Description

The present invention relates to an impurity measuring method of measuring the type and amount of an impurity adhered on the surface of an object to be measured, especially, a semiconductor substrate.

It is well known that when an impurity such as sodium (Na), potassium (K) or iron (Fe) is contained in a thin film, e.g., an oxide film formed on a semiconductor substrate, electrical characteristics of a semiconductor element are significantly adversely affected even if an amount of the impurity is very small. Therefore, in order to improve the electrical characteristics of the semiconductor element, mixing of the impurity from the substrate surface must be reduced as small as possible. For this purpose, a degree of contamination on the substrate surface must be correctly analyzed and measured.

The degree of contamination on the substrate surface is conventionally measured by using Secondary Ion Mass Spectrometry (SIMS), Auger Electron Spectroscopy (AES) or Neutron Activation Analysis (NAA). Since these methods require a large-scale, expensive measuring instrument, an analysis cost is increased. In addition, a skill is required in an analyzing operation. Also, since each analyzing method uses an electron or light beam, local analysis can be performed, but the degree of contamination on the overall surface cannot be estimated.

For this reason, in place of the above instrumental analyzing methods, a method of easily measuring the degree of contamination on the overall substrate surface is proposed. In this method, an oxide film having a predetermined thickness is formed beforehand on the surface of a substrate and dissolved by using a hydrofluoric acid vapor, and the resultant solution is recovered to measure an impurity by using a spectroscopic analyzer. This method is called vapor phase decomposition (VPD), (see Japanese Journal of Applied Physics, Supplements 30.09.1984, TOKYO JA, p.281; A. SHIMAZAKI ET AL.: "Chemical Analysis of Ultratrace Impurities in SiO_2 Films").

The above method, however, requires an oxide film formation step. In this oxide film formation step, an impurity is mixed from an oxidation atmosphere into an oxide film, the impurity evaporates from the substrate surface into the oxidation atmosphere, or the impurity contained in the substrate is diffused to the surface. For this reason, this method is undesirable in terms of reliability in analysis values.

In another conventional method, without forming an oxide film on the surface of a substrate by an oxidation step, the overall substrate is dipped in a hydrofluoric acid solution to dissolve a natural oxide film naturally formed on the substrate surface, and the resultant solution is recovered to measure an impurity amount by using a spectroscopic analyzer.

In this method, however, since an extremely large amount of the hydrofluoric acid solution is required for recovering the impurity, the concentration of the impurity contained in the solution is significantly decreased, and therefore analysis sensitivity and precision are degraded. In addition, according to this method, the hydrofluoric acid solution is contaminated by the impurity adhered on a vessel with very high probability.

It is an object of the present invention to provide an impurity measuring method which can measure an amount of an impurity adhered on the surface of an object to be measured with high sensitivity and precision and which realized a low analysis cost and high reliability.

An impurity measuring method of the present invention is characterized in that a stick obtained by cooling and solidifying a solution into a rod-like shape is brought into contact with the surface of an object to be measured to give a relative movement between the stick and the object to be measured, thereby dissolving a natural oxide film formed on the surface of the object to be measured and recovering an impurity scattered on the surface of the object to be measured while the solution is held at the distal end portion of the stick. After the stick is brought into contact with the overall surface of the object to be measured, the solution recovered at the distal end portion of the stick is analyzed, thereby measuring an amount of the impurity adhered on the surface of the object to be measured.

In the measuring method of the present invention, the stick is kept in contact with the surface of the object to be measured to give a relative movement between the stick and the object to be measured. Therefore, dissolution of the natural oxide film formed on the surface of the object to be measured and recovery of the resultant solution can be simultaneously performed.

In addition, since the recovered solution is not brought into contact with anything but the surface of the object to be measured, only the natural oxide film containing the impurity on the surface of the object to be measured is dissolved in the solution. Therefore, highly reliable measurement can be performed with high sensitivity and precision by using the solution having a proper amount and a sufficient impurity concentration.

According to the present invention, there is provided an impurity measuring method which can measure an impurity adhered on an object to be measured with high sensitivity and precision and

which realizes a low measurement cost and high reliability.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a view showing an arrangement of an apparatus used for carrying out a method of the present invention.

An embodiment of the present invention will be described in detail below with reference to the accompanying drawing.

Fig. 1 shows an apparatus for carrying out a method of the present invention. A silicon semiconductor substrate 10 as an object to be measured is placed on a support table (not shown) and horizontally rotated together with the support table. A stick 11 is brought into contact with the surface of the rotating substrate 10.

The stick 11 is prepared by cooling and solidifying a solution, for dissolving a natural oxide film containing an impurity adhered on the substrate surface and having a hydrophobic nature with respect to the substrate surface, into a rod-like shape. An example of the solution is a hydrofluoric acid (HF) solution having a concentration of 0.5% to 2%.

The stick 11 is chucked and held by a chuck 12 so that its distal end portion is brought into contact with the surface of the substrate 10. The chuck 12 is driven so that the stick 11 horizontally moves from the periphery of the substrate 10 toward the center of rotation or vice versa.

