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Recycling a slurry for reuse in chemical mechanical planarization of tungsten wafer: Effect of chemical adjustments and comparison between static and dynamic experiments

F. Testa [a,b], C. Coetsier [a,1], E. Carretier [a], M. Ennahali [b], B. Laborie [b], P. Moulin [a,*]

[a] Aix Marseille Université, Laboratoire de Mécanique, Modélisation et Procédés Propres (M2P2 – UMR-CNRS 7340), Europôle de l'Arbois, BP. 80, Bâtiment Laennec, Hall C, 13545 Aix en Provence Cedex 04, France
[b] KEMESYS, 125 ZA Verdalai, 13790 Peynier, France

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ABSTRACT

Recycling abrasive slurry that has been used in chemical mechanical polishing (CMP) is one of the options for reducing the cost of manufacturing microchip processors. We use ultrafiltration which is a method of choice to recycle silica (SiO_2)-based slurry. Taking into account that the chemical composition of abrasive slurry plays an important role in tungsten CMP (W-CMP), chemical adjustments have to be made so that the concentrated after used slurry can be reused. In this study, we investigate the effects of chemical additives (iron catalyst, oxalic acid as complexing agent and surfactants as stabilizers) in slurry that has been retreated by ultrafiltration. Experiments are conducted both under static and dynamic conditions and results are compared to better understand the effect of chemical adjustments on the main performances of W-CMP. An optimal chemical adjustment is proposed through a design of experiments evaluation to obtain a concentrated after used and chemically adjust slurry comparable to the operational point of use slurry.

1. Introduction

Chemical mechanical polishing (CMP) is a process that is used to planarize wafers for microelectronic applications. CMP involves polishing the metallic surface of the wafer with a pad while adding slurry. Polishing slurry is one of the most costly consumables in the CMP process. For this reason, the recycling of CMP slurries has become a new challenge for the microelectronic industry and has been investigated for the past 12 years [1–4].

Slurries usually consist of an abrasive material such as silica, alumina or ceria and an aqueous medium that facilitates the suspension of the abrasive particles [5,6]. In the case of tungsten polishing (W-CMP), the aqueous medium contains a strong oxidizer (hydrogen peroxide) and an iron catalyst such as ferric nitrate [7]. The removal of the tungsten layer is achieved by chemical as well as mechanical action. The oxidizer mixture induces the passivation of the tungsten upper layer. The removal of the oxidized tungsten layer requires two processes: passivation/abrasion and chemical dissolution [8,9]. Moreover, it is known that the dissolution static etch rate has to be low to prevent corrosion and planarization defects [10,11]. Other additives may be included in the chemical composition for a better control of the slurry stability and of the tungsten layer formation and removal kinetics [12–14]. The addition of carboxylic acids as complexing agents or stabilizers has been proposed in order to reduce the kinetics of the iron catalyzed oxidation [12,14,15]. The addition of surfactants also helps to stabilize the polishing slurry and prevents settling, flocculation and decomposition of the silica particles [16]. It improves wafer polishing uniformity [14,17,18].

In this study, an attempt is made to recycle commercially available acidic silica-based slurry used for the polishing of tungsten

Abbreviations: *A*, wafer surface (cm^2); Å, angström; aq., aqueous; *C*, concentration ($mol\ L^{-1}$); C_0, initial concentration ($mol\ L^{-1}$); CMP, chemical and mechanical polishing; CUFS, post-filtrated and concentrated after used slurry; CUS, concentrated after used slurry; CVD, chemical vapor deposition; di., desirability (%); *D0*, Defectivity (number of particles deposited on a wafer); DOE, design of experiments; *w*, tungsten weight loss (g); eq., equivalent (1 eq. = 0.36 mM); I or Fe, iron, ferric nitrate; in, inches; *K*, rate constant for H_2O_2 decomposition (h^{-1}); Lp_0, initial permeability ($L\ h^{-1}\ m^{-2}\ bar^{-1}$); MWCO, molecular weight cut-off (kDa); *n*, number of experiments; NU, within wafer non uniformity (%); Ox. Ac., oxalic acid; Pat., patent; POU, slurry at point of use, reference; ρ, tungsten thin deposit layer density ($kg\ m^{-3}$); RR, dynamic removal rate ($Å\ min^{-1}$); *S*, membrane area (m^2); SDS, sodium dodecyl sulfate; SRR, static removal rate ($Å\ min^{-1}$); surf., surfactants; *t*, time (minutes); T, time (hours); TMP, trans membrane pressure (bar); US, used slurry; *W*, tungsten.

