



Method of regulating the titre of a solution, device
for controlling said regulation and system comprising
such a device

5 Technical field and prior art

The invention relates to the field of chemical regulation, in particular the chemical regulation of slurries or compounds of material in suspension and/or of various chemical products (acids, bases, organic
10 compounds) in solution.

Such products are used, for example, in the semiconductor industry where they serve in the chemical-mechanical polishing of semiconductor wafers
15 or substrates.

Some of these slurries or these suspensions use a compound whose concentration decreases over time, for example by decomposition by chemical reaction (this is
20 the case with H_2O_2) or by evaporation (NH_4OH).

It is therefore necessary in this case to regulate the titre of chemical product(s) (H_2O_2 , NH_4OH) of this slurry.

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The current techniques for regulating slurries employ a buffer tank 4 and a mixing tank 2, as illustrated schematically in Figure 1. The products leaving the buffer tank are then taken into a delivery system 8 and
30 are used in operations such as the abovementioned polishing operations.

The operation of the tanks 2 and 4 may be described in the case of H_2O_2 .

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The tanks 2, 4 operate between a high level ($Level_{max}$) and a hysteresis level which triggers the filling.



They are regulated in terms of H_2O_2 titre (%wt).

The filling of the buffer tank 4 takes place when the hysteresis level is reached, with slurry that comes from the mixing tank 2.

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The slurry delivery system is composed of a continuous circulation loop, as described in Patent US 6 125 876, which prevents the slurry from stagnating in the network and makes it possible to regulate the pressure to the equipment by means of a pressure sensor. The feed and the return in this loop are at the base of the buffer tank 4.

The mixing tank 2 is fed with "pure" slurry and with hydrogen peroxide (for example 31% H_2O_2). It is regulated in terms of titre before each transfer of product into the buffer tank 4.

The hydrogen peroxide titre is regulated by provision of 31 wt% H_2O_2 .

The titration operations carried out on the buffer tank 4 use a potentiometric titrator 7 or sometimes two titrators.

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The titrator takes a measurement of the titre periodically (that can be parameterized). Its operation can be described in conjunction with Figure 2. This figure shows three titration levels, namely a high level (maximum value), a low level (minimum value) and a setpoint value to be reached.

If the titre is below the setpoint (Case 1 in Figure 1), a readjustment is made by adding the lacking amount of H_2O_2 .

Should the titre be above the setpoint (Cases 2 and 4 in Figure 1), no regulating action is taken.

Should the titre be above the maximum value (Case 3 in Figure 1), a second check is carried out. If this confirms that the titre is too high, an alarm is triggered. If the titre proves to be normal after the
5 second check, no regulating action is taken.

Should the titre be below the minimum value (Case 5 in Figure 1), a second check is carried out. If this confirms that the titre is too low, an alarm is
10 triggered. If the titre proves to be normal after the second check, no regulating action is taken.

Triggering an alarm results in the delivery system 8, and therefore the production being stopped.
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Moreover, each titrator employs, in particular, elements such as electrodes and capillaries.

The measurement taken furthermore depends on the titration reactants and on any drift of the electrodes or capillaries. There are therefore many sources of error.
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Furthermore each titrator represents in general an overall cost of about 10% of the overall cost of the production plant on which it is mounted.
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Each titrator is also a source of breakdowns and therefore entails substantial operating costs.
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A problem that arises is to find a novel system of regulating the titration of suspensions, especially within the context of the fabrication of production units for semiconductor wafers or substrates, which is
35 free of the abovementioned drawbacks.

Summary of the invention

The invention provides a method for regulating the

titre of a solution, in which a predetermined amount of a product contained in the solution is added to the solution according to a time interval proportional to the product of the delayral degradation coefficient D of the said product in solution and the total volume V_t of the solution at the time of the addition.

This method depends only on the calculation of the addition interval, which depends only on the measurement of the total volume of the solution. This measurement may be performed in an analogue manner.

The method according to the invention entails a much lower cost than the method employing a titrator, and is also not a source of breakdowns, unlike known titrators. It does not employ electrodes that can drift and it does not depend on titration reactants either.

