

Description

Title of Invention: METHOD FOR MANUFACTURING SOLAR CELL

Technical Field

[0001]

The present invention relates to a method of manufacturing a solar cell, and in particular, relates to a method for forming a porous layer on a surface of a silicon substrate.

Background Art

[0002]

As an alternative energy to coal, petroleum and the like, solar light has attracted attention as a clean and inexhaustible energy source, and the popularization of solar cells for converting the light energy of the solar light into electrical energy has been increasingly expected.

[0003]

An infinite number of fine concavities and convexities (hereinafter, referred to as a "texture") having a function of effectively taking in solar light are formed on a surface of a solar cell. In the case of monocrystalline silicon, a texture having pyramidal structures can be easily obtained by etching a Si (100) surface with an alkaline solution. In contrast, in the

case of polycrystalline silicon, various crystalline orientations appear on a silicon substrate surface, and thus, it is difficult to form a uniform texture on the entire silicon substrate surface as on the monocrystalline silicon.

[0004]

As a method for forming a texture on a surface of a silicon substrate made of polycrystalline silicon, a method for forming a porous layer on a surface of a silicon substrate by immersing the silicon substrate in a mixed aqueous solution of an oxidizing agent and hydrofluoric acid, containing metal ions, is disclosed (for example, Patent Literature 1). Moreover, a method is disclosed (for example, Patent Literature 2) which includes a first step of immersing a silicon substrate in a mixed aqueous solution of an oxidizing agent and hydrofluoric acid, containing metal ions, to form a porous layer on a surface of the silicon substrate and a second step of immersing and etching the surface of the silicon substrate after the first step in a mixed acid mainly containing hydrofluoric acid and nitric acid, to form a texture.

[0005]

According to the above-described Patent Literature 2, the silicon substrate having a texture formed by the method of the above-described Patent Literature 1 has a problem in that the surface of the silicon substrate

changes the color while the reflectance is low, and as a result, properties of a solar cell drastically deteriorate. On the other hand, the above-described Patent Literature 2 discloses that, in the method of the Patent Literature 2, after the same step as in the above-described Patent Literature 1, the surface of the silicon substrate is immersed and etched in the mixed acid mainly containing hydrofluoric acid and nitric acid so as to form a texture, and thereby a clean silicon surface can be obtained while maintaining a reflectance reducing effect and metal on the bottom of holes can also be removed, and therefore, the effect that a solar cell having high battery characteristics can be manufactured is obtained.

Citation List

Patent Literature

[0006]

Patent Literature 1: Japanese Patent No. 3925867

Patent Literature 2: Japanese Patent No. 4610669

Summary of Invention

Technical Problem

[0007]

However, in both the above-described Patent Literatures 1 and 2, by immersing the silicon substrate in the mixed aqueous solution of an oxidizing agent and

hydrofluoric acid, containing the metal ions, deposition of the metal ions and etching proceed simultaneously on the surface of the silicon substrate, and thus, it is difficult to manage the amount of the metal ions adhering and the amount etched. Variation in the amount of the metal ions adhering causes variation in the density of holes formed by the etching. Moreover, variation in the amount etched causes variation in the size of the holes formed by the etching. The variation in the amount of the metal ions adhering and the amount etched is caused not only on the entire silicon substrate surface but also among a plurality of silicon substrates using the same mixed aqueous solution due to deterioration of the mixed aqueous solution. Therefore, there was a problem in that, in the above-described Patent Literatures 1 and 2, it is difficult to form a texture having uniform size and density on the surface of the silicon substrate because the variation in the amount of the metal ions adhering and the amount etched is caused.

[0008]

Therefore, it is an object of the present invention to provide a method of manufacturing a solar cell, by which a texture can be formed on a surface of a silicon substrate more uniformly.

Solution to Problem

[0009]

The method of manufacturing a solar cell according to a first aspect of the present invention is a method of manufacturing a solar cell, in which a porous layer is formed on a surface of a silicon substrate by etching with metal ions, including the steps of: immersing the silicon substrate in a first aqueous solution containing hydrofluoric acid to remove a natural oxide film on the surface of the silicon substrate; immersing the silicon substrate from which the natural oxide film has been removed in a second aqueous solution containing the metal ions and not containing oxidizing agent and hydrofluoric acid to deposit the metal ions on the surface of the silicon substrate by electroless plating; and immersing the silicon substrate having the metal ions deposited on the surface in a third aqueous solution containing hydrofluoric acid and hydrogen peroxide water to form the porous layer on the surface of the silicon substrate by a catalytic reaction with the metal ions, wherein, in the step of depositing the metal ion on the surface of the silicon substrate, a concentration of the metal ions is measured and then the concentration of the metal ion is controlled to be constant.

