

**Role of amino-acid adsorption on Silica and Silicon Nitride surfaces
during STI CMP**

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Abstract

Selectivity (Oxide/Nitride polish rate) is a critical factor during Chemical Mechanical Polishing (CMP) of Shallow Trench Isolation (STI) structure and it can be modified by adding amino acids to the slurry. The role of adsorption of the amino acids L-Proline and L-Arginine, on silicon dioxide and silicon nitride surfaces was characterized as a function of pH and concentration using Thermo Gravimetric analysis (TGA). The results suggest that the adsorption behavior does not correlate with the polishing behavior of STI CMP and hence it may not play a key role in changing the selectivity.

Chemical Mechanical Planarization (CMP) is an essential step in microelectronic chip fabrication [1,2]. It consists of moving the surface to be polished against a rotating pad in presence of slurry (a mixture of abrasive particles and chemicals). Shallow Trench Isolation (STI) is one of the steps in the chip fabrication used for electrically isolating the devices (transistors, diodes etc) from each other [3]. CMP is a key step in STI process [4] and it involves removal of excess silicon dioxide (oxide), as shown in the schematic Fig. 1.

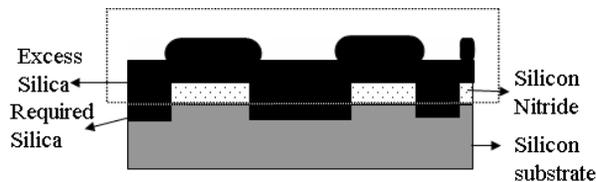


Fig.1. Schematic Diagram showing Shallow Trench Isolation process

A thin nitride layer is used to protect the areas where transistors will be formed later. Typically ceria based slurries at alkaline pH are used for STI polish [5]. The slurry normally polishes both oxide and nitride layers, but the nitride layer should not be removed for optimal process. Certain additives are known to increase the oxide/nitride polish rate ratio (selectivity) dramatically [5-7]. Amino acids like L-proline in the slurry suppress the nitride polish rate but do not alter the oxide polish rate, thus providing high polish rate selectivity. Other amino acids like L-arginine suppress the oxide polish rate as well as the nitride polish rate and hence required selectivity can not be achieved. [6]. However, the exact mechanism of action is not clear in both the cases.

It is suggested that the adsorption of the additives on the surfaces of interest (i.e. silicon dioxide and silicon nitride) may play a role in modifying the polishing behavior

[2,6]. The adsorption of the two amino acids L-proline and L-arginine, which alter the silicon dioxide and silicon nitride polish rates differently, are investigated in this work and the implications are discussed.

Experimental

Samples preparation:

In all the experiments, fumed silica particles CAB-O-SIL EH-5 (Cabot-Sanmar Ltd., India) of dry surface area of 380 m²/g and silicon nitride particles of dry surface area of 9.4 m²/g (Sigma Aldrich, USA) were used as sample surfaces for the adsorption of L-proline and L-arginine (AR grade, Merck India, India). A limited set of experiments were also carried out with silica particles of lower surface area (6.15 m²/g, -325 mesh silica from Sigma Aldrich, USA) for comparison. Although silicon dioxide and silicon nitride layers are present as thin films in the STI polish scheme, fine particles were used for the adsorption studies since they provide relatively large surface area. The surface area and pore size distribution were measured using CE-Sorptometer 1990.

For sample preparation, 2 g of the particles was mixed with in solution of 50 ml of de ionized water and different wt% (0, 2, 4, 6, and 8) of amino acids (L-Proline and L-Arginine) and stirred well. The pH was adjusted with KOH or HCl. The solution was filtered through a Whatmann filter paper (GF/A) using a vacuum pump. The precipitate was put in an oven and dried at 125° C for four hours, to remove the moisture present in the sample. The dried precipitate was ground to a fine powder and stored in a desiccator. Silica particles of lower surface area were utilized in experiments conducted at pH of 11 with amino acids of 6 and 8 wt% only. All other samples were prepared at three different pH values (9, 10 and 11).

