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# (54) HIGHLY CRYSTALLINE SILVER POWDER AND METHOD FOR PRODUCTION THEREOF

(57) An object of the present invention is to provide highly crystalline silver powder which is **characterized in** fine particles, showing high dispersibility, it's particle size distribution is not excessively sharp but relatively broad and crystallites are large; and a method for producing the same. In order to achieve the object, a method for producing highly crystalline silver powder is **characterized in that** mixing a first aqueous solution and a second aqueous solution, wherein the first aqueous solution contains silver nitrate, a dispersing agent and nitric acid, and the second solution contains ascorbic acid. For dispersing agent, polyvinylpyrrolidone or gelatin is preferred. Highly crystalline silver powder produced by the above-described method is preferred to be a crystallite diameter of 300 Å or more, an average particle diameter $D_{50}$ in the range from 0.5 μm to 10 μm, and a thermal shrinkage rate for the length direction after heating at 700°C in the range from -3% to 3%. For ratio $D_{90}/D_{10}$ of the silver powder is preferred to be in the range from 2.1 to 5.0.

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## Description

### Technical Field

**[0001]** The present invention relates to highly crystalline silver powder and a method for producing the same, and more specifically, to highly crystalline silver powder preferable for production of a conductive paste that can significantly reduce the size of the electrode or circuit of, for example, a chip devices, plasma display panel and the like with high density, high accuracy and high reliability. In particular it can enable to form a minute wiring or a thin and flat coating film with high density, high accuracy and high reliability. It is because the silver powder is composed of fine particles, has high dispersibility, particle size distribution is not excessively sharp but is relatively broad, and crystallites are large. So when it is used as the material for the conductive paste, the dispersibility of the silver powder and the filling properties of the paste are excellent, and then the size of the electrode or circuit formed from the thick silver film can be reduced, and the thick silver film obtained from the conductive paste excels in thermal shrinkage resistance, and has low specific resistance (resistivity).

### Background Art

**[0002]** Heretofore, as a method for forming an electrode or circuit of an electronic part or the like, there has been known a method to form a circuit by printing a conductive paste wherein silver powder, which is a conductive material, is dispersed in a paste, on a substrate, and baking or curing the paste to form a thick silver film. However in recent years, due to the improvement in functions of electronic equipment, so called down sizing and wiring density increase of electronic devices have been demanded; consequently, it has been desired that silver powder, which is the material for the conductive paste, excels in filling properties and dispersibility despite of fine particles when used in the conductive paste. In the present invention, dispersibility means the difficulty of aggregating the primary particles of the silver powder with each other, unless otherwise specified such as the dispersibility of silver powder in a paste. For example, the state of high dispersibility means the state wherein there is little or no proportion of primary particles are aggregated with each other; and the state of low dispersibility means the state wherein there is much proportion or all of aggregated primary particles are aggregated with each other.

**[0003]** A substrate on which the above-described conductive paste is printed is normally used in a part of a ceramic substrate where heat generation is large, such as the IC package. However, when the conductive paste is printed on the ceramic substrate, since the thermal shrinkage of the ceramic substrate is generally different from the thermal shrinkage of the thick silver film formed from the conductive paste, there is possibility wherein the thick silver film is separated from the ceramic substrate, or the substrate itself is deformed. Therefore, it is preferable that the rate of the thermal shrinkage of the ceramic substrate is as close to the rate of the thermal shrinkage of the thick silver film formed from the conductive paste.

**[0004]** As a cause of the thermal shrinkage of the above-described thick silver film in such baking process, it is considered that the silver powder in the conductive paste causes sintering during baking. Specifically, it is considered that the silver powder is a polycrystalline construction composed of fine crystallites, and when the conductive paste containing silver powder is baked for the formation of the thick silver film, the fine crystallites in the silver powder are sintered, and dimension change between before and after formation of the sintered thick silver film cause thermal shrinkage. Therefore, in order to obtain a conductive paste containing silver powder with less thermal shrinkage, it is desirable that the crystallites in the silver powder are as large as possible so as to minimize the sintering of the crystallites.

**[0005]** In recent years, the improvement of the highfrequency signal characteristics of circuits and the improvement of dimensional stability of substrates before and after sintering are demanded, and for this, as a substrate on which the thick silver film is formed, an LTCC (low temperature co-baked ceramic) substrate has been used substituting the above-described ordinary ceramic substrates. Furthermore, since the LTCC substrate is obtained by sintering a green sheet of the LTCC substrate with a conductive paste containing a low-resistance conductor such as silver powder together, compared with the technique to form the circuit of a thick silver film by printing a conductive paste using the above-described ordinary ceramic substrate, the number of sintering steps is less, the film thickness of the ceramic dielectric can be easily controlled, the conductor resistance of the circuit formed from the conductive paste is lowered, and the coplanarity of the substrate can be easily improved. However, since the LTCC is much excellent in dimensional stability, silver powder, which is the material of the conductive paste used in it is strongly required to have less thermal shrinkage, and therefore, it is strongly desired that the crystallites in the silver powder be large.

**[0006]** If the crystallites in the silver powder are large as described above, the content of impurities in the silver powder is generally lowered, and thereby the specific resistance of the circuit formed from the thick silver film is easily lowered; therefore, this is also preferable in the aspect that the conductive paste containing silver powder can be used not only in the circuit formed by baking as described above, but also in the circuit formed without baking.

**[0007]** As described above, it is desired for silver powder used in the conductive paste, that the silver powder which is composed of fine particles, having high dispersibility, whose particle size distribution is not excessively sharp but relatively broad, and the crystallites are large.

**[0008]** Whereas in Patent Document 1 (Japanese Patent Laid-Open No. 2000-1706), a method for producing highly crystalline silver powder wherein an aqueous solution of silver nitrate and a solution prepared by dissolving acrylic acid monomer in an aqueous solution of L-ascorbic acid are mixed and allowed to react simultaneously. According to the above-described method, highly crystalline silver powder whose crystallite size is 400 Å or more, and the range of the particle diameters is as narrow as 2 to 4 μm can be obtained.

