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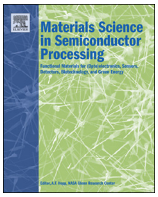

Effect of lanthanum doping in ceria abrasives on chemical mechanical polishing selectivity for shallow trench isolation

B.V.S. Praveen [a], Byoung-Jun Cho [c], Jin-Goo Park [b,c], S. Ramanathan [a,*]

[a] *Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036, India*
[b] *Department of Materials Engineering, Hanyang University, Ansan 426 791, Republic of Korea*
[c] *Department of Bionano Technology, Hanyang University, Ansan 426 791, Republic of Korea*

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ABSTRACT

Amino acids, when used with ceria based slurries, yield high selectivity in shallow trench isolation chemical mechanical polishing (CMP). However, the presence of impurities in the abrasives also plays a role in determining the selectivity. Experiments were performed with two different ceria abrasives, one with high purity and the other with controlled lanthanum doping. Various amino acids were evaluated in order to identify the nature of interaction between the additives and the abrasives. The abrasives were further characterized using transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. The removal rate results show that glycine and proline are sensitive to the La doping in the ceria abrasive whereas the other amino acids studied suppress the nitride removal irrespective of the purity of the abrasives. Thermo-gravimetric analysis shows that the extent of adsorption of glycine or proline on ceria depends on the presence of La doping, whereas the other amino acids adsorb equally well on ceria abrasives with or without La doping.

1. Introduction

As the size of the devices in microelectronic chips shrinks down, the density of the transistors increases rapidly posing a stringent requirement on device isolation [1–3]. Shallow trench isolation (STI) [4–5] technology isolates the transistors by creating shallow trenches and filling the trenches with silicon dioxide, which acts as an insulator. The excess material deposited over the surface is removed by chemical mechanical polishing (CMP) [6]. During CMP, the oxide has to be polished in such a way that the active areas are not damaged. Hence silicon nitride is used as a stop layer to prevent excess polishing. The selectivity, which is defined as the ratio of removal rate of silicon dioxide to silicon nitride, needs to be high for a successful STI CMP process.

Ceria based slurries are reported to yield high removal rates [7–8], when compared to silica based slurries [9–11]. Even though ceria based slurries yield high polish rates, high selectivity can be achieved only when certain chemicals are added to the slurry. These additives suppress the silicon nitride removal without significantly altering the silicon dioxide removal. To explain the suppression of silicon nitride polishing by the additives, various hypotheses have been proposed in the literature. America and Babu [3] proposed that the suppression of the nitride polish by the amino acid L-proline was due to the inhibition of the silicon nitride hydrolysis because of formation of hydrogen bonding between the oxygen atoms of carboxylic group and the silicon atoms on the surface. Carter and Johns [12] proposed a site blocking mechanism on the surface of silicon nitride, which prevents further hydrolysis and subsequent Si–O$^-$ reactivity with ceria. Adsorption studies performed on two

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[*] Corresponding author. Tel.: +91 44 2257 4171; fax: +91 44 2257 0509.
E-mail address: srinivar@iitm.ac.in (S. Ramanathan).

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different amino acids (L-proline and L-arginine), on silicon dioxide and silicon nitride surfaces, showed that both the additives adsorb to equal extent on the surface of silicon dioxide as well as silicon nitride [13]. While L-proline suppresses only nitride polishing, L-arginine suppressed both oxide and nitride polishing. This indicates that adsorption of amino acids on the nitride surface is not the sole mechanism of high selectivity. Manivannan and Ramanathan [14] showed that hydrogen peroxide suppressed both the oxide and the nitride removal in ceria based slurries, in the pH range of 7–10. However, the removal rates were unaffected in silica based slurries with hydrogen peroxide. In another study, Manivannan and Ramanathan [15] reported that ceria slurry with DL aspartic acid as additive showed suppression of oxide and nitride polish rates for pH values less than 4 and both oxide and nitride were polished when pH was maintained more than 5. At the intermediate pH, between 4 and 5, the nitride removal rate was suppressed suggesting the presence of chemically active sites on the surface of ceria which are being blocked by amino acids. Penta et al. [16] reported that amino acid gets protonated in a selective pH range. This leads to the formation of hydrogen bond and subsequent suppression of silicon nitride polishing. They also reported that weak hydrogen bonds were formed between silicon dioxide and amino acids, resulting in enhanced oxide polishing. However, later studies showed that when nitride wafers were polished using slurries containing different ceria abrasives but with the same additives, the polishing results were different [17]. Glutamic acid yielded high selectivity regardless of the type of abrasive used for polishing. However, L-proline yielded high selectivity only with certain abrasives. It was reported that the purity level of the ceria abrasives depended on the source, leading to the speculation that the presence of La in the ceria abrasive might have led to low selectivity in slurries with L-proline. However, the different abrasives employed in that study were not synthesized by the same process and thus other causes such as crystallinty or porosity could not be excluded. In another study, a ceria slurry containing L-proline was reported to polish silicon nitride, but the purity of the ceria abrasive employed in that study is not known [12].