After each addition of product, the time interval before the next injection may be calculated.

Thus, it is possible, after a certain period of time less than the addition interval, to measure the total volume of the solution. If this volume has not varied, the same predetermined amount of product is again injected or added. If the total volume has decreased, a new addition time is calculated according to the same calculation rule.

The invention also relates to a device for controlling the regulation of the titre of a solution, this solution containing a product, comprising means for controlling the injection of a predetermined amount of the said product into the said solution according to a time interval, called the addition interval, proportional to the product of the delayral degradation coefficient D of the said product in solution and the total volume V_t of the solution at the time of the addition.

The invention also relates to a system for regulating the titre of a solution, comprising a device as above, and means for determining a fill volume in a container
5 containing the said solution. These means for determining a fill volume may be analogue means.

Such a regulating system may furthermore include an electrode titration device.

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The invention also relates to a system for producing a chemical solution, comprising:

- a regulating system as above;
- means for delivering the said solution.

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According to the invention, a system for producing semiconductor substrates includes a unit for polishing the said substrates and a system for producing a chemical polishing solution as above.

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Brief description of the figures

The features and advantages of the invention will become more clearly apparent on reading the description
25 as follows of several embodiments given by way of non-limiting examples. The description refers to the appended figures in which:

- Figure 1 shows a known regulating system;
- Figure 2 shows various states of filling of a
30 tank;
- Figure 3 shows a regulating system according to the invention;
- Figure 4 shows decomposition curves for a product in a tank; and
- 35 - Figure 5 shows a device for injecting a product, especially in a system according to the invention.

Detailed description of embodiments of the invention

Figure 3 shows a diagram of a regulating system according to the invention. This diagram, like that in
5 Figure 1, relates to the regulation of slurries (or compounds of material in suspension and/or various chemical products in a solution) in a semiconductor wafer or substrate production unit. The references 2, 4, 6 and 8 denote elements identical or equivalent to
10 those of Figure 1.

Table 1 below summarizes the abbreviations used in the present description, illustrated (non-restrictingly) with a few numerical values in the right-hand column.

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Indices:

- i : initial
- add : added
- meas : measured
- 20 - slur : slurry
- m : slurry/hydrogen peroxide mixture
- mix : mixing tank
- targ : target or desired value
- pure : undiluted

Table 1

<u>Parameters</u>	<u>Definition</u>	<u>Unit</u> <u>Values</u>	<u>Type</u>	<u>Value</u> <u>Example</u>
Deg_{buffer}	Amount of H_2O_2 degradation in the slurry in the buffer tank	$\%H_2O_2/day$	Measured value on the curve	0.189 $\%H_2O_2/day$
Deg_{mix}	Amount of degradation of H_2O_2 in the slurry in the mixing tank	$\%H_2O_2/day$	Measured value on the curve	0.189 $\%H_2O_2/day$
$Diff_{mix}$	Maximum difference for the mixing tank between the last H_2O_2 titre analysis and the new one	$\%H_2O_2$	Calculation	0.06%
$K/K_{mix}/K_{buffer}$	Coefficient of addition of the 100 ml dose of H_2O_2 in the slurry for a mixing tank/buffer tank	$\%H_2O_2$	Calculation	0.16%
$M_{H_2O_2, add}$	Mass of H_2O_2 to be added to the tank	kg	Calculation	523 kg
$M_{slurry, i}$	Mass of slurry in the tank before analysis	kg	Measurement	1123 kg
$M_{added\ slurry}$	Mass of slurry to be added to the tank	kg	Calculation	523 kg
M_{tank}	Maximum weight of slurry in the tank	kg	Parameters	1360 kg
$Level_{max}$	Maximum permissible level in the tank	% of filling	Parameters	95%
$Level_{working}$	Permissible working level in the tank	% of filling	Parameters	90%
$Level_{hyst}$	Range of variation in the mixing tank/buffer tank	% of filling	Parameters	35%
$Level_{min}$	Minimum permissible level in the tank	% of filling	Parameters	60%
$Level_{tank}$	"Current" level in the mixing tank	% of filling	Measurement	68%
$Level_{slurry}$	Level of slurry to be added to the tank	% of filling	Calculation	10%