**[0009]** Patent Document 1: Japanese Patent Laid-Open No. 2000-1706 (page 1)

## Disclosure of the Invention

### Problems to be Solved by the Invention

**[0010]** However, although the silver powder described in Patent Document 1 is composed of fine particles with large crystallites, it is difficult that the thermal shrinkage at a high temperature of for example about 700°C is sufficiently reduced. The silver powder has a large thermal shrinkage at a high temperature even if the crystallites are sufficiently large, and the reason is estimated to be caused by that the range of the particle diameters of the silver powder is between 2 and 4 μm, and since the particle size distribution is excessively sharp, gaps are formed between the particles of the silver powder, and the filling of the silver powder is lowered. Therefore, when the silver powder was used to prepare a conductive paste to form a thick silver film or to form a circuit using an LTCC substrate, the dimension change between before and after forming the circuit was enlarged causing a problem of warpage in an ordinary ceramic substrate or LTCC substrate, particularly the LTCC substrate.

**[0011]** Therefore, it is an object of the present invention to provide highly crystalline silver powder composed of fine particles, having high dispersibility, whose particle size distribution is not excessively sharp but relatively broad, and the crystallites are large; and a method for producing the same.

### Means for Solving the Problems

**[0012]** Under such a situation, the present inventors carried out keen studies, and found to complete the present invention. It is that if silver powder is produced using a method to mix a first aqueous solution containing silver nitrate, a dispersing agent and nitric acid, and a second aqueous solution containing ascorbic acid, highly crystalline silver powder composed of fine particles, having high dispersibility, whose particle size distribution is not excessively sharp but relatively broad, and the crystallites are large. And it can make the thick silver film obtained from the conductive paste excel in thermal shrinkage resistance, can be obtained.

**[0013]** Specifically, the present invention provides a method for producing highly crystalline silver powder which is characterized in that mixing a first aqueous solution and a second aqueous solution, wherein the first aqueous solution contains silver nitrate, a dispersing agent and nitric acid, and the second solution contains ascorbic acid.

**[0014]** The present invention also provides the method for producing highly crystalline silver powder characterized in that the dispersing agent is polyvinylpyrrolidone.

**[0015]** The present invention function provides the method for producing highly crystalline silver powder characterized in that the dispersing agent is a gelatin.

**[0016]** The present invention still further provides the method for producing highly crystalline silver powder characterized in that the first aqueous solution when it contains 100 parts by weight of silver nitrate, it further contains 5 parts by weight to 60 parts by weight of polyvinylpyrrolidone and 35 parts by weight to 70 parts by weight of nitric acid.

**[0017]** The present invention also provides the method for producing highly crystalline silver powder characterized in that the first aqueous solution when it contains 100 parts by weight of silver nitrate, it further contains 0.5 parts by weight to 10 parts by weight of gelatin and 35 parts by weight to 70 parts by weight of nitric acid.

**[0018]** The present invention further provides the method for producing highly crystalline silver powder characterized in that the first aqueous solution contains 100 parts by weight of silver nitrate, ascorbic acid contained in the second aqueous solution to be mixed with the first aqueous solution is 30 parts by weight to 90 parts by weight.

**[0019]** The present invention still further provides the method for producing highly crystalline silver powder characterized in that the second aqueous solution contains 100 parts by weight of ascorbic acid, nitric acid contained in the first aqueous solution to be mixed with the second aqueous solution is 40 parts by weight to 150 parts by weight.

**[0020]** The present invention also provides highly crystalline silver powder characterized in that the powder is produced by the method for producing highly crystalline silver powder.

**[0021]** The highly crystalline silver powder produced by the method for producing highly crystalline silver powder is characterized in that the powder has a crystallite diameter of the powder is 300 Å or more.

**[0022]** The highly crystalline silver powder is characterized in that an average particle diameter $D_{50}$ of the powder is in the range from 0.5 μm to 10 μm. (where $D_{50}$ is a median diameter (μm) calculated as 50% of volume cumulative distributions examined by a laser diffraction scattering particle size distribution measuring method).

**[0023]** The highly crystalline silver powder is characterized in that a thermal shrinkage rate of the powder after heating at 700°C is in the range from -3% to 3%.

**[0024]** The highly crystalline silver powder is characterized in that a ratio $D_{90}/D_{10}$ of the powder is in the range from 2.1 to 5.0 (where $D_{10}$ is diameter (μm) at 10% of volume cumulative distributions and $D_{90}$ is diameter (μm) at 90% of volume cumulative distributions examined by a laser diffraction scattering particle size distribution measuring method, respectively).

**[0025]** The highly crystalline silver powder is characterized in that a crystallite diameter is 300 Å or more, an average particle diameter $D_{50}$ is in the range from 0.5 μm to 10 μm, and a thermal shrinkage ratio after heating at 700°C in the length direction is in the range from -3% to 3%.

**[0026]** The highly crystalline silver powder is characterized in that a ratio $D_{90}/D_{10}$ of the powder is in the range from 2.1 to 5.0 (where $D_{10}$ is diameter (μm) at 10% of volume cumulative distributions and $D_{90}$ is diameter (μm) at 90% by volume of cumulative distributions examined by a laser diffraction scattering particle size distribution measuring method, respectively).

## Advantage of the Invention

**[0027]** Since the highly crystalline silver powder according to the present invention is of fine particles, has high dispersibility, and whose particle size distribution is not excessively sharp and relatively broad, and crystallites are large. And when it is used as a material for a conductive paste, the dispersibility of the silver powder to the conductive paste and the filling property of the conductive paste with the silver powder in can be excellent; an electrode, circuit and the like can be finer; the thick silver film obtained from the conductive paste can be excellent in thermal shrinkage resistance; and the resistivity thereof can be lowered. The method for producing the highly crystalline silver powder according to the present invention can efficiently produce the above-described highly crystalline silver powder according to the present invention.