In the present work, we synthesized two kinds of ceria particles, one with high purity and other containing La using identical process and with controlled reactant species. This ensured that the abrasives were similar to the maximum possible extent with only the La content being different. The abrasives were characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photo-electron spectroscopy (XPS). Polishing experiments were conducted using various amino acids as additives, in slurries containing both types of ceria abrasives. The polishing results show that some of the additives such as L-proline and glycine are sensitive while other additives are robust to the presence of impurity in providing high selectivity. Thermo-gravimetric analysis was performed to study the interaction between the additives and the ceria abrasives. The results show that the adsorption of proline or glycine on ceria depends on the La doping in ceria abrasives, where as other amino acids adsorbed equally well on both types of ceria.

2. Experimental methods

2.1. Sol–gel synthesis of ceria particles

Cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, Alfa Aesar, UK), citric acid ($C_6H_8O_7$, Merck, India) and aqueous ammonia (NH_4OH, Fischer Scientific, India) were used for the synthesis of ceria. The sol–gel synthesis process was adopted from Du et al. [18]. Cerium nitrate and citric acid in the molar ratio of 1:3 were dissolved in deionized water (DIW) resulting in a colorless solution. The solution was mixed homogeneously using a magnetic stirrer with simultaneous addition of aqueous ammonia until the pH increases to 7. As the pH was adjusted, the solution color changed from colorless to brown. After one hour of stirring, the solution was dehydrated using a hot plate maintained at temperature of more than 150 °C. As the water evaporated, a gel was formed at the bottom of the beaker. After some time, there was a sudden increase in temperature and the gel turned into a yellow color powder. This powder was collected, crushed using mortar and pestle and calcined at 350 °C for 12 h to remove traces of unreacted citric acid and ammonia. The powder was again calcined for 12 h at 900 °C to enhance the crystalline nature. The particle size was reduced by wet milling for 3 h in a high-energy ball mill (Pulverisette 6, Fritsch GmbH, Germany) using tungsten carbide balls with a ball to powder weight ratio of 10:1 and toluene as a medium. The milled powder was oven dried at 85 °C for 4 h and used in the polishing experiments. The above process was repeated to prepare lanthanum doped ceria with a mole ratio of 1:9 of lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$, Alfa Aesar, UK) and cerium nitrate. The sol–gel synthesized pure ceria is designated as ceria-SG and La doped ceria as ceria-SGL.

2.2. Chemical mechanical polishing

One inch couponed wafers of silicon dioxide and silicon nitride (Semi-wafer Inc., Taiwan) were polished using a bench-top Struers (Labopol-5/Laboforce-3). The carrier and turntable speed were maintained at 250 rpm and 100 rpm respectively. Slurries were prepared with ceria abrasives at a concentration of 0.25 wt%. For most of the amino acids, the additive concentrations were maintained at 200 mM, which was chosen based on trial experiments. For glutamic acid and aspartic acid, the concentrations were maintained at 20 mM. Due to the low solubility limit of these two amino acids, higher concentrations were not employed. The pH of the slurry was maintained at 5 using either KOH or H_2SO_4. The pad was initially soaked in deionized (DI) water for a day and conditioned until consistent results were obtained. After each run, the pad was again conditioned using a silicon carbide grit paper. The slurry was fed on to the surface of the polishing pad at a flow rate of 60 mL/min using a peristaltic pump. For each experimental run, polishing was done for one minute. F20-UV thin film analyzer was used to measure the thickness of the wafer before and after the polishing experiments. Polishing experiments were repeated at least three times and the average value along with standard deviation was reported.