(19) Europäisches
Patentamt
European
Patent Office
Office européen
des brevets

(11) **EP 3 276 042 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
**31.01.2018 Bulletin 2018/05**

(21) Application number: **16768841.5**

(22) Date of filing: **23.03.2016**

(51) Int Cl.:
***C23C 18/18*** $^{(2006.01)}$ ***H05K 3/18*** $^{(2006.01)}$

(86) International application number:
**PCT/JP2016/059264**

(87) International publication number:
**WO 2016/152938 (29.09.2016 Gazette 2016/39)**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**
Designated Extension States:
**BA ME**
Designated Validation States:
**MA MD**

(30) Priority: **24.03.2015 JP 2015061779**

(71) Applicant: **OM Sangyo Co., Ltd.**
**Okayama 700-0971 (JP)**

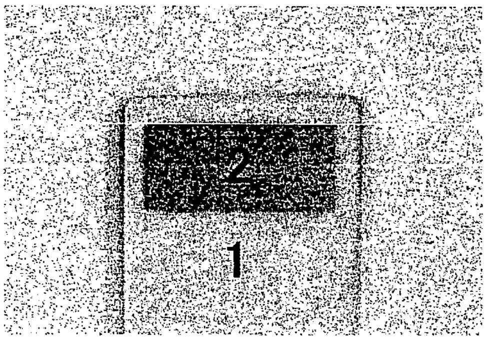
(72) Inventors:
- **NISHIMURA, Yoshiyuki**
  **Okayama-shi**
  **Okayama 700-0971 (JP)**
- **MIYAKE, Rie**
  **Okayama-shi**
  **Okayama 700-0971 (JP)**
- **FUKUDA, Chisa**
  **Okayama-shi**
  **Okayama 700-0971 (JP)**
- **TAKAMIZAWA, Masao**
  **Okayama-shi**
  **Okayama 700-0971 (JP)**
- **MITOOKA, Yutaka**
  **Okayama-shi**
  **Okayama 701-1296 (JP)**

(74) Representative: **Müller-Boré & Partner**
**Patentanwälte PartG mbB**
**Friedenheimer Brücke 21**
**80639 München (DE)**

# (54) METHOD FOR PRODUCING PLATED ARTICLE

(57) There is provided a method for producing a plated article in which a plating film pattern is formed on the surface of a glass substrate, comprising a first step of irradiating a partial area of the surface of the glass substrate with a pulsed laser; a second step of attaching an electroless catalyst on the surface of the glass substrate; a third step of selectively deactivating or selectively removing the catalyst attached to the unirradiated area with the pulsed laser in the glass substrate; and a fourth step of nonelectrolytically plating the glass substrate after the third step to selectively form a plating film in the irradiated area with the pulsed laser. The method allows for easily producing a plated article in which a highly adherent plating film pattern is formed on the surface of the glass substrate.

[FIG. 2]



EP 3 276 042 A1

Printed by Jouve, 75001 PARIS (FR)

## Description

### TECHNICAL FIELD

**[0001]** The present invention relates to a method for producing a plated article in which a plating film pattern is formed on the surface of a glass substrate.

### BACKGROUND ART

**[0002]** Conventionally, paper phenol substrates, paper epoxy substrates, glass epoxy substrates, ceramic substrates or the like have been used as a substrate for a circuit used for products such as home electric appliances and transport devices. These substrates are properly used depending on performance and a cost needed to a product because electric properties, mechanical properties and a price are different from each other. Recently, a glass substrate has got much attention as a substrate for a circuit, and there have been attempts for forming a metal film pattern on the surface of a glass substrate. A glass substrate has advantages that it is highly thermally stable compared with substrates conventionally used and is inexpensive.

**[0003]** Patent Reference No. 1 has described a selective plating method wherein the surface of an insulative substrate to be plated is irradiated with an energy beam, that is, a predetermined area of the substrate surface is irradiated with the energy beam, then a liquid containing a substance to be precipitation nuclei in chemical plating as a compound is contacted with the surface of the insulative substrate, the substrate is washed for removing the residual liquid, and then the surface irradiated with the energy beam is contacted with a predetermined chemical plating solution to deposit metal over the area of the adherend by chemical plating. There is described that it allows for forming a complicated and fine metal deposition pattern.

**[0004]** However, Patent Reference No. 1 has not described or suggested that in the plating method, a metal film pattern is formed on the surface of a glass substrate.

**[0005]** Patent Reference No. 2 has described a method for forming a metal interconnection in which the metal interconnection is formed over the surface of an insulator, wherein using a picosecond laser beam with a pulse width of picosecond level or a femtosecond laser beam with a pulse width of femtosecond level as a laser beam, the surface of a silver-containing insulator which is transparent to the above laser beam is irradiated with the laser beam; silver ions in the irradiated area are reduced to generate silver atoms in the irradiated area; the insulator in which the above laser beam irradiation has generated silver atoms in the irradiated area is immersed in an electroless plating solution kept at a predetermined temperature; and using the silver atoms as catalyst nuclei, a metal is precipitated to deposit a metal film over the above insulator, forming a metal interconnection. In Examples therein, there is described an example where a photosensitive glass is used as an insulator. It has been described that a metal interconnection can be thus formed with simple processes and a small number of steps.