Level _{H2O2}	Level of H ₂ O ₂ to be added to the tank	% of filling	Calculation	1%
N _{buffer}	Stirring power number in the buffer tank	number	Parameters	-5_0
N _{mix}	Stirring power number in the mixing tank	number	Parameters	-5_0
N _{titration, mix}	Successive titration number of the mixing tank during an off-spec analysis before a fault is triggered	number	Parameters	1-4
Slurry _m	Mixing of on-spec H ₂ O ₂ and slurry			
Amount _{fill}	% Level in the tank	%	Measurement	65.5%
Time _{inter-analysis}	Time before the new analysis of the mixing tank after an off-spec titre	day	System value	2 day
Time _{additions/analysis}	Determination of the time between the end of the H ₂ O ₂ additions and the analysis of the in-tank H ₂ O ₂ titre	minutes	Parameters	40 min
Time _{buffer inject} Time _{mix inject}	Time between each new injection of H ₂ O ₂ into the tank for the doses added.	minutes	System value	35 min
Time _{inject mix}	Time since last titration of the mixing tank	0-21 days	System value	Existent
Titre _{H2O2, pure} Titre _{H2O2, targ}	Desired (target) H ₂ O ₂ titre in the tank	wt%	Parameters	4.2%
Titre _{H2O2, i}	H ₂ O ₂ titre to be used for the additions	wt%	Parameters	31%
Titre _{H2O2, meas}	H ₂ O ₂ titre measured in the tank	wt%	Parameters	4.18%
Titre _{pure H2O2}	H2O2 titre used in pure form, undiluted			
	Minimum value of the desired H ₂ O ₂ titre in the tank	wt%	Parameters	4.15%

$\text{Titre}_{\min}$	Maximum value of the desired H ₂ O ₂ titre in the tank	wt%	Parameters	4.25%
$\text{Titre}_{\max}$	Precise volume of the 100 ml H ₂ O ₂ injection dose	milli-litres	Parameters	104 ml
V1	Precise volume of the 900 ml H ₂ O ₂ injection dose	milli-litres	Parameters	875 ml
V2	Precise volume of the 9000 ml H ₂ O ₂ injection dose	milli-litres	Parameters	9012 ml
V3	Volume of Slurry _m in the buffer tank	% fill	System value	78%
V_{buffer}	Volume of the tank - volume of slurry			
$V_{\text{total buffer}}$				
$\text{Vol}_{\text{H}_2\text{O}_2, i}$	Volume of concentrated H ₂ O ₂ to be added to the mixing tank	litres	Calculation	65 litres
$\text{Vol}_{\text{added slurry}}$	Volume of slurry to be added to the mixing tank	litres	Calculation	261 litres
$\rho_{\text{H}_2\text{O}_2, i}$	Density of H ₂ O ₂ to be used for the additions	kg/m ³	Fixed value	1.11 kg/m ³
ρ_{slurry}	Density of the slurry	kg/m ³	Fixed value	1.043 kg/m ³
K_{mix}	Theoretical degradation per day of the H ₂ O ₂ titre in the mixing tank for a full tank	%H ₂ O ₂ /D 0 - 0.4	Parameters	new

The buffer tank 4 is regulated as follows.

An injection of a predetermined volume (for example, 100 ml) is programmed at a time interval that depends on several parameters:

1 - on K, coefficient of addition of the 100 ml of H_2O_2 dose for the slurry:

K depends on:

- the maximum volume in the buffer tank,
- the precise volume of the H_2O_2 dose to be added and in principle, on the stirring rate in the tank;

2 - on the volume in the tank in question at the time of the addition, i.e. $V_{\text{total-buffer}} = V_{\text{tbuffer}} \times \text{Factor}_{\text{fill}}$;

3 - on the daily H_2O_2 degradation coefficient $\text{Deg}_{\text{buffer}}$ in the tank.