In such an apparatus, the stick 11 is sequentially dissolved by:

(1) an intersurface pressure between the stick and the substrate surface induced upon rotation of the substrate 10;

(2) a chemical reaction between the stick and the oxide film or the like on the substrate surface; and

(3) heating of the substrate 10.

A solution 13 wets the substrate surface and the substrate surface maintains its hydrophilic nature while the natural oxide film (not shown) formed on the substrate surface in contact with the solution 13 is present. When the natural oxide film is dissolved by the solution 13, however, fluorine (F) and hydrogen (H) adhere and terminate on the substrate surface to increase a hydrophobic nature. For this reason, the solution 13 is repelled by the substrate surface. Meanwhile, the solution 13 is kept hydrophilic with respect to the stick 11. Therefore, the solution 13 is held around the distal end portion of the stick 11 and moved with the stick 11.

When the stick 11 is brought into contact with the overall surface of the substrate 10 to dissolve the natural oxide film, the impurity scattered on the substrate surface is recovered together with the solution 13 at the distal end portion of the stick 11. Thereafter, the recovered solution 13 is sampled and analyzed by chemical analysis using a spectroscopic analyzer to measure the type and amount of the impurity, thereby determining a degree of contamination of the substrate 10.

Since the above method according to the embodiment of the present invention does not require an expensive measuring instrument, a measurement cost can be decreased. In addition, the stick 11 is kept in contact with the surface of the substrate 10. Therefore, dissolution of the natural oxide film formed on the substrate surface and recovery of the solution 13 can be simultaneously performed, thereby reducing a measurement time.

The recovered solution 13 is not brought into contact with anything but the substrate surface, and therefore only the natural oxide film containing the impurity on the substrate surface is dissolved therein. For this reason, since the solution 13 has a proper amount and a sufficient impurity concentration, highly reliable measurement can be performed with high sensitivity and precision upon chemical analysis using a spectroscopic apparatus.

The present invention is not limited to the above embodiment but can be variously modified. For example, in the above embodiment, the present invention is applied to measurement of an impurity on the surface of a semiconductor substrate. The method of the present invention, however, can be applied to general measurement of a degree of contamination on the surface of a metal. In additon, the type of the solution constituting the stick can be arbitrarily selected in accordance with the type of object material.

Examples of the solution constituting the stick are

(1) HF

(2) $HF + HNO_3$

(3) $HF + H_2O_2$

(4) $HCl + H_2O_2$

Furthermore, when the stick is to be brought into contact with the surface of an object to be measured, the object to be measured may be heated to accelerate dissolution of the stick.

Claims

1. An impurity measuring method comprising the steps of:

   (A) bringing a stick (11), prepared by cooling and solidifying a solution into a rod-like shape, into contact with the surface of an object (10) to be measured to give a relative movement between said stick (11) and said object (10) to be measured, thereby dissolving an oxide film or the like formed on the

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which realizes a low measurement cost and high reliability.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a view showing an arrangement of an apparatus used for carrying out a method of the present invention.

An embodiment of the present invention will be described in detail below with reference to the accompanying drawing.

Fig. 1 shows an apparatus for carrying out a method of the present invention. A silicon semiconductor substrate 10 as an object to be measured is placed on a support table (not shown) and horizontally rotated together with the support table. A stick 11 is brought into contact with the surface of the rotating substrate 10.

The stick 11 is prepared by cooling and solidifying a solution, for dissolving a natural oxide film containing an impurity adhered on the substrate surface and having a hydrophobic nature with respect to the substrate surface, into a rod-like shape. An example of the solution is a hydrofluoric acid (HF) solution having a concentration of 0.5% to 2%.

The stick 11 is chucked and held by a chuck 12 so that its distal end portion is brought into contact with the surface of the substrate 10. The chuck 12 is driven so that the stick 11 horizontally moves from the periphery of the substrate 10 toward the center of rotation or vice versa.

In such an apparatus, the stick 11 is sequentially dissolved by:

(1) an intersurface pressure between the stick and the substrate surface induced upon rotation of the substrate 10;

(2) a chemical reaction between the stick and the oxide film or the like on the substrate surface; and

(3) heating of the substrate 10.

A solution 13 wets the substrate surface and the substrate surface maintains its hydrophilic nature while the natural oxide film (not shown) formed on the substrate surface in contact with the solution 13 is present. When the natural oxide film is dissolved by the solution 13, however, fluorine (F) and hydrogen (H) adhere and terminate on the substrate surface to increase a hydrophobic nature. For this reason, the solution 13 is repelled by the substrate surface. Meanwhile, the solution 13 is kept hydrophilic with respect to the stick 11. Therefore, the solution 13 is held around the distal end portion of the stick 11 and moved with the stick 11.

When the stick 11 is brought into contact with the overall surface of the substrate 10 to dissolve the natural oxide film, the impurity scattered on the substrate surface is recovered together with the solution 13 at the distal end portion of the stick 11. Thereafter, the recovered solution 13 is sampled and analyzed by chemical analysis using a spectroscopic analyzer to measure the type and amount of the impurity, thereby determining a degree of contamination of the substrate 10.