## Best Mode for Carrying Out the Invention

### (Highly Crystalline Silver Powder According to the Present Invention)

**[0028]** The highly crystalline silver powder according to the present invention is substantially granular powder. The average particle diameter $D_{50}$ of the highly crystalline silver powder according to the present invention is 0.5 μm to 10 μm, preferably 1 μm to 5 μm. It is preferable that the average particle diameter $D_{50}$ is within the above-described range because when the silver powder is used in a conductive paste, the filling of the silver powder in the conductive paste is excellent, and the circuit or the like formed from the thick silver film can be made finer. On the other hand, the average particle diameter $D_{50}$ less than 0.5 μm is not preferable because the collection of the silver powder becomes difficult; and the average particle diameter $D_{50}$ exceeding 10 μm is not preferable because the silver powder is often aggregated. Here, the average particle diameter $D_{50}$ means the volume average particle diameter measured by a laser diffraction scattering method, that is, the particle diameter at 50% cumulative distribution.

**[0029]** The highly crystalline silver powder according to the present invention has a crystallite diameter of 300 Å or more, preferably 350 Å to 600 Å. It is preferable that the crystallite diameter is within the above-described range because when the conductive paste containing the silver powder is applied onto a ceramic substrate, and baked to form a circuit or the like composed of a thick silver film, the thermal shrinkage of the thick silver film between before and after baking becomes close to the thermal shrinkage of the ceramic substrate, and the effect to suppress the separation of the thick silver film from the ceramic substrate, or the deformation of the ceramic substrate due to the dimension change of the thick silver film is large.

**[0030]** On the other hand, it is not preferable that the crystallite diameter is less than 300 Å, because when the conductive paste is applied onto a ceramic substrate, and baked to form a circuit or the like composed of a thick silver film, the shrinkage of the thick silver film between before and after baking becomes larger than the shrinkage of the ceramic substrate, and the thick silver film is easily separated from the ceramic substrate or the ceramic substrate is easily deformed due to the dimension change of the thick silver film. Here, the crystallite diameter means the average crystallite diameter obtained from the half-value width of the diffraction angle of each crystal face obtained by conducting X-ray diffraction for silver powder sample.

**[0031]** The $D_{90}/D_{10}$ of the highly crystalline silver powder according to the present invention is normally 2.1 to 5.0, preferably 2.5 to 4.7. In the present invention, $D_{10}$ is diameter (μm) at 10% by volume cumulative distributions, and $D_{90}$ is diameter (μm) at 90% by volume cumulative distributions examined by a laser diffraction scattering particle size distribution measuring method, respectively. The $D_{90}/D_{10}$ is an indicator to indicate fluctuation, and a large $D_{90}/D_{10}$

indicates that the fluctuation of particle size distribution is large. It is preferable that $D_{90}/D_{10}$ is within the above-described range, because the particle size distribution of the silver powder is not excessively sharp, but is relatively broad, and when a circuit is formed with a conductive paste using the silver powder, the filling properties of the silver powder and the thermal shrinkage resistance of the circuit becomes excellent, specifically the dimension change of the circuit between before and after baking is easily reduced.

**[0032]** On the other hand, it is not preferable that $D_{90}/D_{10}$ is less than 2.1, because the particle size distribution becomes excessively sharp, and when a circuit is formed with a conductive paste using the silver powder, the filling properties of the silver powder easily becomes inferior, specifically, the dimension change of the circuit between before and after baking easily becomes large. It is also not preferable that $D_{90}/D_{10}$ exceeds 5.0, because the particle size distribution of the silver powder becomes excessively broad to make silver powder filling properties inferior when forming a circuit using a conductive paste using the silver powder, and thus the thermal shrinkage resistance of the circuit is easily deteriorated, specifically, the dimension change of the circuit between before and after baking easily becomes large.

**[0033]** The thermal shrinkage of the highly crystalline silver powder according to the present invention at 700°C in the length direction is normally in the range from -3% to 3%, preferably in the range from -2% to 2%. In the present invention, the thermal shrinkage at 700°C in the length direction means the thermal shrinkage of a pellet in the length direction measured using thermomechanical analysis (TMA) in a sample in which silver powder is formed into a pellet.

**[0034]** In the highly crystalline silver powder according to the present invention, the resistivity of the silver coating film baked at a relatively low temperature, for example 300°C, is low. Specifically, even if the highly crystalline silver powder is sintered at a low temperature, the resistivity of the sintered article can be easily reduced. The reason why the resistivity of the silver coating film thus baked at 300°C is estimated to be because the movement of electrons in the silver powder is smoothened due to large crystallite diameter.

**[0035]** The specific surface area of the highly crystalline silver powder according to the present invention is normally 0.10 $m^2/g$ to 1.0 $m^2/g$, preferably 0.20 $m^2/g$ to 0.90 $m^2/g$. The specific surface area of less than 0.10 $m^2/g$ is not preferable because the formation of the finer electrode or circuit composed of a thick silver film tends to be difficult. The specific surface area exceeding 1.0 $m^2/g$ is also not preferable because the formation of paste of silver powder tends to be difficult. The specific surface area in the present invention is the BET specific surface area.

**[0036]** The tap density of the highly crystalline silver powder according to the present invention is normally 3.8 $g/cm^3$ or more, preferably 4.0 $cm^3$ to 6.0 $cm^3$. The tap density within the above-described range is preferable because the filling of the silver powder in the paste of the highly crystalline silver powder is favorable in the preparation of the conductive paste to facilitate the preparation of the conductive paste, and on the coating film formation of the conductive paste, adequate gaps are formed between the particles of the highly crystalline silver powder to facilitate binder removal from the coating film on baking the coating film and to improve the density of the baked film, and as a result, the resistance of the thick silver film can be easily lowered. The highly crystalline silver powder according to the present invention can be produced by the following method.