As regards the buffer tank, the time between two injections is given by:

$$\text{Time}_{\text{inject buffer}} = K \times \text{Deg}_{\text{buffer}} \times V_{\text{buffer}}.$$

A controller (for example, a programmed micro-controller) carries out the calculation, after each H_2O_2 injection, of the delay before the next injection. This controller comprises means for storing the various data used for the calculation and a microprocessor that carries out the desired calculations and manages and controls the various product injections.

Moreover, a measurement of the volume in the tank 4 is made, for example by conventional analogue means.

After the calculated delay, the controller performs a test on the new measured volume in the tank:

- if there is no change in level (for example within $\pm 4\%$), the predetermined dose is then injected;
- if there is a decrease in level (product was consumed since the last addition), the controller re-

calculates the injection delay according to the new volume. The time already elapsed is subtracted from the new delay so as to determine at what moment the new addition will be made; and

- 5 • upon filling the buffer tank, the addition operation is initialized at "time = 0" and the calculation of the time is repeated according to the new level (no addition at $t = 0$).

- 10 In fact, K depends on the specifications of the tank (height, diameter, volume) and on the stirring rate, whereas the degradation coefficient Deg itself depends on K and on the volume ratio of energy dissipated in the slurry (in W/m^3).

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The coefficient K and the degradation curve for a given tank are determined in the following manner.

- 20 The H_2O_2 degradation measurements are made as a function of the level in the tank. A curve of the type of those illustrated in Figure 4 is then obtained.

The method used is as follows:

- 25 - fill the tank to 90% with a slurry mixture whose H_2O_2 titre is known (about 4.2%);
 - wait 24 hours and then measure the titre again;
 - purge the tank in order to vary the level and reset the mixture to the titre (about 4.2%);
 - wait 24 hours and then measure the titre again;
30 - repeat several times in order to obtain enough points; and
 - deduce therefrom decomposition curve for the H_2O_2 in the tank as a function of its fill level.

- 35 The coefficient K is the coefficient of the exponential function found. Thus, in Figure 4, one curve has as coefficient $K = 0.1613$ and the other $K = 0.0644$.

The curve giving the variations in the degradation

coefficient D as a function of the fill factor is identical or similar to that expressing the variations in the degradation coefficient D as a function of a stirring rate for a fixed level in the tank. This is because, in one case the energy (W) is varied and in the other case the volume (m^3) is varied. However, these two variables are of the same order of magnitude. If both the stirring rate and the level in the tank are varied at the same time, a representation in the form of isolevels is obtained and therefore one with several curves. In all cases, these variables do not depend on the H_2O_2 dose.

In order to add a further safety factor to the system described above, it is also possible to add a measurement by a conventional titrator or an electrode titrator.

The H_2O_2 addition is then always made as described above, but regular analysis by the titrator allows the measurement to be validated.

The operation is then as below, the various cases being those in Figure 2.

Case 1: should the titre be below the setpoint, re-adjustment as in the mode of regulation by the titrator (already described above in the introduction).

Case 2: should the titre be above the setpoint, no action.

Case 3: should the titre be above the maximum value, a second measurement is taken:

- if this confirms that the titre is too high, an alarm is triggered, and additions are stopped;
- if at the second measurement the titre appears normal, no action is undertaken.

Case 4: should the titre be similar to the maximum value (for example greater than the maximum value - 0.01%), a second measurement is taken:

- if this confirms that the titre is too high, an alarm is triggered and additions are stopped;
- if at the second measurement the titre appears normal, no action is undertaken.

Case 5: should the titre be below the minimum value, a second measurement is taken:

- if this confirms that the titre is too low, an alarm is triggered and the titre is adjusted;
- if at the second measurement the titre appears normal, no action is undertaken.

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The foregoing description relates to the buffer tank 4.

The mixing tank 2 is regulated in terms of H_2O_2 titre (wt%) before each filling of the buffer tank and in terms of fill (%) after each transfer to the buffer tank 4.

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The filling of this tank 2 and its setting to the titre take place in the following manner.