**[0006]** However, in the plating method described in Patent Reference No. 2, a special glass substrate must be used, and such a glass substrate is more expensive than substrates conventionally used. Therefore, there is a limit on widely disseminating a circuit using this substrate.

### PRIOR ART REFERENCES

#### Patent References

**[0007]**

Patent Reference No. 1: JP 60-149783 A
Patent Reference No. 2: JP 2008-41938 A

### SUMMARY OF THE INVENTION

#### PROBLEMS TO BE SOLVED BY THE INVENTION

**[0008]** To solve the above problems, an objective of the present invention is to provide a method for easily producing a plated article in which a highly adherent plating film pattern is formed on the surface of a glass substrate.

#### MEANS FOR SOLVING THE PROBLEMS

**[0009]** The above problems can be solved by providing a method for producing a plated article in which a plating film pattern is formed on the surface of a glass substrate, comprising a first step of irradiating a partial area of the surface of the glass substrate with a pulsed laser; a second step of attaching an electroless catalyst on the surface of the glass substrate; a third step of selectively deactivating or selectively removing the catalyst attached to the unirradiated area with the pulsed laser in the glass substrate; and a fourth step of nonelectrolytically plating the glass substrate after the third step to selectively form a plating film in the irradiated area with the pulsed laser.

**[0010]** Here, it is preferable that a pulse width of the pulsed laser is $1\times10^{-8}$ to $1\times10^{-4}$ sec. It is also preferable that the plating film is at least one selected from the group consisting of nickel, copper, silver, gold, palladium, platinum, rhodium, ruthenium, tin, iron, cobalt and alloys thereof.

**[0011]** It is preferable that in the third step, the glass substrate contacts a solution containing a compound deactivating the catalyst or a compound removing the catalyst.

**[0012]** It is preferable that in the third step, a compound deactivating the catalyst is a sulfur compound. Here, it is preferable that the sulfur compound is a compound having at least one functional group selected from the group consisting of a thiocarbonyl group, a thiol group and a sulfide group.

**[0013]** Furthermore, it is also preferable that a compound removing the catalyst is a chelate compound or cyanide. Here, it is preferable that the compound removing the catalyst is at least one chelate compound selected from the group consisting of an amino acid, an amino alcohol, a polyamine, a polycarboxylic acid and a polyketone.

## EFFECTS OF THE INVENTION

**[0014]** According to the present invention, a plated article in which a highly adherent plating film pattern is formed on a glass substrate can be easily produced.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0015]**

FIG. 1 shows an example of a pulsed laser irradiation method.
FIG. 2 is a microscopic image of a plated article in Example 1.
FIG. 3 is a microscopic image of the appearance of the plated article in Example 1 after the tensile test.
FIG. 4 is a microscopic image of a plated article in Example 2.
FIG. 5 is a microscopic image of a plated article in Comparative Example 1.

## MODES FOR CARRYING OUT THE INVENTION

**[0016]** The present invention relates to a method for producing a plated article in which a plating film pattern is formed on the surface of a glass substrate. The production method according to the present invention comprises the following first to fourth steps. There will be described each step.

**[0017]** In a first step, a partial of the surface of a glass substrate is irradiated with a pulsed laser. Examples of the glass substrate used in the first step include, but not limited to, a soda-lime glass, a borosilicate glass and a quartz glass. These glass substrates can be appropriately selected, depending on an application of a plated article. When a cost is emphasized, a soda-lime glass is suitable. When thermal stability emphasized, a quartz glass and a borosilicate glass are suitable and a quartz glass is more suitable. When reducing the amount of impurities contained in a glass substrate is emphasized, a quartz glass and a borosilicate glass are suitable, and a quartz glass is more suitable. There are no particular restrictions to a thickness of a glass substrate, and it is generally 0.02 to 5 mm. There are no particular restrictions to its shape. A glass substrate whose mechanical strength has been improved by heating can be also used. Examples of such a glass substrate include a physically tempered glass which is produced by heating and then rapidly cooling a glass to generate compression stress in the proximity of the surface, and a chemically tempered glass which is produced by heating a glass while the glass is subjected to ion-exchange treatment for introducing alkali ions having a large ion radius in the surface of the glass to generate compression stress in the proximity of the surface of the glass.

**[0018]** In the present invention, it is important to use a pulsed laser. The use of a pulsed laser allows for inducing multiphoton absorption in even a transparent substrate such as a glass. Multiphoton absorption is accelerated with a larger peak power (W) of laser. When an energy is the same, a peak power (W) is larger as a pulse width is shorter, and therefore, a shorter pulse width is preferable. Based on this point of view, a pulse width (sec) of a pulsed laser is preferably $1\times10^{-4}$ sec or less, more preferably $1\times10^{-7}$ sec or less, further preferably $1\times10^{-9}$ sec or less, particularly preferably $1\times10^{-10}$ sec or less. Thus, with a very short pulse width, a peak powder of a laser can be sufficiently increased to initiate multiphoton absorption. The lower limit of a pulse width of a pulsed laser is, but not limited to, generally $1\times10^{-18}$ sec, suitably $1\times10^{-15}$ sec. Then, by setting the system such that a laser processing point (focus) is the surface of a glass substrate, the surface of the glass substrate can be processed.

