Retreatment of silicon slurry by membrane processes

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ABSTRACT

The purpose of the present study is to develop a process to regenerate the polish liquid used in Chemical and Mechanical Polishing (CMP), called "slurry", and more specifically Silicon CMP slurry. Physico-chemical analyses show a considerable dilution of slurry through washing waters used in polishing. Thus, this effluent has been characterised for a better identification of the deviations from the slurry of reference (Point Of Use). Hence, the principle is to regenerate this effluent by membrane processes. The ultrafiltration results obtained at laboratory scale have led to the development of an industrial prototype. An optimal utilisation of this treatment allows completing a two-step process: the reconcentration by ultrafiltration and a chemical adjustment by addition of concentrated slurry. A stable behaviour of the slurry at the different steps of the process has been observed. Polishing results are similar with retreated and POU slurries. Furthermore, the functioning at industrial scale permits to maintain the performances obtained on the laboratory pilot.

1. Introduction

The purpose of CMP (Chemical and Mechanical Polishing) is to transform the wafer surface to be polished by a chemical action, then to remove this modified layer by a mechanical action [1,2]. The cost of this process is determined by the cost of consumables [3,4] particularly the polish liquid, the slurry [5–7]. A slurry consists of an abrasive, normally silica, alumina or ceria, an aqueous medium that facilitates the suspension of particles and in certain application an oxidizing agent [3,8,9]. Each CMP application has its own specific slurry. There are two main types of slurry used to flatten a surface layer. The first type of slurry is basic with a pH between 10 and 11, it permits to polish both silicon and silicon dioxide. The second one

is acid combined to an oxidizing agent permits to polish the layer by passivating the metal, then by dissolving the metallic film thus formed.

Many studies aim to reduce the cost of these consumables [1]. Researches [10] have demonstrated that 90% of slurry is not degraded during CMP, therefore, the possibility of recycling the used slurry has been considered. However, the important amounts of deionised water used to wash the wafers during the polishing process raise several drawbacks. The abrasive concentration of the effluent after polishing is reduced and it does not allow obtaining the same quality of polishing. Those large amounts of effluent implie considerable retreatment costs.

Two groups of processes have been classified enabling to reuse only the abrasive or the recuperated slurry after polishing. The first group aims to perform a rough pretreatment of the effluent then to readjust it by injection of concentrated slurry and/or adding different chemical components [6,11,12]. This pretreatment consists of a single filter to remove any debris which can also be associated to a cyclone to obtain a particular particle size. The control of those additions does not consider the concentration variations of the collected slurry involving concentration variations of retreated slurry. Bibby et al. show that results are similar to those obtained with the slurry of reference with a saving of slurry at about 80% [1]. These different methods are applied for the oxide slurry with vast specifications on CMP parameters, in particular concerning defectivity.

The second group applies ultrafiltration process for different purposes. Corlett and Roberson employ ultrafiltration with

important concentration factors for the separation of solid and liquid phases [13]. Thus, the permeate is used for CMP rinsing waters and the solid is dispatched for other less restrictive CMP usages. Ndiaye et al. have studied the possibility to use polysulfone hollow fibers to concentrate liquid waste mainly composed of slurry to reduce the volume of waste sent to Municipal Wastewater Treatment Plant [14]. Chang et al. employ a coupled UF/RO in order to reuse an oxide slurry [15]. The mounted device aims to recuperate silica particles by ultrafiltration and the pH buffering agent by reverse osmosis. The reverse osmosis permeate is used as deionised water. However, a KOH chemical adjustment and an addition of new slurry can be done if the pH of the retreated effluent or the silica concentration does not comply with standards. The results of CMP with recycled slurry as well as the nature of the membranes employed are not mentioned.

The purpose of this study is to develop a reliable and adaptable process to reuse slurries in order to reduce cost and environmental impact due to the release of fine particles. The results are based on a reliable and relevant characterization. They are given at both laboratory and industrial scale. Evidently, a comparison of CMP performances, as validation of steps for the reused slurry employed, is shown.

2. Material and methods

2.1. Slurry characterization

This work is about the retreatment of slurry used for the polishing of silicon wafers. In this study the silica particles whose size is between 40 and 80 nm are spread in a basic medium, a colloidal suspension where silica is amorphous. The silica concentration is about 2.2% (wt.%) prepared from concentrated slurry called "Con", diluted 20 times with deionised water. This slurry will be called Point Of Use (POU) and feeds the polisher (Fig. 1).

The slurry is characterized at different steps:

- before the developed process: Concentrated slurry (Con), Point of use (POU) and Collected (Col) (Fig. 1),
- after the developed process: re-concentrated (Rec), after adjustment (Adj) and after post-filtration or retreated slurry (Ret) (Fig. 2b).

The pH, the conductivity and the turbidity were measured directly from the slurry sample. The measurement on dry extract was achieved by accurate weighting on a 200 g of slurry. After 30 h at 110 °C in the oven, the remaining solid was weighted over again
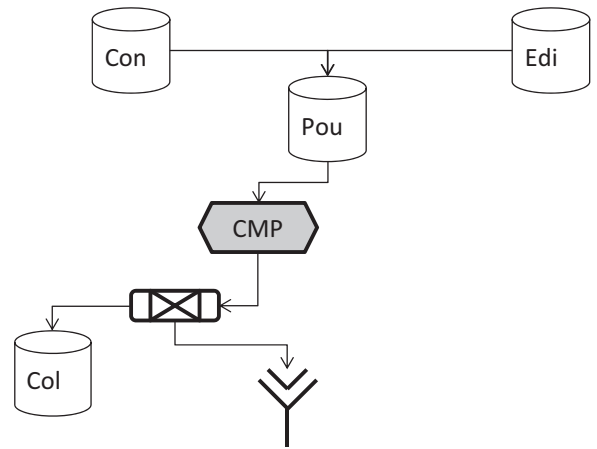

Fig. 1. Different types of slurry before treatment.

and the value of dry extract corresponds to the solid weight related to the total weight. In this study the solid weight is assimilated to the silica weight due to the low conductivity of the sample. For this slurry, a linear calibration of silica concentration according to turbidity has been drawn in order to control the re-concentration of slurry by measuring turbidity which is easier and quicker to run at industrial level [13,14]. This calibration was done for a constant particle size. The particle distribution done by a ZetaSizer Nano-S Granulometeris given in number and volume in order to evaluate the presence of agglomerates. The range of particle measured by this device is from 0.6 nm to 6 μm. This measurement was measured on a sample without previous dilution to avoid any modification of the value since dilution has an effect on agglomeration and on the size of particles in suspension.