Advantageous Effects of Invention

[0010]

According to the first aspect of the present invention, prior to the formation of the porous layer by etching, the metal ions are deposited on the surface of the silicon substrate. Accordingly, the metal ions can be deposited on the surface of

the silicon substrate more uniformly than in the conventional procedure in which deposition of metal ions and etching take place simultaneously. Then, the porous layer is formed on the surface of the silicon substrate by the catalytic reaction of the metal ions. Accordingly, by controlling the immersion time of the silicon substrate and the ratio of the hydrofluoric acid to the hydrogen peroxide water, the size of holes formed by the catalytic reaction can be controlled. Therefore, a texture having more uniform size and density can be formed on the surface of the silicon substrate. In addition, by controlling the concentration of the metal ions contained in the second aqueous solution more reliably, variation in the amount of the metal ions adhering can be suppressed on the whole.

Brief Description of Drawings

[0011]

Figure 1 is a perspective view showing an overall structure of a solar cell according to the present embodiment;

Figure 2 is a flowchart showing a method of manufacturing a solar cell according to the present embodiment;

Figure 3 is a SEM image of a silicon substrate surface having metal ions deposited;

Figure 4 is a SEM image of the silicon substrate surface showing an example in which a porous layer is formed, in the manufacturing method according to the present embodiment;

Figure 5 is a SEM image of a texture formed on the silicon substrate surface by etching the porous layer with mixed acid mainly containing fluoronitric acid, in

the manufacturing method according to the present embodiment;

Figure 6 is a SEM image of the silicon substrate surface showing a comparative example by a conventional producing method;

Figure 7A is a photograph of the silicon substrate surface subjected to etching by adding 0 ml hydrogen peroxide water to hydrofluoric acid;

Figure 7B is a photograph of the silicon substrate surface subjected to etching by adding 100 ml of hydrogen peroxide water to hydrofluoric acid;

Figure 7C is a photograph of the silicon substrate surface subjected to etching by adding 200 ml of hydrogen peroxide water to hydrofluoric acid;

Figure 7D is a photograph of the silicon substrate surface subjected to etching by adding 300 ml of hydrogen peroxide water to hydrofluoric acid; and

Figure 8 is a graph showing a measurement result of the reflectance of the silicon substrate shown in Figures 7A to 7D.

Reference Signs List

[0012]

- 1 solar cell
- 2 silicon substrate
- 3 porous layer

Description of Embodiments

[0013]

Hereinafter, an embodiment according to the present invention will be described in detail with reference to the drawings. A solar cell 1 shown in Figure 1 includes a silicon substrate 2 that performs photoelectric conversion and a porous layer 3 obtained by processing a surface of the silicon substrate 2 into a texture shape, and converts light incident from a light receiving surface on which the porous layer 3 is formed into electrical energy in the silicon substrate 2. The light incident on the surface of the silicon substrate 2 repeats transmission and reflection, and as a result, the porous layer 3 introduces more light into the silicon substrate 2 compared to a flat silicon substrate surface. It is generally known that the fine texture formed on the porous layer 3 can more efficiently confine the incident light when its height and density are uniform than when they are non-uniform. It is to be noted that the height of the texture means a height difference between concavities and convexities in the texture, and the density means the number of the concavities or the convexities per unit area of the texture. The solar cell 1 according to the present embodiment is characterized in that a fine texture is formed on the porous layer 3 more uniformly than in conventional solar cells, but otherwise it has the same configuration as the conventional ones.

[0014]

Actually, in the solar cell 1, although not shown in the drawing, with respect to the p-type silicon substrate, a diffusion layer, an antireflection film, and a grid electrode are formed in order on the side of the light receiving surface on which the porous layer 3 is formed, and a back surface electric field layer and a back surface electrode are formed in order on the side of the back surface. The antireflection film is formed on a surface of the porous layer 3 so as to suppress light reflection. The antireflection film is composed of, for example, a single layer structure film of a titanium oxide (TiO_2) film or a silicon nitride (SiN) film formed by a chemical vapor deposition (CVD) method or the like.

[0015]

Next, a method for forming the porous layer 3 will be described with reference to Figure 2. In the following description, the concentration is represented by mass%.