**[0019]** It is preferable that an average output power at a processing point is 0.01 to 1000 W. If an average output power at a processing point is less than 0.01 W, a highly adherent plating film may not be obtained. If an average output power at a processing point is more than 1000 W, a glass substrate may be significantly damaged. A repetition frequency of a pulsed laser is generally, but not limited to, 1 kHz to 1000 MHz.

**[0020]** There are no particular restrictions to the type of a-laser; for example, solid laser such as YAG laser, fiber laser and semiconductor laser; and gas laser such as carbon dioxide laser and excimer laser. There are no particular restrictions to a wavelength of a pulsed laser, and it can be appropriately selected depending on the type of a glass substrate used and is generally 100 to 12000 nm. In the light of easiness of pulsed oscillation, YAG laser is preferable and neodymium YAG laser is more preferable. In neodymium YAG laser, a laser beam with a wavelength of 1064 nm which is called as a fundamental wave (first harmonic) is generated. Using a wavelength conversion device, a laser beam with a wavelength of 532 nm called as a second harmonic, a laser beam with a wavelength of 355 nm called as a third harmonic, and a laser beam with a wavelength of 266 nm called as a fourth harmonic can be obtained. In the production method of the present invention, any of the first to the fourth harmonics can be appropriately selected depending on the purpose.

**[0021]** Then, a partial area of the surface of a glass substrate is irradiated with a pulsed laser. There are no particular restrictions to a method of irradiating a glass substrate with a pulsed laser, and for example, the method shown in FIG. 1 can be employed. FIG. 1 shows an example of a pulsed laser irradiation method. As shown in FIG. 1, an area of the surface of a glass substrate to be irradiated is set. In a subsequent step, a plating film is to be selectively formed only in an area irradiated with a pulsed laser, that is, this irradiation area. Then, a laser is irradiated from the point indicated by St in the x direction (the right direction in FIG. 1) at a predetermined scan rate, then the laser is moved by a predetermined interval in the y direction (the upper direction in FIG. 1), then the laser is irradiated in the -x direction (the left direction in FIG. 1) at a predetermined scan rate, and then again the laser is moved by a predetermined interval in the y direction. An irradiation spot diameter corresponds to a laser beam diameter, but irradiation spots do not have to be mutually overlapped and there may be an interval between irradiation spots. In this method, a scan rate and an interval (pitch interval) can be appropriately adjusted to regulate the laser irradiation amount per unit area.

**[0022]** In the light of adherence of a plating film, an arithmetic mean roughness (Ra) of a glass surface irradiated with a pulsed laser is preferably 0.1 μm or more, more preferably 0.2 μm or more. If Ra is excessively large, strength of a plated article may be deteriorated, and therefore, Ra is preferably 10 μm or less, more preferably 5 μm or less. Herein, Ra is determined in accordance with JIS B 0601 (2001).

**[0023]** Next, in a second step, an electroless catalyst is attached to the surface of the glass substrate. There are no particular restrictions to the electroless catalyst as long as it contains a metal element which can exert catalysis to an electroless plating solution. Examples of the metal element include palladium (Pd), silver (Ag), copper (Cu), nickel (Ni), aluminum (Al), iron (Fe), cobalt (Co), zinc (Zn), gold (Au), platinum (Pt) and tin (Sn). These metal elements can be appropriately selected, depending on the type of an electroless plating solution used in a fourth step. Then, after the treatment with an aqueous solution containing the above metal element, the glass substrate can be treated with an aqueous solution containing a reducing agent to activate the electroless catalyst.

**[0024]** Next, in a third step, the catalyst attached to the area which has not been irradiated with the pulsed laser in the glass substrate is selectively deactivated or selectively removed.

**[0025]** There are no particular restrictions to a method for removing the catalyst In the third step; for example, conducting an ultrasonic treatment to the glass substrate or washing the surface of the glass substrate with flowing water. However, in the light of more selective deactivating or removing the catalyst attached to the area which has not been irradiated with the pulsed laser, preferably employed are a method where the glass substrate is contacted with a solution containing a compound capable of deactivating the catalyst, and a method where the glass substrate is contacted with a solution containing a compound capable of removing the catalyst. Examples of a method for contacting the glass substrate with a solution include a method where the glass substrate is immersed in a solution containing a compound deactivating the catalyst, a method where the glass substrate is immersed in a solution containing a compound removing the catalyst, a method where a solution containing a compound deactivating the catalyst is applied to the glass substrate, and a method where a solution containing a compound removing the catalyst is applied to the glass substrate.

