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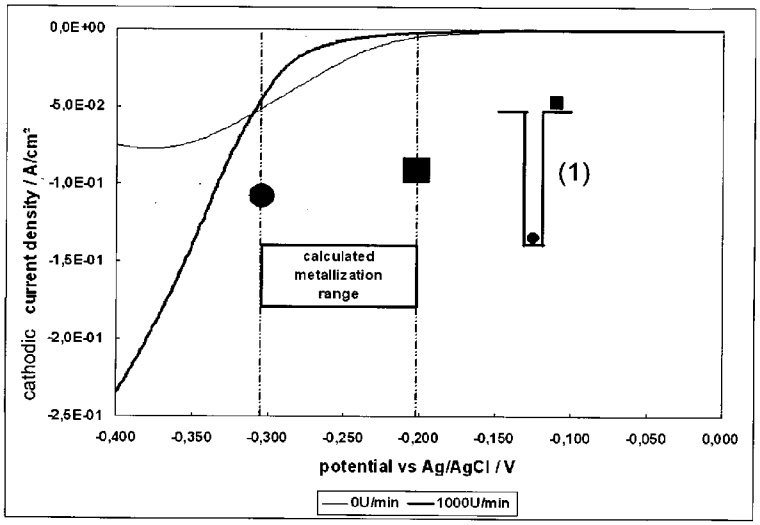
(54) Title: METHOD FOR MONITORING THE FILLING PROPERTIES OF A COPPER ELECTROLYTE

(57) Abstract: The present invention concerns a method for monitoring the via filling properties of copper electrolytes. The method comprises the steps of calculating a cathodic current density range and/or the corresponding potential range for a given via geometry, recording a current-voltage diagram in the cathodic current range of the current for at least two different rotation speeds of the rotating disc electrode within the potential range calculated for said given via geometry.

Fig. 2



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Method for monitoring the filling properties of a copper electrolyte

Field of the Invention

The present invention is related to a method for monitoring the via filling properties of a copper electrolyte during use.

Background of the Invention

Electroplating of copper from acidic plating baths is a long known process and utilized e.g. in the manufacture of printed circuit boards, IC substrates and silicon based microelectronic devices.

Electroplating of copper is applied to form electrically conductive circuitry and contact areas for soldering and bonding operations. Such uses of copper electroplating are often associated with filling of a via such as through-silicon vias (TSVs), through-glass vias (TGVs), through-ceramic vias (TCVs), blind micro vias (BMVs) and through holes (THs). Both BMVs and TSVs are vias having one opening whereas THs have an opening on both sides of a substrate. TGVs and TCVs can be vias having one opening or vias having an opening on both sides of the substrate.

Different organic additives such as brighteners, carriers and levellers must be added to acidic copper electrolytes in order to fulfil the requirements for filling such vias. Hence, the concentration of such organic additives and their breakdown products in a copper electrolyte need to be monitored during use of the plating bath to ensure a stable performance by e.g. replenishing organic additives or dumping parts of or the whole plating bath.

A standard method to monitor such organic additives is cyclic voltammetric stripping (CVS) which can be used as an on-line method, i.e. providing continuously data on the organic additives during use of the copper electrolyte. However, the accuracy of said method is limited. Especially in case more challenging substrate features have to be plated with copper such methods fail: according to CVS measurements the concentrations of the organic additives are still in the recommended range but the via filling properties investigated by microscopic inspection of cross-sectioned recessed structures reveals incomplete filling with copper or undesired voids inside such incompletely filled recessed structures.

Other methods known in prior art are electrochemical measurement techniques which use information obtained by convection-dependent adsorption of such additives on an electrode surface:

An electrochemical method for monitoring via filling properties is described by T.-H. Tsai and J.-H. Huang ("Copper electrodeposition in a through-silicon via evaluated by rotating disc electrode techniques", J. Micromech. Microeng. 20 (2010), pp. 1 to 5). The electrochemical measurements shown in Fig. 1 are used to simulate the mass-transfer environment on a wafer substrate surface, at the bottom of shallow vias, and the deep vias, respectively. The geometry of a given via and the different current densities present e.g. on top of the substrate surface and the bottom of a via are not taken into account. The method disclosed herein was only demonstrated for a copper electrolyte comprising as additives PEG (a typical carrier-suppressor additive) and SPS (a typical brightener-accelerator additive). The electrolytes investigated did not contain any leveller additives.

A method for analysing a copper electroplating solution is disclosed in US 7,820,535 B2. The time-dependent potential change at a cathodic current of -0.1 to -20 A/dm^2 is determined and the data obtained are approximated according to the Boltzmann`s function. In this method only one cathodic current

value is applied. Hence, the cathodic current distribution present in case of a substrate having vias can not be observed by such a method.

A method for evaluating the filling performance of a copper plating formula using a galvanostat method is disclosed by W.-P. Dow and Chen-Wei Liu ("Evaluating the filling performance of a copper plating formula using a simple galvanostat method", Journal of the Electrochemical Society 153 (2) C190-C194 (2006)). According to this method only one current value is applied. Hence, the current distribution present in case of a substrate having vias can not be observed by such a method.

Objective of the Invention

Therefore it is the objective of the present invention to provide a method for monitoring the via filling properties of a copper electrolyte during use of said copper electrolyte which is especially sensitive to leveller additives and their respective break-down products.

Summary of the Invention

The present invention concerns a method for monitoring the via filling properties of a copper electrolyte. The method can be used to monitor the via filling properties during use of a copper electrolyte in production of e.g., printed circuit boards, IC substrates and semiconductor-based microelectronic devices. The method can also be used for screening of new leveller additives for copper electrolytes and quality control of leveller additives.

The method for monitoring the filling properties of a copper electrolyte comprises the steps of

a) Providing a substrate having at least one via,

b) Calculating the required cathodic current density value on the bottom area (2) of the at least one via having one opening at an applied cathodic

current density on top (3) of the substrate surface to completely metal fill the via,

wherein the required cathodic current density value on the bottom (2) of a via having one opening is calculated by the formula

$$[\text{required cathodic current density on the bottom area (2) of a via}] =$$

$$\left(\frac{[\text{volume of the via to be filled}]}{(\text{desired volume of copper on top (1) of said via})}\right)$$

$$\cdot [\text{predefined cathodic current density applied on top (3) of the substrate surface}]$$

or

calculating the required cathodic current density in the centre (5) of a via having an opening on both sides of the substrate at a predefined cathodic current density on top (3) of the substrate surface to conformally metal fill the via

wherein the required cathodic current density value in the centre (5) of a via having an opening on both sides of the substrate is calculated by the formula

$$\left[\begin{array}{l}\text{required cathodic current density in the centre (5) of a via having} \\ \text{an opening on both sides of the substrate}\end{array}\right] =$$

$$\left(\frac{[\text{desired copper thickness in the centre (5) of a via having an opening on both sides of the substrate}]}{[\text{desired copper thickness on top (3) of the substrate surface}]}\right)$$

$$\cdot [\text{predefined cathodic current density applied on top (3) of the substrate surface}]$$

and thereby deriving the cathodic current density range where the influence of leveller additive(s) and corresponding break-down products of a given copper electrolyte on via filling properties is obtainable

wherein said cathodic current density range ranges from the cathodic current density applied to the substrate surface to the calculated cathodic current density on the bottom (2) of said via in case the via is selected from vias having one opening and

wherein said cathodic current density range ranges from the applied cathodic current density on top of the substrate to the calculated cathodic current density in the centre (5) of the via in case the via has an opening on both sides of the substrate,

c) Recording a current-voltage profile in the cathodic current range of the current by linear sweep voltammetry for at least two different rotating speeds of the rotating disc electrode in a three electrode set-up

and

d) Obtaining the via filling properties of the given copper electrolyte for a given via geometry from the data recorded in step c) in the cathodic current density range as calculated in step b)

by comparing the current-voltage profiles recorded in step c) in the cathodic current density range obtained in step b).