The adjustment of the retreated slurry was done by addition of concentrated slurry "Con", its turbidity is 20 times superior to POU slurry. The amount of slurry to be added is determined by the dissolved compounds or salts of the slurry knowing that the amount of silica is the same than the slurry POU. The concentration variation of dissolved chemical compounds is a function of the slurry dilution factor collected at CMP waste which is not modified by the ultrafiltration step since salts are not retained. An R ratio allows quantifying these dissolved compounds; the R value corresponds to the ratio of dissolved compounds in the retreated slurry compared to the same studied in the POU slurry. Technically, it is assimilated as a dissolved chemical concentration. This concentration of reconcentrated slurry, called Rec is equivalent to that of the
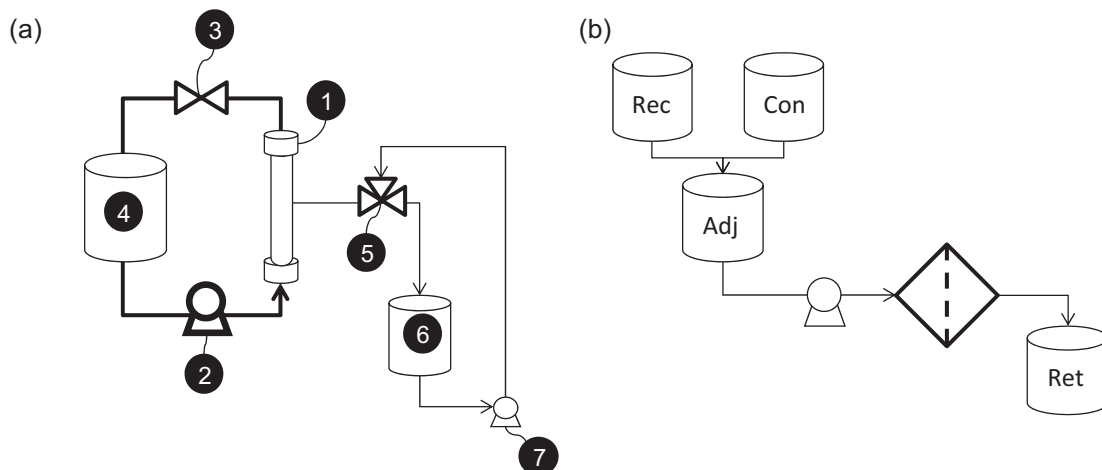

Fig. 2. Laboratory ultrafiltration plant (a) and different types of slurry after treatment (b).

1: CMP Machine

2, 6: diverters valve controlled by turbidity

3: tank of collected slurry

4, 6, 11, 14: pump

5: filter, membrane barrier

8: UF membrane

9: reconcentration loop

10: tank of retreated slurry

12: post filtration 1μm
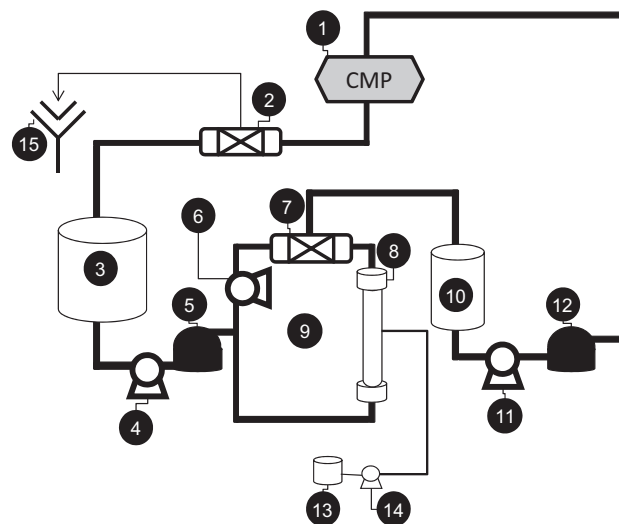
13: permeate tank

15: neutralization plant

Fig. 3. Industrial plant.

collected slurry called Col. This equivalency is due to ultrafiltration properties which do not retain dissolved salts and small stabilizer type molecules. This concentration of the slurry Rec is obtained by measuring the turbidity of the collected slurry where the dilution factor of dissolved compounds is the same for silica. The volume of concentrated slurry to be added is determined by the concentration of collected slurry and by the ratio of dissolved chemicals required. Therefore, it results in the concentration factor to be applied for the ultrafiltration step. The retreated slurry, ready to be sent to the polisher is called Ret. The only difference between this slurry and the adjusted slurry, "Adj", is the passage through the post filtration step (Fig. 2b).

2.2. Laboratory pilot

The feasibility of the re-concentration process was tested on an ultrafiltration pilot (Fig. 2a). It consists of a 100 L (4) tank of concentrate, and one of permeate, 50 L (6). The centrifugal pump (2) supplies the membrane module (1) from the concentrate tank (flow rate: 5 m³ h⁻¹). The permeate can be used to backwash the membrane module using a pump (7) providing a flow of 500 L h⁻¹. The rates of these two pumps are controlled and are measured by flow meters. Pressure gauges to measure the pressure on the two fluids and a valve at the exit of the membrane (3) are used to determine the TMP (transmembrane pressure). The laboratory pilot is equipped with a polysulfone hollow fiber module (1 m², permeability = 200 L h⁻¹ m⁻² bar⁻¹, MWCO = 100 kDa). The tests were performed with open loop at constant volume and with TMP of 0.3 bar. The feed rate is set at about 3 m³ h⁻¹ and backwashes are completed at the end of filtration. Backwashes were carried out with the permeate at a transmembrane pressure of 1 bar. The permeability of the module is verified to assess the membrane regeneration performances with time and to complete a new backwash if necessary. Reconcentrated slurry, called "Rec", is adjusted with concentrated slurry, called "Con", and is post filtered before use in CMP (Fig. 2b). Post filtration is carried out on a pilot with an air pump and a filter cartridge with a cut-off of 1 μm (polypropylene).

2.3. Industrial prototype

Apart from CMP machine (1), a first diverter valve (2), restricted to turbidity allows the recovery of an effluent more concentrated in silica. The collected effluent comes into a 1 m³ tank (3) then dispatched to the industrial prototype (Fig. 3). This one was set up to

perform large-scale tests. This operation differs from the one on laboratory (discontinuous flow operation with open loop) with a re-concentration occurring in a loop (9) to continuously provide a retreated effluent. This ultrafiltration pilot is a REI model from the AQUASOURCE Company. This pilot was modified by including a diverter valve (7) controlled by turbidity measurement. The collected slurry is sent to the re-concentration loop (9) by a pump (4). A filter (5) is installed to remove any debris that may damage the module. Then a recirculation pump (6) allows the re-concentration in the membrane loop (8). The silica concentration in the effluent is measured on line in the loop using a turbidity meter (TURB 02, Endress Hauser, sensor CUS 31). This system allows, through a valve restricted to turbidity (7), the recovery of slurry reprocessed at the desired concentration. The re-concentrated slurry is sent to a 200 L tank (10) by mixing it with the concentrated slurry before adjustment. The filtration area is 7 m² for one hollow fiber module and the operating conditions are similar to those of the laboratory pilot. The membranes are cellulose acetate hollow fibers with an internal diameter equal to 1.4 mm, a water permeability of 200 L h⁻¹ m⁻² bar⁻¹ and a MWCO of 100 kDa. The adjustment with the concentrated slurry is made in the mixing tank and the amount is determined by the ratio of dissolved chemical compounds described in Section 2.1. A step of post filtration at 1 μm (12) is performed to remove any residue that may damage the wafers [16,17]. Then the re-treated slurry can supply CMP polisher through a pressurized loop with continuous recirculation and extraction towards the polisher identical to the industrial ones. A recovery tank of permeate (13) and its extraction pump (14) enable to do the backwashes at the beginning and at the end of the treatment.