* Corresponding author. Tel.: +33 4 42 90 85 01; fax: +33 4 42 90 85 15.
E-mail address: philippe.moulin@univ-amu.fr (P. Moulin).
[1] Present address: Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique (CNRS-UMR 5503), 118 route de Narbonne, F-31062 Toulouse, France.

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wafers. The properties of the used slurry are disrupted after CMP. Abrasive particles and chemical components are highly diluted during the rinsing steps of the CMP process. However, only a small fraction of the slurry is degraded [19] and it could be regenerated through a concentration step. A few studies exist concerning the regeneration of oxide CMP slurry by filtration [20]. In view of the abrasive particle size, the ultrafiltration (UF) process seems to be one of the most suitable processes for the recycling of silica based slurry [21–23]. In addition to the economic interest of recycling slurry, an environmental benefit arises from the potential reduction of waste water volume by ultrafiltration [23]. The problem was that with this process only the abrasive particles are regenerated but the initial chemical composition of the slurry is not recovered. Oxidizing and stabilizing properties are not maintained in the concentrated used slurry (CUFS). It is a major drawback, especially in the case of W-CMP slurry, for which the chemical composition plays a major role in the chemical and mechanical polishing. As reviewed by several authors, the chemical composition of W-CMP slurry is a determining factor in obtaining uniform and non-defective polishing [5,24,25]. Moreover, in our case, recycling slurry has to be directly operational and all the settings related to the polishing process have to stay unchanged. First experiments were conducted in static conditions where the chemically adjusted slurries were compared to the original slurry as reference [26]. Results confirm the importance of chemistry: (i) the addition of ferric nitrate ensured the passivation of the tungsten layer, obtaining static removal rate similar to that of the reference slurry, but conducted to rapid decomposition of the oxidizer due to the presence of metal impurities in the recycled slurry [27] (ii) the addition of carboxylic acid ensured the increase of the pot lifetime of the recycle slurry (preventing the rapid degradation of hydrogen peroxide) but increased the static etch rate (related to dissolution). From these results it emerged the need to make perfectly balanced chemical adjustments between catalyst and complexing agent in order to ensure the recovering of the specific chemical properties (balance between dissolution and passivation) and the stability of the original slurry [20].

Thus, we performed different chemical adjustments on concentrated after used slurry, mainly taking care on the effect of chemistry in order to prevent corrosion and allow soft oxidation of the metal surface by passivation. Carrying out experiments on site under dynamic conditions, we evaluated the influence of additives on the main CMP parameters: removal rate, within wafer non-uniformity and Defectivity, and also the stability of the slurry. Comparing the results obtained under static and dynamic conditions, we were able to discriminate the effect of chemistry on the mechanical removal of tungsten. Validation of the results through design of experiments methodology helps in the identification of the optimal chemical adjustment that has to be made on the recycled slurry to fulfilled industrial polishing requirements to some extent.