The method according to the present invention may further comprises the step of

e)1 replenishing the leveller additive in case the cathodic current at a given potential obtained in step c) in the cathodic current density range defined in step b) for the higher rotation speed is higher than or equal with the cathodic

current at said potential for the lower rotation speed in case the via is selected from vias having one opening

or

e)2 replenishing the leveller additive in case the cathodic current at a given potential obtained in step c) in the cathodic current density range defined in step b) for the higher rotation speed at said potential and for the lower rotation speed differ from each other in case the via has an opening on both sides of the substrate.

The method according to the present invention utilizes different rotation speeds of a rotating disc electrode in a three electrode set-up combined with the cathodic current density applied to the top of the substrate surface and the calculated current density on the bottom of a via with a specific geometry. Accordingly, both the cathodic current density on the top surface of the substrate and the calculated cathodic current density on the bottom of a via are used to define those region of the data measured in step b) which carry the influence of the leveller additive(s) and the respective break down products in case the via has one opening.

For vias having two openings such as through vias, both the cathodic current on top of the substrate surface and the calculated and desired cathodic current density in the center of a via having two openings are used to define those region of data measured in step b) which carry the influence of the leveller additive(s) and the respective break down products.

Brief Description of the Figures

Figure 1 shows a via of TSV-type and the definition of the terms "bottom of a via" and "on top of the substrate surface" (a) and a via of TH-type and the definition of the terms "in the centre of the via" and "on top of the substrate surface" (b).

Figure 2 shows the correlation between calculated cathodic current density on the bottom of a TSV and on top of substrate surface and the data range expressed in potential values of a current voltage profile in the cathodic current range of the current providing the required information on via filling properties.

Figure 3 shows current-potential profiles in the cathodic current range of the current obtained at different rotation speeds of the rotating disc electrode for a copper electrolyte comprising a leveller additive in case of a BMV to be filled (a) and a corresponding micrograph of a cross-sectioned copper filled BMV (b).

Figure 4 shows current-potential profiles in the cathodic current range of the current obtained at different rotation speeds of the rotating disc electrode for a copper electrolyte comprising a leveller additive in case of a BMV to be filled (a) and a corresponding micrograph of a cross-sectioned copper filled BMV (b).

Figure 5 shows current-potential profiles in the cathodic current range of the current obtained at different rotation speeds of the rotating disc electrode for a copper electrolyte comprising a leveller additive in case of a TSV to be filled (a) and a corresponding micrograph of a cross-sectioned copper filled TSV (b).

Figure 6 shows current-potential profiles in the cathodic current range of the current obtained at different rotation speeds of the rotating disc electrode for a copper electrolyte comprising a leveller additive in case of a TSV to be filled (a) and a corresponding micrograph of a cross-sectioned copper filled TSV (b).

Figure 7 shows data from current-potential profiles in the cathodic current range of the current obtained for an acidic copper electrolyte during use for characteri-

zation of TSV filling over a period of three weeks of plating showing the ratio (quotient) of potential and cathodic current values for two different rotation speeds of the RDE at -210mV subtracted from each other and plotted against the processing time (a) and corresponding micrographs of cross-sectioned copper filled TSVs (b).

Detailed Description of the Invention

The method according to the present invention utilizes two general principles:

The cathodic current density during electroplating of copper into a via (1) having one opening such as a TSV or BMV is higher at the bottom (2) of said via than on the top of the substrate surface (3). The definition of the terms "bottom" (2) of a via (1) and "top" (3) of the substrate surface in case of a via having one opening is shown in Fig. 1 (a).

For example, a TSV having a depth of 25 µm and a diameter of 5 µm requires 25 min for filling when applying a cathodic current density of -0.2 A/dm^2 which corresponds also to the cathodic current density present on top (3) of the substrate surface (assumptions: 100 % current efficiency and potential effect neglected). The cathodic current density required at the bottom (2) of said TSV needs to be 20 times higher than on the top (3) of the substrate surface in case the copper deposit on top of the substrate surface shall have a thickness of 1.2 µm. The value of 20 is obtained by dividing the volume of said TSV completely filled with copper

$$V_{TSV} = \left(\frac{5\mu m}{2}\right)^2 \cdot \pi \cdot 25\mu m = 490.8\mu m^3$$

by the volume of the copper deposit on top of the substrate surface (in this example a deposit having a height of 1.2 µm and a diameter of 5 µm)

$$V_{Surface} = \left(\frac{5\mu m}{2}\right)^2 \cdot \pi \cdot 1.2\mu m = 23.6\mu m^3$$

$$\frac{V_{TSV}}{V_{Surface}} \approx 20$$

With Farady`s law and the applied cathodic current density $I_{Surface}$ to the top of substrate surface of -0.2 A/dm^2

$$\frac{I_{TSV}}{I_{Surface}} = \frac{V_{TSV}}{V_{Surface}}$$

the required cathodic current density on the bottom (2) of the via I_{TSV} is calculated as

I_{TSV} = -0.2 A/dm^2 · 20 = -4 A/dm^2 for the exemplary TSV geometry.

The same method for obtaining the relevant cathodic current density or respective cathodic current or potential range for assessing the via filling properties of a copper electrolyte in the current-voltage profiles in the cathodic current range of the current is applied for vias of BMV type.

The cathodic current density in a BMV (1) having a depth of 80 µm, a diameter of 100 µm and a desired copper layer of 20 µm thickness on top of the substrate must be in average four times higher on the bottom (2) of the BMV than on top (3) of the substrate surface in order to obtain a complete filling of said BMV.

Mass transfer inside a via having one opening such as a BMV or TSV is only caused by diffusion of additives such as leveller additives, whereas mass transfer on top of the substrate is mainly caused by convection. Hence, the absolute cathodic current density must be higher at a given potential without convection than with convection of the electrolyte. Only in such a case the desired via filling can be achieved. Accordingly, when the absolute cathodic current density at a given potential without convection is lower than or equal with the cathodic current density at the same potential with convection of the electrolyte, leveller ad-

ditive(s) have to be added (replenished) to the copper plating bath in order to reach or maintain the desired via filling properties.

The method according to the present invention makes use of the above described behaviour: Different electrolyte convection situations are simulated by different rotating speeds of a rotating disc electrode (RDE) in a three electrode set-up. E.g., a rotating speed of 0 rpm resembles to no electrolyte convection and a rotation speed of > 0 rpm resembles to convection of the electrolyte. Notably, different electrolyte convection situations can be simulated with a first rotation speed of e.g. 100 rpm and a second rotation speed of e.g. 1000 rpm or vice versa.

In order to eliminate the contribution of other bath ingredients such as copper ions on the obtained rotation dependent current-potential profiles in the cathodic current range of the current only those portions of said profiles are used for assessing the via filling properties where no mass transfer related contributions of other bath ingredients such as copper ions are observed. The current-potential profile ranges of interest are calculated as described above for the exemplary TSV geometry of 25 µm depth, 5 µm diameter and a 1.2 µm thick layer of copper on top of the TSV as well as an applied cathodic current density of -0.2 A/dm^2.