(Method for producing the Highly Crystalline Silver Powder According to the Present Invention)

**[0037]** The method for producing the highly crystalline silver powder according to the present invention is to mix a first aqueous solution containing silver nitrate, a dispersing agent and nitric acid, and a second aqueous solution containing ascorbic acid.

**[0038]** The first aqueous solution in the present invention is an aqueous solution containing silver nitrate, a dispersing agent and nitric acid. As the water used for the preparation of the first aqueous solution, pure water, ion-exchanged water, ultra-pure water or the like is preferable for preventing impurities to be mixed. The silver nitrate used in the present invention is not specifically limited, but either solid or an aqueous solution can be used.

**[0039]** The examples of dispersing agents used in the present invention include polyvinylpyrrolidone (PVP), gelatin, polyethylene glycol, polyvinyl alcohol and the like. In the present invention, the term "gelatin" is used in the concept including glue. Among the dispersing agents used in the present invention, polyvinylpyrrolidone and gelatin are preferable because the thermal shrinkage resistance of silver powder can be particularly elevated. In the present invention, by compounding the dispersing agent in the first aqueous solution, the dispersion of the silver powder can be improved, and there is the effect of making the silver powder have fine particles, and making the particle size distribution not excessively sharp and relatively broad.

**[0040]** The nitric acid used in the present invention is not specifically limited, but either concentrated nitric acid or diluted nitric acid can be used. In the present invention, since the rate of the reaction to form silver from silver ions is controlled to be relatively slow by compounding sulfuric acid in the first aqueous solution, there is the effect of making the particle size distribution not excessively sharp and relatively broad, and enlarging the crystallites. If silver powder is produced without compounding nitric acid, the rate of the reaction to form silver from silver ions is excessively rapid and the reaction starts immediately, the obtained silver powder has a smaller particle diameters, and the crystallite diameter tends to be reduced compared with the case to produce the silver powder by compounding nitric acid as in the present invention.

**[0041]** When the dispersing agent is polyvinylpyrrolidone, the first aqueous solution contains normally 5 parts by weight to 60 parts by weight, preferably 15 parts by weight to 50 parts by weight, and more preferably 20 parts by weight to 40 parts by weight of polyvinylpyrrolidone to 100 parts by weight of silver nitrate. It is preferable that the compounding quantity of polyvinylpyrrolidone is within the above-described range, because the dispersion of the silver powder is improved, and the particle size distribution of the silver powder tends to be not excessively sharp but to be relatively broad. On the other hand, it is not preferable that the compounding quantity of polyvinylpyrrolidone is less than 5 parts by weight, because the obtained silver powder is easily aggregated; and it is not preferable that the compounding quantity of polyvinylpyrrolidone exceeds 60 parts by weight, because the impurity concentration in the obtained silver powder is easily elevated, environment is easily contaminated, and the production costs tend to be high.

**[0042]** When the dispersing agent is gelatin, the first aqueous solution contains normally 0.5 part by weight to 10 parts by weight, preferably 1 part by weight to 8 parts by weight, and more preferably 2 parts by weight to 6 parts by weight of gelatin to 100 parts by weight of silver nitrate. It is preferable that the compounding quantity of gelatin is within the above-described range, because the dispersion of the silver powder is improved, and the particle size distribution of the silver powder tends to be not excessively sharp but to be relatively broad. On the other hand, it is not preferable that the compounding quantity of gelatin is less than 0.5 parts by weight, because the obtained silver powder is easily aggregated; and it is not preferable that the compounding quantity of gelatin exceeds 10 parts by weight, because the impurity concentration in the obtained silver powder is easily elevated, environment is easily contaminated, and the production costs tend to be high.

**[0043]** When the dispersing agent is polyvinylpyrrolidone, the first aqueous solution contains normally 1 part by weight to 10 parts by weight, preferably 2 parts by weight to 4 parts by weight of gelatin to 100 parts by weight of water. It is preferable that the compounding quantity of polyvinylpyrrolidone is within the above-described range, because the dispersion of the silver powder is improved, and the particle size distribution of the silver powder tends to be not excessively sharp but to be relatively broad. On the other hand, it is not preferable that the compounding quantity of polyvinylpyrrolidone is less than 1 parts by weight, because the obtained silver powder is easily aggregated; and it is not preferable that the compounding quantity of polyvinylpyrrolidone exceeds 10 parts by weight, because the impurity concentration in the obtained silver powder is easily elevated, environment is easily contaminated, and the production costs tend to be high.

**[0044]** When the dispersing agent is gelatin, the first aqueous solution contains normally 0.1 parts by weight to 5 parts by weight, preferably 0.4 parts by weight to 2 parts by weight of gelatin to 100 parts by weight of water. It is preferable that the compounding quantity of gelatin is within the above-described range, because the dispersion of the silver powder is improved, and the particle size distribution of the silver powder tends to be not excessively sharp but to be relatively broad. On the other hand, it is not preferable that the compounding quantity of gelatin is less than 0.1 part by weight, because the obtained silver powder is easily aggregated; and it is not preferable that the compounding quantity of gelatin exceeds 5 parts by weight, because the impurity concentration in the obtained silver powder is easily elevated, environment is easily contaminated, and the production costs tend to be high.

**[0045]** The first aqueous solution contains normally 35 parts by weight to 70 parts by weight, preferably 40 parts by weight to 60 parts by weight, and more preferably 48 parts by weight to 54 parts by weight of nitric acid to 100 parts by weight of silver nitrate. It is preferable that the compounding quantity of nitric acid is within the above-described range, because the dispersion of the silver powder is improved, and the particle size distribution of the silver powder tends to be not excessively sharp but to be relatively broad. On the other hand, it is not preferable that the compounding quantity of nitric acid is less than 35 parts by weight, because the crystallization ability of the silver powder is easily lowered; and it is not preferable that the compounding quantity of nitric acid exceeds 70 parts by weight, because the obtained silver powder is easily aggregated. In the present invention, the compounding quantity of nitric acid means the compounding quantity converted to concentrate nitric acid of a concentration of 61%.