**[0026]** In the third step, when the glass substrate is contacted with a solution containing a compound deactivating the catalyst, the compound is preferably a sulfur compound. The inventors prepared a glass substrate to which a palladium catalyst was attached, and chemical compositions of the surface of the glass substrate before and after immersion in a solution containing a sulfur compound were analyzed using a photoelectron spectrometer (XPS). As a result, it was found that palladium was present on the substrate surface even after immersion in a solution containing a sulfur compound. It was also found that a peak position derived from palladium moved after immersion in a solution containing a sulfur compound. Assuming that the results indicate that a sulfur atom coordinates palladium, the inventors infer that it causes deactivation of the palladium catalyst.

**[0027]** Preferably, the above sulfur compound is a compound having at least one functional group selected from the group consisting of a thiocarbonyl group, a thiol group and a sulfide group. A sulfur compound having a thiocarbonyl group can be thiourea. Examples of a sulfur compound having a thiol group include triazine thiol, mercapto benzothiazole, mercaptoacetic acid and thiocyanic acid. Examples of a sulfur compound having a sulfide group include dimethyl sulfide and methionine.

**[0028]** If a concentration of a solution containing a sulfur compound is too low, the catalyst may not be selectively deactivated. Based on this point of view, a concentration of the sulfur compound is preferably 0.001 ppm or more. If a concentration of the sulfur compound is too high, the catalyst attached to the area irradiated with a pulsed laser may be also deactivated. Based on this point of view, a concentration of the sulfur compound is preferably 100 ppm or less.

**[0029]** A solvent used for a solution containing a compound deactivating the catalyst is generally, but not limited to, water or an alcohol. When a glass substrate is immersed in a solution containing a compound deactivating a catalyst, a temperature of the solution in which the glass substrate is immersed is generally, but not limited to, 5 to 90 °C. A time of immersing glass substrate is generally, but not limited to, 1 sec to 30 min. A method for applying a solution containing a compound deactivating a catalyst can be application of the solution to a glass substrate by spraying.

**[0030]** In the third step, when a glass substrate is contacted with a solution containing a compound removing a catalyst, the compound is preferably a chelate compound or a cyanide. In the light of handleability, the compound removing a catalyst is preferably at least one chelate compound selected from the group consisting of amino acids, amino alcohols, polyamines, polycarboxylic acids and polyketones. Examples of an amino acid include alanine, arginine, asparagine, aspartic acid, cysteine, glutamine, glutamic acid, glycine, histidine, isoleucine, leucine, methionine, phenylalanine, proline, serine, threonine, tryptophan, tyrosine and valine. Examples of an amino alcohol include triethanolamine. Examples of a polyamine include ethylenediamine. Examples of a polycarboxylic acid include citric acid, succinic acid, maleic acid, fumaric acid, tartaric acid and potassium tartrate. Examples of a polyketone include acetylacetone.

**[0031]** The inventors prepared a glass substrate to which a palladium catalyst was attached, and chemical compositions of the surface of the glass substrate before and after immersion in a solution containing a chelate compound were analyzed using a photoelectron spectrometer (XPS). As a result, it was found that the palladium catalyst was removed from the substrate surface by immersion in a solution containing a chelate compound. The solution after immersion of the glass substrate was analyzed using an ICP emission analyzer, and it was found that the solution contained palladium.

**[0032]** Examples of the cyanide include potassium cyanide and sodium cyanide.

**[0033]** If a concentration of the chelate compound or the cyanide is too low, the catalyst may not be selectively removed. Based on this point of view, a concentration of the chelate compound or the cyanide is preferably 0.001 M or more. If a concentration of the chelate compound or the cyanide is too high, the catalyst attached to the area irradiated with a pulsed laser may be also removed. Based on this point of view, a concentration of the chelate compound or the cyanide is preferably 3 M or less.

**[0034]** A solvent used for a solution containing a compound removing the catalyst is generally, but not limited to, water or an alcohol. When a glass substrate is immersed, a temperature of the solution in which the glass substrate is immersed is generally, but not limited to, 5 to 90 °C. A time of immersing glass substrate is generally, but not limited to, 1 sec to 30 min. A method for applying a solution containing a compound removing a catalyst can be application of the solution to a glass substrate by spraying.

**[0035]** In a fourth step, nonelectrolytic plating is conducted, after the third step, to selectively form a plating film only in the irradiated area with the pulsed laser. Here, the plating film is preferably made of at least one selected from the group consisting of nickel, copper, silver, gold, palladium, platinum, rhodium, ruthenium, tin, iron, cobalt and alloys thereof. An alloy as used herein refers to an alloy containing at least one of the above metal elements in 50 % by mass or more.

**[0036]** Examples of nonelectrolytic plating used in the fourth step include electroless nickel plating, electroless copper plating, electroless silver plating, electroless gold plating, electroless palladium plating, electroless platinum plating, electroless rhodium plating, electroless ruthenium plating, electroless tin plating, electroless iron plating, electroless cobalt plating or electroless plating of an alloy thereof. Electroless alloy plating as used herein refers to nonelectrolytic plating involving the system containing at least one metal element in 50 % by mass or more. Varying the type of nonelectrolytic plating, this process can be conducted in multiple batches.