TG analysis:

TGA was performed with Perkins instruments, TGA 7 Model to quantify the amount of adsorption. The samples were heated from room temperature to 800° C at 10° C/min in N₂ atmosphere. The weight loss is accounted by the loss of moisture and amino acid. The weight loss due moisture is calculated by performing TGA for blank particle surfaces (without amino acids) at different pH values.

Results

TGA is has been used to quantify the adsorption of glycine on silica surfaces at various pH values [8]. Fig 2.a and 2.b show the adsorption isotherm of L-Proline and L-Arginine on silica surface respectively. The adsorbed quantities do not vary significantly with pH for both amino acids. On silica, L-proline adsorbs to a larger extent than L-Arginine. The experiments conducted with silica of lower surface area also showed that both amino acids adsorb to similar extent on the oxide surface (Results not shown).

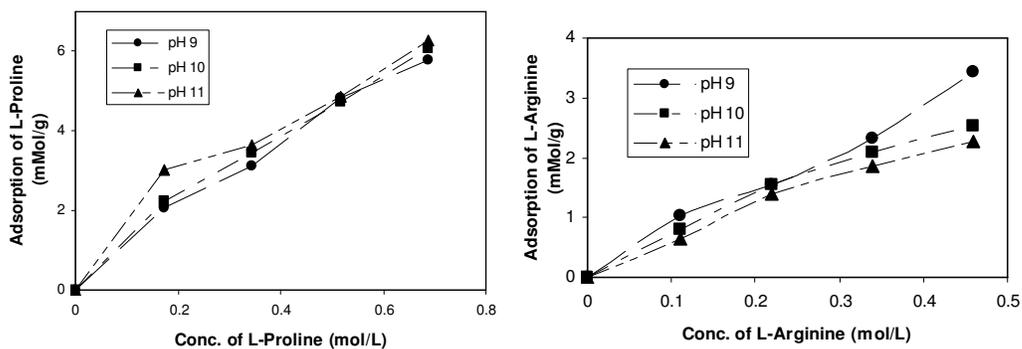


Fig. 2. Adsorption isotherm of amino acids on Silica at pH 9, 10 and 11. The amino acids are (a) L-Proline and (b) L-Arginine

Fig. 3.a and 3.b show the adsorption isotherms of both the amino acids on silicon nitride surface. Again, the adsorption does not vary significantly with pH for L-Proline

and L-Arginine. On silicon nitride, both L-Proline and L-Arginine are adsorbed more or less to the same extent.

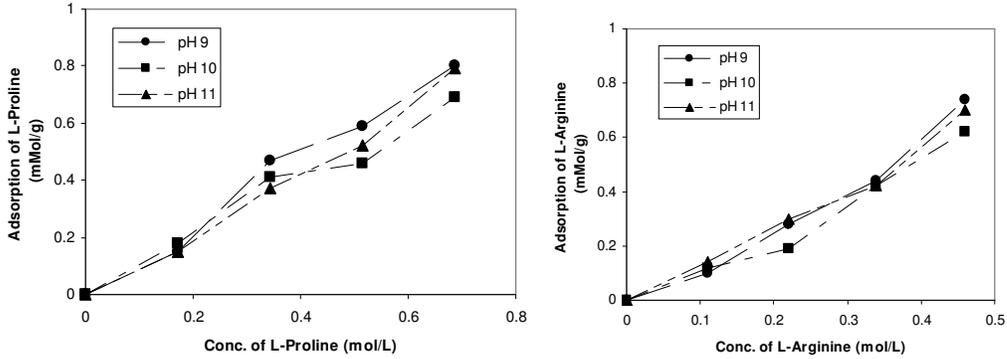


Fig.3. Adsorption isotherm of amino acids on Silicon Nitride at pH 9, 10 and 11. The amino acids are (a) L-Proline and (b) L-Arginine

Discussion:

The polishing of silica and silicon nitride is usually performed with ceria or silica based slurries. Ceria based slurries exhibit high removal rates, even though ceria is softer than either silica or silicon nitride and this is believed to be due to chemical interaction between ceria and silicon dioxide [9,10]. Cerium in the ceria particles may not be fully co-ordinated and the uncoordinated valence electron may interact with the silica. Silicon nitride polish mechanism is believed to involve hydrolysis of the nitride surface to form ammonia and a thin layer of silica [11, 12]. The silica will be subsequently removed by the abrasive. High polish rates of silicon nitride are also observed with zirconium dioxide and to a lesser extent with titanium dioxide abrasives [9,11]. It is worth noting that both zirconium and titanium exhibit multiple valencies and may have uncoordinated valence

electrons. However, the exact nature of the interaction between the abrasive and the work surface is not clear.