[0016]

Firstly, in step SP1, the silicon substrate 2 is immersed in a first aqueous solution containing hydrofluoric acid, and a natural oxide film on the surface of the silicon substrate 2 is removed. The volume ratio of the first aqueous solution in this case is HF (at a concentration of 50%): H_2O = 400 ml to 5000 ml:1200 ml to 15000 ml, and the immersion time may be 60

seconds to 360 seconds. It is to be noted that the first aqueous solution is intended only to remove the natural oxide film on the surface of the silicon substrate 2, and thus, does not contain metal ions.

[0017]

Next, in step SP2, the silicon substrate 2 is immersed in a second aqueous solution containing metal ions, and the metal ions are deposited on the surface of the silicon substrate 2 by electroless plating. As the metal ions, for example, Ag ions can be applied. In the case where the Ag ions are applied as the metal ions, the second aqueous solution can be produced by using AgNO_3 as a metal ion-containing agent. The volume ratio of the second aqueous solution in this case is the metal ion-containing agent (at a concentration of $1\text{E-}4\text{ M}$ to $8\text{E-}4\text{ M}$): H_2O = 5.0 ml to 15 ml:5000 ml to 15000 ml. As conditions of the electroless plating, for example, the immersion time may be 300 seconds, and the temperature of the second aqueous solution may be 26°C . The electroless plating is performed while the concentration of the metal ions contained in the second aqueous solution is measured and the concentration of the metal ions is controlled to be constant. The concentration of the metal ions can be measured by, for example, an electric resistance method. It is to be noted that the second aqueous solution is intended only to deposit the metal ions on the surface of the silicon substrate 2, but not to form the porous layer

3 on the surface of the silicon substrate 2, and thus, it does not contain an oxidizing agent and hydrofluoric acid.
[0018]

In the case of the present embodiment, since the second aqueous solution contains the metal ions but does not contain an oxidizing agent and hydrofluoric acid, the concentration of simple metal ions can be measured. Therefore, in the manufacturing method according to the present embodiment, the concentration of the metal ions can be measured more easily than in the conventional procedure using an aqueous solution containing an oxidizing agent and hydrofluoric acid in addition to metal ions. By controlling the concentration of the metal ions contained in the second aqueous solution in this manner, the amount of the metal ions to be deposited on the surface of the silicon substrate 2 can be controlled more reliably.

[0019]

In this connection, in a conventional method in which a silicon substrate is immersed in a mixed aqueous solution of an oxidizing agent and hydrofluoric acid, containing metal ions, the electric resistance value is measured as a sum of respective resistance values of the metal ions, the oxidizing agent, and the hydrofluoric acid, and the resistance value of only the metal ions cannot be directly measured, and thus, it was difficult to measure the concentration of simple metal ions.

[0020]

Moreover, in the case of the present embodiment, the electroless plating is preferably performed while making the second aqueous solution flow. For example, although not shown in the drawing, a storage tank in which the second aqueous solution is stored and a plating tank in which electroless plating is performed communicate by two pipes, and the second aqueous solution may be circulate between the storage tank and the plating tank by a pump (hereinafter, referred to as a "pump circulator"). Furthermore, although not shown in the drawing, the second aqueous solution may be stirred by a stirrer in the plating tank. In this manner, in the present embodiment, by performing the electroless plating while making the second aqueous solution flow, the metal ions can be deposited on the surface of the silicon substrate 2 more reliably and at a uniform density.

[0021]

Next, in step SP3, the silicon substrate 2 is immersed in a third aqueous solution containing hydrofluoric acid and hydrogen peroxide water. In the silicon substrate 2, a hydrogen reduction reaction of the hydrogen peroxide water due to catalytic action of the metal ions which adhere to the surface proceeds. Accordingly, electrons are extracted from the surface of the silicon substrate 2 in contact with the metal ions so as to compensate the increase in the electron consumption.

As a result, positive holes are generated in the silicon substrate 2 to cause oxidative dissolution of the silicon substrate. In this manner, an infinite number of holes are formed on the surface of the silicon substrate 2, and the porous layer 3 is formed by the holes (concavities) and parts in which the holes are not formed (convexities). The volume ratio of the third aqueous solution in this case is HF (at a concentration of 50%):H₂O₂ (at a concentration of 30%):H₂O = 400 ml to 4000 ml:400 ml to 2000 ml:10000 ml to 20000 ml. By controlling the immersion time of the silicon substrate 2, the size of the holes constituting the porous layer 3 is controlled. For example, if the holes (concavities) are large, the height difference from the parts in which the holes are not formed (convexities) becomes large, and thus, the height of the texture becomes large. It is to be noted that the third aqueous solution is intended only to form the porous layer 3 on the surface of the silicon substrate 2 by etching, but not to deposit the metal ions on the surface of the silicon substrate 2, and thus, it does not contain the metal ions.