Since the above method according to the embodiment of the present invention does not require an expensive measuring instrument, a measurement cost can be decreased. In addition, the stick 11 is kept in contact with the surface of the substrate 10. Therefore, dissolution of the natural oxide film formed on the substrate surface and recovery of the solution 13 can be simultaneously performed, thereby reducing a measurement time.

The recovered solution 13 is not brought into contact with anything but the substrate surface, and therefore only the natural oxide film containing the impurity on the substrate surface is dissolved therein. For this reason, since the solution 13 has a proper amount and a sufficient impurity concentration, highly reliable measurement can be performed with high sensitivity and precision upon chemical analysis using a spectroscopic apparatus.

The present invention is not limited to the above embodiment but can be variously modified. For example, in the above embodiment, the present invention is applied to measurement of an impurity on the surface of a semiconductor substrate. The method of the present invention, however, can be applied to general measurement of a degree of contamination on the surface of a metal. In additon, the type of the solution constituting the stick can be arbitrarily selected in accordance with the type of object material.

Examples of the solution constituting the stick are

(1) HF

(2) $HF + HNO_3$

(3) $HF + H_2O_2$

(4) $HCl + H_2O_2$

Furthermore, when the stick is to be brought into contact with the surface of an object to be measured, the object to be measured may be heated to accelerate dissolution of the stick.

Claims

1. An impurity measuring method comprising the steps of:

(A) bringing a stick (11), prepared by cooling and solidifying a solution into a rod-like shape, into contact with the surface of an object (10) to be measured to give a relative movement between said stick (11) and said object (10) to be measured, thereby dissolving an oxide film or the like formed on the

surface of said object (10) to be measured;
(B) bringing said stick (11) into contact with the overall surface of said object (10) to be measured by the relative movement while said solution is held at a distal end portion of said stick, thereby recovering an impurity adhered on the surface of said object (10) to be measured by said solution (13) held at the distal end portion of said stick (11); and
(C) analyzing said recovered solution (13) to measure the type and amount of the impurity adhered on the surface of said object (10) to be measured.

2. A method according to claim 1, characterized in that a stick (11) prepared by cooling and solidifying a solution of one of HF, HF + HNO_3, HF + H_2O_2, and HCl + H_2O_2 is used.

Patentansprüche

1. Verfahren zum Messen einer Verunreinigung, welches die Stufen umfaßt:
(A) Inkontaktbringen eines Stabes (11), der durch Abkühlen und Verfestigen einer Lösung in eine stabähnliche Form hergestellt ist, mit der Oberfläche eines zu messenden Objekts (10), wobei eine relative Bewegung zwischen dem Stab (11) und dem zu messenden Objekt (10) entsteht, wodurch ein auf der Oberfläche des zu messenden Objekts (10) gebildeter Oxidfilm oder dgl. gelöst wird;
(B) Inkontaktbringen des Stabes (11) mit der Gesamtoberfläche des zu messenden Objekts (10) durch die Relativbewegung, während die Lösung an einem distalen Endteil des Stabes gehalten wird, wodurch eine an der Oberfläche des zu messenden Objekts (10) anhaftende Verunreinigung durch die an dem distalen Endteil des Stabes (11) gehaltene Lösung (13) gewonnen wird; und
(c) Analysieren der gewonnenen Lösung (13), um Art und Menge der an der Oberfläche des zu messenden Objekts (10) anhaftenden Verunreinigung zu messen.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß ein Stab (11), der durch Abkühlen und Verfestigen einer Lösung aus der Gruppe aus HF, HF + HNO_3, HF + H_2O_2 und HCl + H_2O_2 hergestellt ist, verwendet wird.

Revendications

1. Procédé de mesure d'impuretés comprenant les étapes consistant à :
(A) mettre une barre (11), préparée par refroidissement et solidification d'une solution sous forme d'une barre, en contact avec la surface d'un objet (10) à mesurer pour produire un mouvement relatif entre ladite barre (11) et ledit objet (10) à mesurer, pour dissoudre un film d'oxyde ou analogue formé sur la surface dudit objet (10) à mesurer,
(B) mettre ladite barre (11) en contact avec toute la surface dudit objet (10) à mesurer par suite du mouvement relatif tandis que ladite solution est maintenue au niveau de l'extrémité distale de ladite barre, pour recueillir une impureté qui adhère sur la surface dudit objet (10) à mesurer grâce à ladite solution (13) maintenue à l'extrémité distale de ladite barre (11), et
(C) analyser ladite solution (13) recueillie pour mesurer le type et la quantité de l'impureté qui adhère sur la surface dudit objet (10) à mesurer.

2. Procédé selon la revendication 1, caractérisé par l'utilisation d'une barre (11) préparée par refroidissement et solidification d'une solution parmi HF, HF + HNO_3, HF + H_2O_2 et HCl + H_2O_2.