of this invention, they are found to form excellent thick films from the point of view not only of their mechanical strength but their electrical properties resulting from excellent film density as well.

The following examples are presented by way of illustration and not limitation:

EXAMPLE 1

20.2 grams of sponge gold are admixed with 100 ml. HCl (37–38% HCl concentration) and 30 ml. HNO_3 (70–71% HNO_3 concentration). The admixture is then heated for a period of 1 hour at a temperature just below the boiling point of the admixture. After 1 hour, all sponge gold has been dissolved in the acid medium. The heat is then increased to the extent that the solution boils vigorously. As the solution boils, an additional 200 ml. HCl is added over a period of about 1½ hours. The distillate coming from the boiling solution is constantly removed during this time and after this 1 ½ hour period, about 130 ml. of solution remain. This boiling process removes substantially all traces of nitric acid from the solution as evidenced by a lack of brown gases emitted at the end of the boiling period. The solution is then cooled to room temperature and filtered to remove any solids contained therein. The filtered solution is then diluted with distilled water so as to form a 200 ml. solution.

A sodium sulfite solution is formulated by dissolving 30 grams of Na_2SO_3 in 200 ml. distilled water. 2 ml. of butyl stearate are then measured out. The temperature of all ingredients is then adjusted to about 25° C.

The 200 ml. solution of gold is then placed in a 1 liter glass-baffled reaction vessel and 200 ml. of distilled water are added thereto to bring the total volume of the solution to 400 ml. Agitation is begun using a marine type propeller at about 200 rpm. The 2 ml. of butyl stearate are then added and agitation is allowed to proceed for about 3 minutes to insure adequate dispersion of the particle size inhibitor substantially homogeneously throughout the solution. The 200 ml. solution of Na_2SO_3 is then added over a period of 10 seconds to the solution and agitation is allowed to proceed for about 1 minute after the addition of the Na_2SO_3 solution is completed. Agitation is then discontinued and a precipitate is found to exist in the vessel which is substantially pure gold. The mixture is then filtered to obtain the precipitate using a standard Buechner funnel. The precipitate is then repeatedly washed with distilled water and air-dried at 100° C. for about 48 hours. The product so formed is found to be a dense gold powder having a bulk density within the range of 6.8 – 7.5 grams/cc. and having a particle size distribution of

less than 0.6 microns – 0%
less than 2 but > .6 microns — 20%
less than 2.8 but > 0.6 microns — 50%
less than 5.0 but > 0.6 microns — 98.8%
greater than 5.8 microns — 0%

A printing paste was formulated from the powder previously made by admixing 96 parts by weight of the gold powder with 4 parts by weight of a lead barium borosilicate glass consisting of: (by weight) 15% SiO_2, 10% B_2O_3, 40% PbO, 20% BaO and 15% ZnO. The average particle size of this glass binder admixed with the gold powder was about 1 micron. This glass powder-glass binder admixture was then added to a liquid organic vehicle consisting of 15% by weight N-4 ethyl cellulose and 85% by weight of a mixture of 2 parts by weight butyl Carbitol acetate (diethyl glycol monobutyl ether acetate) and 1 part by weight isoamyl salicylate. The vehicle was mixed with the glass powder-glass binder admisture in an amount of 10% by weight vehicle to 90% by weight gold and glass binder. The paste so formulated was printed by a conventional screen printing technique onto a known alumina substrate and dried at 100° C. for 15 minutes, thereafter fired at 875° C. peak for 5 minutes with an 8-minute heat-up and cool-down period. The resultant film exhibited high film density and was in every respect an excellent thick film microelectronic conductor. The above example through further experimentation is found to be highly reproducible.

EXAMPLE 2

Essentially the same procedure is followed as in Example 1 except a stoichiometric amount of Na_2SO_3 (20.9 grams in a 200 ml. solution of water) was em-

ployed to precipitate the gold. The resulting powder had the requisite particle size and bulk density to form an excellent thick film microelectronic conductor.

EXAMPLE 3

Essentially the same procedure is followed as in Example 1 except that the solution was adjusted to 20 grams of gold per 600 ml. of solution by adding 400 ml. of distilled water prior to precipitation. 1.2 ml. of oleic acid is employed as the particle size inhibitor and the addition rate of the Na_2SO_3 solution is 200 ml. over a 60 second period. The resulting gold powder had the requisite particle size and bulk density to form a high quality thick film microelectronic conductor.

I claim:

1. A method of forming a gold powder having a bulk density greater than about 5.0 grams/cc. and an average particle size of less than about 20 microns comprising:

A. dissolving a gold-bearing material in an acid comprised of HCl and HNO_3;

B. adding to the solution formed in (A) an effective amount of an emulsifying agent capable of coating freshly formed gold particles and prevent coalescing and cold-welding thereof and keep the average size of said gold particles less than about 20 microns; and

C. precipitating the gold from said solution to provide said gold powder.

2. A method of forming a gold powder in accordance with claim 1 wherein the bulk density of the powder is greater than about 6.8 grams/cc. and the average particle size of the powder is less than about 5 microns.

3. A method in accordance with claim 1 which also includes the step of removing the precipitate from said solution and drying said precipitate to form a substantially dry, pure gold powder.

4. A method in accordance with claim 1 wherein said precipitation is effected by the addition of a reducing agent to said solution.

5. A method in accordance with claim 4 wherein said reducing agent is added rapidly to said solution and said addition is accompanied by agitation of the solution in an amount sufficient to place the solution in turbulent flow.

6. A method in accordance with claim 1 which also includes the step of, prior to adding the emulsifying agent to said solution, heating said solution at a temperature below its boiling point for a sufficient period of time to remove substantially all nitric acid therefrom.

7. A method in accordance with claim 6 which also includes the step of adjusting the concentration of the solution prior to precipitation such that the concentration of the gold in the solution is in an amount of from about 1 part by weight gold: 2.5 parts by volume solution to about 1 part by weight gold: 100 parts by volume solution.

8. A method in accordance with claim 7 wherein the concentration of gold is adjusted prior to precipitation to an amount of about 1 part by weight gold: 20 parts by volume solution.

9. A method in accordance with claim 1 wherein said gold bearing material is substantially pure refined gold and said acid is aqua regia.

10. A method in accordance with claim 9 wherein the ratio of HCl: HNO_3 is about 2:1.

11. A method in accordance with claim 1 wherein said emulsifying agent is an ester of a fatty acid.

12. A method in accordance with claim 11 wherein said emulsifying agent is a fatty acid represented by the formula $C_nH_{2_{n+1}}COOH$ wherein n is greater than 10.

13. A method in accordance with claim 1 wherein said emulsifying agent is butyl stearate.

14. A method in accordance with claim 1 wherein said emulsifying agent is a fatty acid and is employed in an amount of 1 part by volume inhibitor to 500 parts by volume solution.

15. A method in accordance with claim 1 wherein said precipitation is carried out at a temperature not exceeding about 50° C.

16. A method as defined in claim 1 in which the emulsifying agent is an alkyl ester of an aliphatic monocarboxylic acid, the acid having 12 to 22 carbon atoms and the alkyl group having two to six carbon atoms.

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