In general, the industrial prototype includes a modified ultrafiltration pilot and other elements permitting the retreatment of the slurry collected from the line to the CMP polisher of retreated slurry.

2.4. CMP and test conditions

CMP equipment consists of a rotating plate covered with a pad (polishing material). The pad keeps the abrasive grains from the slurry sent at a controlled flow. The polishing plate is held by a plate holder. The holder and the plate are set in rotation and animated by an oscillating or sweeping movement (Fig. 4). During polishing, the force applied to the holder is transmitted to the wafer that is in contact with the pad soaked in slurry. The combination of these chemical and mechanical actions allows the wafer planarization.
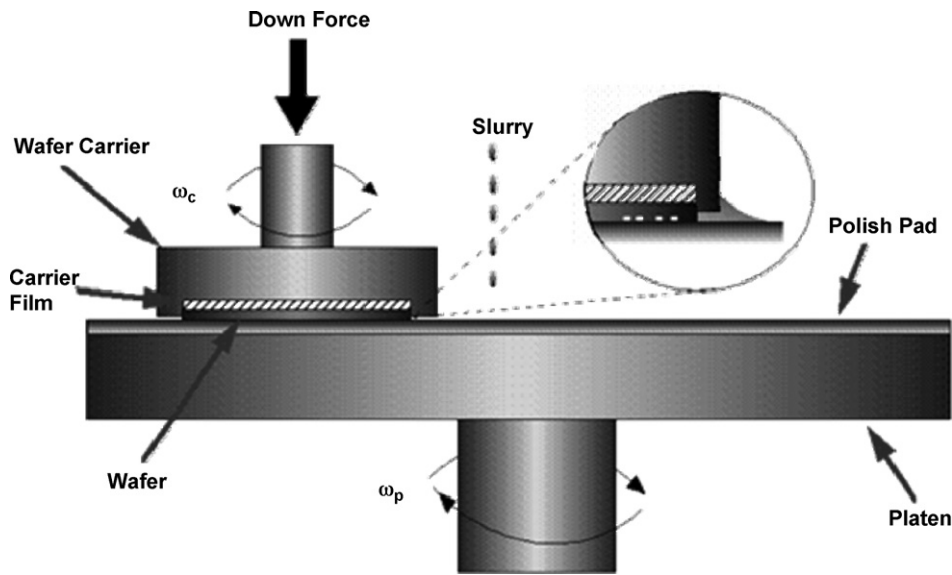
Fig. 4. CMP apparatus.

Standard silicon polishing process occurs in two steps: rough polishing and finishing polishing. The polishing basic sequence includes (i) conditioning of the plate at the beginning of the process, (ii) polishing, (iii) a rinse period of 2 min and (iv) the pad brushing every two polishing sequences. This study concerns the rough polishing slurry whose function is essentially to remove silicon. The rough polishing time is set in intervals from 3–30 min depending on the initial state of the wafer to be treated. The finishing polishing, set at shorter intervals, is designed to improve the wafer surface with minor material removal.

Water rinsing phases produce a significant dilution of the slurry after polishing. In a conventional process, this effluent is dispatched to a pH neutralization step prior to discharging to a Municipal Wastewater Treatment Plant. Those large amounts of polluted effluents entail serious environmental costs.

Rough polishing tests with the retreated slurry are carried out in a production machine with the production conditions described in section 2.4. The polisher is a MECAPOL PRESI 1200, the polishing time tested is 12 min, the polished wafers are 8′ diameter and the process steps are identical to those of production. This device consists of two holders turning on the same pad. Each holder contains three wafers of 8′. The wafers are analyzed after the finishing polishing step for a better compliance of industrial standards. The evaluated parameters of CMP output are material removal or RR (Removal Rate), the uniformity of this removal or TTV (Total Thickness Variation), defectiveness and surface roughness or Haze. These criteria are measured on the production units after a finishing polishing step. A specific procedure has been developed to obtain a significant influence of the impact of a retreated slurry on these parameters. Two batches of 60 wafers were prepared, one for the POU slurry and another for the retreated slurry. For each one of these batches, the wafers were divided into three categories depending on the quality of their surface (Table 1). Defects are analyzed through an optical method for analyzing light scattering with SP1-TBI model supplied by KLA-Tencor. There are two sorts of defects: restricted defects and extended defects. LPD (Light Point Defect) corresponds to restricted defects usually associated with particles deposited on the wafer and LPD-N corresponds to those due to the crystalline structure of the wafer or identified as such. They are measured for different sizes of resolution down to 0.09 μm for the smallest one. The category "1" contains the wafer with fewer defects. Two types of extended defects may be present on a wafer: scratches characterized by their number and total length within a wafer and areas ($\geq$0.7 μm) characterized by their number and total area on a wafer. Clusters of non-classifiable small particles by the device can be assimilated to those types of defects. The surface roughness is indirectly measured by the same device by adding low frequency rays normally diffused to the incident rays. Its measurement is given in ppm according to the number of incident rays sent to the wafer. The Sum Of All Defects (SOA) measurement, at a given particle size permitting to rapidly evaluate the quality of polishing in view of the different defaults, is regularly monitored. The wafers of the tests were measured before and after polishing and the following parameter was calculated:

$$\Delta SOA = SOA_{after\,Polishing} - SOA_{before\,Polishing}$$

The purpose of polishing consists in improving the wafer surface or at least keep the same quality of the wafer, the lower the number of defects, the better the quality of polishing.

Table 1
Wafers classification used for the quality test.