A different situation is present if the via has an opening on both sides of the substrate such as a TH because an electrolyte flows through said via from both front and backside of the substrate. Thus, when applying the method according to the present invention to monitor the filling properties of a copper electrolyte in a via having an opening on both sides of the substrate the cathodic current density and cathodic current measured for at least two different rotating speeds of the rotating disc electrode in a three electrode set-up should match within a narrow range within the predetermined measurement range in order to obtain the desired filling. The cathodic current density ratio in the centre of a via having an opening on both sides of the substrate and on top of the corresponding sub-

strate surface are calculated by the same method as in case of a via having one opening. The definition of the terms "centre" (5) for via having an opening on both sides of the substrate is shown in Fig. 1 (b). Conformal metal filling means that a TH is plated with copper wherein the plated copper layer has a homogeneous layer thickness inside the TH.

For example, in case of a rotating disc electrode having an active surface of 7.1 mm^2 a cathodic current density of -0.2 A/dm^2 (= $-0.2 \cdot 10^{-2}$ A/cm^2) corresponds to a cathodic current of approx. -0.14 mA and a cathodic current density of -4 A/dm^2 (= $-4 \cdot 10^{-2}$ A/cm^2) to a cathodic current of approx. -2.84 mA.

The cathodic current values of -0.14 mA and -2.84 mA obtained for a RDE having an active surface of 7.1 mm^2 by the method described above define the cathodic current range wherein the relevant information on via filling properties of a given copper electrolyte are obtained in the current-voltage profiles in the cathodic current range of the current for a TSV with 25 µm depth and 5 µm diameter, a 1.2 µm thick copper layer on top of the TSV, an applied cathodic current density of -0.2 A/dm^2 and a desired filling time of 25 min.

The potential range of interest is obtained by deriving 1. the potential value for the bottom of the TSV (1) from the current-voltage curve in the cathodic current range of the current at for example 0 rpm at $-4 \cdot 10^{-2}$ A/cm^2 and 2. the potential value for the top of the substrate surface from the current-voltage curve in the cathodic current range of the current at for example 1000 rpm at $-0.2 \cdot 10^{-2}$ A/cm^2. Accordingly, the potential range of interest for this specific via geometry ranges from about -0.3 V vs. Ag/AgCl to about -0.2 V vs. Ag/AgCl. This is shown in Fig. 2.

The same method to obtain the cathodic current range of interest and the corresponding potential range in the current-voltage profiles in the cathodic current range of the current as described above can be applied to any other via geometries.

Next, current-voltage profiles in the cathodic range of the current are recorded by means of linear sweep voltammetry (LSV).

A three electrode set-up consisting of a rotating disc electrode (RDE) having a copper surface, a reference electrode (e.g., a Ag/AgCl reference electrode) and a counter electrode which is preferably a platinum electrode is used for the method according to the present invention.

The rotating disc electrode can for example be a copper electrode or a platinum electrode which has a copper surface. A platinum electrode can be used after deposition of a copper layer from e.g. a copper electrolyte which is free of organic additives onto the entire surface of said electrode by a controlled deposition.

Next, the three electrode set-up is contacted with the copper electrolyte comprising a leveller additive.

In a preferred embodiment of the present invention the RDE having a copper surface is conditioned in the copper electrolyte comprising a leveller additive prior to the LSV measurement. Conditioning can be for example achieved by applying a current of e.g., $-0.4\ A/dm^2$ for 300 s at a rotation speed of 0 rpm. Such a conditioning step is optional and depends on the kinetics of the interacting organic additives in the respective copper electrolyte.

A current-voltage profile in the cathodic current range of the current without other than natural electrolyte convection (0 rpm) is measured followed by measuring of a current-voltage profile in the cathodic current range of the current under controlled convection (> 0 rpm). The controlled convection is adjusted by a calibrated rotating disc electrode (RDE). The comparison of the current-voltage profiles in a current range defined by the process under consideration (filling of vias having a defined size with copper by electroplating) is an indicator for the filling performance of the copper electrolyte including the influence of filling behaviour of leveller additives and break-down products thereof.

Hence, the LSV measurement is done for at least two different rotation speeds of the RDE. The rotation speeds to be applied depend on the equipment used for said purpose. Preferably, one rotation speed of 0 to 100 rpm and another rotation speed of more than 100 rpm are applied for each individual LSV scan (or vice versa). Preferably, one rotation speed of the rotating disc electrode ranges from 0 to 100 rpm and a second rotation speed of the rotating disc electrode of more than 100 rpm are applied in step c).

The scan speed is set to a value which leads to the required accuracy of the method and the maximum time allowed due to conditions of copper electrolyte use during production. Furthermore, the scan speed must allow a quasi-stationary adsorption of leveller additives and their break-down products on the surface of the RDE. Hence, a scan speed in the range of 0.1 to 50 mV/s for each LSV measurement cycle is preferred.

Different methods for data analysis are available for the method according to the present invention:

The curves obtained by dividing the data obtained at the higher rotating speed of the RDE by the data obtained at the lower rotating speed of the RDE are plotted against the cathodic current values obtained by either the higher rotating speed or the lower rotating speed. The data obtained from such plots can be further treated in order to obtain the desired information on via filling properties of a copper electrolyte. The area below and above the zero line are numerically integrated within the cathodic current range which depends on the geometry of the via to be filled with copper. The absolute sum indicates the via filling properties of the copper electrolyte under consideration. In case the via is a TSV or a BMV, the higher the absolute sum, the better is the via filling.

Another method for data analysis comprises plotting the data obtained by the method according to the present invention as curves showing the ratio of potential and cathodic current (i.e., resistivity) against potential.

Still another method for data analysis comprises the steps of a) selecting a potential value in the LSV diagram which is within the calculated potential range for the given via geometry and b) subtracting the cathodic current or cathodic current density value at said potential value obtained for a first rotation speed rpm 1 from said value obtained for a second rotation speed rpm 2 wherein rpm 2 < rpm 1. Such a procedure is for example useful when monitoring a copper electrolyte during use with the method according to the present invention. In case the via to be filled with copper is a TSV or a BMV a declining curve shows worsening of the via filling properties of a given electrolyte, i.e. the concentration of the active leveller additive is declining. A stable concentration of the active leveller additive is indicated by a curve having no slope. A modification of said method of data analysis is applied in example 5 and shown in Fig. 7 wherein the ratio of potential and cathodic current values for two different rotation speeds of the RDE at -210 mV are substracted from each other and plotted against the processing time, i.e. the electroplating time applied to a electrolyte. This data analysis method is particularly suitable to monitor the leveller additive concentration indirectly during use of a copper electrolyte during production of printed circuit boards, metallization of semiconductor wafers and the like.

The three electrode set-up can be prepared for a new measurement using the following procedure: The electrodes are rinsed with water, preferably deionised water and the copper layer deposited during the LSV scans is removed by e.g. immersing the RDE in diluted HNO_3 followed by rinsing with water.

The three electrode set-up can now be used for measuring the via filling properties of another batch of copper electrolyte.

A test protocol according to one embodiment of the present invention which allows the measurement of via filling properties of different batches of copper electrolytes is summarized in Table 1.

After finishing the measurement of one copper electrolyte batch (step 5), the three electrode set-up is prepared for the measurement of another copper electrolyte batch (steps 6 to 9 and then steps 1 to 4).

Table 1: Test protocol for the measurement of different batches of a copper electrolyte using the same three electrode set-up:

Step	Description
1	Cleaning and characterisation of the RDE
2	Providing a copper surface on the RDE
3	Transfer of the RDE
4	Conditioning of the copper surface of the RDE in the copper electrolyte under consideration
5	Characterisation of the electrolyte under consideration by means of LSV
6	Rinsing the RDE
7	Copper stripping from the RDE
8	Rinsing of the RDE
9	Transfer of the RDE; continue with step 1 or end of the method

Examples

The following non-limiting examples further illustrate the present invention.