25

First, a mixture is prepared. The level in the tank 2 is maintained between:

- a level $Level_{min} = Level_{max} - Level_{hyst}$ (F1) and
- 30 - a level $Level_{working} = Level_{max} \times 0.95$ (F2),

where 0.95 is a safety factor allowing the H_2O_2 titre to be adjusted without the high level in the mixing tank being exceeded.

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The level in the tank decreases as $Slurry_{mix}$ is transferred from the mixing tank 2 to the buffer tank 4. The level is reset after each fill if the final level in the mixing tank 2 reaches the value $Level_{min}$.

The product in the mixing tank 2 is prepared with Slurry_p ("pure" slurry with no H₂O₂) and 31 wt% hydrogen peroxide.

- 5 This preparation is carried out so as to obtain a level in the mixing tank such that:

$$\text{Level}_{\max} \times 0.95 = (\text{Level}_{\text{initial}} + \text{Level}_{\text{slurry}} + \text{Level}_{\text{H}_2\text{O}_2}) \quad (\text{F3})$$

- 10 The H₂O₂ to be added by filling the mixing tank 2 is calculated using the following formula (F4):

$$\text{Titre}_{\text{H}_2\text{O}_2} = \text{Vol}_{\text{H}_2\text{O}_2, i} \times \rho_{\text{H}_2\text{O}_2, i} \times \text{titre}_{\text{H}_2\text{O}_2, i} / (\text{Vol}_{\text{H}_2\text{O}_2, i} \times \rho_{\text{H}_2\text{O}_2, i} + \text{Vol}_{\text{added slurry}} \times \rho_{\text{slurry}}).$$

- 15 The following formula for calculating the hydrogen peroxide to be added to the mixing tank is then obtained:

$$M_{\text{H}_2\text{O}_2, \text{add}} = M_{\text{slurry}, i} \times \text{Titre}_{\text{H}_2\text{O}_2, \text{targ}} / (\text{Titre}_{\text{H}_2\text{O}_2, i} - \text{Titre}_{\text{H}_2\text{O}_2, \text{targ}}) \quad (\text{F5}).$$

20

In practice, the various filling steps are carried out in the following manner:

1) the line for filling the mixing tank with the slurry is firstly rinsed (delay);

- 25 2) then the tank is filled with the slurry: M_{added slurry} according to the formula (F6):

$$M_{\text{slurry}, \text{add}} = M_{\text{tank}} \times (\text{Level}_{\max} \times 0.95 - \text{Level}_{\text{initial}}) \times \text{Titre}_{\text{H}_2\text{O}_2, \text{targ}} / (\text{Titre}_{\text{H}_2\text{O}_2, i} - \text{Titre}_{\text{H}_2\text{O}_2, \text{targ}}) \quad (\text{F6});$$

- 30 3) next, the line for filling the mixing tank with DIW is rinsed (delay);

4) the valve for filling the mixing tank is then rinsed with DIW (delay);

5) next, the tank is filled with H₂O₂ (M_{H₂O₂, add})

where:

- 35 M_{H₂O₂, add} = M_{tank} × (Level_{max} × 0.95 - Level_{initial} × Titre_{pureH₂O₂} / Titre_{H₂O₂}) (F7);

6) waiting while the mixing tank homogenizes (waiting time = Time_{additions/analysis});

7) next, the mixing tank is analysed and its titre

obtained: $\text{Titre}_{\text{H}_2\text{O}_2, \text{meas}}$

- if $\text{Titre}_{\min} \leq \text{Titre}_{\text{H}_2\text{O}_2, \text{meas}} \leq \text{Titre}_{\max}$, validation of the mixing tank - the procedure passes to stage 10)

- if $\text{Titre}_{\text{H}_2\text{O}_2, \text{meas}} \leq \text{Titre}_{\max}$:

5 - carry out another analysis for confirmation ($N_{\text{titration, mix}}$),

 - if confirmation, an alarm is triggered and a request for operator intervention is generated,

- if $\text{Titre}_{\text{H}_2\text{O}_2, \text{meas}} < \text{Titre}_{\min}$, a titre is adjusted and

10 then the procedure passes to stage 8):

