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The pH-dependant attachment of ceria nanoparticles to silica using surface analytical techniques

K. Dawkins, B.W. Rudyk, Z. Xu, K. Cadien*

Department of Chemical and Materials Engineering, University of Alberta, ECERF 7-034, 9107 – 116 Street, Edmonton, Alberta, Canada T6G 2V4

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ABSTRACT

The adhesion and removal of ceria particles to a silica surface was investigated with the use of X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and auger electron spectroscopy (AES) measurements. A model is presented based on electrophoretic mobility measurements of ceria slurry and silica particles at different pH's. XPS results show that at acidic pH values, ceria is present on silica surfaces, but at alkaline pH values, far less ceria is present, or no ceria is present in the extreme case. SEM results corroborated the XPS results showing uniform distribution of ceria particles on silica surface at pH 6 while a clean silica surface is observed at pH 12. However, SEM images show agglomeration of ceria particles occurring at the isoelectric point of ceria at ~pH 9.6. High resolution Ce 3d XPS analysis indicates that ceria present on the surface is composed ~31% Ce(III) and ~69% Ce(IV). AES mapping done at specific points on the silica surface validated both XPS and SEM results. Based on XPS, SEM and AES analyses, it is clear that an alkaline pH is necessary to minimize particulate contamination of silica surface by ceria.

1. Introduction

Over the past decade, ceria particles have attracted significant attention due to their physical and chemical properties which have proven to be very useful especially in integrated circuit fabrication technology such as chemical mechanical polishing (CMP) [3–7]. Cerium oxide is ambiguous, containing multiple valences of which the most commonly used are: cerium (III) oxide, Ce_2O_3 or cerium (IV) oxide, CeO_2. However, the most prevalent form in which cerium oxide exists is CeO_2 [1], which enhances chemical action on oxide surfaces. For the remainder of this paper we will use cerium oxide and ceria, interchangeably, to refer to CeO_2.

CeO_2 possesses a fluorite structure with a lattice constant of 0.541 nm [1]. The earliest use of cerium oxide was as a hydrocarbon catalyst during the high temperature cleaning process of self-cleaning ovens [2]. Cerium oxide based slurries have been used for decades in glass and optical lens polishing [3,4]. Recently, ceria based slurries have emerged as important abrasives in CMP applications such as shallow trench isolation (STI), liquid crystal display (LCD) and interlayer dielectrics (ILD) applications [3–7]. STI is an isolation technique used for semiconductor devices with small line widths and high transistor density [5]. STI embeds field oxide into silicon and establishes an abrupt, near vertical interface between the oxide and active-area regions hence preventing “bird's peak” which results from the lateral encroachment of oxide into the active area of the substrate below the nitride mask which is used in the local oxidation of silicon (“LOCOS”) process [5]. The STI process starts with growing pad oxide on a silicon wafer, followed by deposition of a nitride layer, lithography and patterning, and then a shallow trench is etched into the silicon substrate using the patterned nitride layer as a mask. This is followed by liner oxidation, and CVD oxide gap fill [5]. The last steps include oxide CMP to remove the overburden silicon dioxide (stopping on the nitride) followed by nitride strip [5]. Ceria abrasives are used widely in STI CMP slurries due to their high selectivity [4–7], that is, the oxide removal rate is high while the nitride removal is low. Ceria particles have the ability to absorb silicate ions in the removal of silica during the CMP process. Ceria based slurries have higher polish rates than silica based slurries and, at the same time, improved surface finish [4,7]. Several studies have been done to investigate the mechanism of both the high selectivity of ceria slurries and the CMP of silica surfaces by ceria abrasives [3–11,14] yet no exact polishing mechanism is known for CeO_2. Most of these studies were based on the adhesion/interaction of the ceria abrasive with the silica substrate. The “chemical tooth” model was proposed by Cook [8] for glass polishing, which is said to be responsible for the high oxide removal. In this model, a temporary chemical bond initially exists between the ceria abrasives and the silica substrate which is said

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* Corresponding author. Tel.: +1 780 492 7380; fax: +1 780 492 2881.
E-mail address: kcadien@ualberta.ca (K. Cadien).

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to be responsible for the removal of the silica during the polishing process, as shown in Eq. (1) below:

$$\mathrm{Ce{-}OH} + \mathrm{Si{-}O^-} \leftrightarrow \mathrm{Si{-}O{-}Ce} + \mathrm{OH^-} \quad (1)$$

However, Cook's explanation is only a theoretical explanation of the removal of silica in the CMP process. Furthermore, Osseo-Asare et al. [9], in their study, concluded that the adsorption phenomenon is responsible for the material removal mechanism. To explain the nature of ceria/silica interaction, Abiade et al. [4] examined the effect of ceria slurry pH on silica removal. Using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) to examine particle–surface interaction, they showed that the removal of silica is strongly dependent on the pH of the ceria slurry with the maximum removal occurring near the isoelectric point of the slurry.