**[0046]** The second aqueous solution in the present invention is an aqueous solution containing ascorbic acid. As the water used for the preparation of the first aqueous solution, pure water, ion-exchanged water, ultra-pure water or the like is preferable for preventing impurities to be mixed. As the ascorbic acid used in the present invention, either L-isomer or D-isomer can be used.

**[0047]** In the production method according to the present invention, the above-described first aqueous solution and second aqueous solution are mixed to deposit highly crystalline silver powder in the blended solution. The examples of mixing modes include a method wherein the first aqueous solution is agitated and the second aqueous solution is mixed thereto. As the method to add the second aqueous solution, the entire quantity of the second aqueous solution can be added to the first aqueous solution at once, or the second aqueous solution can be gradually added to the first aqueous solution a little at a time. When the dispersing agent in the first aqueous solution is polyvinylpyrrolidone, the method to add the entire quantity of the second aqueous solution to the first aqueous solution is preferable because the silver powder composed of fine particles, whose particle size distribution is not excessively sharp but is relatively broad can be easily obtained; when the dispersing agent in the first aqueous solution is gelatin, the method to add the second aqueous solution gradually to the first aqueous solution a little at a time is preferable because the particle diameter of silver powder can be easily controlled.

**[0048]** In mixing the first aqueous solution and the second aqueous solution, the solutions are mixed so that the quantity of ascorbic acid contained in the second aqueous solution is normally 30 parts by weight to 90 parts by weight, preferably 40 parts by weight to 80 parts by weight, and more preferably 50 parts by weight to 75 parts by weight to 100 parts by weight of silver nitrate contained in the first aqueous solution. It is preferable that the compounding quantity of ascorbic acid to silver nitrate is within the above-described range because the yield of the silver powder is easily elevated. On the other hand, it is not preferable that the compounding quantity of ascorbic acid to 100 parts by weight silver nitrate is less than 30 parts by weight, because reduction is insufficient and the yield of the silver powder is easily lowered; and it is not preferable that the compounding quantity of ascorbic acid to 100 parts by weight silver nitrate exceeds 90 parts by weight, because environment is easily contaminated, and the production costs tend to be high.

**[0049]** In mixing the first aqueous solution and the second aqueous solution, the solutions are mixed so that the silver ion concentration in the obtained mixed solution is normally 10 g/l to 80 g/l, preferably 30 g/l to 65 g/l. It is preferable that the silver ion concentration in the blended solution is within the above-described range because the yield of the silver powder is high and the obtained silver powder is difficult to aggregate. On the other hand, it is not preferable that the silver ion concentration is less than 10 g/l, the productivity of the silver powder tends to be worsened; and it is not preferable that the silver ion concentration exceeds 80 g/l, the silver powder is easily aggregated.

**[0050]** In mixing the first aqueous solution and the second aqueous solution, the solutions are mixed so that the quantity of nitric acid contained in the first aqueous solution is normally 40 parts by weight to 150 parts by weight, preferably 50 parts by weight to 120 parts by weight, and more preferably 65 parts by weight to 100 parts by weight to 100 parts by weight of ascorbic acid contained in the second aqueous solution. It is preferable that the compounding quantity of nitric acid to ascorbic acid is within the above-described range because the yield of the silver powder is easily elevated. On the other hand, it is not preferable that the compounding quantity of nitric acid to 100 parts by weight ascorbic acid is less than 40 parts by weight, because it is difficult to sufficiently increase the crystallite diameter of the obtained silver powder; and it is not preferable that the compounding quantity of nitric acid to 100 parts by weight ascorbic acid exceeds 150 parts by weight, the obtained silver powder is easily aggregated.

**[0051]** It is preferable that silver powder deposited in the blended solution by mixing the first aqueous solution and the second aqueous solution is grown in the blended solution by continuing agitation normally for further 3 minutes or more, preferably 5 minutes to 10 minutes, because the particle diameter, particle size distribution and dispersion of the silver powder are easily within the specific ranges of the silver powder according to the present invention. After filtering the silver powder obtained in the blended solution using filtering means, for example, a Nutsche, the filtered product is washed with pure water and dried to obtain the highly crystalline silver powder according to the present invention.

**[0052]** The above-described highly crystalline silver powder according to the present invention can be used as the material for a conductive paste that can form electrodes or circuits of, for example, chip devices, plasma display panels, glass ceramic packages, ceramic filters and the like; in particular, it can be suitably used as the material for a conductive paste not only for ordinary ceramic substrates, but also for LTCC substrates as substrates forming the circuit, utilizing the very small thermal shrinkage of the silver powder. The method for producing highly crystalline silver powder according to the present invention can also be used for producing highly crystalline silver powder according to the present invention.

**[0053]** Although the examples will be described below, these examples should not be construed to limit the present invention.

## Example 1

**[0054]** 10 g of PVP (K-value: 30), 50g of silver nitrate and 24.6 g of concentrated nitric acid (concentration: 61wt%) were added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a first aqueous solution (first aqueous solution A). In addition, 35.8 g of ascorbic acid was added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a second aqueous solution (second aqueous solution A). The compositions of the first aqueous solution and the second aqueous solution are shown in Table 1 and Table 2.

Next, the second aqueous solution A was added to the stirring first aqueous solution A at once, after that, stirring was continued for 5 minutes to grow particles in the blended solution. Thereafter, stirring was stopped to settle the particles in the blended solution. After settling the particles, the supernatant of the blended solution was disposed, and the rest of blended solution was filtered using a Nutsche. Then the filtered product was rinsed with pure water and dried, and then highly crystalline silver powder was obtained.

