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Role of ionic strength in chemical mechanical polishing of silicon carbide using silica slurries

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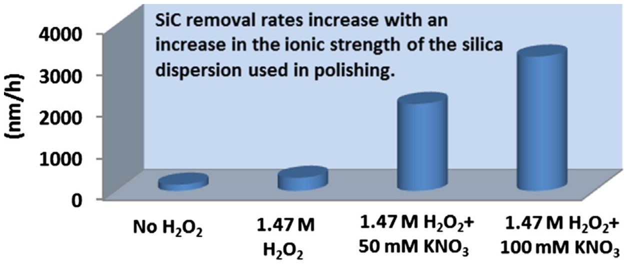
HIGHLIGHTS

- Silica dispersions for chemical mechanical polishing of SiC surfaces were investigated.
- Dispersions that resulted in high amorphous SiC removal rates are reported.
- The ionic strength of the dispersion was found to strongly affect material removal.
- A removal mechanism based on particle–surface electrostatic interaction is proposed.
- Observed difference in the rates of Si and C removal has implications in polishing of crystalline SiC.

GRAPHICAL ABSTRACT



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ABSTRACT

Silicon carbide thin films, though of widespread use in microelectronic engineering, are difficult to process by chemical mechanical polishing (CMP) because of their hardness and chemical inertness. This report discusses the development of slurries based on silica abrasives that resulted in high amorphous SiC (a-SiC) removal rates (RRs). The ionic strength of the silica dispersion was found to play a significant role in enhancing material removal rate, while also providing very good post-polish surface-smoothness. For example, the addition of 50 mM potassium nitrate to a pH-8 aqueous slurry consisting of 10 wt% of silica abrasives and 1.47 M hydrogen peroxide increased the RR from about 150 nm h^{-1} to about 2100 nm h^{-1}. The role of ionic strength in obtaining such high RRs was investigated using surface ζ-potentials measurements and X-ray photoelectron spectroscopy (XPS). Evidently, H_2O_2 promoted the oxidation of Si and C to form weakly adhered species that were subsequently removed by the abrasive action of the silica particles. The effect of KNO_3 in increasing material removal is attributed to the reduction in the electrostatic repulsion between the abrasive particles and the SiC surface because of screening of surface charges by the added electrolyte.

1. Introduction

Amorphous SiC (a-SiC) is widely used in microelectronic devices and micro electromechanical systems (MEMS) designed for harsh environments [1–6]. It is also being pursued for applications in thin-film photovoltaics [7,8]. Due to their excellent chemical resistance and ease of deposition at a low temperature, a-SiC thin films

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can also be used as masking layers in various etch processes during advanced semiconductor device fabrication [9,10]. In all these applications, smoothening of the SiC surface, necessary for uniform growth and processing of subsequent deposited layers, is essential and can, in principle, be achieved using chemical mechanical planarization (CMP). However, SiC is a hard and inert material that is difficult to polish. Hence, there has been a substantial research effort aimed at developing slurries to polish SiC at reasonably high rates of material removal but with minimal surface damage [11–19]. While almost all of the previous studies on SiC CMP focused on the development of slurries for 6H–SiC or 3C–SiC, our goal here is CMP of a-SiC surfaces. On the basis of surface composition, a-SiC is comparable to the **a** or **m** face in 6H–SiC as it has both Si and C atoms on its surface [20].

Early attempts to polish SiC relied on severe mechanical and thermal stress generated by using a high concentrations of abrasives (as much as 30 wt% silica particles), high pressure (such as 6 psi), and high temperature (by heating the substrate, polishing conditioner, and the slurry) during polishing [11–13]. Not surprisingly, such methods resulted in a poor surface finish and many surface defects. Later, the use of different oxidizers was shown to improve the polishing rate as well as the surface quality of the post-polish SiC surfaces, but the removal rates (RRs) remained relatively low, below 500 nm h^{-1} [11,13,17,21]. It was suggested that the mechanism for the polishing SiC in the presence of an oxidizer follows the sequence of an initial oxidation of the surface Si species into SiO_2, followed by its removal by abrasion [16,21]. However, a clear understanding of the polishing mechanism, in particular, the fate of carbon during the CMP, has not yet emerged.