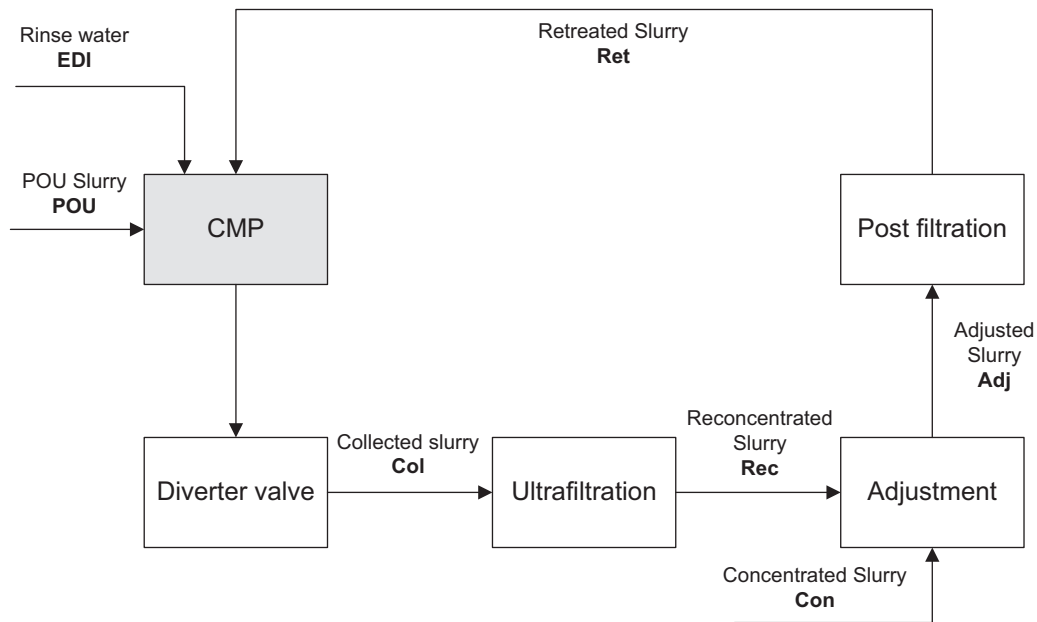| Class	Number of wafers	Criteria				
		Total area	LPD (μm)			LPD-N (μm)
1	36	$\geq$1μm	0.12	0.16	0.2	0.12
2	18	$\leq$10	$\leq$80	$\leq$45	$\leq$25	$\leq$200
3	6	$\leq$10	$\leq$100	$\leq$45	$\leq$25	$\leq$800
		–	$\leq$250	$\leq$210	$\leq$180	$\leq$5000

Fig. 5. Steps of retreatment Process.

3. Results and discussion

3.1. Characterization of slurries reference/collection

This process is thus divided in four major steps: collecting, re-concentration by ultrafiltration, addition of concentrated slurry to adjust the concentrations and post filtration in order to remove any agglomerates (Fig. 5). Though these steps are presented separately, they remain connected and inseparable. The concentration of dissolved compounds of the retreated slurry is determined by the dilution factor (DF) of the collected slurry since ultrafiltration does not concentrate salts. Therefore, a separated collection was implemented to obtain retreated slurry with enough dissolved compounds quantity to meet the CMP requirements. That is why the characteristics of the collected slurry depending on the time of recovery have been studied to determine the optimum slot for the slurry collection.

The silica concentration and silica mass flow of the collected slurry increase during polishing and also increase during the rinse cycle (Fig. 6). A piston flow occurs in the slurry-collecting bowl when a large amount of rinse water is sent. The solid concentration and mass flow of the collected slurry increase throughout the polishing step from 0 to 720 s to reach at the end of polishing the same values for the injected POU slurry. Considering concentration and flow rate, at the end of polishing step the entire volume of rinse water in the collecting bowl was removed to obtain similar slurry to that of POU. Once the rinse cycle begins ($t = 720$ s), the silica concentration decreases abruptly contrary to mass flow rate that still increases for 1 min. From $t = 820$ s, the collected slurry becomes quite diluted and therefore the amount of silica low. Almost 80% of the total amount of recovered slurry is collected during 2 min of the rinse cycle, from 720 s to 820 s. In order to maintain a dissolved chemical ratio above 0.5, a recovery time slot which enables to gather about 85% of the total amount of silica sent to the polisher with a maximum dilution factor of 3 was selected. Thus, the effluent is collected between 360 s and 820 s.

Thus, environmental releases can be reduced in volume, exceeding 30% and also in pollutants with a low slurry concentration.
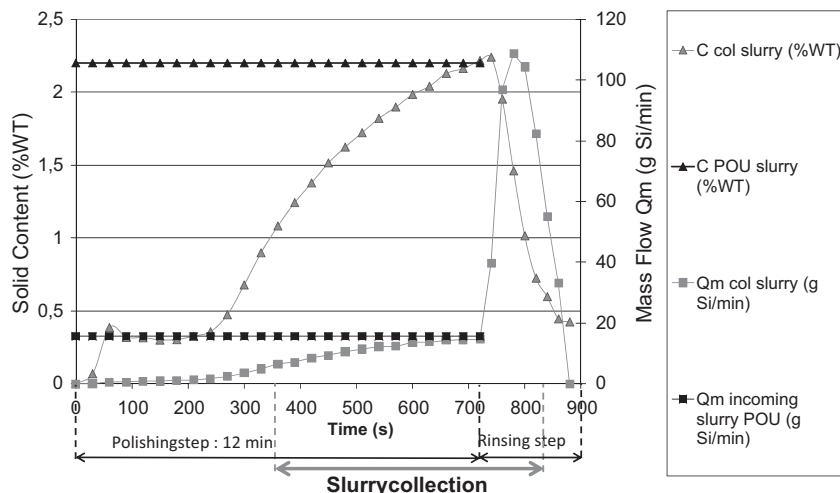

Fig. 6. Variations of Solid Content and mass flow as a function of time [polishing time = 12 min].

Table 2
Slurries characteristics.

Parameter	Col	Rec	Con	Adj	Ret	POU	POU range
Solid contents (% wt)	0.71	1.37	44.0	2.21	**2.20**	**2.2**	2.1–2.3
Turbidity (NTU)	388	673	Out of range	946	886	920	850–950
pH	9.62	9.63	11.09	9.95	9.97	10.31	10.2–10.6
Conductivity (μS cm^{-1})	233.7	248.1	3170	489	382.2	415.6	350–400
$R^{Si}_{analysed\ slurry}$	0.32	0.62	20.0	1.0	1.0	1	
$R^{ch}_{analysed\ slurry}$	0.32	0.32	20.0	0.64	**0.64**	**1.0**	

The physico-chemical analyses prove a good conservation of the slurry properties after polishing with the implementation of a separated collection (Table 2). The dry extract of the collected slurry is 0.71% compared to 2.2% of POU slurry. The pH and conductivity are similar to those of POU slurry with even better stability of the slurry. The granulometry of the collected slurry is also conserved in number and volume (Fig. 7). The slight shifts in granulometry distribution come primarily from concentration difference between the collected slurry (Col) and POU slurry. The granulometry of the slurry is neither altered by polishing nor by dilution of the slurry with rinse water.