 - check that $\text{Titre}_{\text{H}_2\text{O}_2, \text{targ}} - \text{Titre}_{\text{H}_2\text{O}_2, \text{meas}} < \text{Diff}_{\text{mix}}$ (where Diff_{mix} is the maximum difference in the case of the mixing tank between the last determination of the H_2O_2 titre and the new one),

15 - carry out another determination for confirmation ($N_{\text{titration, mix}}$);

8) the titre is then adjusted, the adjustment steps being the following:

20 • calculation of the H_2O_2 volume to be added using formula (F8),

- H_2O_2 addition for adjustment (as a result of the decrease in the H_2O_2 titre) and

- waiting for homogenization of the mixing tank (waiting time = $\text{Time}_{\text{additions/analysis}}$);

25 9) the mixing tank is analysed in order to confirm that the titre is within specification; and

10) there is then a wait for a demand to fill the buffer tank.

30 The titre of the tank 2 is regulated in the following manner. In fact, the same calculating method is used to calculate the mass of hydrogen peroxide to be added to the mixing tank 2 in order to regulate the titre:

$$M_{\text{H}_2\text{O}_2, \text{add}} = M_{\text{slurry, i}} \times (\text{Titre}_{\text{H}_2\text{O}_2, \text{targ}} - \text{Titre}_{\text{H}_2\text{O}_2, \text{meas}}) / (\text{Titre}_{\text{H}_2\text{O}_2, \text{i}} - \text{Titre}_{\text{H}_2\text{O}_2, \text{targ}}) \quad (\text{F8})$$

35

The successive steps are then the following:

1) Analysis of the mixing tank. Hence the titre obtained: $\text{Titre}_{\text{H}_2\text{O}_2, \text{targ}}$

- if $\text{Titre}_{\min} \leq \text{Titre}_{\text{H}_2\text{O}_2, \text{meas}} \leq \text{Titre}_{\max}$, then

validation of the mixing tank, and the procedure passes to step 10)

- if, $\text{Titre}_{\text{H}_2\text{O}_2, \text{meas}} > \text{Titre}_{\text{max}}$:
 - carry out another analysis for confirmation
- 5 ($N_{\text{titration, mix}}$)
 - if confirmation, alarm and request intervention by an operator,
- if $\text{Titre}_{\text{H}_2\text{O}_2, \text{meas}} < \text{Titre}_{\text{min}}$, the titre is adjusted and the procedure passes to step 8):
- 10 - then check that $\text{Titre}_{\text{H}_2\text{O}_2, \text{targ}} - \text{Titre}_{\text{H}_2\text{O}_2, \text{meas}} < \text{Diff}_{\text{mix}}$ (where Diff_{mix} is the maximum difference for the mixing tank between the last determination of the H_2O_2 titre and the new one),
 - carry out another analysis for confirmation
- 15 ($N_{\text{titration, mix}}$);
- 2) adjustment of the titre:
 - calculation of the H_2O_2 volume to be added using formula (F8),
 - H_2O_2 addition for adjustment (as a result of the
 - 20 decrease in the H_2O_2 titre),
 - waiting for the mixing tank to homogenize (waiting time = $\text{Time}_{\text{additions/analysis}}$);
 - 3) analysis of the mixing tank in order to confirm that the titre is within specification; and
 - 25 4) waiting for a request to fill the buffer tank.

The buffer tank 4 is, for its part, constantly regulated in terms of H_2O_2 titre (wt%) and in terms of filling (%).

30

The level in the tank is maintained between:

- a level: $\text{Level}_{\text{min, i}} = \text{Level}_{\text{max}} - \text{Level}_{\text{hyst}}$ (F1)

and

- a level: $\text{Level}_{\text{working}} = \text{Level}_{\text{max}} \times 0.95$ (F2)

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where 0.95 is a safety factor that allows the H_2O_2 titre to be adjusted without the high level being exceeded in the mixing tank.

The level in the tank 4 decreases as product is

consumed by the equipment.

It is then filled with $Slurry_m$ which comes from the mixing tank 2, as soon as its level goes below the
5 level $Level_{hyst}$.