**[0037]** As described above, a production method of the present invention allows for precisely forming a desired plating film pattern on the surface of a glass substrate without using a special glass substrate. As demonstrated in Examples later, a pattern was formed by a pulsed laser and then, by nonelectrolytically plating, a plating film was formed in an area irradiated with the laser. However, if the third step is omitted, a plating film was formed not only in the area irradiated with a laser but also in the area unirradiated with a laser (Comparative Example 1). According to the production method of the present invention, a catalyst attached to an area unirradiated with a laser can be selectively deactivated or selectively removed, so that a plating film can be selectively formed only in the area irradiated with a laser.

**[0038]** A plating film formed by the production method of the present invention has excellent adherence. Recent trend to size reduction and higher performance of end products has led to stricter requirement for performance of a plated article and thus a plated article having a finer film pattern. However, as a pattern pitch is finer, a plating film is required to have higher adherence. Therefore, for providing a plated article having a fine film pattern, the use of the production method of the present invention is very beneficial.

**[0039]** Following the fourth step, the production method of the present invention can comprise an additional step. Such an additional step can be electrolytic plating or various surface processings. Examples of electrolytic plating include electrolytic nickel plating, electrolytic copper plating, electrolytic silver plating, electrolytic gold plating, electrolytic palladium plating, electrolytic tin plating, electrolytic iron plating, electrolytic bismuth plating, electrolytic platinum plating, electrolytic rhodium plating, electrolytic ruthenium plating, electrolytic zinc plating and electrolytic plating of alloys thereof. Electrolytic alloy plating as used herein refers to electrolytic plating involving the system containing at least one metal element in 50 % by mass or more. Examples of various surface processings include metal spraying by a cold spraying process and applying a metal paste. Examples of a metal used include copper, tin, gold, silver, nickel, iron, palladium, ruthenium, rhodium, iridium, indium, zinc, aluminum, tungsten, chromium, magnesium, titanium, silicon or alloys thereof. These additional steps can be conducted more than once and the steps can be identical or different. Furthermore, after the fourth step, mechanical strength of a glass substrate can be improved by heating.

EXAMPLES

**[0040]** The present invention will be further detailed, but not limited to, with reference to Examples.

Example 1

[Laser irradiation]

(Glass substrate)

**[0041]** A soda-lime glass with a size of 76 mm (length) × 26 mm (width) ×1.1 mm (thickness) ("Matsunami slide glass S7213") was prepared as a glass substrate.

(Processing method)

**[0042]** A pulse oscillation solid-state laser "Talisker HE" from Coherent Japan Inc. was used.

Wavelength: 355 nm
Average output power: 2 W
Average output power at a processing point: 0.8 W
Pulse width: 20 picosecond
Frequency: 50 kHz

**[0043]** Then, as shown in FIG. 1, the glass substrate was irradiated with a pulsed laser. Specifically, a 20 mm×10 mm irradiation area was set in the surface of the glass substrate. To this irradiation area, a pulsed laser was irradiated from the point indicated by St in the x direction to the right end of the irradiation area at a scan rate of 100 mm/sec. Then, the pulsed laser was moved by 15 μm in the y direction, and the pulsed laser was irradiated in the -x direction to the left end of the irradiation area at a scan rate of 100 mm/sec. This process was repeated to irradiate the whole irradiation area with the pulsed laser.

**[0044]** After the pulsed laser irradiation, observation of the surface of the glass substrate demonstrated that as shown in FIG. 1, the area was processed such that there was a sequence of spots (recesses). A diameter of one spot was determined to be about 15 μm.

[Nonelectrolytic plating]

(Pre-treatment)

**[0045]** The laser processed glass substrate was immersed in an aqueous solution of potassium hydroxide (concentration: 50 g/L) kept at 50 °C for 5 min. Then, the glass substrate was washed with ion-exchanged water. Subsequently, the glass substrate was immersed in a conditioning solution (concentration: 50 mL/L, "THRU-CUP MTE-1-A" from C. Uyemura & Co., Ltd.) kept at 50 °C for 5 min. Then, glass substrate was washed with ion-exchanged water.

(Electroless catalyst adhesion)

**[0046]** The pre-treated glass substrate was immersed in a palladium catalyst solution (concentration: 50 mL/L, "Activator A-10X" from C. Uyemura & Co., Ltd.) at room temperature for 1 min. Then, the glass substrate was washed with ion-exchanged water three times.

(Activation)

**[0047]** The glass substrate with the palladium catalyst was immersed in an aqueous solution of sodium hypophosphite (concentration: 0.27 M) kept at 50 °C for 30 sec, to activate the palladium catalyst. Then, the glass substrate was washed with ion-exchanged water.

(Catalyst deactivation)

**[0048]** The activated glass substrate was immersed in an aqueous solution of thiourea (concentration: 0.1 ppm) kept at 50 °C for 1 min, to deactivate the palladium catalyst attached to the area unirradiated with the pulsed laser. Then, the glass substrate was washed with ion-exchanged water three times.

(Electroless Ni plating)

**[0049]** The glass substrate was immersed in an electroless Ni-plating solution, pH 4.4 kept at 75 °C for 35 min, for electroless Ni plating, to form an electroless Ni-plating layer with a film thickness of 5 μm on the surface of the glass substrate. Then, the substrate was washed with ion-exchanged water three times. A composition of an electroless Ni-plating solution was as follows.