3.2. Ratio influence of dissolved chemicals

The influence of R ratio has been evaluated on the characteristics obtained during polishing: RR and TTV. As it was previously mentioned, only R ratio concerning the concentration of dissolved chemical compounds was evaluated. This ratio is always equal to 1 for the silica concentration, which is identical in the recycled slurry and the slurry POU (Table 3). A simple addition of concentrated slurry permits to obtain RR and TTV values within the specifications in several reports reviewed. Since there concentration of the dissolved compounds or salts is not possible with ultrafiltration, dissolved chemicals concentration of the collected slurry reduces all the more the collected slurry is diluted. Tested ratios were 0.55, 0.75 and 1 (Fig. 8). With the increase of the R ratio, it appears an increase in material removal. An R ratio = 0.75 is satisfactory to obtain material removal within the specifications. It appears that TTV is found within the specifications regardless of R ratio value. pH variations, conductivity, turbidity and even dry solids extract have no influence on TTV (Table 3). These parameters increase with R and therefore with the addition of concentrated slurry. Only the
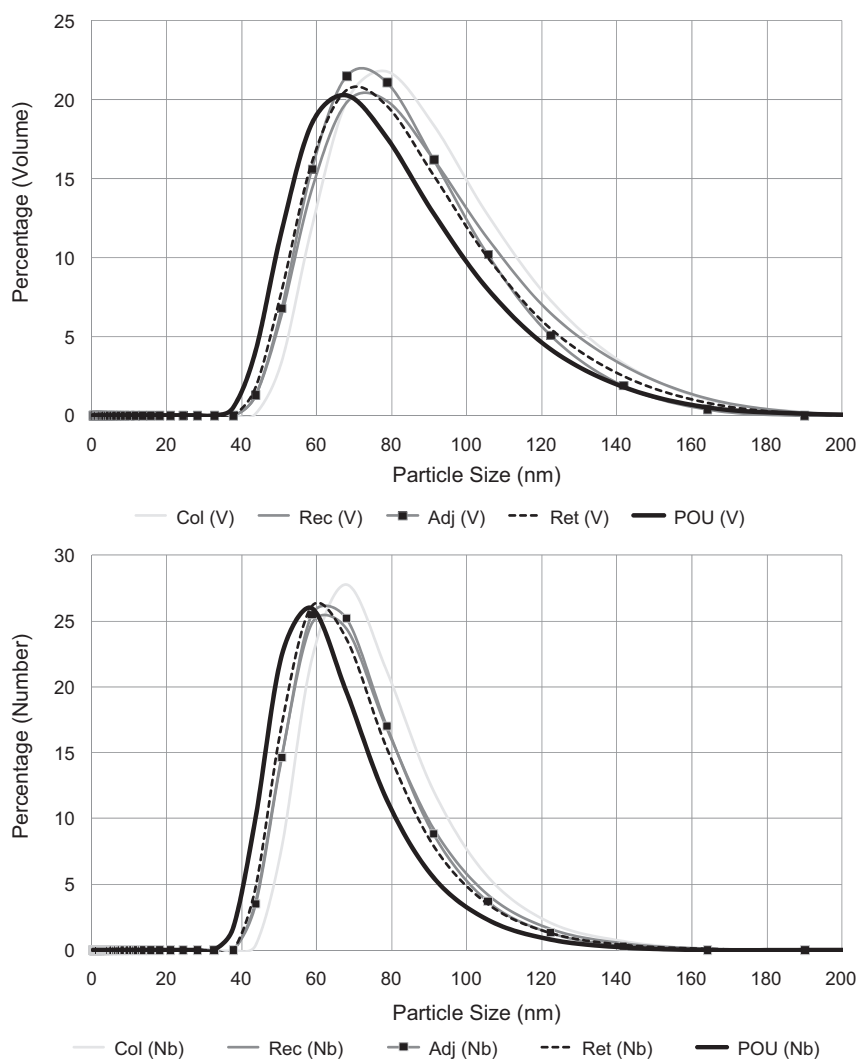

Fig. 7. Slurries particle size distributions.

Table 3
Analyses slurries with different dissolved chemicals ratios.

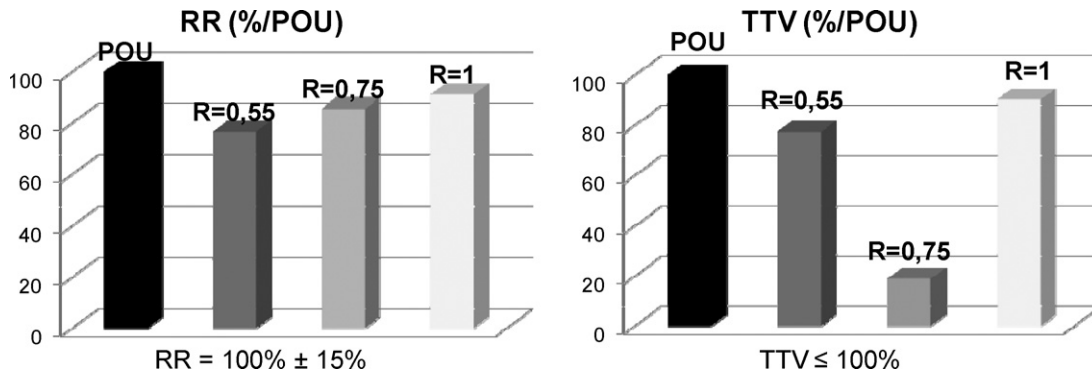| Parameter	POU	Collected	$R = 0.55$	$R = 0.75$	$R = 1$
% added slurry/retretraited			0	1.09%	2.50%
Solid content (% wt)	2.1–2.3	0.88	2.18	2.69	3.51
Turbidity (NTU)	850–950	455	944	1023	1085
pH	10.2–10.6	9.74	9.77	9.97	10.16
Conductivity ($\mu S\,cm^{-1}$)	350–400	295	306	373	520

Fig. 8. RR and TTV variations for different % of added slurry or R [polishing time = 12 min].

ratio conductivity of 0.75 lies within a range of production which seems to improve TTV. Whatever the ratio, the pH is below the range without degradation of the polishing results. Granulometry also remains close to that of POU slurry regardless the ratio R tested (Fig. 9). Only the collected slurry varies faintly due to a silica concentration slightly lower. Granulometry, centred in number and volume, gives evidence the good stability of the slurry.

3.3. Process for reprocessing laboratory

The process aims to re-concentrate the collected slurry by ultrafiltration, keeping the particles larger than 10 nm and adjusting the silica concentration by addition of concentrated slurry to compensate the dilution factor 3 observed (Table 2). This adjustment also enables to increase the concentration of dissolved chemical compounds. For the ultrafiltration step, the permeate flux remains constant depending on time: one hour of filtration around 55 L h^{-1} m^{-2}. This permeate flux obtained only at a TMP = 0.3 bar corresponds to a decrease in permeability of 10% compared to the initial permeability (Fig. 10). Volumic Concentration Factor (VCF) being 2, turbidity is multiplied by 2 between the beginning and the end of filtration step. Conductivity remains constant as well as pH during filtration since salts are not retained by ultrafiltration. The permeate turbidity is close to 0, corroborating the retention of silica particles in the membrane. It appears that a simple water backwash is effective and recovers a permeability close to that of a new membrane for the different tests completed (Fig. 11). The second step aims to re-concentrate by a factor 2 the dissolved compounds and thus obtaining a better stability of the retreated effluent. The amount to be added is thus defined in Section 2.1. The characteristics of the different slurries are discussed in Section 3.4.