Experimental set-up and general procedure

A three electrode set-up consisting of a rotating disc electrode (RDE) having a copper surface, a Ag/AgCl reference electrode and a platinum counter electrode was used throughout all experiments. The counter electrode was separated by a salt bridge throughout all steps.

Linear sweep voltammetry (LSV) with a scan speed of 10 mV/s and different rotating speeds of the RDE was applied.

The LSV measurements were compared with micrographs of cross-sectioned, copper filled recessed structures in order to prove the accuracy of the method according to the present invention.

The data derived from LSV measurement at different rotating speeds of the RDE was investigated using the following procedure:

The cathodic current range considered for obtaining the required information on via filling properties of the copper electrolyte under investigation was calculated from the depth and diameter values of the vias to be filled, the desired thickness of the copper layer on top of the substrate surface and the cathodic current density applied to the top of the substrate surface.

Next, the LSV measurement was performed at a rotating speed of the RDE of 0 rpm and 1000 rpm. The scanned potential range was in for all three rotating speeds from + 0.1 V to – 0.6 V vs. Ag/AgCl reference electrode.

The whole test protocol used throughout all examples is summarized in Table 2.

Table 2: Test protocol applied throughout all examples.

Step	Description	Electrolyte	Technique	Parameters
1	Cleaning and characterisation of the RDE	0.5 M H_2SO_4	Cyclic voltammetry	Potential range: 0.3 V → 1.2 V → - 0.18 V → 0.3 V; Scan number: approx. 200 Scan rate: 1 V/s Rotation

				speed: 0 rpm
2	Deposition of copper on the RDE	Electrolyte of steps 4 and 5 without organic additives	Galvanostatic Chrono Potentiometry (GCP)	Deposition cathodic current: $-2.5\ A/dm^2$ Deposition time: 60 s Rotation speed: 1000 rpm
3	Transfer			three electrode set-up transfer in electrolyte of step 5
4	Conditioning of the copper layer	Electrolyte under consideration	GCP	Deposition cathodic current: $-0.14\ A/dm^2$ Deposition time: 300 s Rotation speed of RDE: 0 rpm and 1000 rpm
5	Electrolyte characterisation	Electrolyte under consideration	LSV	Potential range: 0.1 V to – 0.4 V Scan rate: 10 mV/s Rotation speed of RDE: 0 rpm and 1000 rpm
6	Rinsing	Deionised		three elec-

		water (DI water)		trode set-up
7	Copper stripping from RDE	HNO_3:DI water = 1:1		RDE
8	Rinsing	DI water		RDE
9	Transfer			three electrode set-up transfer to electrolyte of step 1

Example 1

The via filling properties of an acidic copper electrolyte comprising a leveller additive suitable for via filling were determined using the test protocol according to Table 2.

The data obtained for a first rotation speed of the RDE of 0 rpm and a second rotation speed of the RDE of 1000 rpm for the calculated potential range required for a BMV having a given geometry is shown in Fig. 3 (a).

Here, the absolute cathodic current density is lower in case of a rotation speed of 1000 rpm compared to those absolute cathodic current density obtained at a rotation speed of the RDE of 0 rpm, i.e. no rotation.

A good correlation between the copper electrolyte characterization by means of LSV and the cross-sectioned samples investigated by optical microscopy was observed (Fig. 3 (b)). The micrograph shows a completely filled BMV.

Example 2

The via filling properties of an acidic copper electrolyte comprising a leveller additive not suitable for via filling were determined using the test protocol according to Table 2.

The data obtained for a first rotation speed of the RDE of 0 rpm and a second rotation speed of the RDE of 1000 rpm for the calculated potential range required for a BMV having a given geometry is shown in Fig. 4 (a).

Here, the cathodic current density at a rotation speed of 1000 rpm is higher in the potential range of approx. -0.3 V to approx. -0.24 V than and equal in the potential range of approx. -0.24 V to -0.21 V with the curve obtained for a rotation speed of 0 rpm.

A good correlation between the copper electrolyte characterization by means of LSV and the cross-sectioned samples investigated by optical microscopy was observed (Fig. 4 (b)). The micrograph shows an incompletely filled BMV.

Example 3

The via filling properties of an acidic copper electrolyte comprising a leveller additive suitable for via filling were determined using the test protocol according to Table 2.

The data obtained for a first rotation speed of the RDE of 0 rpm and a second rotation speed of the RDE of 1000 rpm for the calculated potential range required for a TSV having a given geometry is shown in Fig. 5 (a).

Here, the absolute cathodic current density is lower in case of a rotation speed of 1000 rpm compared to those absolute cathodic current density obtained at a rotation speed of the RDE of 0 rpm.

A good correlation between the copper electrolyte characterization by means of LSV and the cross-sectioned samples investigated by optical microscopy was observed (Fig. 5 (b)). The micrograph shows a completely filled TSV.

Example 4

The via filling properties of an acidic copper electrolyte comprising a leveller additive not suitable for via filling were determined using the test protocol according to Table 2.

The data obtained for a first rotation speed of the RDE of 0 rpm and a second rotation speed of the RDE of 1000 rpm for the calculated potential range required for a TSV having a given geometry is shown in Fig. 6 (a).

Here, the absolute cathodic current density at a rotation speed of 1000 rpm is higher in the potential range of approx. -0.31 V to -0.25 V compared to those absolute cathodic current density obtained at a rotation speed of the RDE of 0 rpm and equal in the potential range of approx. -0.25 V to -0.21 V.

A good correlation between the copper electrolyte characterization by means of LSV and the cross-sectioned samples investigated by optical microscopy was observed (Fig. 6 (b)). The micrograph shows an incompletely filled TSV.

Example 5

The via filling properties of an acidic copper electrolyte comprising a leveller additive suitable for via filling were determined during use of said copper electrolyte. The test protocol according to Table 2 was applied.

The data obtained for a low rotation speed of the RDE of 0 rpm were subtracted from the data obtained from a high rotation speed of the RDE of 1000 rpm at a potential of -210 mV which is within the calculated potential range required for a TSV having the given geometry (Fig. 7 a).

The data obtained show a drop of the curve which corresponds to declining via filling properties of the copper electrolyte during use.

Corresponding micrographs of cross sectioned samples are shown in Fig. 7 b wherein the TSV filling after three weeks use of the electrolyte is insufficient. This corresponds well to the drop shown in the curve in Fig. 7 a.