For the obtained silver powder, $D_{10}$, $D_{50}$, $D_{90}$, $D_{100}$, SD, crystallite diameter, specific surface area, tap density, thermal shrinkage and resistivity were measured using the following methods and $D_{90}/D_{10}$ was calculated. The results are shown in Table 3 to Table 6.

**[0055]** ($D_{10}$, $D_{50}$, $D_{90}$, $D_{100}$, SD) : 10%, 50%, 90% and 100% were indicated as $D_{10}$ (μm), $D_{50}$ (μm), $D_{90}$ (μm), $D_{100}$ (μm) are particle diameters when the cumulative distributions measured by a laser diffraction scattering method using

[Micro Track HRA] manufactured by Nikkiso Co., Ltd. were, respectively, and SD is the standard deviation in the particle size distribution.

(Crystallite diameter): X-ray diffraction on the powder was performed using an X-ray diffraction apparatus [RINT 2000/PC] manufactured by Rigaku Corporation, and the crystallite diameter was calculated from the half-value width of the peak of diffraction angle obtained on each crystal faces.

(Specific surface area): It is a B.E.T. specific surface area measured by [Monosorb] manufactured by Yuasa-Ionics Co., Ltd.

(Tap density): Tap density was measured by tapping the sample using [Tap Denser] manufactured by Kuramochi Kagaku Kikai Seisakusyo Co., Ltd.

(Thermal shrinkage): A columnar pellet was prepared by compressing the silver powder, and the TMA analysis of the pellet was conducted using TMA/SS 6300 manufactured by Seiko Instruments Inc., in air at a temperature elevation rate of 10°C/min within the range between room temperature and 850°C to measure thermal shrinkage of the pellet in the length direction. The measuring temperatures were 300°C, 500°C and 700°C.

(Resistivity): A mixed solvent was prepared by mixing 95 parts by weight of terpineol and 5 parts by weight of ethyl cellulose, a paste was prepared by mixing 15 parts by weight of the mixed solvent and 85 parts by weight of the sample powder, and the paste was baked at 300°C to prepare a silver coating film having a thickness of about several $\mu$m. Other silver coating films were prepared in the same manner as described above except that the baking temperatures were 400°C and 500°C instead of 300°C.

Then, after measuring the resistance ($\Omega$) of the silver coating films by four-terminal network method using (MILLIOHM METER manufactured by Hewlett-Packard), the resistivity p ($\Omega \cdot$m) was obtained from the cross-sectional area of the silver coating films and the length between the terminals. Example 2

**[0056]** 20 g of PVP (K-value: 30), 50g of silver nitrate and 24.6 g of concentrated nitric acid (concentration: 61%) were added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a first aqueous solution (first aqueous solution B). In addition, 35.8 g of ascorbic acid was added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a second aqueous solution (second aqueous solution A). The compositions of the first aqueous solution and the second aqueous solution are shown in Table 1 and Table 2.

Next, the second aqueous solution A was added to the first aqueous solution B in at once, after that, stirring was continued for 5 minutes to grow particles in the blended solution. Thereafter, stirring was stopped to settle the particles in the blended solution. After settling the particles, the supernatant of the blended solution was filtered using a Nutsche. Then, the filtered product was rinsed with pure water and dried, and then highly crystalline silver powder was obtained.

For the obtained silver powder, $D_{10}$, $D_{50}$, $D_{90}$, $D_{100}$, SD, crystallite diameter, specific surface area, tap density, thermal shrinkage and resistivity were measured in the same manner as in Example 1 using the following methods and $D_{90}/D_{10}$ was calculated. The results are shown in Table 3 to Table 6.

Comparative Example 1

**[0057]** 10 g of PVP (K-value: 30) and 50g of silver nitrate were added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a first aqueous solution (first aqueous solution C). In addition, 26 g of ascorbic acid was added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a second aqueous solution (second aqueous solution B). The compositions of the first aqueous solution and the second aqueous solution are shown in Table 1 and Table 2.

Next, the second aqueous solution B was added to the stirring first aqueous solution C at once, after that, stirring was continued for 5 minutes to grow particles in the blended solution. Thereafter, stirring was stopped to settle the particles in the blended solution. After settling the particles, the supernatant of the blended solution was disposed, and the rest of blended solution was filtered using a Nutsche. Then the filtered product was rinsed with pure water and dried, and then highly crystalline silver powder was obtained.

For the obtained silver powder, $D_{10}$, $D_{50}$, $D_{90}$, $D_{100}$, SD, crystallite diameter, specific surface area, tap density, thermal shrinkage and resistivity were measured in the same manner as in Example 1 using the following methods and $D_{90}/D_{10}$ was calculated. The results are shown in Table 3 to Table 6. Example 3

**[0058]** 1.0 g of gelatin (manufactured by Nitta Gelatin Inc.), 50g of silver nitrate and 24.6 g of concentrated nitric acid (concentration: 61%) were added into 250 g of pure water at room temperature, and then, heated up to 50°C and dissolved by stirring to prepare a first aqueous solution (first aqueous solution D). In addition, 26.4 g of ascorbic acid was added into 250 g of pure water at room temperature, and dissolved by stirring to prepare a second aqueous solution (second aqueous solution C). The compositions of the first aqueous solution D and the second aqueous solution C are shown in Table 1 and Table 2.

