



## Synthesis of Fe metal precipitated colloidal silica and its application to W chemical mechanical polishing (CMP) slurry

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### ARTICLE INFO

#### Article history:

Received 5 March 2010

Accepted 28 April 2010

Available online 4 May 2010

#### Keywords:

W CMP

Fe precipitation on colloidal silica

Slurry stability

Removal rate

Selectivity

### ABSTRACT

The objective of this paper is to develop a new method of Fe (metal) precipitation on colloidal silica to overcome the stability problem, which would be responsible in producing defects, with commercially available fumed silica slurry containing Fe ions. The slurry was developed by using sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) as a raw material and the concentration of precipitation of metal was controlled by addition of Fe salt ( $\text{Fe}(\text{NO}_3)_3$ ). To compare the concentration of precipitated Fe with directly added Fe ions in slurry solutions, static electrochemical and peroxide decomposition experiments were performed. Although the performance of the Fe precipitation appeared to be lower than Fe ion addition during these experiments, nearly equal removal rate was observed due to the dynamic condition during polishing. The Fe precipitated colloidal silica particles at the concentration of 52 ppm showed the similar W removal rate and selectivity of W to TEOS (tetraethylorthosilicate) to commercially available fumed silica slurry containing externally added Fe ions. The introduction of Fe particle precipitation on colloidal silica particles would result in a longer shelf life time and hence lower defect level in W CMP.

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### 1. Introduction

W (tungsten) has been a widely used material for the formation of contact, via and hole for connecting the inter-layer metal lines in IC fabrication due to its excellence in filling vias by Chemical Vapor Deposition (CVD) [1–5]. In this application, the tungsten deposited by CVD above the insulator layer must be planarized by chemical mechanical polishing (CMP) process to form contacts and vias [6–8]. During the CMP process the chemicals present in W CMP slurry develop a tungsten oxide layer onto the surface and this surface is mechanically abraded by abrasive particles [7]. The CMP process must provide a high removal rate and good planarity through the simultaneous actions of chemical dissolution and mechanical abrasion [7,9]. Apart from the W surface polishing, the slurry should also provide high selectivity with TEOS [10].

The slurry chemistry plays a major role in removing the W material by CMP process [4,5,8,10–14]. Usually an oxidizer is added to W slurry since it plays a key role in increasing the removal rate by forming the passive tungsten oxide layer which is softer than W material [10,15,16]. Different oxidizers such as  $\text{H}_2\text{O}_2$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{KIO}_3$ ,  $\text{KMnO}_4$ ,  $\text{KNO}_3$  and periodic acid ( $\text{H}_5\text{IO}_6$ ) have been investigated for tungsten CMP [7,8,10–14,17–19]. Generally  $\text{Fe}(\text{NO}_3)_3$  is an effective oxidizer followed by  $\text{H}_2\text{O}_2$ . Though  $\text{Fe}(\text{NO}_3)_3$  has the highest oxidation potential, its application is nor-

mally restricted to the very low pH region due to its limited stability in aqueous solutions [8]. It was observed that  $\text{Fe}(\text{NO}_3)_3$  showed the better stability and excellent corrosion effect in the hydrogen peroxide solution [12]. Hence, peroxide as oxidizer and Fe ions as catalyst is the more suitable combination for W polishing [4,5,13]. But Fe ion slurry has limited stability at higher pH (>5). Depending on the choice of the oxidizing agent, the catalyst, the abrasive and other useful additives, the polishing slurry can be tailored to provide effective polishing to metal layers.

The W slurry should consist of suitable abrasives with appropriate chemicals to meet the requirements. Traditionally alumina particles were used to polish the W surface. Alternative abrasives for W polishing were proposed since alumina particles would produce defects during the process such as scratches due to its hard nature [14]. Silica particles were found to be suitable replacement of alumina particles. Colloidal silica and fumed silica are the two types of silica that are commonly used. Fumed silica suffers from the high instability problem, which would cause the silica particles to get agglomerated and hence produces more defects, whereas colloidal silica has been known to be stable and well suspended slurry [4,9]. Reduction of all types of surface defects, especially scratch formation, has become a critical element of the fabrication processes [20–22].

Colloidal silica plays a key role as a polishing slurry for CMP process. Several attempts have been done in modifying these slurries to make it suitable for the CMP process for different materials and applications. Armini et al. developed the composite silica shell

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by coating polymers on colloidal silica [20]. Recently several studies were performed on precipitating the metals on the colloidal silica particles for the application of CMP process. The precipitation of several metals like Fe [23], Al [24], Ce [25], Mg [26] on colloidal silica particles has been performed for different applications. In particular, the coating of the catalyst to the abrasive to enhance the chemical reaction between oxidizing agent and the metal to be polished during CMP process has been carried out extensively [27–32].

In this study, colloidal silica particles were synthesized using sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) as raw material with and without Fe precipitation by ion exchange process. To estimate the performance of Fe precipitation to the colloidal silica particles on W CMP, electrochemical and peroxide decomposition tests were performed and compared with external Fe ion addition. The composition of Fe precipitate was optimized to achieve similar W removal rate and selectivity (W/TEOS) as obtained by commercially available fumed silica slurry having externally added Fe ions.

## 2. Materials and methods

Fig. 1 shows the synthetic procedure of Fe precipitated colloidal silica (30 nm) by adding  $\text{Fe}(\text{NO}_3)_3$ . Dilute water glass solution ( $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ ) of 10 wt.% in the aqueous form was used as raw material for the synthesis of colloidal silica. De-sodium ion was performed in the cation exchange resin to exchange the sodium ion with hydrogen ion to obtain the silicic acid solution. From this solution synthesis of colloidal silica was performed by conducting nucleation polymerization and particle growth using KOH at  $100^\circ\text{C}$  for 2–4 h. A size of 20–40 nm colloidal silica particle were obtained in the pH range of 10–11.