"ELN240 M2" from Electroplating Engineers of Japan Ltd. (EEJA): 150 mL/L
"ELN240 M1" from Electroplating Engineers of Japan Ltd. (EEJA): 50 mL/L
"ELN240 R3" from Electroplating Engineers of Japan Ltd. (EEJA): 6 mL/L

(Immersion Au plating)

**[0050]** The glass substrate having an Ni-plating layer was immersed in a gold plating solution ("PRECIOUS-FAB IGS8000SPF" from EEJA) kept at 55 °C for 10 min, for forming an immersion Au plating layer with a thickness of 0.05 μm over the Ni plating layer, to provide a plated article.

[Evaluation]

(Surface observation)

**[0051]** The surface of the plated article obtained was observed by a microscope. The image obtained is shown in FIG. 2. In FIG. 2, 1 is the glass substrate, and 2 is an immersion gold-plating film. As shown in FIG. 2, by "catalyst deactivation", a plating film was selectively formed only in the area irradiated with a pulsed laser.

(Adhesion test)

**[0052]** An adhesion test was conducted in accordance with a solder testing described in JIS H8504. Here, an L-shaped clasp was an oxygen free copper plate with a thickness of 0.5 mm. It was press-molded into a predetermined shape such that an area to be soldered is 5 mmx5 m, which was then nickel-plated to a film thickness of 3 μm as a base layer and then gold-plated to a film thickness of 0.05 μm. Separately, a solder was applied to the surface of the plated article (φ 8 mm×t 0.2 mm), and then heated at 300 °C for 1 min. Then, the L-shaped clasp and the plated article were bonded via a solder to provide a test piece. The test piece obtained was mounted to a tensile tester "3382 floor model testing system" from Instron Corporate, and an adhesion test was conducted. A solder was a lead-free solder paste "TSC-254-5042SF 12-1" from Tarutin Kester Co., Ltd. FIG. 3 is an image after the tensile test. As shown in FIG. 3, the plating film was stripped together with the glass.

Example 2

**[0053]** In "electroless catalyst adhesion", a time of immersion in a palladium catalyst solution was changed to 2 min and "catalyst removal" was conducted in place of "catalyst deactivation". In "catalyst removal", a plated article was produced as described in Example 1, except that an activated glass substrate was immersed in an aqueous solution of glycine (concentration: 0.05 M) at room temperature for 30 sec, and its surface was observed by a microscope. FIG. 4 shows an image obtained. In FIG. 4, 1 is a glass substrate, and 2 is an immersion Au plating film. As shown in FIG. 4, by "catalyst removal", a plating film was selectively formed only in the area irradiated with a pulsed laser. Then, an adhesion test was conducted as described in Example 1. As a result, the plating film was stripped together with the glass.

Example 3

**[0054]** A plated article was produced as described in Example 1, except that a glass substrate was replaced with a 76 mm×26 mm×1.1 mm borosilicate glass ("Matsunami slide glass S1127"). Then, an adhesion test was conducted as described in Example 1. As a result, the plating film was stripped together with the glass.

Example 4

**[0055]** A glass substrate was irradiated with a pulsed laser as described in Example 1, except that a glass substrate was replaced with a reinforced glass with a size of 70 mm (length)×30 mm (width)×0.55 mm (thickness) ("Dragontrail" from AGC: Asahi Glass Co., Ltd.) and in pulsed laser irradiation, an average output power at a processing point was 1.1 W, a travel distance in the y direction was 6 μm and a scan rate was 300 mm/sec. "Dragontrail" is a chemically reinforced glass, in which $Na^+$ in the glass surface is replaced with $K^+$.

**[0056]** Using a color 3D laser microscope "VK-9700" (observation magnification: 50) from KEYENCE Corporation, an arithmetic mean roughness (Ra) of the area irradiated with a pulsed laser was measured in accordance with JIS B 0601(2001). As a result, Ra was 0.41 μm.

**[0057]** After measuring a surface roughness, a plating film was formed on the surface of the glass substrate as described in Example 2. As a result, a plating film was selectively formed only in the area irradiated with a pulsed laser. Then, an adhesion test was conducted as described in Example 1, and the plating film was stripped together with the glass.

Example 5

**[0058]** A glass substrate was irradiated with a pulsed laser as described in Example 4, except that in pulsed laser irradiation, an average output power at a processing point was 1.1 W, a travel distance in the y direction was 10 μm, and a scan rate was 50 mm/sec. Then, an arithmetic mean roughness (Ra) of the area irradiated with a pulsed laser was measured as described in Example 4. As a result, Ra was 2.81 μm.

**[0059]** After measuring a surface roughness, a plating film was formed on the surface of the glass substrate as described in Example 2. As a result, a plating film was selectively formed only in the area irradiated with a pulsed laser. Then, an adhesion test was conducted as described in Example 1, and the plating film was stripped together with the glass.