2. Experimental

2.1. Slurry concentration and characterization

The reference slurry was silica (SiO_2)-based slurry from Cabot, Semi-Sperse® W2000 (SSW2000), which is used for standard W-CMP process. It contains silica abrasive particles (<200 nm, 1.8 wt.%) in acidic conditions (pH 2.65 ± 0.05) and hydrogen peroxide (2.70 ± 0.05 wt.%) as oxidizer. The slurry to be recycled is collected after use at the outlet of the CMP process. A diverter valve automatically controlled by the polishing time was adapted to the Chemical–Mechanical Planarization system and allowed an effluent to be recovered which was more concentrated than the used effluent [28]. The slurry was retreated in a semi industrial ultrafiltration pilot plant equipped with a module containing hollow polysulfone fibers ($S = 1\ m^2$, MWCO = 100 kDa, $Lp_0 = 200$ - $L\ h^{-1}\ m^{-2}\ bar^{-1}$) [23]. The filtration flux was stabilized around $50\ L\ h^{-1}\ m^{-2}$ for a low Trans Membrane Pressure (TMP = 0.3 bar) implying low energy consumption and fouling. Post filtration was carried out on a polypropylene cartridge (0.5 μm cut-off, Pentair Industrial) in order to eliminate agglomerates. The slurry suspensions – collected used slurry (named US), concentrated by ultrafiltration after used slurry (named CUS) and post-filtrated concentrated slurry (named CUFS) – were characterized at each step of the recycling process and compared to the point of use (named POU) slurry taken as reference. The slurry characterization was obtained from measurements of physicochemical parameters such as pH (Microprocessor pH-meter HI 221, HANNA Instruments France), conductivity (CDM 210 Conductivity meter with temperature compensation, MeterLab and CDC 745-9 conductivity cells, 2-pole, Radiometer Analytical) and turbidity (Turb 550 IR, WTW). Dry weight suspensions were obtained after complete dehydration (30 h at 110 °C) of samples in a compact muffle furnace (LE 2/11/R6, Nabertherm GmbH). The dry solid content was related to the silica concentration only, since the concentration of chemical compounds was low. *Turbidity* (NTU) was used as an indicator of the amount of suspended solids in the slurry sample. Turbidity values were correlated to silica percentage (wt.%) and gave a good indication of the amount of silica particles in the slurry [22]. Iron content was evaluated by colorimetric o-*Phenanthroline* method. Hydrogen peroxide titration was carried out using potassium permanganate (ChemLab NV) in acidic solution on a Titroline easy dispenser (SCHOTT Instrument GmbH). The hydrogen peroxide decomposition rate (K) gave an indication of the pot lifetime of the slurry (stability).

Range values for the slurry physicochemical parameters before and after the filtration steps are summarized in Table 1. The concentration of colloidal silica by ultrafiltration led to the regeneration of the physical properties – silica content and particle size distribution – so that they were identical to those of the POU reference slurry. Turbidity and granulometry were analyzed to validate the retreatment process.

The dilution of the slurry during the CMP process also led to the reduction of the conductivity and to an increase in pH. In accordance with previous studies, the silica particles were retained thanks to an ultrafiltration membrane cutoff of 100 kDa whereas the ion concentrations remained constant throughout the filtration step [22,26]. Moreover, the chemical components were only partially recovered due to loss during the CMP cleaning steps and during the ultrafiltration. pH and conductivity were corrected by chemical adjustments. Addition of ferric nitrate, carboxylic acid or H_2O_2 alone tended to decrease the pH and increase the conductivity.

Particle size distributions in volume and in number were estimated by laser granulometry measurements over the particle diameter range 0.6 nm–6 μm on Zetasizer Nano-S (Malvern Instruments). Average particle sizes for the original slurry and the treated slurry, both without dilution, are shown in Table 2.

Table 1
Physico-chemical characteristics of the point of use slurry and after used and after concentration by ultrafiltration slurry [26].

Physico-chemical parameters	Turbidity (NTU)	Si content (wt.%)	pH	Conductivity ($\mu s\ cm^{-1}$)
POU	**880–990**	**1.78–1.85**	**2.55–2.70**	**800–1000**
US	130–570	0.17–0.80	2.58–3.32	230–910
CUS	960–1030	1.48–2.09	2.49–3.10	300–900
CUFS	**960–1040**	**1.48–2.17**	**2.50–3.20**	**220–1100**