CLAIMS

1. A method for monitoring the filling properties of a copper electrolyte comprising the steps of

a) Providing a substrate having at least one via,

b) Calculating the required cathodic current density value on the bottom area (2) of the at least one via having one opening at an applied cathodic current density on top (3) of the substrate surface to completely metal fill the via,

wherein the required cathodic current density value on the bottom (2) of a via having one opening is calculated by the formula

$$[\text{required cathodic current density on the bottom area (2) of a via}] =$$

$$\left(\frac{[\text{volume of the via to be filled}]}{(\text{desired volume of copper on top (3) of said via})}\right)$$

$$\cdot [\text{predefined cathodic current density applied on top (3) of the substrate surface}]$$

or

calculating the required cathodic current density in the centre (5) of a via having an opening on both sides of the substrate at a predefined cathodic current density on top (3) of the substrate surface to conformally metal fill the via

wherein the required cathodic current density value in the centre (5) of a via having an opening on both sides of the substrate is calculated by the formula

$$\left[\begin{array}{l}\text{required cathodic current density in the centre (5) of a via having}\\ \text{an opening on both sides of the substrate}\end{array}\right] =$$

$$\left(\frac{\left[\text{desired copper thickness in the centre (5) of a via having an opening on both sides of the substrate}\right]}{\left[\text{desired copper thickness on top (3) of the substrate surface}\right]}\right)$$

$$\cdot \left[\text{predefined cathodic current density applied on top (3) of the substrate surface}\right]$$

and thereby deriving the cathodic current density range where the influence of leveller additive(s) and corresponding break-down products of a given copper electrolyte on via filling properties is obtainable

wherein said cathodic current density range ranges from the cathodic current density applied to the substrate surface to the calculated cathodic current density on the bottom (2) of said via in case the via is selected from vias having one opening and

wherein said cathodic current density range ranges from the applied current density on top of the substrate to the calculated cathodic current density in the centre (5) of the via in case the via has an opening on both sides of the substrate,

c) Recording a current-voltage profile in the cathodic current range of the current by linear sweep voltammetry for at least two different rotating speeds of the rotating disc electrode in a three electrode set-up

and

d) Obtaining the via filling properties of the given copper electrolyte for a given via geometry from the data recorded in step c) in the cathodic current density range as calculated in step b)

by comparing the current-voltage profiles recorded in step c) in the cathodic current density range obtained in step b).

2. Method according to claim 1 wherein one rotation speed of the rotating disc electrode ranges from 0 to 100 rpm and another rotation speed of the rotating disc electrode of more than 100 rpm are applied in step c).

3. Method according to any of the foregoing claims comprising the further step

e)1 replenishing the leveller additive in case the absolute cathodic current at a given potential obtained in step c) in the cathodic current density range calculated in step b) for the higher rotation speed is higher than or equal with the absolute cathodic current at said potential for the lower rotation speed in case the via is selected from vias having one opening.

4. Method according to claims 1 and 2 comprising the further step

e)2 replenishing the leveller additive in case the absolute cathodic current at a given potential obtained in step c) in the cathodic current density range calculated in step b) for the higher rotation speed at said potential and for the lower rotation speed differ from each other in case the via has an opening on both sides of the substrate.

5. Method according to any of the foregoing claims wherein the surface of the rotating disc electrode consists of copper.

6. Method according to any of the foregoing claims wherein the scan speed in step c) is in the range of 0.1 to 50 mV.

FIGURES

Fig. 1 (a)

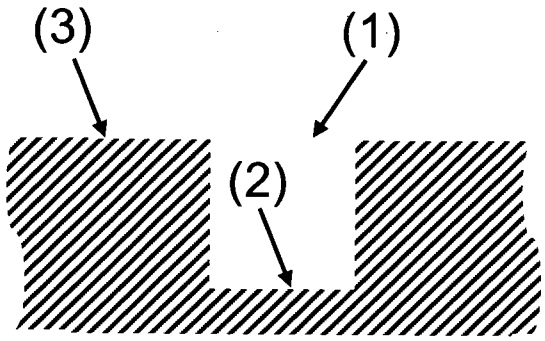


Fig. 1 (b)

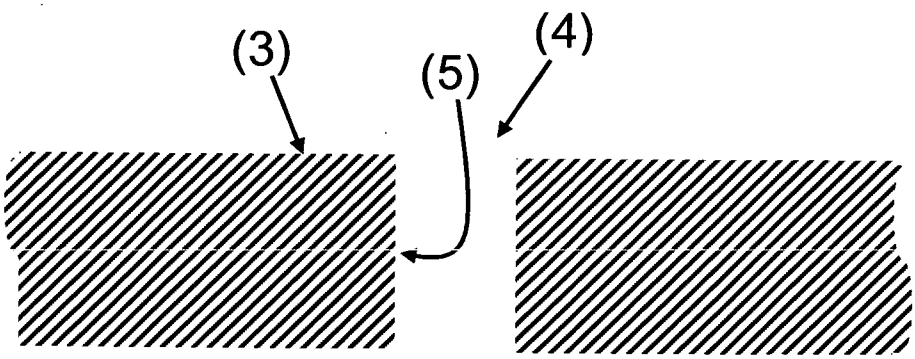


Fig. 2

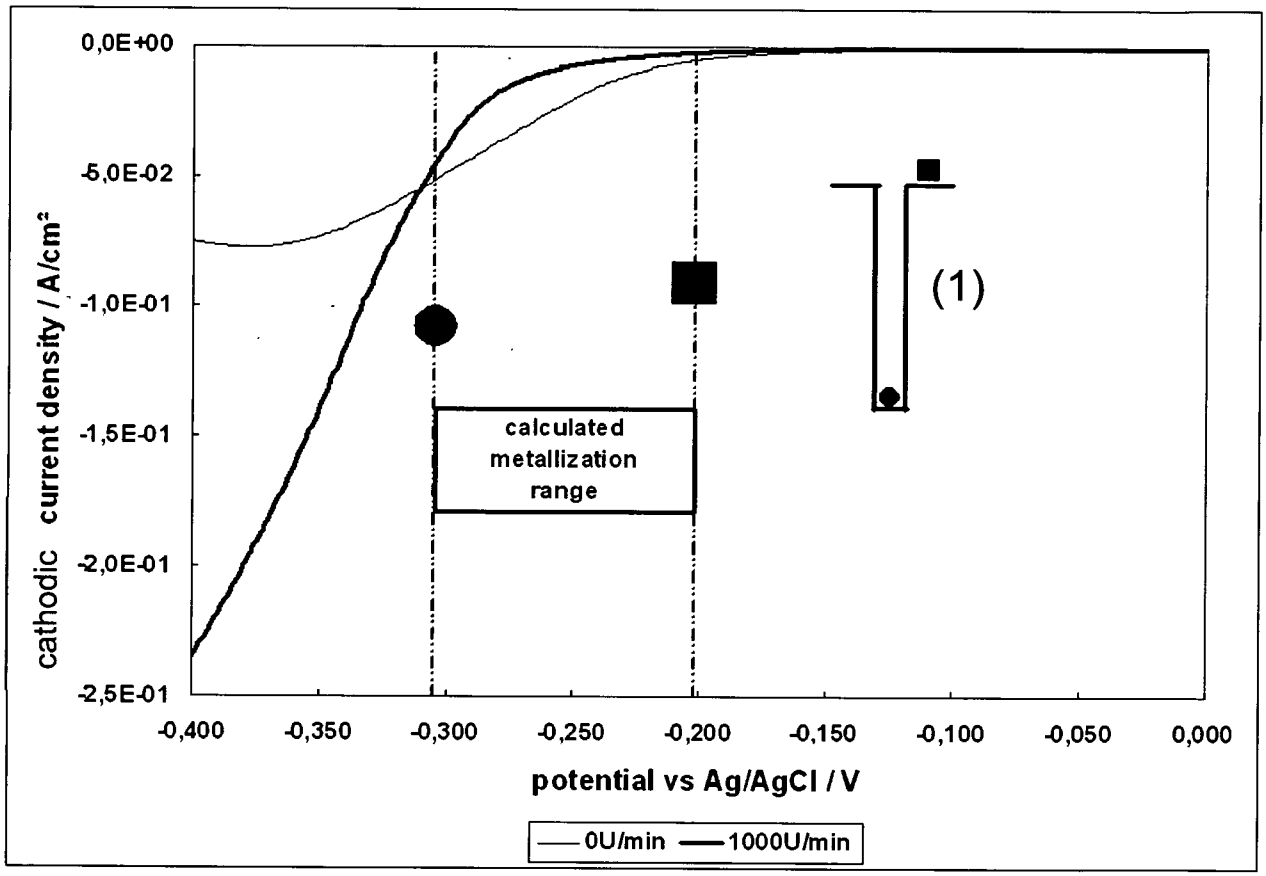
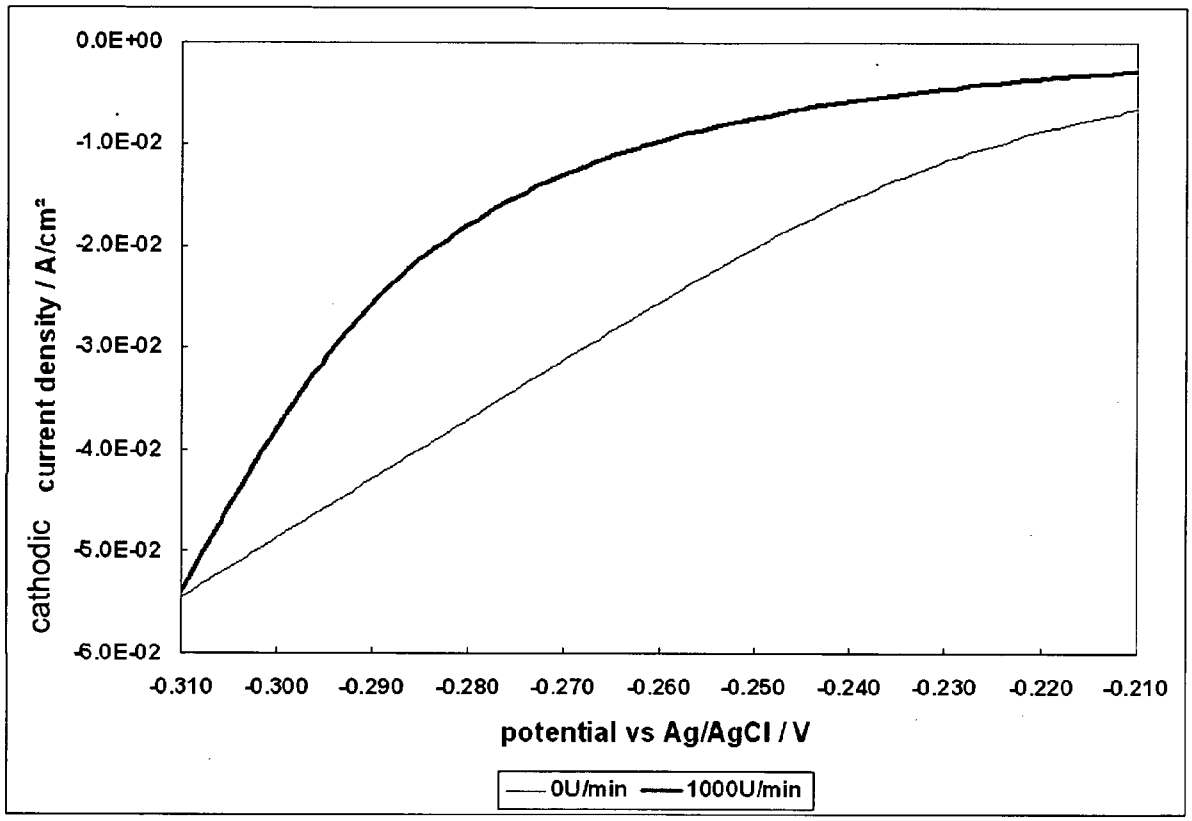