[0022]

The concentration of the hydrogen peroxide water in the third aqueous solution is preferably suppressed to a concentration at a degree not suppressing etching of the metal ions so as to form the porous layer 3 more reliably. Specifically, the concentration of the hydrogen peroxide

water is preferably 25 to 50% with respect to the concentration of the hydrofluoric acid. Since the hydrogen peroxide water has a stronger force to deprive the silicon substrate of electrons than the metal ions, at a concentration of the hydrogen peroxide water more than 50%, the etching rate by the hydrogen peroxide water is faster than the etching rate by the catalytic action of the metal ions, the entire surface of the silicon substrate is oxidized to become a mirror surface, and the porous layer is not formed. Moreover, in the case where the hydrogen peroxide water has the concentration with respect to the hydrofluoric acid of outside the above-described range, that is, in the case where the concentration with respect to the hydrofluoric acid is more than 50% and the concentration with respect to the hydrofluoric acid is less than 25%, the reflectance cannot be decreased.

[0023]

As described above, in the method of manufacturing the solar cell 1 according to the present embodiment, prior to the formation of the porous layer 3 by etching, the silicon substrate 2 is immersed in the second aqueous solution containing the metal ions and the metal ions are deposited on the surface of the silicon substrate 2. Accordingly, the metal ions can be deposited on the surface of the silicon substrate 2 more uniformly than in

the conventional procedure in which deposition of metal ions and etching take place simultaneously.

[0024]

Furthermore, since the second aqueous solution contains the metal ions but not an oxidizing agent and hydrofluoric acid as it does in the conventional procedure, the concentration of the metal ions can be measured more easily. Therefore, in the present embodiment, by controlling the concentration of the metal ions contained in the second aqueous solution more reliably, the metal ions can be deposited in the surface of one silicon substrate 2 uniformly, and moreover, even in the case of using the same second aqueous solution for a plurality of silicon substrates 2, the metal ions can be deposited on surfaces of the plurality of silicon substrates 2 uniformly, and thus, variation in the amount of the metal ions adhering can be suppressed on the whole.

[0025]

Moreover, in the present embodiment, after depositing the metal ions on the surface of the silicon substrate 2, the silicon substrate 2 is immersed in the third aqueous solution containing the hydrofluoric acid and the hydrogen peroxide water, and the porous layer 3 is formed on the surface of the silicon substrate 2 by a catalytic reaction of the metal ions. In this manner, by controlling the immersion time of the silicon substrate 2 and the ratio of the hydrofluoric acid to the hydrogen

peroxide water, the size of the holes formed by the catalytic reaction can be controlled. Therefore, in the present embodiment, the texture having a more uniform height can be formed on the surface of the silicon substrate 2.

[0026]

After depositing the metal ions on the surface of the silicon substrate 2, the silicon substrate 2 is immersed for predetermined time in the third aqueous solution in which the concentrations of the hydrofluoric acid and the hydrogen peroxide water are managed and the porous layer 3 is formed on the surface of the silicon substrate 2, and thus, the texture can be formed on the surface of the silicon substrate 2 more uniformly.

[0027]

The third aqueous solution for forming the porous layer 3 deteriorates in proportion to the number of processed silicon substrates 2 and thus needs to be replaced, but in the present embodiment, the third aqueous solution is separate from the second aqueous solution containing the metal ions and thus the metal ions need not to be disposed of as in a conventional manner, the management of the aqueous solutions can be simplified.

[0028]

It is to be noted that the following steps may be added after the above-described step SP3. That is, in

step SP4, washing with water is performed, and in step SP5, the silicon substrate 2 is immersed in a fourth aqueous solution containing hydrofluoric acid and nitric acid and etching is performed. In the present embodiment, this can have an effect of removing the metal ions. In this case, the volume ratio of the fourth aqueous solution is HF (at a concentration of 50%):HNO₃ (at a concentration of 69%):H₂O = 100 ml to 500 ml:600 ml to 3000 ml:10000 ml to 50000 ml. The immersion time may be 240 seconds to 360 seconds.

[0029]

Next, in step SP6, washing with water is performed, and then, the silicon substrate 2 is immersed in an alkaline chemical solution and a stain film is removed (step SP7). The stain film means a blackish brown film formed on the surface of the silicon substrate 2 by etching. Finally, by performing washing with water, the silicon substrate 2 including the porous layer 3 according to the present embodiment can be obtained (step SP8).

