

METHOD FOR RECOVERING AU FROM IODINE-BASED ETCHING WASTE AND RECYCLING ETCHING SOLUTION

5 TECHNICAL FIELD

[0001] The present invention generally relates to the treatment of a spent iodine-based etching solution which is discharged during the microfabrication of Au thin films in various semiconductor components, and particularly relates to a method for recovering Au from iodine-based etching waste and simultaneously recycling the etching solution in a stable and efficient manner.

BACKGROUND

[0002] Au and other highly conductive materials are used as the wiring of various semiconductor components. Au wiring is formed by depositing a film via the PVD method or the like and thereafter microfabricating the deposited film via wet etching. At that time, the used etching solution contains expensive Au. Here, an iodine-based etching solution is often used as the etching solution in the foregoing process, and Au is recovered from the iodine-based etching solution based on methods such as chemical reduction using various reducing agents, displacement precipitation using metal powders, or electrowinning.

[0003] Meanwhile, with the iodine-based etching solution after Au recovery, the triiodide ions (I_3^-) that exhibit etching ability are reduced and become iodide ions (I^-); as a result, the etching ability becomes deteriorated, which has made it difficult to reuse the iodine-based etching solution after Au recovery.

In the light of the issues, Patent Document 1 subjects the spent etching solution to electrolysis treatment using a diaphragm so as to recover Au; also Patent Document 1 oxidizes the reduced iodide ions (I^-) to obtain triiodide ions (I_3^-) so as to restore the etching ability, namely, to recycle the etching solution.

[0004] Nevertheless, with the method of Patent Document 1, the current density will change pursuant to the lapse of the treatment time, thus problems occurred. On the cathode side, the pH will increase due to the electrolysis of water associated with the increase in the current density and the etching ability will consequently deteriorate

on the one hand; and on the anode side, the pH will decrease due to the electrolytic decomposition of water associated with the increase in the current density, and the etching ability will become excessive on the other hand. Furthermore, on the anode side, iodine (I₂) becomes precipitated on the electrode, the concentration of the iodide ions (I⁻) in the solution consequently deteriorates, and it has been difficult to recycle the etching solution in a stable and efficient manner.

PRIOR ARTDOCUMENTS

PATENT DOCUMENTS

[0005]

[Patent Document 1] Japanese Unexamined Patent Application Publication No. H3-202484

[Patent Document 2] Japanese Patent No. 5669995

SUMMARY OF THE INVENTION

TECHNICAL PROBLEM

[0006] As described above, performing electrolysis in a stable and efficient manner was difficult due to changes in the electrolysis conditions when recovering Au from a spent etching solution containing Au and recycling the etching solution. Meanwhile, Patent Document 2 describes a technique in that both increasing recovery rate of Au and restoring ability of the etching solution are possible by maintaining the cathode potential and the anode potential during the electrolysis to be within a certain range. Nevertheless, the method of Patent Document 2 has the following problems. For example, complicated control is required for precisely suppressing the pH of the solution to be within ± 0.5 before and after treatment, and much time is required for treatment since the cathode potential is low at -0.7 V or more.

[0007] The present invention aims to resolve these problems, and an object of this invention relates to a method for recovering Au from a spent iodine-based etching solution containing Au and also recycling the iodine-based etching solution; and particularly to provide a method for recycling a spent iodine-based etching solution in a stable and efficient manner without precise pH control.

SOLUTION TO PROBLEM

[0008] In order to achieve the foregoing object, as a result of intense study, the present inventor discovered that it is possible to suppress the electrolysis of water and the precipitation of iodine without a precise pH adjustment but by properly adjusting the current density of the cathode and the current density of the anode; and thereby recover Au, and simultaneously recycle the etching solution in a stable and efficient manner. The present inventor provides the following aspects based on the findings.

1) A method for electrolytically recovering Au from a spent iodine-based etching solution containing Au and simultaneously recycling the etching solution, wherein a cathode potential is set from -0.75 V to -0.95 V (reference electrode: Ag/AgCl), and a ratio of a current density of an anode relative to a current density of a cathode is set from 3 to 50, but excluding 3.

EFFECT OF THE INVENTION

[0009] According to embodiments of the present invention, it is possible to electrolytically recover Au from a spent iodine-based etching solution containing Au; and in a method for recycling the spent etching solution, it is also possible to suppress the electrolysis of water and the precipitation of iodine by properly adjusting the current density of the cathode and the anode. The method yields a superior effect of recovering Au and simultaneously recycling the etching solution in a stable and efficient manner.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Fig. 1 is a schematic diagram of the reaction process of the Au-containing spent etching solution.

Fig. 2 is a schematic diagram of the treatment flow of the Au-containing spent etching solution.