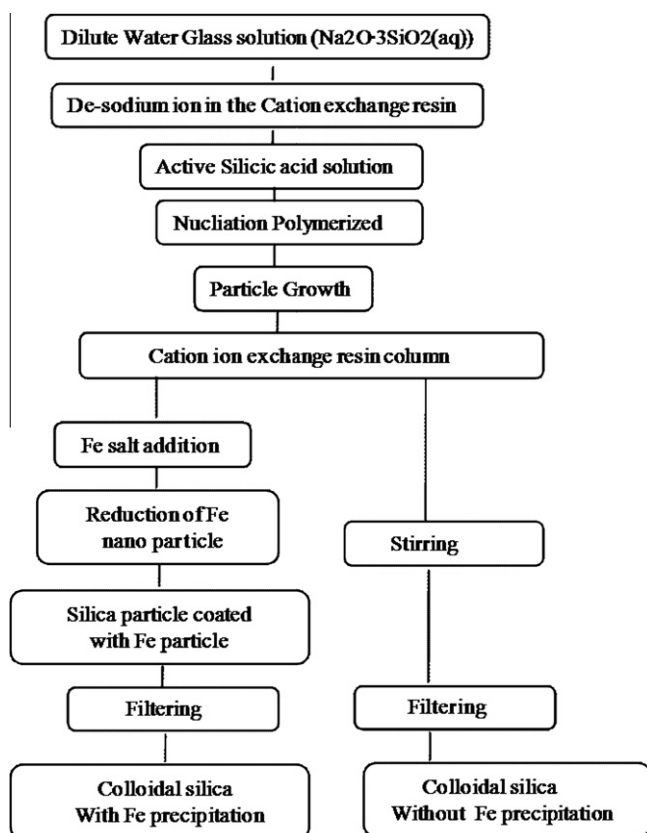


Fig. 1. Flow chart for colloidal silica slurry preparation with and without Fe particles.

The solution was made acidic in the pH range of 3–4, by exchanging the surface to  $\text{H}^+$  in the cation exchange resin. Since Fe salt could exist ionic state in the acidic condition and would exist as bulk in the basic or neutral state. In the case, where no precipitation is intended the colloidal silica particles were obtained directly by stirring followed by filtering. Based on desired impurity level, the Fe salt in the range of 20–100 ppm was added and mixed for 10 min. The Fe salt was reduced to 1–2 nm Fe particles at room temp with stirring for 1 h. Fe nano particles were adsorbed on the surface of silica. Since size of Fe particle was too small (1 nm), they mostly tend to adsorb on the oxide surface because of surface attractive forces and available large surface area. The schematic mechanism of precipitation of Fe particle is shown in Fig. 2. Finally the colloidal silica particles of 3 wt.% with Fe ion precipitation at pH of 5–7 were obtained by filtering at room temperature. It was believed that the slurry would be stable at lower pH because of lower wt.% of silica. The fundamental study showed, as discussed later in the text, better stability. Hence no modification to the silica particles was performed. Colloidal silica particles were obtained with different Fe precipitation of 10, 15, 35, 52 and 100 ppm. Multiple concentration and dilution processes with ion exchange columns were performed to obtain the desired Fe concentration level in colloidal silica. The precipitated Fe concentration on colloid was controlled by the concentration of Fe salt during the synthesis process. The concentration of colloidal silica was controlled by measuring its specific gravity. For comparison,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (98 wt.%, Junsei Chemical Co., Japan) was used to control the concentration of Fe ions in non Fe precipitated silica slurry during the experiments.

Hydrogen peroxide was used as an oxidizer for the subsequent experiments. To estimate the performance of Fe precipitation on colloidal silica, the decomposition of peroxide (2 wt.%) was studied at room temperature and compared as a function of time with and without Fe precipitation on colloidal silica. The concentration of  $\text{H}_2\text{O}_2$  was measured by general redox titration method [33]. The titration was carried out by using Permanganate. For the comparison, Fe ions were added to non Fe precipitated colloid. Three different concentrations (15 ppm, 35 ppm and 52 ppm) of both Fe precipitation and Fe ion were used for these experiments.

The potentiodynamic polarization tests were performed using a potentiostat (Model 273A, Princeton Applied Research, USA). During the potentiodynamic scans, the working electrode potential was varied with a scanning rate of 1 mV/s from  $-500$  mV/SCE (Saturated Calomel Electrode) to  $+1000$  mV/SCE in the positive direction, in order to measure the electrochemical corrosion potential

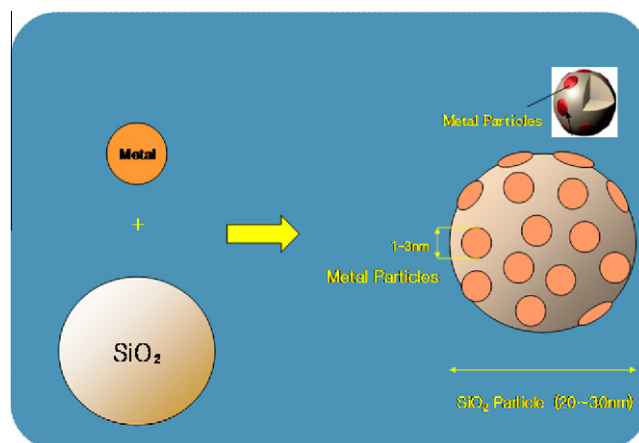


Fig. 2. The schematic diagram for precipitation mechanism of Fe particles on silica particles.

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