3.4. Industrial prototype

The retreatment performances in presence of the re-concentration loop are equivalent to those obtained in batch on the laboratory pilot (Fig. 12). In order to validate the functioning
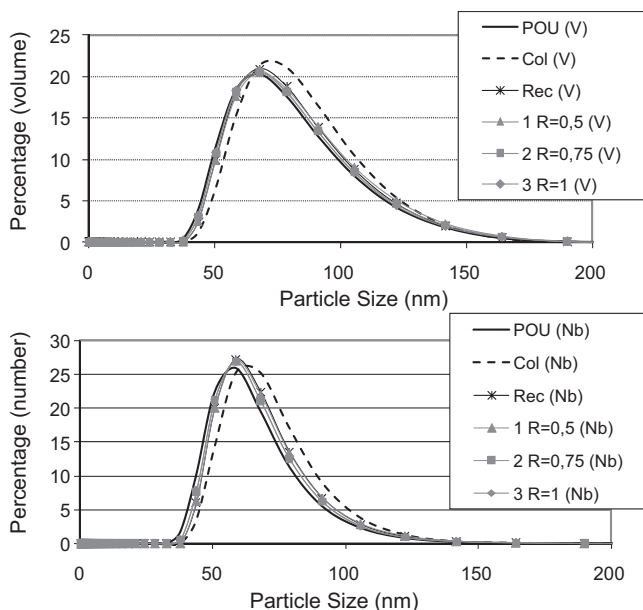

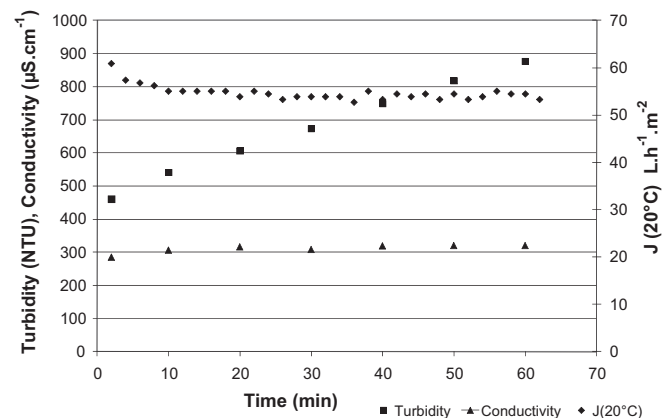**Fig. 9.** Variations of particle size distribution as a function of R.

Fig. 10. Variations of permeate flux, turbidity and conductivity values as a function a time [TPM = 0.3 bar].
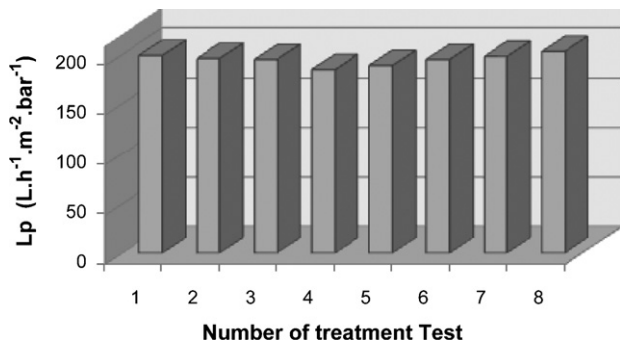
Fig. 11. Variation of the membrane permeability.

of the system with a deconcentrating valve, the experiments were performed for important concentration factors, about 10. To take into account a very large variation of the collected slurry at CMP output, the developed process has to be flexible. Reconcentration through ultrafiltration is divided into two stages: (i) before the permanent filtration step and (ii) the permanent running with production of concentrated slurry at the desired concentration. Before the permanent filtration step, the turbidity increases from about 50 to 850 NTU which is the aimed turbidity. The initial turbidity value of the slurry to be reconcentrated is lower than that of the collected slurry due to the presence of backwash permeate in the filtration loop. The increase of turbidity in the loop results in a decrease of permeate flux. In the second step, once the silica concentration is reached, the production phase can start. Two modes of the prototype operation were tested. For the functioning with continuous opened valve, a percentage of the valve opening was chosen in order to recover at continuous low-flow an effluent with constant concentration. For the operation mode with the valve restricted to turbidity, an opening and closing slot of the valve is programmed according to a range of turbidity. In this second mode, turbidity fluctuations also lead to fluctuations in filtration flow. These fluctuations are caused pulses created by the opening of the valve. The advantage of the second mode, at industrial place, compared to the first one is the independence of the aimed slurry concentration in relation to the concentration of the slurry initially collected.

Concerning the two operating modes; continuous opened valve or valve opening restricted to turbidity, it is possible to re-concentrate the slurry 10 times without a decrease of the permeate flux. Filtration flows, about 60 L h^{-1} m^{-2}, are similar for both operating modes. These flows are also similar to those obtained at laboratory scale. TMP for both operation modes is low, about 0.25 bar. For the prototype as a function of the results, back-washes during the cycle were cancelled and carried out only at the beginning and at the end of retreatment of a volume of 1 m^3 of slurry.

As for the process proposed in laboratory, ultrafiltration is followed by the step of slurry adjustment. The addition of concentrated slurry is performed in an agitation tank as described in Section 2.1. The post filtration phase at 1 μm finishes the retreatment of slurry. The analyses of slurries at the output of different stages of the process were performed for retreatment obtaining polishing results presented in Section 3.5. For the silica concentrations of different slurries, turbidity and solid extract measurements show that reconcentration by 2 through ultrafiltration was well controlled (Table 2) respectively from 388 to 673 NTU and from 0.71% to 1.37%. The adjustment with the concentrated slurry confirms the reliability of this turbidity measurement with a dry extract on the retreated slurry equal to the POU slurry. There is good correlation between the weight of dry extract and turbidity measurement which can be useful to monitor the silica concentration in line during the ultrafiltration treatment. Results at post filtration level, at 1 μm, combined with proper granulometry conservation, are correlative to the good results obtained for defectiveness (Section 3.5). Concerning pH and conductivity measurements, the adjustment with the concentrated slurry enables to increase the pH from 9.6 to almost 10. This pH is slightly below the range but has no negative effect on CMP results. The conductivity of the retreated slurry equal to 382.2 μS cm^{-1} is within the POU slurry range after the stages of adjustment to concentrate slurry and post filtration.