Fig. 3 is a photograph of Comparative Example 1), showing the precipitation of iodine on the anode after electrolysis.

DESCRIPTION OF THE EMBODIMENTS

[0011] A schematic diagram of the treatment (reaction process) of a spent etching solution containing Au of the present invention is shown in Fig. 1. As shown in Fig. 1, an electrolytic bath is separated into an anode chamber and a cathode chamber by a diaphragm i.e. cation-exchange membrane, and an iodine-based etching solution containing Au (Au-containing spent etching solution) is supplied to the cathode chamber, and an etching solution after Au recovery in which iodine has been reduced (from I_3^- to I^-) is supplied (transferred) to the anode chamber. Subsequently, Au is recovered in the cathode chamber and the etching solution is recycled in the anode chamber.

[0012] Fig. 2 shows a schematic diagram of the treatment flow of the spent etching solution containing Au. As shown in Fig. 2, the Au-containing spent etching solution supplied to the cathode chamber is recovered by precipitating Au on the cathode based on electrolytic treatment. Meanwhile, the spent etching solution after Au recovery in which iodine has been reduced (from I_3^- to I^-) is supplied (transferred) to the anode chamber, and the etching solution is made to be reusable by oxidizing the etching solution into triiodide ions (I_3^-), which exhibit etching ability, based on electrolytic treatment.

[0013] Meanwhile, when the current density increases in the electrolytic treatment, there is a problem in that the electrolysis of water occurs and causes pH to increase on the cathode side, thereby causing the etching ability of the recycled etching solution to deteriorate. Moreover, in the anode chamber, there is a problem in that pH will decrease and cause the etching ability of the recycled etching solution to become excessive. Further, in the anode chamber, there is a problem in that the iodine becomes precipitated on the electrode pursuant to lower pH, which causes the concentration of the iodide ions in the recycled etching solution to decline.

[0014] The present inventor gained the knowledge that the above side reactions such as electrolysis of water and precipitation of iodine can be effectively suppressed by controlling the current density on the cathode side by the potential of the cathode and controlling the current density on the anode side by the current density ratio of the anode and the cathode. Here, there is no need to strictly control pH as with conventional technologies. Based on the findings, the present invention is characterized by setting the cathode potential from -0.75 V to -0.95 V (reference electrode: Ag/AgCl), and the ratio of the current density of the anode relative to the

current density of the cathode from 3 to 50, but excluding 3.

[0015] In the present invention, the potential of the cathode is preferably set to be -0.95 V or more and -0.75 V or less (reference electrode: Ag/AgCl). When the potential of the cathode exceeds -0.75 V, the treatment time of electrolysis will increase and the production efficiency will deteriorate. Meanwhile, when the potential of the cathode is less than -0.95 V, the electrolysis of water will become notable on the cathode side. Note that, as a method of controlling the cathode potential, there is a method of constantly measuring the potential difference between the reference electrode and the cathode, and reflecting the result in the output voltage of a rectifier based on feedback control.

[0016] Moreover, the ratio of the current density of the anode relative to the current density of the cathode is preferably within a range of 3 to 50 (but excluding 3). When the ratio deviates from the foregoing range, there is a problem in that the electrolysis of water will occur due to the increase in the current density, thereby causing the etching ability of the recycled etching solution to become excessive pursuant to the decrease in pH, and there is also a problem in that the iodine becomes precipitated on the anode. Note that the current density ratio may be adjusted, as described later, by the area ratio of the respective electrodes, namely by the ratio of areas that are immersed with the electrolytic solution.

[0017] Preferably, pH of the cathode chamber and the anode chamber immediately before electrolytic treatment is adjusted to 4 to 6. When pH immediately before electrolytic treatment falls outside the range of 4 to 6, the recycling ability of the etching solution will deteriorate or become excessive. By setting pH immediately before electrolysis to be within the foregoing range, the recovery of Au and simultaneously recycling the etching solution can be performed in a stable and efficient manner. In order to suppress changes in pH, pH may also be adjustable by adding an acid solution such as sulfuric acid to the cathode chamber, or adding an alkali solution such as caustic soda to the anode chamber.

Examples

[0018] The Examples and Comparative Examples of the present invention are now explained. Note that the following Examples merely illustrate representative examples,

and it should be understood that the present invention is not limited to these Examples, and the present invention should be interpreted within the technical scope described in this specification.

5 Example 1

[0019] In an electrolytic bath in which a cathode chamber and an anode chamber are separated with a cation-exchange membrane, 500 mL of an Au-containing etching solution was supplied to the cathode chamber.