0,0E+00
-5,0E-02
-1,0E-01
-1,5E-01
-2,0E-01
-2,5E-01
cathodic current density / A/cm²
-0,400
-0,350
-0,300
-0,250
-0,200
-0,150
-0,100
-0,050
0,000
potential vs Ag/AgCl / V
calculated metallization range
(1)
0U/min
1000U/min

Fig. 3 (a)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-1.0E-02
-2.0E-02
-3.0E-02
-4.0E-02
-5.0E-02
-6.0E-02
cathodic current density / A/cm²
-0.310
-0.300
-0.290
-0.280
-0.270
-0.260
-0.250
-0.240
-0.230
-0.220
-0.210
potential vs Ag/AgCl / V
0U/min
1000U/min

Fig. 3 (b)

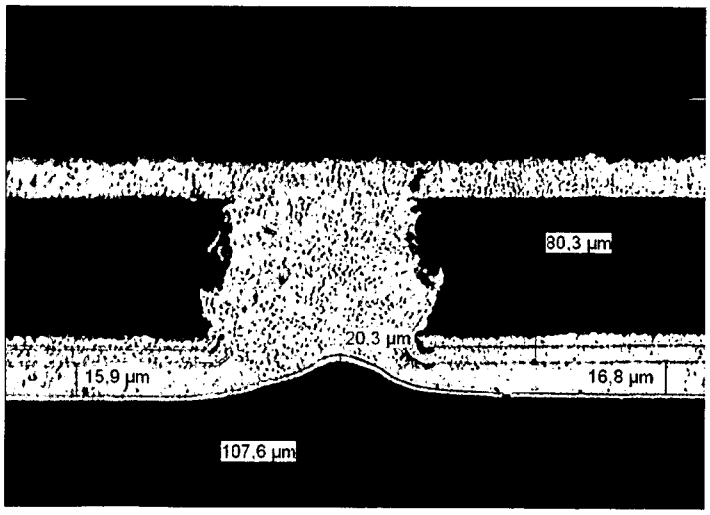
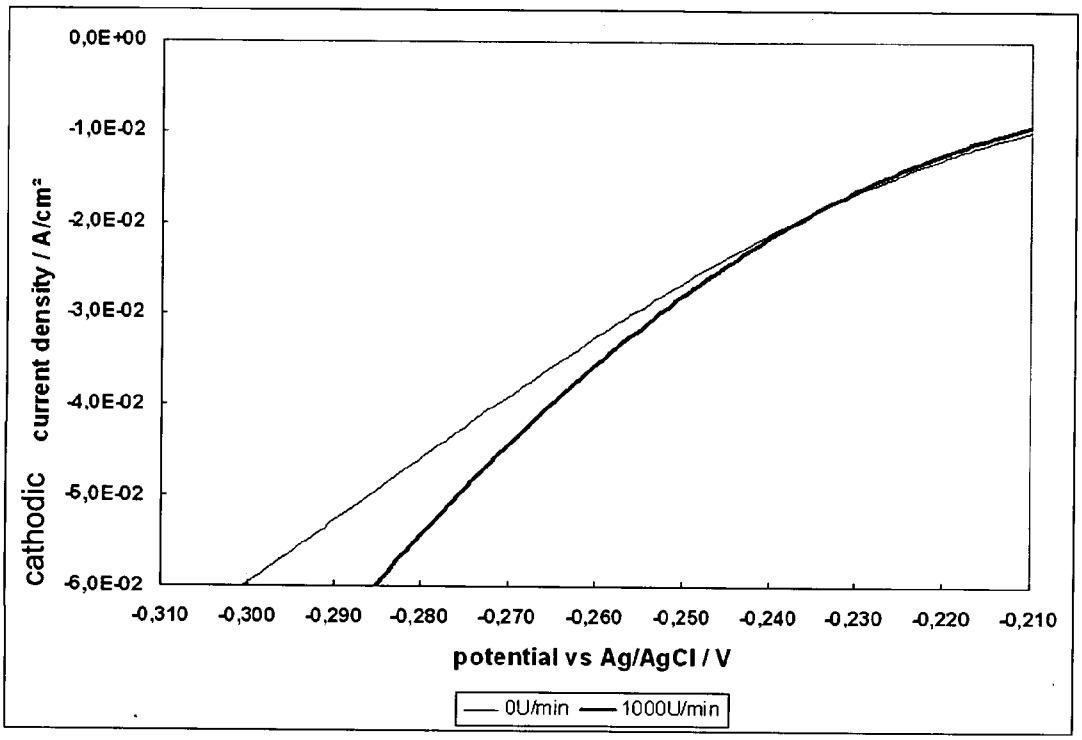

