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# 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

*Abbreviations:* Adj, adjusted slurry; Col, collected slurry; Con, concentrated slurry; POU, point of use slurry; Rec, reconcentrated slurry; Ret, retreated slurry; CMP, chemical and mechanical polishing; DF, dilution factor; LPD, light point defect; MWCO, molecular weight cut off; NTU, nephelometric turbidity unit; POU, point of use slurry; R or $R^{ch}$, ratio of dissolved chemical compounds within the slurry to be recycled on the concentrated chemical compounds dissolved in the POU slurry; RO, reverse osmosis; RR, removal rate; $R^{Si}$, ratio of silica concentration within the slurry to be recycled on the silica concentration in the POU slurry. This ratio is always equal to 1 when referring to retreated slurry; SOA, sum of all defects; TMP, trans membrane pressure; TTV, total thickness variation; UF, ultrafiltration; VCF, volumic concentration factor.

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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

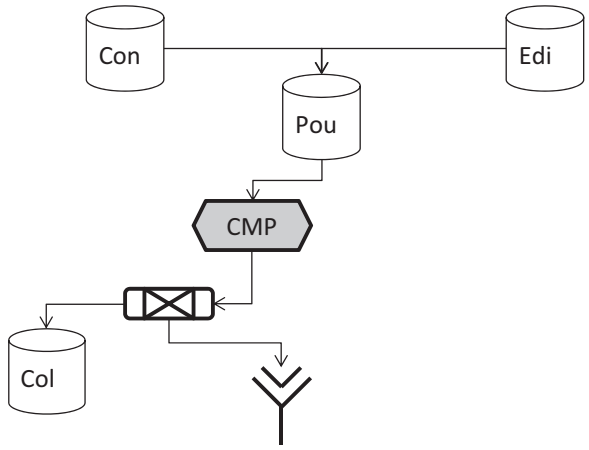


**Fig. 1.** Different types of slurry before treatment.

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

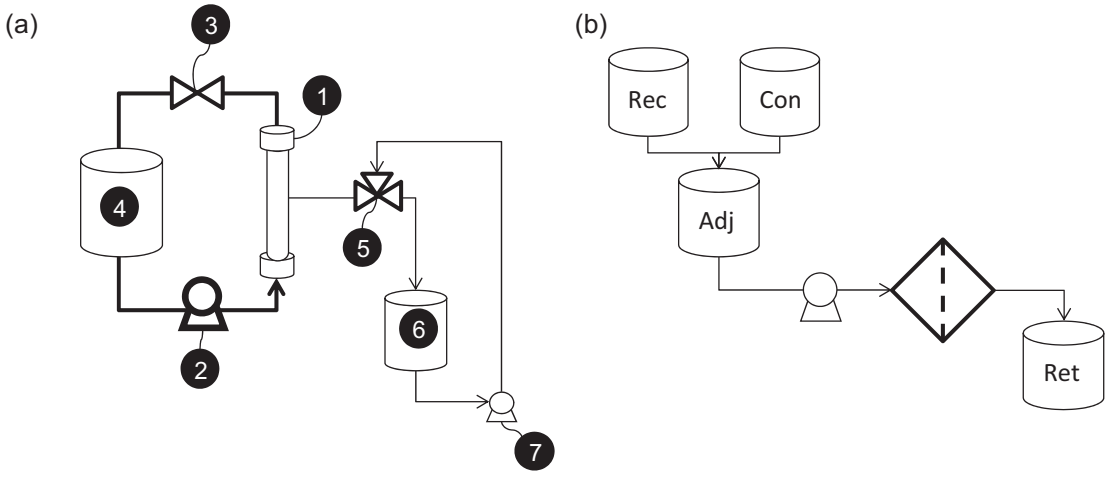


**Fig. 2.** Laboratory ultrafiltration plant (a) and different types of slurry after treatment (b).