10 The Au-containing etching solution consists of the following components:
KI (0.25 mol/L) + I₂ (0.14 mol/L) + Au (0.03 mol/L)

Meanwhile, 500 mL of a solution after Au recovery (after iodine reduction) was supplied to the anode chamber.

15 The solution after Au recovery (after iodine reduction) consists of the following component:
KI (0.25 mol/L)

[0020] Ti was used as the cathode (i.e. counter electrode), Ti coated with IrO₂ was used as the anode (i.e. working electrode), and Ag/AgCl was used as the reference electrode. Here, the immersion area of the Ti electrode was set to 20 cm², the immersion area of the IrO₂ electrode was set to 62 cm², and the area ratio (current density ratio) of the cathode and the anode was set to 3.1. Subsequently, the cathode potential was set to -0.75 V, the solution was maintained at 20°C, and electrolytic treatment was performed. Electrolysis was ended at the point in time that the current value fell below 5 mA.

[0021] By performing the foregoing electrolytic treatment, the recovery rate of Au in the cathode chamber was 95.9%. The change in pH before and after electrolysis was checked; and pH was 5.16 before electrolysis and pH was 4.95 after electrolysis in the anode chamber, and pH was 5.61 before electrolysis and pH was 4.88 after electrolysis in the cathode chamber, and it was possible to suppress the electrolysis of water. Then the etching ability of the etching solution after recycling was checked: 12.22 g of Au was dissolved (Au concentration at 5.82 g/L) in an etching solution

having a liquid measure of 2.10 L. It was confirmed that the recycled etching solution was reusable as Au etching solution.

Example 2

[0022] The immersion area of the Ti electrode was set to 2 cm², the immersion area of the IrO₂ electrode was set to 100 cm², the area ratio (current density ratio) of the cathode and the anode was set to 50, and electrolytic treatment was performed under the same conditions as Example 1.

By performing the foregoing electrolytic treatment, the recovery rate of Au in the cathode chamber was 96.3%. The change in pH before and after electrolysis was checked; and pH was 5.01 before electrolysis and pH was 4.98 after electrolysis in the anode chamber, and pH was 5.11 before electrolysis and pH was 5.13 after electrolysis in the cathode chamber, and it was possible to suppress the electrolysis of water. Then the etching ability of the etching solution after recycling was checked: 12.31 g of Au was dissolved (Au concentration was 5.73 g/L) in an etching solution having a liquid measure of 2.15 L. It was confirmed that the recycled etching solution was reusable as Au etching solution.

Example 3

[0023] The cathode potential was set to -0.95 V, and electrolytic treatment was performed under the same conditions as Example 1.

By performing the foregoing electrolytic treatment, the recovery rate of Au in the cathode chamber was 96.1%. The change in pH before and after electrolysis was checked; and pH was 4.99 before electrolysis and pH was 4.31 after electrolysis in the anode chamber, and pH was 4.99 before electrolysis and pH was 5.88 after electrolysis in the cathode chamber, and it was possible to suppress the electrolysis of water. Then the etching ability of the etching solution after recycling was checked; 11.99 g of Au was dissolved (Au concentration was 5.76 g/L) in an etching solution having a liquid measure of 2.08 L. It was confirmed that the recycled etching solution was reusable as Au etching solution.

Comparative Example 1

[0024] The immersion area of the Ti electrode was set to 40 cm², the immersion area of the IrO₂ electrode was set to 80 cm², the area ratio of the wetted area of the anode relative to the wetted area of the cathode was set to 2, and electrolytic treatment was performed under the same conditions as Example 1.

The change in pH before and after electrolysis was checked, and pH was 4.55 before electrolysis and pH was 1.71 after electrolysis in the anode chamber, and pH was 5.14 before electrolysis and pH was 1.69 after electrolysis in the cathode chamber, and pH increased due to the electrolysis of water. Moreover, hydrogen ions also migrated to the cathode chamber, and pH had similarly increased. Furthermore, as shown in Fig. 3, iodine precipitated on the anode after electrolysis.

Industrial Applicability

[0025] A method for recovering Au from a spent iodine-based etching solution containing Au and recycling the etching solution based on the diaphragm electrolytic treatment method enables to be carried out in a stable and efficient manner according to embodiments of the present invention. The method also has a superior effect of considerably reducing the time required for electrolysis and improves the production efficiency. The method of the present invention is useful in recycling materials in the fields of electronic devices, electronic components, substrates and semiconductors.

CLAIMS

[Claim 1] A method for electrolytically recovering Au from a spent iodine-based etching solution containing Au and simultaneously recycling the etching solution, wherein a cathode potential is set from -0.75 V to -0.95 V (reference electrode: Ag/AgCl), and a ratio of a current density of an anode relative to a current density of a cathode is set from 3 to 50, but excluding 3.