80,3 µm
20,3 µm
15,9 µm
16,8 µm
107,6 µm

Fig. 4 (a)


0,0E+00
-1,0E-02
-2,0E-02
-3,0E-02
-4,0E-02
-5,0E-02
-6,0E-02
cathodic current density / A/cm²
-0,310
-0,300
-0,290
-0,280
-0,270
-0,260
-0,250
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-0,230
-0,220
-0,210
potential vs Ag/AgCl / V
0U/min
1000U/min

Fig. 4 (b)

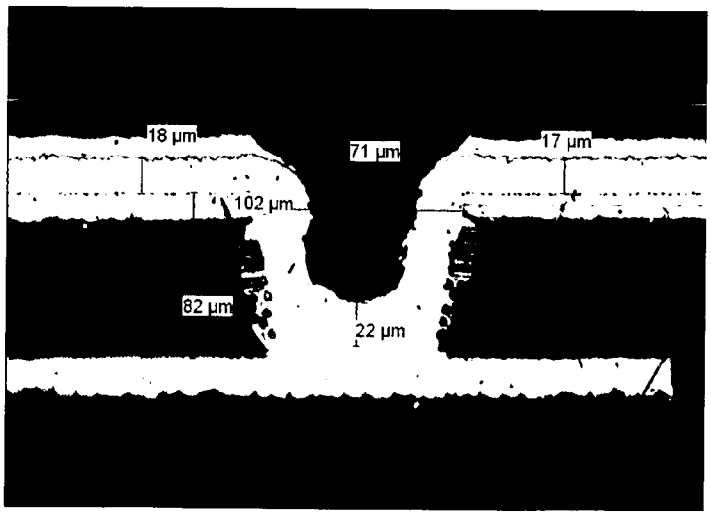
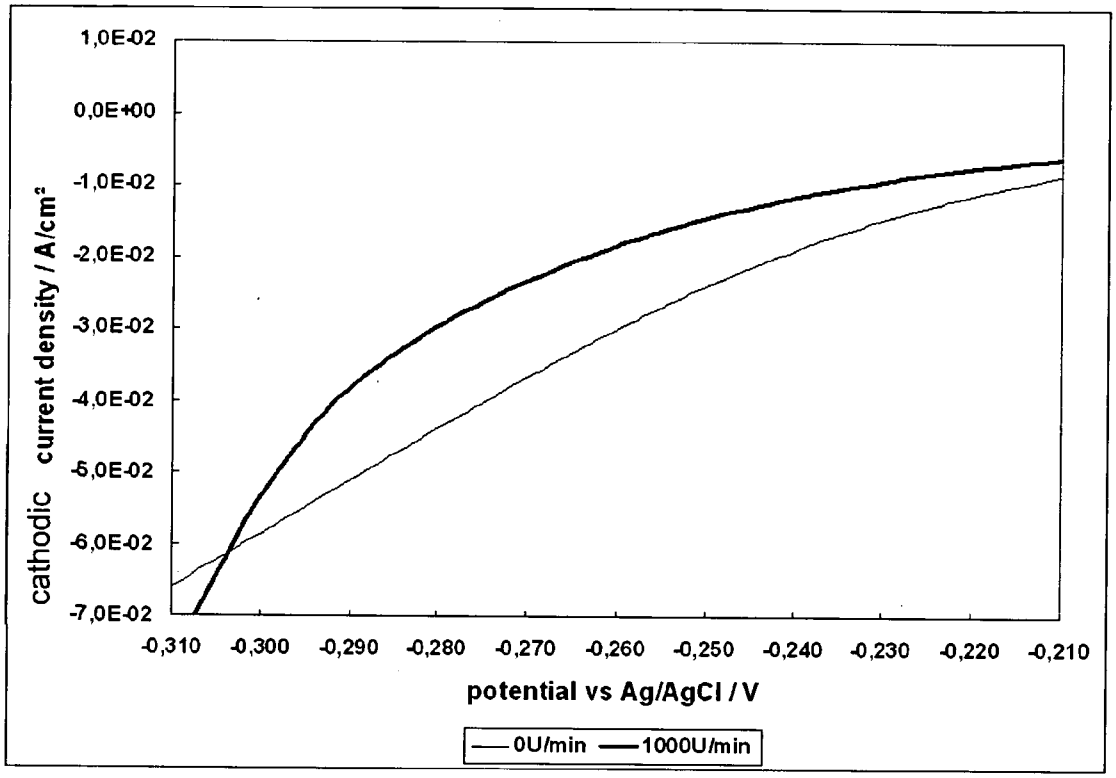

18 µm
71 µm
17 µm
102 µm
82 µm
22 µm

Fig. 5 (a)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0,0E+00
-1,0E-02
-2,0E-02
-3,0E-02
-4,0E-02
-5,0E-02
-6,0E-02
-7,0E-02
cathodic current density / A/cm²
-0,310
-0,300
-0,290
-0,280
-0,270
-0,260
-0,250
-0,240
-0,230
-0,220
-0,210
potential vs Ag/AgCl / V
0U/min
1000U/min

Fig. 5 (b)

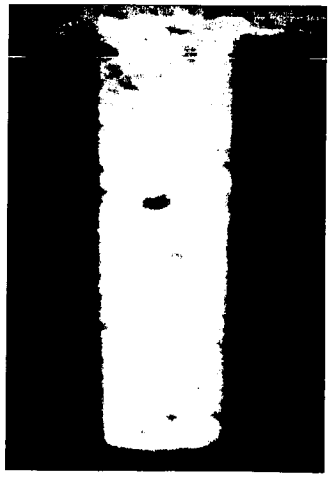
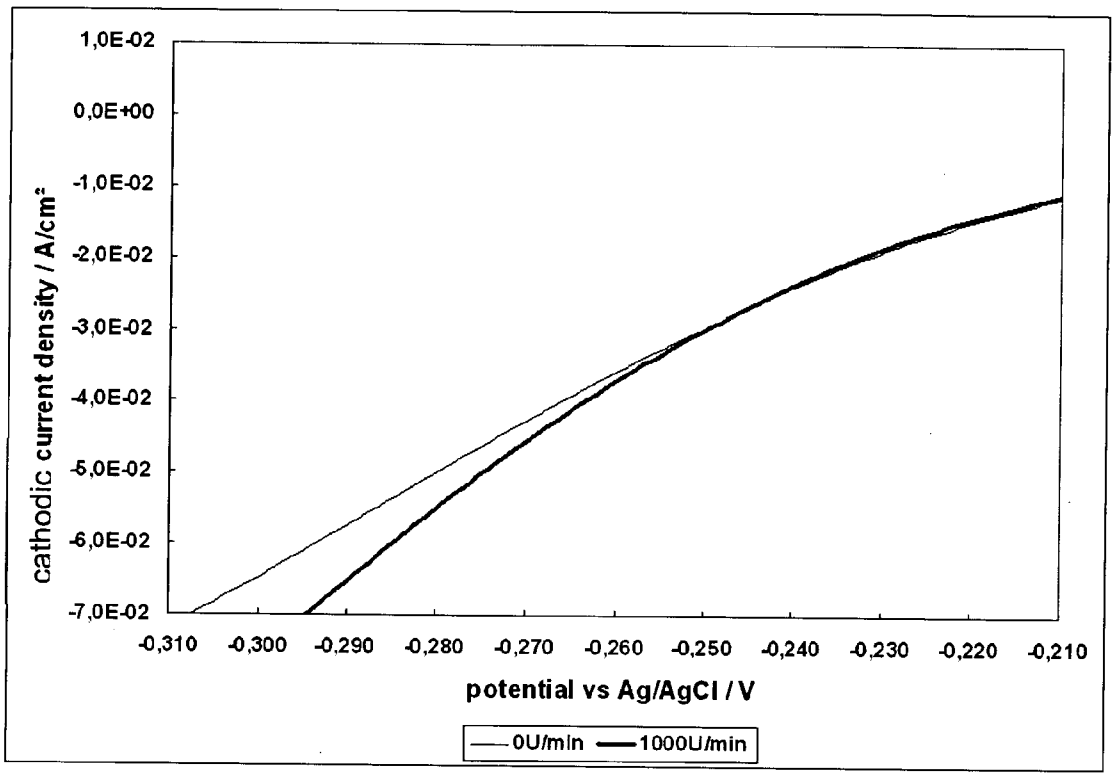