[0030]

Next, an example of the method of manufacturing the solar cell 1 according to the above-described embodiment will be described. In this example, a p-type silicon substrate was used for the silicon substrate 2. The silicon substrate 2 was immersed in the first aqueous solution in which the volume ratio was adjusted to HF (at

a concentration of 50%):H₂O = 1200 ml:10000 ml for 300 seconds, and the natural oxide film was removed. Next, the silicon substrate 2 was immersed in the second aqueous solution in which the volume ratio was adjusted to AgNO₃ (at a concentration of 3E-4 M):H₂O = 3 ml:10000 ml in a standing state, and the metal ions were deposited on the surface of the silicon substrate 2 by the electroless plating. As plating conditions in this case, the immersion time was 300 seconds, and the temperature of the second aqueous solution was 26°C. Moreover, the second aqueous solution was made to flow around the silicon substrate 2 by the pump circulator. It is to be noted that the concentration of the metal ions was measured by a resistance measuring device for measuring aqueous solution resistance.

[0031]

A SEM (Scanning Electron Microscopic) image of a silicon substrate surface 2A having the metal ions deposited in this manner is shown in Figure 3. As can be seen in the drawing, according to the method of manufacturing the solar cell 1 according to the present embodiment, metal ions 4 can be deposited on the silicon substrate surface 2A more uniformly.

[0032]

Next, the silicon substrate 2 was immersed in the third aqueous solution in which the volume ratio of the hydrofluoric acid and the hydrogen peroxide water was

adjusted to HF (at a concentration of 50%):H₂O₂ (at a concentration of 30%):H₂O = 1200 ml:600 ml:10000 ml, and the porous layer 3 was formed on the surface of the silicon substrate 2 by the catalytic reaction of the metal ions. A SEM image of the surface of the silicon substrate 2 on which the porous layer 3 was formed in this manner is shown in Figure 4. As can be seen in the drawing, according to the method of manufacturing the solar cell 1 according to this example, the texture 3 can be formed on the surface of the silicon substrate 2 more uniformly.

[0033]

Next, the silicon substrate 2 on which the porous layer is formed was immersed in the fourth aqueous solution in which the volume ratio of the hydrofluoric acid and the nitric acid was adjusted to HF (at a concentration of 50%):HNO₃ (at a concentration of 69%):H₂O = 400 ml:3000 ml:6000 ml, and etching was performed. A SEM image of the surface of the silicon substrate 2 which was subjected to the etching in this manner is shown in Figure 5. As can be seen in the drawing, according to the method of manufacturing the solar cell 1 according to this example, the texture can be formed on the surface of the silicon substrate 2 more uniformly.

[0034]

A comparative example was produced in which deposition of metal ions and etching took place simultaneously, with respect to the above-described example. In the comparative example, a p-type polycrystalline silicon wafer (boron dope, 1 to 3 Ωcm , 15 × 15 cm square, thickness of 280 μm) was provided as a silicon substrate, and a damaged layer on the surface of the silicon substrate was removed with alkali. Then, etching was performed for 3 minutes in a tank containing a chemical solution given by: HF (at a concentration of 50%):H₂O₂ (at a concentration of 30%):H₂O:AgNO₃ (0.1 M) = 400 ml:200 ml:1600 ml:4.4 ml ([Ag⁺] = 2E-4 M), with the silicon substrate placed upright. Then, after water washing and drying of the silicon substrate, etching was performed for 3 minutes with mixed acid having the volume ratio of HF (at a concentration of 50%):HNO₃ (at a concentration of 69%):H₂O: = 1:9:15. A SEM image of the comparative example produced in this manner is shown in Figure 6. As can be seen in the drawing, according to the comparative example, a large number of nano-sized square holes 10 were formed, and it could be confirmed that variation in the size of a texture was large.

[0035]

Next, the influence of the concentration of the hydrogen peroxide water in the third aqueous solution on formation of the porous layer was examined. Six kinds of the third aqueous solutions in each of which 0 ml, 100 ml,

200 ml, 300 ml, 400 ml, and 500 ml of hydrogen peroxide water (at a concentration of 50%) was added with respect to an aqueous solution of hydrofluoric acid having the volume ratio of HF (at a concentration of 50%):H₂O = 400 ml:800 ml were produced. The silicon substrate having the metal ions deposited was immersed in each of the third aqueous solutions for 10 minutes, and etching was performed. The etched silicon substrate surface was observed. As a result, as shown in Figure 7, it was found that, as the amount of the hydrogen peroxide water added is increased, the silicon substrate surface becomes a mirror surface.