Despite the many advantages of using ceria slurry, it is difficult to remove ceria particles from silica surfaces during CMP cleaning steps. CeO_2 removal from the SiO_2 surface is critical because remaining particles cause defects [10], and the STI process occurs at a very sensitive location in the process, that is, at the transistor level. In the CMP process, micro-scratches are one of the main problems in the planarization of SiO_2 surfaces that is caused by contaminants or the use of crushed abrasives. However, the nature of this scratch formation is not fully understood. Volkov et al. [11], in their study of the adhesion of ceria abrasive on silica surfaces during the CMP process, showed a correlation between adhesion and the creation of scratches, specifically higher adhesion correlates with a higher number of defects. They went on to propose that the agglomeration of abrasive particles also causes the number of defects to increase. The interaction between CeO_2 abrasives and SiO_2 surface can be explained by electrostatic and van der Waals forces. In the semiconductor industry, defect minimization is a major challenge and also of great interest especially in the manufacture of sub 15 nm devices. From the literature [10] it is understood that defects are formed mainly due to the interaction between the slurry and wafer surface during the CMP process. Therefore, defects can be reduced through a fundamental understanding of the slurry particle–wafer surface interaction to enable the removal of the particles. Zhang et al. [12] suggested that the slurry composition can be designed in such a way that prevents particles from depositing onto the wafer surface during the CMP process and that a repulsive electrostatic force is necessary to inhibit particle-wafer deposition. This can be achieved by measuring the zeta potential between the abrasive and the film surface as function of pH. A repulsive electrostatic force can be reached when both abrasive and wafer surfaces have the same sign. Additives/chelating agents can also be used in the slurry to modify its pH/zeta potential and also will minimize particulate contamination arising from particle-wafer interaction. Zhang et al. [12] studied the effect of using a common pH/chelating agent, citric acid, to control alumina particle deposition on tungsten and oxide surfaces. They found that the use of citric acid can minimize alumina contamination significantly on both tungsten and oxide surfaces. It has also been stated that the pH of the solution is critical to the adhesion and removal of particles from surfaces [10]. Furthermore, based on a study of Cu CMP, it was concluded that alkaline slurry is required to control particulate contamination. However, in practice changing the slurry pH can be detrimental to the CMP process.

XPS is an effective technique for surface analysis and has been used extensively in many areas of surface and materials analysis due to the exceptional combination of compositional and chemical information that it provides. SEM, along with Auger emission spectroscopy (AES) imaging and point analysis, were applied to obtain information about wafer surface topography and composition of the multi-elemental sample, at various pH levels (pH 6, 9, and 12) chosen based on the results of the zeta potential determination. The experimental analysis of the effect of pH on ceria–silica interaction for the subsequent removal of ceria abrasives from silica surfaces will be useful to obtain clean silica surfaces and to design slurries that limit contact between abrasive and substrate during the CMP process. To the best of our knowledge, there are no other studies which employ these surface characterization techniques to understand the mechanism of residual CeO_2 contamination and removal.

2. Experimental procedures

2.1. Ceria slurry preparation

The ceria slurry used in this study, namely CeO_2, from Nyacol Nano Technologies, had a 20 wt% ceria concentration. De-ionized water (Milli-Q UV PLUS), referred to as Milli-Q water, was used for slurry dilution to 5 wt% concentration. The pH of solutions/suspensions was measured by an Accumet Basic AB15 pH metre, which was calibrated each time prior to use. Citric acid and potassium hydroxide were used to adjust the pH of suspensions. A silicon oxide wafer which was cleaved into three 1 cm × 1 cm pieces was used as the substrate for this experiment. The substrate was dipped into the ceria suspension for 1 min at a stirring speed of 286 revolutions/min. It was then rinsed in Milli-Q water for 1 min at a flow rate of 250 mL/min and dried in air.

2.2. Zeta potential measurements

In order to measure the surface charge of the particles in the slurry and on the wafer surface, the zeta potentials of ceria and silicon dioxide particles were measured over a wide pH range (3–12) using a Nano ZS Zetasizer from Malvern Inc. The suspensions used were prepared by a dilution of the original slurries to approximately 1 wt% for ceria and 0.5 wt% for silica using Milli-Q water. The pH of the suspensions was adjusted using citric acid and potassium hydroxide. The zeta potential measurement recorded was an average of three consecutive measurements for each sample. The refractive indices used were 1.457, 1.33 and 2.1 for silica, water and ceria, respectively, while the absorptivity was set at 0.01 for silica and 0.05 ceria. All measurements were done at room temperature (25 °C). The viscosity was set at 8.872×10^{-4} Pa s.

2.3. Particle size distribution

Particle size and size distribution of the ceria slurry was found using a Malvern Nano ZS Zetasizer, which was previously used for the zeta potential measurements. The ceria suspension used was prepared by dilution of the original slurry to 0.5 wt% using Milli-Q water and the pH was adjusted to approximately 4 ± 0.03. A small disposable cuvette was used to hold the suspension. All measurements were done at room temperature, 25 °C. The refractive index was set at 2.1 and 1.33 for ceria and water, respectively. Again, the final measurement recorded was an average of three consecutive measurements. The average particle size was determined to be ~5 nm at pH 4 (Fig. S1 in supplementary information), and is consistent with the particle size given by the slurry supplier. At pH 4, the particles were mono-dispersed and therefore show little or no agglomeration.

Supplementary Fig. S1 related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2015.03.170.

2.4. XPS measurements

All XPS measurements (except pH 12 survey spectrum – discussed below) were completed using a Kratos Axis Ultra spectrometer equipped with a monochromatic Al Kα ($h\nu = 1486.7$ eV)