Comparative Example 1

**[0060]** A plated article was produced as described in Example 1, without conducting "catalyst deactivation" or "immersion Au plating", and its surface was observed by a microscope. FIG. 5 shows the image obtained. In FIG. 5, 31 indicates an Ni plating film formed in the area irradiated with a pulsed laser, and 32 indicates an Ni plating film formed in the area unirradiated with a pulsed laser in the glass substrate. As shown in FIG. 5, without conducting "catalyst deactivation" or "catalyst removal", a plating film was formed on the whole surface of the glass substrate. Furthermore, the Ni plating film formed in the area unirradiated with a pulsed laser was easily stripped by an adhesive cellophane tape.

Comparative Example 2

**[0061]** A glass substrate was irradiated with a pulsed laser as described in Example 4, except that in pulsed laser irradiation, an average output power at a processing point was 1 W, a travel distance in the y direction was 10 μm, and a scan rate was 300 mm/sec. Then, an arithmetic mean roughness (Ra) of the area irradiated with a pulsed laser was measured as described in Example 4. As a result, Ra was 0.03 μm.

**[0062]** After measuring a surface roughness, a plating film was formed on the surface of the glass substrate as described in Example 2. As a result, a plating film was selectively formed only in the area irradiated with a pulsed laser, but the plating film could be easily stripped by an adhesive cellophane tape.

## EXPLANATION OF LETTERS OR NUMERALS

**[0063]**

1: Glass substrate
2: Immersion Au plating film
31: Ni plating film formed in the area irradiated with a pulsed laser
32: Ni plating film formed in the area unirradiated with a pulsed laser in the surface of a glass substrate

## Claims

1. A method for producing a plated article in which a plating film pattern is formed on the surface of a glass substrate, comprising
a first step of irradiating a partial area of the surface of the glass substrate with a pulsed laser;
a second step of attaching an electroless catalyst on the surface of the glass substrate;
a third step of selectively deactivating or selectively removing the catalyst attached to the unirradiated area with the pulsed laser in the glass substrate; and
a fourth step of nonelectrolytically plating the glass substrate after the third step to selectively form a plating film in the irradiated area with the pulsed laser.

2. The production method as claimed in Claim 1, wherein a pulse width of the pulsed laser is $1\times10^{-18}$ to $1\times10^{-4}$ sec.

3. The production method as claimed in Claim 1 or 2, wherein the plating film is at least one selected from the group consisting of nickel, copper, silver, gold, palladium, platinum, rhodium, ruthenium, tin, iron, cobalt and alloys thereof.

4. The production method as claimed in any of Claims 1 to 3, wherein in the third step, the glass substrate contacts a solution containing a compound deactivating the catalyst or a compound removing the catalyst.

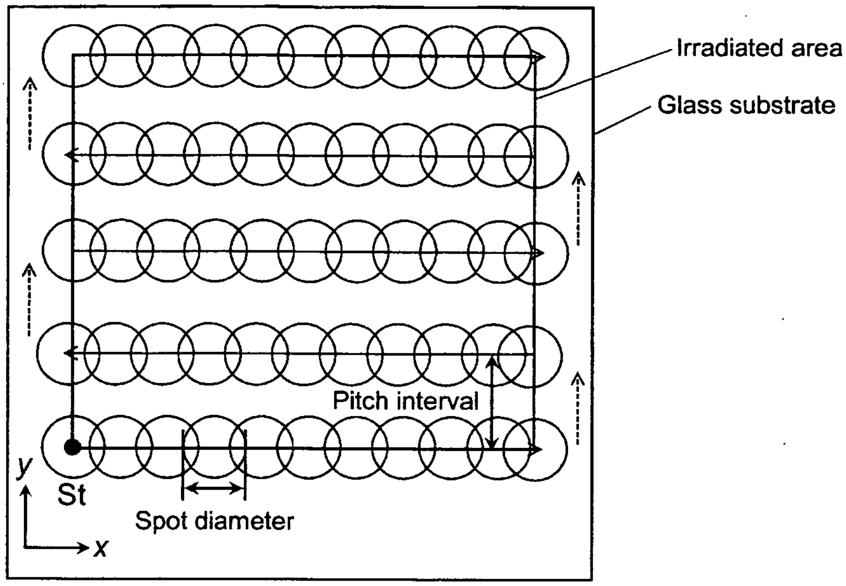
5. The production method as claimed in any of Claims 1 to 4, wherein in the third step, a compound deactivating the catalyst is a sulfur compound.

6. The production method as claimed in Claim 5, wherein the sulfur compound is a compound having at least one functional group selected from the group consisting of a thiocarbonyl group, a thiol group and a sulfide group.

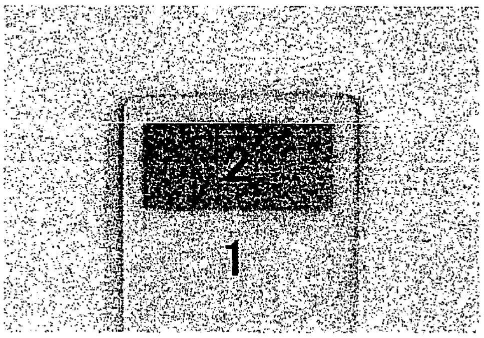
7. The production method as claimed in any of Claims 1 to 4, wherein a compound removing the catalyst is a chelate compound or cyanide.