The effect of addition of amino acids on polish rate selectivity has been explained by proposing that adsorption plays a key role [5-7]. According to that hypothesis, if the additive adsorbs on silicon nitride but not on silica, it would prevent the hydrolysis of the nitride. The silicon nitride being harder than silica will not be removed easily by the abrasive, while the oxide polish rate will remain unaffected. Thus the oxide to nitride polish rate selectivity would be enhanced by additives which selectively adsorb on silicon nitride and prevent its hydrolysis. On the other hand, if the additive adsorbs on silica as well as silicon nitride, then it would prevent the interaction between abrasive and the work surface, thus reducing the polish rate in both cases [6, 7]. The quantification of adsorption of various additives can be used to confirm or refute the hypothesis.

The total amount of amino acid adsorbed on the surface of silica and silicon nitride depends on the surface charge and the surface area available for adsorption [13]. At alkaline pH range of 9 to 11, surface charge of L-proline and L-Arginine are positive [14]. Since the point of zero charge (PZC) of silica is nearly at pH 2.0 and that of silicon nitride at pH 7, both surfaces have negative charge in the alkaline pH range [15]. Hence, it is expected that the amino acids would be attracted by both the work surfaces. The adsorbed quantities (mMol/g) of amino acids is very much less on silicon nitride surface when compared to silica surface, mainly because the surface area available is much more ($380 \text{ m}^2/\text{g}$) for silica compared to silicon nitride ($9.4 \text{ m}^2/\text{g}$). If the silica adsorbent is porous, the amino acid trapped in the pores would not be removed during vacuum filtration and it would lead to ambiguous data. Thus it is essential to verify that the

measured quantities represent the true adsorption and not the trapped amino acids. Fumed silica used in these experiments is made of aggregates of very small (5 nm to 40 nm) primary silica particles. A pore size distribution analysis of the sample indicates that the pore size is 5 Angstroms. Both L-Arginine and L-Proline in hydrated state are likely to be larger than 5 Angstroms and are not likely to be trapped in the pores. The results of adsorption studies of amino acids on silica with low surface area confirm that L Arginine and L-Proline adsorb to similar extent on silica regardless of the surface area of the adsorbent.

During STI polishing L-Proline does not affect silica polish rate but decreases silicon nitride polish rate whereas L-Arginine decreases both silica and silicon nitride polish rates [6]. The adsorption studies reported here indicate that both L-Arginine and L-Proline adsorb onto silica and silicon nitride surface to similar extents. Hence it is unlikely that the inhibition of nitride and oxide polish by L-Arginine and the inhibition of nitride polish alone by L-Proline can be explained by the adsorption mechanism.

The selectivity enhancement studies published so far have utilized only ceria based slurries [5-7]. Based on the adsorption results, it is proposed that the change in selectivity with the addition of amino acids may be due to modification of the chemical mechanism of removal and is not linked to the adsorption on the work surfaces alone. A deeper understanding of the chemical mechanism is necessary to explain the changes in selectivity with the addition of amino acids.

Conclusions:

Adsorption studies of L-Proline and L-Arginine on silica indicate that the effect of amino acids on changing the selectivity of STI CMP is complex. Both L-Proline and L-

Arginine adsorb to equal extent on oxide and nitride surface, even though L-Arginine suppresses the polishing of both oxide and nitride, while L-Proline suppresses the polishing of nitride surface only. Hence adsorption of the amino acids on the work surface alone does not explain the change in the oxide to nitride polish rate selectivity.

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Figure captions

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