The filling steps are carried out as follows:

- 1) request to fill the mixing tank 2;
- 2) - mixing tank 2 not ready: on standby
- 10 - mixing tank 2 ready: proceed to step 3);
- 3) rinsing of the line for filling the buffer tank with $Slurry_m$ and then filling of the buffer tank with $Slurry_m$ until the level $Level_{max} \times 0.95$;
- 4) rinsing of the line for filling the mixing tank
- 15 with DIW (delay).

The formula for regulating the titre in the buffer tank 4, making it possible to calculate the amount of hydrogen peroxide to be added, is the same as in the
20 mixing tank:

$$M_{H_2O_2,add} = M_{slurry,i} \times (Titre_{H_2O_2,targ} - Titre_{H_2O_2,meas}) / (Titre_{H_2O_2,i} - Titre_{H_2O_2,targ}) \quad (F8).$$

The hydrogen peroxide is added to the buffer tank via
25 metering tanks on the product return.

A valve system called a "block and bleed" system is used for adding hydrogen peroxide while preserving the tank from any in-line leaks which would add hydrogen
30 peroxide to the buffer tank when filling the mixing tank with peroxide.

The titre is regulated using the method already explained above.

35 As regards the titration of the mixing tank 2, this takes place in the following manner. The permissible value with respect to the difference between two determinations carried out on the mixing tank depends

on a parameter Deg_{mix} (H_2O_2 degradation coefficient).

The H_2O_2 titre degradation coefficient in the mixing tank 2 itself depends on the stirring in the tank and
5 on the level in the tank.

This is because although the stirring rate in the tank is constant the energy dissipated per unit volume can vary. Consequently, the rate of degradation in the tank
10 depends on its slurry level.

The degradation curve is therefore a power curve (typical of stirring phenomena).

15 It is therefore possible to estimate the H_2O_2 titre reduction in the tank between two determinations:

- mixing tank difference in % = Diff_{mix}
- mixing tank degradation in %/per day = Deg_{mix}

where $\text{Deg}_{\text{mix}} = K_{\text{mix}} \times \text{Level}_{\text{mix tank}}$;

20 - time since last titration in days = $\text{time}_{\text{mix inject}}$
 $\text{Diff}_{\text{mix}} = \text{Deg}_{\text{mix}} \times \text{Time}_{\text{mix inject}}$.

If a determination of the titre indicates that the titre is too low in the mixing tank 2 ($\text{Titre}_{\text{H}_2\text{O}_2, \text{targ}} -$
25 $\text{Titre}_{\text{H}_2\text{O}_2, \text{meas}} < \text{Diff}_{\text{mix}}$), the system triggers a titre readjustment by H_2O_2 addition.

If a determination indicates that the titre is too high in the mixing tank, the system triggers, after
30 successive confirmation, a "mixing tank titre too high" alarm which disappears when the titre becomes normal again.

Another determination carried out on the tank is
35 performed after a $\text{Time}_{\text{inter-analysis}}$ which is calculated as follows:

$$\text{Time}_{\text{inter-analysis}} = \text{Diff}_{\text{mix}} / \text{Deg}_{\text{mix}}.$$

If there is a titration alarm:

During determination of the titre, if the value is such that $\text{Titre}_{\text{H}_2\text{O}_2, \text{targ}} - \text{Titre}_{\text{H}_2\text{O}_2, \text{meas}} > \text{Diff}_{\text{mix}}$, the system triggers (after $N_{\text{titration, mix}}$ successive confirmations) an alarm and requests the intervention by an operator.

5

A titration error with regard to the mixing tank must not stop the system - it must only generate a minor defect (for H hours, a parameter that can be modified) and then a major defect after H hours if there has been
10 no intervention by the operator.

The H_2O_2 additions are made using a system of containers which is filled with product, with venting to atmospheric pressure, followed by pressurization in
15 order to fill one of the two tanks (buffer tank or mixing tank).