8. The production method as claimed in Claim 7, wherein the compound removing the catalyst is at least one chelate compound selected from the group consisting of an amino acid, an amino alcohol, a polyamine, a polycarboxylic acid and a polyketone.

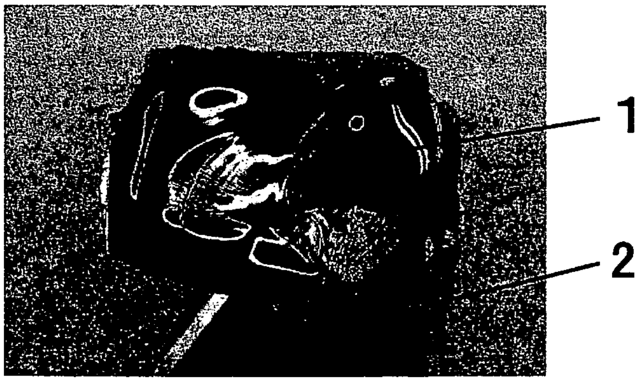
[FIG. 1]



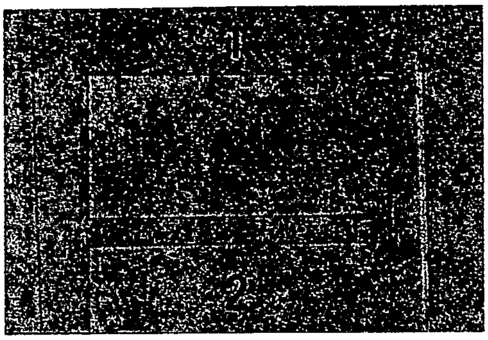
[FIG. 2]



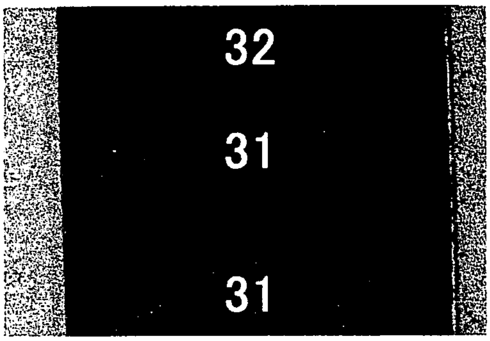
[FIG. 3]



[FIG. 4]



[FIG. 5]



**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2016/059264

A. CLASSIFICATION OF SUBJECT MATTER
*C23C18/18*(2006.01)i, *H05K3/18*(2006.01)i

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)
C23C18/18, H05K3/18

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 | 1996-2016 |
| Kokai Jitsuyo Shinan Koho | 1971-2016 | Toroku Jitsuyo Shinan Koho | 1994-2016 |

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>A | JP 2011-17069 A (Sankyo Kasei Co., Ltd.),<br>27 January 2011 (27.01.2011),<br>claim 1; paragraphs [0020], [0022], [0029] to [0032]<br>& US 2012/0107522 A1<br>claim 1; paragraphs [0021], [0023], [0044] to [0046]<br>& WO 2011/004802 A1 & EP 2453040 A1<br>& CN 102471889 A | 1-3<br>4-8 |
| A | JP 2003-13242 A (Japan Science and Technology Corp.),<br>15 January 2003 (15.01.2003),<br>claim 1; paragraphs [0024] to [0026]<br>(Family: none) | 1-8 |

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

| | |
|---|---|
| Date of the actual completion of the international search<br>11 May 2016 (11.05.16) | Date of mailing of the international search report<br>24 May 2016 (24.05.16) |
| Name and mailing address of the ISA/<br>Japan Patent Office<br>3-4-3,Kasumigaseki,Chiyoda-ku,<br>Tokyo 100-8915,Japan | Authorized officer<br><br>Telephone No. |

Form PCT/ISA/210 (second sheet) (January 2015)

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2016/059264

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | JP 60-149782 A (Inoue Japax Research Inc.),<br>07 August 1985 (07.08.1985),<br>claims 1 to 2, 13 to 14; page 6, upper right column, lines 2 to 7<br>& US 4639378 A<br>claims 1 to 2; column 10, lines 6 to 10<br>& US 4822633 A & EP 151413 A2 | 1-8 |
| A | JP 2008-41938 A (Riken, Japan),<br>21 February 2008 (21.02.2008),<br>claims 1, 3<br>(Family: none) | 1-8 |
| A | JP 6-81153 A (International Business Machines Corp.),<br>22 March 1994 (22.03.1994),<br>claims 1 to 2, 5 to 6<br>& US 5260108 A<br>claims 1, 6, 8 | 1-8 |
| A | JP 6-235169 A (Teijin Ltd.),<br>23 August 1994 (23.08.1994),<br>claim 1; paragraph [0004]<br>(Family: none) | 1-8 |

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

## REFERENCES CITED IN THE DESCRIPTION

### Patent documents cited in the description

- JP 60149783 A **[0007]**
- JP 2008041938 A **[0007]**