Ultrafiltration does not permit to retain the salts and the ratio R is the same before and after ultrafiltration resulting from the dilution factor of the collected slurry, equal to 0.323. The chemical adjustment step allows doubling this ratio going from 0.323 to 0.636 for the retreated slurry. The slurry granulometry is maintained all along the retreatment process (Fig. 7). Granulometric distributions in number and volume are well centred between 60 and 70 nm regardless of the sample analyzed.
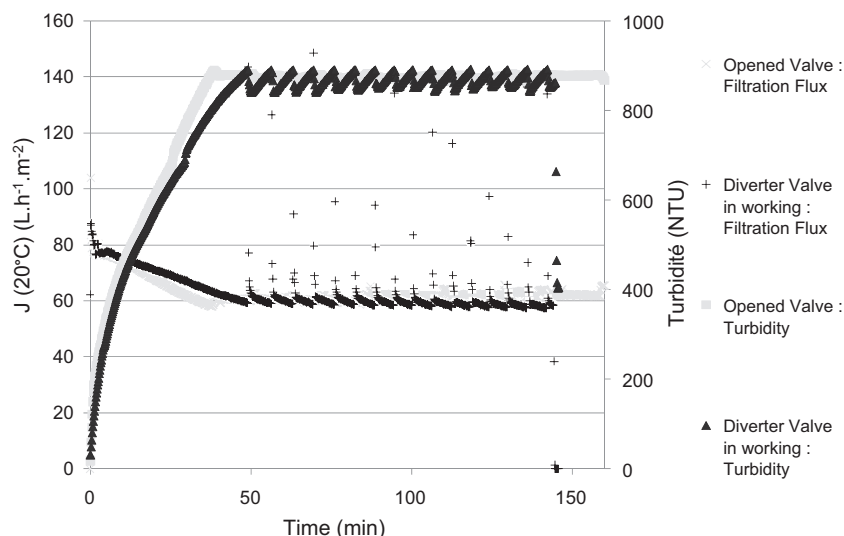

Fig. 12. Influence of the diverter valve on the filtration flux [PTM = 0.25 bar].
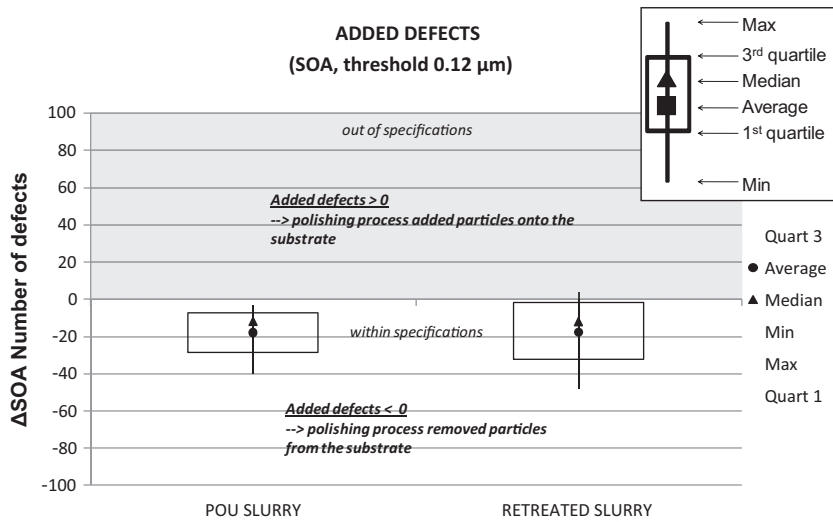
Fig. 13. Comparison of the SOA for retreated and POU slurry for class "1".
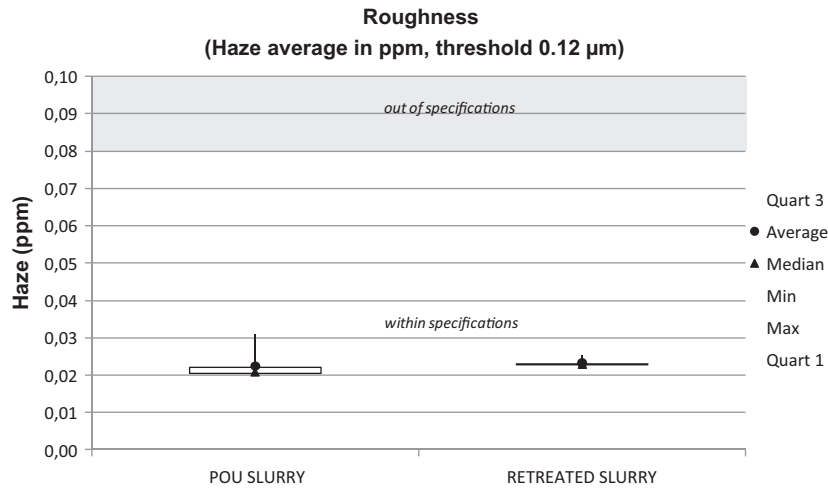

Fig. 14. Comparison of Haze for retreated and POU slurry: class "1".

The absence of aggregates lower than 5 μm gives evidence of the good performance of the slurry in the proposed process. Ultrafiltration, adjustment with concentrated slurry and post filtration steps do not have a negative effect on particle size.

3.5. Results of CMP

Polishing tests with retreated slurry and defectiveness values show a conservation of CMP parameters. Given the RR and TTV
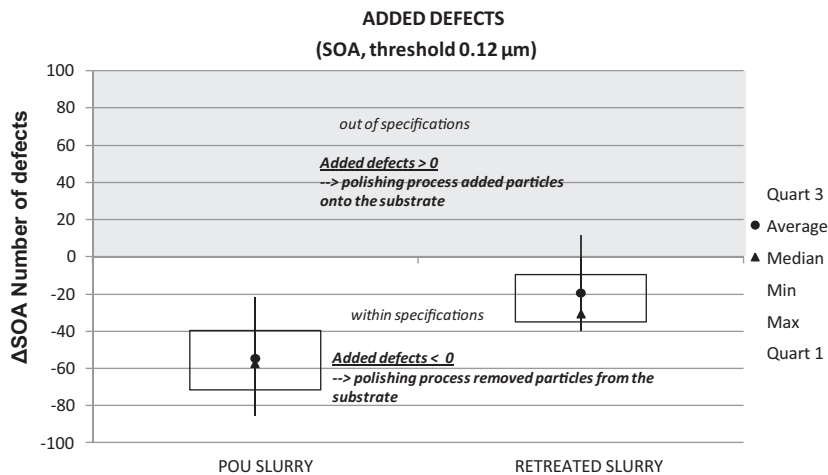

Fig. 15. Comparison of the SOA for retreated and POU slurry for class "2".
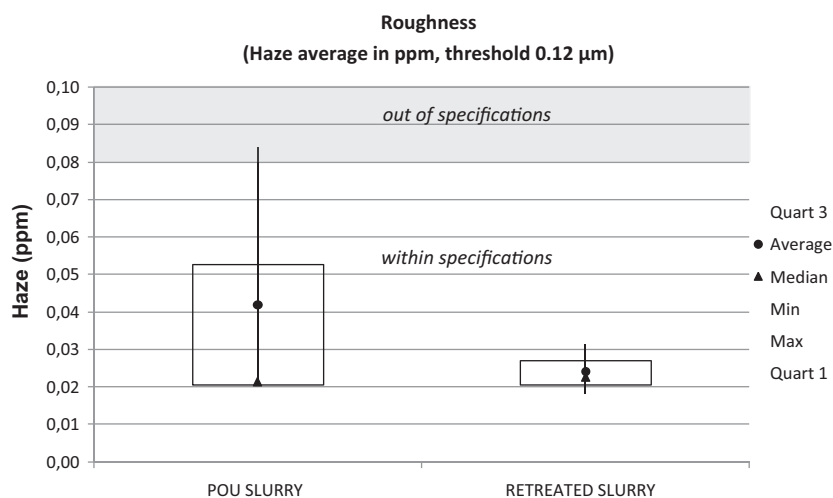
Roughness

(Haze average in ppm, threshold 0.12 μm)

Fig. 16. Comparison of Haze for retreated and POU slurry: class "2".