Next, the second aqueous solution C at room temperature was gradually added to the stirring first aqueous solution D at 50°C in 30 minutes, after that, stirring was continued for 5 minutes to grow particles in the blended solution. Thereafter, stirring was stopped to settle the particles in the blended solution. After settling the particles, the supernatant of the

blended solution was disposed, and the rest of blended solution was filtered using a Nutsche. Then the filtered product was rinsed with pure water and dried, and then highly crystalline silver powder was obtained.
For the obtained silver powder, $D_{10}$, $D_{50}$, $D_{90}$, $D_{100}$, SD, crystallite diameter, specific surface area, tap density, thermal shrinkage and resistivity were measured in the same manner as in Example 1 using the following methods and $D_{90}/D_{10}$ was calculated. The results are shown in Table 3 to Table 6. Example 4

**[0059]** 3.0 g of gelatin (manufactured by Nitta Gelatin Inc.), 50g of silver nitrate and 24.6 g of concentrated nitric acid (concentration: 61%) were added into 500 g of pure water at room temperature, and then, heated up to 50°C and dissolved by stirring to prepare a first aqueous solution (first aqueous solution E). In addition, 25.9 g of ascorbic acid was added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a second aqueous solution (second aqueous solution D). The compositions of the first aqueous solution and the second aqueous solution are shown in Table 1 and Table 2.
Next, the second aqueous solution D at room temperature was gradually added to the stirring first aqueous solution E in 30 minutes, after that, stirring was continued for 5 minutes to grow particles in the blended solution. Thereafter, stirring was stopped to settle the particles in the blended solution. After settling the particles, the supernatant of the blended solution was disposed, and the rest of blended solution was filtered using a Nutsche. Then the filtered product was rinsed with pure water and dried, and then highly crystalline silver powder was obtained.
For the obtained silver powder, $D_{10}$, $D_{50}$, $D_{90}$, $D_{100}$, SD, crystallite diameter, specific surface area, tap density, thermal shrinkage and resistivity were measured in the same manner as in Example 1 using the following methods and $D_{90}/D_{10}$ was calculated. The results are shown in Table 3 to Table 6.

**[0060]**

[Table 1]

| | Water (g) | Kind of dispersing agent | Dispersing agent (g) | Silver nitrate (g) | Concentrated nitric acid (g) | Kind of first aqueous solutions |
|---|---|---|---|---|---|---|
| Example 1 | 500 | PVP | 10 | 50 | 24.6 | A |
| Example 2 | 500 | PVP | 20 | 50 | 24.6 | B |
| Comparative Example 1 | 500 | PVP | 10 | 50 | 0 | C |
| Example 3 | 250 | Gelatin | 1.0 | 50 | 26.4 | D |
| Example 4 | 500 | Gelatin | 3.0 | 50 | 24.6 | E |

**[0061]**

[Table 2]

| | Water (g) | Ascorbic acid (g) | Kind of second aqueous solutions |
|---|---|---|---|
| Example 1 | 500 | 35.8 | A |
| Example 2 | 500 | 35.8 | A |
| Comparative Example 1 | 500 | 26.0 | B |
| Example 3 | 250 | 26.4 | C |
| Example 4 | 500 | 25.9 | D |

**[0062]**

[Table 3]

| | $D_{10}$ (μm) | $D_{50}$ (μm) | $D_{90}$ (μm) | $D_{100}$ (μm) | $D_{90}/D_{10}$ | SD |
|---|---|---|---|---|---|---|
| Example 1 | 2.97 | 6.35 | 10.75 | 22.0 | 3.6 | 3.01 |
| Example 2 | 1.30 | 3.03 | 5.67 | 15.6 | 4.4 | 1.59 |
| Comparative Example 1 | 2.14 | 2.83 | 4.08 | 9.3 | 1.9 | 0.71 |

(continued)

| | $D_{10}$ (μm) | $D_{50}$ (μm) | $D_{90}$ (μm) | $D_{100}$ (μm) | $D_{90}/D_{10}$ | SD |
|---|---|---|---|---|---|---|
| Example 3 | 2.72 | 4.36 | 7.33 | 18.5 | 2.7 | 1.71 |
| Example 4 | 0.76 | 1.27 | 2.28 | 4.6 | 3.0 | 0.57 |

**[0063]**

[Table 4]

| | Crystallite diameter (Å) | Specific surface area ($m^2/g$) | Tap density ($g/cm^3$) |
|---|---|---|---|
| Example 1 | 441 | 0.30 | 4.1 |
| Example 2 | 377 | 0.62 | 4.0 |
| Comparative Example 1 | 258 | 0.62 | 3.8 |
| Example 3 | 545 | 0.20 | 4.4 |
| Example 4 | 441 | 0.72 | 4.8 |

**[0064]**

[Table 5]

| | Thermal shrinkage percentage at 300°C (%) | Thermal shrinkage percentage at 500°C (%) | Thermal shrinkage percentage at 700°C (%) |
|---|---|---|---|
| Example 1 | 0.13 | -2.13 | -2.2 |
| Example 2 | 0.09 | -2.68 | -2.9 |
| Comparative Example 1 | 0.84 | -4.02 | -7.82 |
| Example 3 | 0.27 | 1.08 | 1.13 |
| Example 4 | -0.58 | -1.51 | -1.35 |

**[0065]**

[Table 6]

| | Resistivity of silver coating film baked at 300°C $\rho(\Omega \cdot m)$ | Resistivity of silver coating film baked at 400°C $\rho(\Omega \cdot m)$ | Resistivity of silver coating film baked at 500°C $\rho(\Omega \cdot m)$ |
|---|---|---|---|
| Example 1 | $4.1\times10^{-5}$ | $2.0\times10^{-5}$ | $9.9\times10^{-6}$ |
| Example 2 | $5.2\times10^{-5}$ | $1.5\times10^{-5}$ | $1.2\times10^{-5}$ |
| Comparative Example 1 | $7.2\times10^{-4}$ | $8.9\times10^{-6}$ | $4.8\times10^{-5}$ |
| Example 3 | $9.4\times10^{-6}$ | $8.3\times10^{-6}$ | $9.9\times10^{-6}$ |
| Example 4 | $1.0\times10^{-5}$ | $8.8\times10^{-6}$ | $4.8\times10^{-5}$ |

**[0066]** From Table 1 to Table 5, it is clearly shown that silver powder prepared by using both dispersing agent and nitric acid is highly crystalline with a large crystallite diameter, and thermal shrinkage after heating at 700°C is small. Especially when gelatin is used as the dispersing agent, thermal shrinkage after heating at 700°C is especially small. From Table 6, it is found that silver powder prepared by using both dispersing agent and nitric acid show lower resistivity p on the silver coating film after baked at 300°C when compared with the silver powder prepared without using nitric acid. The reason why is suspected that the movement of electrons in the silver powder of the invention is more smooth because of it is large crystallite diameter.