[0036]

The redox potential of hydrogen peroxide water is 1.78 (V vs. NHE), and is higher than that of metal ions (for example, the redox potential of Ag ions is 0.80 (V vs. NHE)). That is, it can be said that the hydrogen peroxide water has a stronger force to deprive the silicon substrate of electrons than the metal ions. Thus, it is considered that, if the concentration of the hydrogen peroxide water is higher, the etching rate by the hydrogen peroxide water is faster than the etching rate by the catalytic action of the metal ions, and the entire surface of the silicon substrate is oxidized to become a mirror surface.

[0037]

According to the results of this example, when the hydrogen peroxide water was added in an amount of 300 ml or more (Figure 7D), the silicon substrate surface 20D was confirmed to be a mirror surface. In contrast, when the hydrogen peroxide water was added in amounts of 100 ml (Figure 7B) and 200 ml (Figure 7C), the silicon substrate surfaces 20B and 20C had a brownish-red stain. This indicates that the etching by the metal ions was accelerated. In addition, when the hydrogen peroxide water was not added (Figure 7A), the silicon substrate surface 20A had a thin stain with a white turbidity.

[0038]

Next, the etched silicon substrate was irradiated with a light of 800 nm to measure the reflectance. The results are shown in Figure 8. According to the drawing, it could be confirmed that addition of the hydrogen peroxide water in amount of 100 ml or 200 ml decreased the reflectance. Therefore, application to a solar cell of the silicon substrate etched with the third aqueous solution having the hydrogen peroxide water added in an amount of 100 ml or 200 ml can be expected to decrease light loss due to reflection and improve light conversion efficiency.

[0039]

Accordingly, it was confirmed that the porous layer can be formed by adding the hydrogen peroxide water in an amount of more than 100 ml and 200 ml or less, that is,

by setting the concentration of the hydrogen peroxide water at 25% or more and 50% or less relative to the concentration of the hydrofluoric acid.

[0040]

(Modified Example)

The present invention is not limited to the above-described embodiment, and can be appropriately modified within the spirit and scope of the present invention.

For example, the case of Ag ions applied to as the metal ions has been described in the above-described embodiment, but the present invention is not limited thereto, and Au ions, Cu ions, Pt ions, Pd ions and the like can be applied.

CLAIMS

1. A method of manufacturing a solar cell, in which a porous layer is formed on a surface of a silicon substrate by etching with metal ions, the method comprising steps of:

immersing the silicon substrate in a first aqueous solution containing hydrofluoric acid to remove a natural oxide film on the surface of the silicon substrate;

immersing the silicon substrate after removing the natural oxide film therefrom in a second aqueous solution containing the metal ions and not containing oxidizing agent and hydrofluoric acid to deposit the metal ions on the surface of the silicon substrate by electroless plating; and

immersing the silicon substrate having the metal ions deposited on the surface in a third aqueous solution containing hydrofluoric acid and hydrogen peroxide water to form the porous layer on the surface of the silicon substrate by a catalytic reaction with the metal ions, wherein, in the step of depositing the metal ion on the surface of the silicon substrate, a concentration of the metal ions is measured and then the concentration of the metal ion is controlled to be constant.

2. The method of manufacturing a solar cell according to claim 1, wherein the third aqueous solution has a

concentration of the hydrogen peroxide water of 25% to 50% relative to that of the hydrofluoric acid.

3. The method of manufacturing a solar cell according to claim 1 or 2, further comprising a step of immersing the silicon substrate having the porous layer formed thereon in a fourth aqueous solution containing hydrofluoric acid and nitric acid to etch the substrate.

4. The method of manufacturing a solar cell according to any one of claims 1 to 3, further comprising a step of immersing the silicon substrate in an alkaline chemical solution to etch the substrate.

5. The method of manufacturing a solar cell according to any one of claims 1 to 4, wherein, in the step of forming the porous layer on the surface of the silicon substrate,

immersion time for the silicon substrate and
a ratio of the hydrofluoric acid to the hydrogen peroxide water is controlled to control a size of holes forming the porous layer.

6. The method of manufacturing a solar cell according to any one of claims 1 to 5, wherein, in the step of depositing the metal ions on the surface of the silicon

substrate, the second aqueous solution containing the metal ions is flown to perform electroless plating.