Table 4

Comparison of different CMP parameters for retreated and POU slurry.

Parameter	Retreated slurry class "1" Relative error/POU (%)
RR (μm min^{-1})	4.7%
TTV (μm min^{-1})	Improved
Added defects: SOA 0.12 μm	1.2%
Haze 0.12 μm	3%

results presented in Fig. 8, it was decided to set a ratio $R = 0.65$. The retreated slurries and slurry POU permit to obtain similar results for the category "1", which is within specifications for the parameters SOA 0.12 μm (Fig. 13) and includes 36 wafers. Measurements of surface roughness, also for category "1", confirm the good quality of polishing with the retreated slurry with a wide range according to specification (Fig. 14). Haze values of 0.12 μm are between 0.02 and 0.03 ppm with a specification limit of 0.08 ppm. Results are reproducible with a low standard deviation and a median almost equal to the average. CMP, RR, TTV, defectiveness and Haze parameters with retreated slurry permit obtaining results within specifications. The relative error according to the POU value given by tests was calculated and remains below 5% regardless of the parameter (Table 4). TTV seems to be improved for the wafer category "1". Results for categories "2" and "3" are within the specifications industrially required without showing a general evolution (Figs. 15 and 16). These good results raise the need for a larger evaluation sample.

4. Conclusions

CMP results obtained for retreated slurry using the developed process showed the possibility to reuse the slurry at an industrial scale. The characterization of the slurry showed a good preservation of the slurry after polishing and collection steps. A separated collection allows the recovery of an effluent diluted by a maximum of 3. The purpose of the developed retreatment is reconcentration by an ultrafiltration step and a final adjustment with a single addition of concentrated slurry. Different R ratios of dissolved compounds compared to POU slurry were tested to evaluate the optimal ratio, to obtain good RR and TTV results. A ratio of 0.65 allows obtaining these parameters within specifications. The feasibility of this process has been proven on a laboratory pilot then confirmed on the industrial prototype. The ultrafiltration permeate flux is close to 60 L h^{-1} m^{-2} for both scales tested, for a small TMP. The experience in many cycles shows a good regeneration of the membrane with simple water backwash. The addition of concentrated slurry permits to multiply by 2 the concentration of dissolved compounds of the retreated slurry in order to obtain a dissolved chemicals relation of 0.65 compared to POU slurry. Given the variations in the turbidity measurement, the step of post filtration appears to be essential in this process. The characteristics of the retreated slurry at the process output are within the range of POU slurry. Granulometry is maintained during the retreatment process with distributions in number and volume close to POU slurry. The defectiveness parameters obtained during this test with the retreated slurry are similar to those obtained with the POU slurry. Defectiveness was evaluated on a significant number of wafers with different levels of defects. The retreatment process industrially developed enables to treat the large volumes required by CMP process. This first study performed for a single reuse of the slurry provides a saving of 40% of slurry. It is expected to perform multiple reuses of the slurry and thus to increase the profitability of the process.

References

[1] T.F.A. Bibby, J.A. Adams, K. Holland, G.A. Krulik, P. Parikh, CMP CoO reduction: slurry reprocessing, Thin Solid Films 308–309 (1997) 538–542.

[2] J. Larsen-Basse, H. Liang, Probable role of abrasion in chemo-mechanical polishing of tungsten, Wear 233–235 (1999) 647–654.

[3] Y. Li, Microelectronic Applications of Chemical mechanical Planarization, Wiley Interscience, New Jersey USA, 2007.

[4] S. Seal, R.L. Opila, K.B. Sundaram, R. Singh, Chemical Mechanical Planarization IV: Proceedings of the International Symposium, The Electrochemical Society, Inc., Pennington, New Jersey, 2003.

[5] A. Philipossian, E. Mitchell, Slurry utilization efficiency studies in chemical mechanical planarization, Jpn. J. Appl. Phys., Part 42 (2003) 7259–7264.

[6] Y.J. Seo, S.W. Park, N.H. Kim, E.G. Chang, W.S. Lee, Chemical mechanical polishing performances by filtering and retreatment of used silica abrasives slurry, Microelectron. Eng. 77 (2005) 358–364.

[7] W.S. Lee, S.Y. Kim, Y.J. Seo, J.K. Lee, An optimization of tungsten plug chemical mechanical polishing (CMP) using different consumables, J. Mater. Sci. 12 (2001) 63–68.

[8] E. Matijevic, S.V. Babu, Colloid aspects of chemical–mechanical planarization, J. Colloid Interface Sci. 320 (2008) 219–237.

[9] P.B. Zantye, A. Kumar, A.K. Sikder, Chemical mechanical planarization for microelectronics applications, Mater. Sci. Eng., R 45 (2004) 89–220.

[10] A. Philipossian, E. Mitchell, Performing mean residence time analysis of CMP processes, Micro 20 (2002) 85–185.

[11] S. Kurisawa, Slurry recycling apparatus and slurry recycling method for chemical–mechanical polishing technique, US Patent 6183352 (2001).

[12] M. Uto, N. Kondo, Grinding slurry recycling apparatus, US Patent 6547961 (2003).
[13] G.L. Corlett, G.A. Roberson Jr., Method and apparatus for recovery of water and slurry abrasives used for chemical and mechanical planarization, US Patent 6096185 (2000).
[14] P.I. Ndiaye, P. Moulin, L. Dominguez, J.C. Millet, F. Charbit, Treatment of silica effluents: ultrafiltration or coagulation–decantation, J. Hazard. Mater. 116 (2004) 75–81.
[15] J.H. Chang, K.J. Lee, J.G. Park, Slurry recycling system and method for CMP apparatus, US Patent 6866784 (2005).
[16] Y.-J. Seo, S.-Y. Kim, Y.-O. Choi, Y.-T. Oh, W.-S. Lee, Effects of slurry filter size on the chemical mechanical polishing (CMP) defect density, Mater. Lett. 58 (2004) 2091–2095.
[17] Y.-J. Seo, S.-Y. Kim, W.-S. Lee, Advantages of point of use (POU) slurry filter and high spray method for reduction of CMP process defects, Microelectron. Eng. 70 (2003) 1–6.