Fig. 6 (a)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-1,0E-02
-2,0E-02
-3,0E-02
-4,0E-02
-5,0E-02
-6,0E-02
-7,0E-02
cathodic current density / A/cm²
-0,310
-0,300
-0,290
-0,280
-0,270
-0,260
-0,250
-0,240
-0,230
-0,220
-0,210
potential vs Ag/AgCl / V
0U/min
1000U/min

Fig. 6 (b)

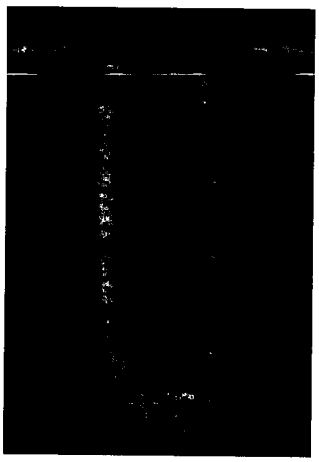


Fig. 7 (a)

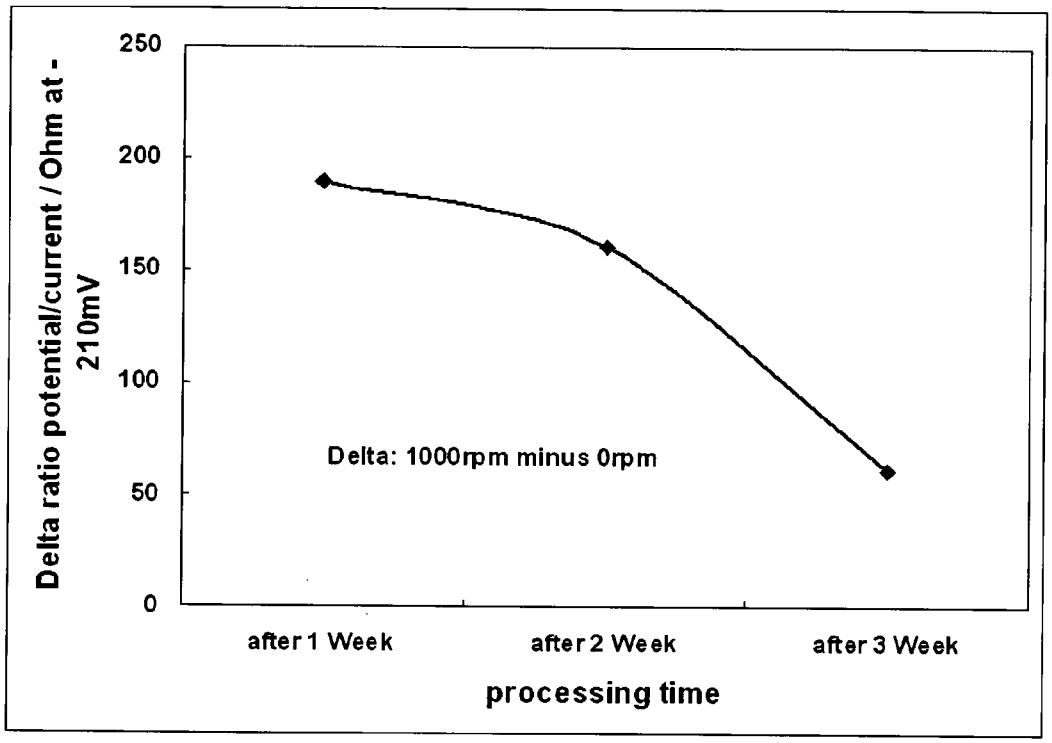
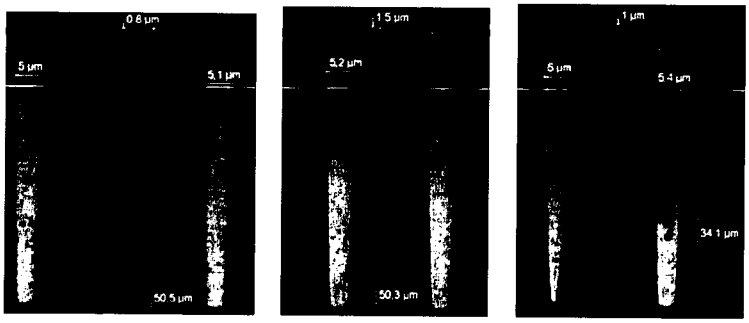


Fig. 7 (b)



After 1 week after 2 weeks after 3 weeks

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/005396

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25D5/02 C25D21/12 H01L21/768
ADD.

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)
C25D H01L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TZU-HSUAN TSAI ET AL: "Copper electrodeposition in a through-silicon via evaluated by rotating disc electrode techniques;Copper electrodeposition in a TSV evaluated by RDE techniques", JOURNAL OF MICROMECHANICS & MICROENGINEERING, INSTITUTE OF PHYSICS PUBLISHING, BRISTOL, GB, vol. 20, no. 11, 15 October 2010 (2010-10-15), page 115023, XP020200027, ISSN: 0960-1317, DOI: 10.1088/0960-1317/20/11/115023 cited in the application the whole document ----- -/--	1-6

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 October 2013	28/10/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Suárez Ramón, C

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	K. KONDO ET AL: "Copper damascene electrodeposition and additives", JOURNAL OF ELECTROANALYTICAL CHEMISTRY, vol. 559, 1 November 2003 (2003-11-01), pages 137-142, XP55084567, ISSN: 1572-6657, DOI: 10.1016/S0022-0728(03)00110-4 the whole document	1-6
X	PREMRATN TAEPHAISITPHONGSE ET AL: "Electrochemical and Fill Studies of a Multicomponent Additive Package for Copper Deposition", JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 148, no. 7, 1 January 2001 (2001-01-01), page C492, XP055084566, ISSN: 0013-4651, DOI: 10.1149/1.1376636 the whole document	1-6
A	WEI-PING DOW AND CHENG-WEI LIU: "Evaluating the Filling Performance of a Copper Plating Formula Using a Simple Galvanostat Method", JOURNAL OF THE ELECTROCHEMICAL SOCIETY, ELECTROCHEMICAL SOCIETY, MANCHESTER, NEW HAMPSHIRE; US, vol. 153, no. 3, 3 February 2006 (2006-02-03), pages C190-C194, XP002662774, ISSN: 0013-4651, DOI: DOI:10.1149/1.2165743 [retrieved on 2006-02-03] the whole document	1-6

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