Industrial Applicability

**[0067]** The highly crystalline silver powder according to the present invention is useful for the material to be contained in a conductive paste for forming electrodes and/or circuits, for example, chip devices, plasma display panels, glass ceramic packages, ceramic filters and the like. Also the method for producing highly crystalline silver powder according to the present invention is useful. Especially, it is shows good performance on LTCC substrate.

## Claims

1. A method for producing highly crystalline silver powder which is **characterized in that** mixing a first aqueous solution and a second aqueous solution, wherein the first aqueous solution contains silver nitrate, a dispersing agent and nitric acid, and the second solution contains ascorbic acid.

2. The method for producing highly crystalline silver powder according to claim 1, wherein the dispersing agent is polyvinylpyrrolidone.

3. The method for producing highly crystalline silver powder according to claim 1, wherein the dispersing agent is a gelatin.

4. The method for producing highly crystalline silver powder according to claim 2, the first aqueous solution when it contains 100 parts by weight of silver nitrate, it further contains 5 parts by weight to 60 parts by weight of polyvinylpyrrolidone and 35 parts by weight to 70 parts by weight of nitric acid.

5. The method for producing highly crystalline silver powder according to claim 3, the first aqueous solution when it contains 100 parts by weight of silver nitrate, it further contains 0.5 parts by weight to 10 parts by weight of gelatin and 35 parts by weight to 70 parts by weight of nitric acid.

6. The method for producing highly crystalline silver powder according to claim 1, when the first aqueous solution contains 100 parts by weight of silver nitrate, ascorbic acid contained in the second aqueous solution to be mixed with the first aqueous solution is 30 parts by weight to 90 parts by weight.

7. The method for producing highly crystalline silver powder according to claim 1, when the second aqueous solution contains 100 parts by weight of ascorbic acid, nitric acid contained in the first aqueous solution to be mixed with the second aqueous solution is 40 parts by weight to 150 parts by weight.

8. Highly crystalline silver powder which is **characterized in that** the powder is produced by the method according to claim 1.

9. The highly crystalline silver powder according to claim 8, wherein crystallite diameter of the powder is 300 Å or more.

10. The highly crystalline silver powder according to claim 8, wherein an average particle diameter $D_{50}$ of the powder is in the range from 0.5 $\mu$m to 10 $\mu$m. (where $D_{50}$ is a median diameter ($\mu$m) calculated as 50% of volume cumulative distributions examined by a laser diffraction scattering particle size distribution measuring method).

11. The highly crystalline silver powder according to claim 8, wherein a thermal shrinkage rate of the powder after heating at 700°C is in the range from -3% to 3%.

12. The highly crystalline silver powder according to claim 8, wherein a ratio $D_{90}/D_{10}$ of the powder is in the range from 2.1 to 5.0 (where $D_{10}$ is diameter ($\mu$m) at 10% of volume cumulative distributions and $D_{90}$ is diameter ($\mu$m) at 90% of volume cumulative distributions examined by a laser diffraction scattering particle size distribution measuring method, respectively).

13. Highly crystalline silver powder which is **characterized in that** a crystallite diameter is 300 Å or more, an average particle diameter $D_{50}$ is in the range from 0.5 $\mu$m to 10 $\mu$m, and a thermal shrinkage ratio after heating at 700°C in the length direction is in the range from -3% to 3%.

14. The highly crystalline silver powder according to claim 13, wherein a ratio $D_{90}/D_{10}$ of the powder is in the range from

2.1 to 5.0 (where $D_{10}$ is diameter ($\mu$m) at 10% of volume cumulative distributions and $D_{90}$ is diameter ($\mu$m) at 90% by volume of cumulative distributions examined by a laser diffraction scattering particle size distribution measuring method, respectively).

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2005/001660

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl$^7$ B22F9/24, 1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl$^7$ B22F9/24, 1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

| | | | |
|---|---|---|---|
| Jitsuyo Shinan Koho | 1922-1996 | Jitsuyo Shinan Toroku Koho | 1996-2005 |
| Kokai Jitsuyo Shinan Koho | 1971-2005 | Toroku Jitsuyo Shinan Koho | 1994-2005 |

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br>Y | JP 01-104338 A (Tanaka Kikinzoku Kogyo Kabushiki Kaisha),<br>21 April, 1989 (21.04.89),<br>Claims<br>(Family: none) | 1,8-14<br>1-14 |
| Y | JP 63-307206 A (Tanaka Kikinzoku Kogyo Kabushiki Kaisha),<br>14 December, 1988 (14.12.88),<br>Claims; examples<br>(Family: none) | 1-14 |
| Y | JP 2000-001706 A (Tanaka Kikinzoku Kogyo Kabushiki Kaisha),<br>07 January, 2000 (07.01.00),<br>Claims; Par. No. [0011]<br>(Family: none) | 1-14 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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|---|---|
| Date of the actual completion of the international search<br>25 April, 2005 (25.04.05) | Date of mailing of the international search report<br>17 May, 2005 (17.05.05) |
| Name and mailing address of the ISA/<br>Japanese Patent Office<br>Facsimile No. | Authorized officer<br>Telephone No. |

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## REFERENCES CITED IN THE DESCRIPTION

### Patent documents cited in the description

- JP 2000001706 A **[0008] [0009]**