This arrangement illustrated in Figure 5 consists of 3 successive containers 20, 22, 24 of volume known to
20 within one millilitre:

- a first container 20 of volume about $V1 = 100 \text{ ml}$, known precisely;
- a second container 22 of volume about $V2 = 900 \text{ ml}$, known precisely;
- 25 - a third container 24 of volume about $V3 = 9000 \text{ ml}$, known precisely.

Example of use in the case of an 11.3 volume of H_2O_2 :

- filling of the containers;
- 30 - draining down to the 10 000 millilitre level ($V1 + V2 + V3$);
- filling of the containers;
- draining down to the 1000 millilitre level ($V1 + V2$);
- 35 - filling of the containers;
- draining down to the 100 millilitre level ($V1$);
- filling of the containers;
- draining down to the 100 millilitre level ($V1$);
- filling of the containers; and

- draining down to the 100 millilitre level (V1);

In fact, the volumes V1, V2 and V3 are not precise multiples of one hundred millilitres - the program of
5 the controller 10 takes this into account when calculating the doses to be added.

In Figure 5, the references 24 and 26 denote valves on a pressurization line and a venting line, respectively.
10 The valves 32 and 34 are valves for rapid addition and slow addition respectively, (via a calibrated orifice). The product is then sent into the tank 2 (valve 36) or the tank 4 (via valves 38 and 40) or else to a draining line via a valve 42.

15 The regulating method according to the invention applies especially to controlling the titre of a chemical solution for polishing semiconductor substrates.

20 A regulating system according to the invention therefore delivers a polishing product to delivery means. This product is then delivered to a substrate polishing unit.

CLAIMS

1. Method for regulating the titre of a solution, in which a predetermined amount of a product contained in the solution is added to the solution according to a time interval, called the addition interval, proportional to the product of the delayral degradation coefficient D of the said product in solution and the total volume V_t of the solution at the time of the addition.
2. Method according to Claim 1, in which, after each addition of product, the time interval before the next injection is calculated.
3. Method according to Claim 2, in which, after a certain period of time less than the addition interval, the total volume of the solution is measured.
4. Method according to Claim 3, in which, if the total volume has decreased, a new addition time is calculated.
5. Method according to one of Claims 1 to 4, the addition interval being equal to $K \times D \times V_t$, where K is a coefficient that depends on the solution stirring speed and on the geometrical characteristics of a container containing the said solution.
6. Method according to one of the preceding claims, in which the degradation coefficient of the said product in solution is measured beforehand according to the degree of filling of a container with the said solution and/or the stirring rate in the said container.
7. Method according to one of Claims 1 to 6, which furthermore includes a determination of the titre of

the solution by an electrode titrator.

8. Method according to Claim 7, which includes the triggering of an alarm when the titre measured by the electrode titrator is below a predetermined minimum value or is above a predetermined maximum value.

9. Method according to Claim 8, in which, before the alarm is triggered, at least two successive measurements are made by the electrode titrator when a measurement by this titrator is below the said maximum value.

10. Method according to one of Claims 1 to 9, in which the solution is a solution for polishing semiconductor substrates.

11. Process for polishing semiconductor substrates, comprising the use of a solution regulated by a method according to one of Claims 1 to 10.

12. Device for controlling the regulation of the titre of a solution, this solution containing a product, comprising means (10) for controlling the injection of a predetermined amount of the said product into the said solution according to a time interval, called the addition interval, proportional to the product of the delayral degradation coefficient D of the said product in solution and the total volume V_t of the solution at the time of the addition.

13. Device according to Claim 12, which furthermore includes means (10) for determining, after each addition of product, the time interval before the next injection.

14. System for regulating the titre of a solution, which comprises a device according to either of Claims 12 and 13 and means for determining a fill

volume in a container containing the said solution.

15. System according to Claim 14, the means for determining a fill volume being analogue means.

16. Regulating system according to Claim 14 or 15, which furthermore includes an electrode titration device.

17. System for producing a chemical solution, comprising:

- a regulating system according to one of Claims 14 to 16;
- means (8) for delivering the said solution.

18. System for producing semiconductor substrates, which includes a unit for polishing the said substrates and a system for producing a chemical polishing solution according to Claim 17.