Li et al. [18] explored the possibility of polishing SiC by electrochemical mechanical planarization using an electrolyte solution consisting of hydrogen peroxide (H_2O_2) and potassium nitrate (KNO_3). They investigated a two-step process in which the SiC surface was exposed first to an electrolyte containing either H_2O_2 or KNO_3 to oxidize the film in the presence of an applied potential, followed by polishing the surface with a silica slurry to remove the oxidized layer. An anodic current density of 1 mA cm^{-2} was found to produce the best surface. While an increased current increased oxide formation, the final surface roughness deteriorated. Several chromium(III) oxide (Cr_2O_3) based slurries were reported [11,12] to give somewhat higher material RRs than their silica counterparts, but are less desirable because of the environmental and health hazards of chromium compounds. Moreover, it was found that the final quality of the surface was better when silica abrasives were used [12].

The low removal rates of SiC result in long polish times, even to remove layers as thin as 100 nm. So slurries that give considerably higher RRs with a good post-polish surface are necessary. Recently several investigators reported high SiC RRs but the slurry compositions were not disclosed [22,23]. Kurokawa et al. [24] used MnO_2 and $KMnO_4$ based slurries and obtained good RRs of 4H–SiC substrates. They also showed that the surface oxidation plays an important role during CMP.

In this work, an aqueous slurry consisting of 10 wt% of colloidal silica particles, H_2O_2 oxidizer (5 wt%, that is, 1.47 M), and KNO_3 (50 mM) at pH 8 was found to give RRs of 2100 nm h^{-1} (35 nm min^{-1}) for a-SiC films with a post-polish RMS surface roughness of approximately 0.5 nm. Furthermore, at the same pH, the RR increased to about 3200 nm h^{-1} (53 nm min^{-1}) when the concentration of KNO_3 was doubled to 100 mM. We discuss herein the role of ionic strength in obtaining such high RRs, and the polishing mechanism, based on material removal rate, ζ-potential, X-ray photoelectron spectroscopy (XPS), and contact angle measurements.

Table 1
Slurry composition.

Component	Concentration
Colloidal Silica, mean diameter 85 nm	10 wt%
Hydrogen peroxide	1.47 M (5 wt%)
KNO_3	0.05 M to 0.5 M
KOH or HNO_3	To adjust pH
Deionized water	Balance

2. Materials and experimental methods

2.1. Chemical mechanical polishing of a-SiC

Amorphous silicon carbide wafers, prepared by plasma-enhanced chemical vapor deposition on Si substrates, were purchased from WRS Materials (San Jose, CA). These 8″ wafers, covered with approximately 100 nm thick a-SiC film, were cut into several 2″ disks for use in the polishing experiments. Silica abrasives (Nexsil® 125A, mean diameter of 85 nm, specific gravity of 1.2, and surface area of 35 $m^2 g^{-1}$) were obtained from Nyacol Nano Technologies, Inc. (Ashland, MA) as a 30 wt% acid-stabilized colloidal dispersion in water. These dispersions were diluted and used at different loadings during slurry preparation. The chemical additives, hydrogen peroxide (aq. H_2O_2, stabilized, CAS no. 7722-84-1, *MW* 34.01 g mol^{-1}, 50 wt%), potassium nitrate (KNO_3, CAS no. 7757-79-1, *MW* 101.1 g mol^{-1}, ≥99%), potassium chloride (KCl, CAS no. 7447-40-7, *MW* 74.55 g mol^{-1}, ≥99%), potassium sulfate (K_2SO_4, CAS no. 7778-80-5, *MW* 174.27 g mol^{-1}, >99%), sodium nitrate ($NaNO_3$, CAS no. 7631-99-4, *MW* 84.99 g mol^{-1}, ≥99%), potassium hydroxide (KOH, CAS no. 1310-58-3, *MW* 56.11 g mol^{-1}, ACS reagent, ≥85%), nitric acid (aq. HNO_3, CAS no. 7697-37-2, *MW* 63.01 g mol^{-1}, 70%), and SiC powder (CAS no. 409-21-2) were obtained from Sigma-Aldrich Corporation and used as received without further purification.

The slurry was prepared by adding the chemical additives to water followed by the addition of abrasives to this solution and mixing using a magnetic stirrer for about 5 min. The composition of a representative slurry is shown in Table 1. The ionic conductivities of the slurries were determined at room temperature using a Malvern Zeta Sizer Nano-ZS instrument.

Polishing of the 2″ wafers was performed on a Center for Tribological Research (CETR) CP-4 polisher using a 9″ pad cut from a standard polyurethane IC-1000 K-groove pad supplied by Dow Electronic Materials (Newark, DE). A 3M-S60, 4″ diamond grit conditioner was used for ex-situ conditioning of the pad. Each polishing experiment was conducted at 4 psi down pressure for either 1 min or 5 min depending on the measured RR. If the RR was below 10 nm min^{-1}, the polishing was done for 5 min, and if the RR was higher, the duration of polishing was 1 min. Each polishing experiment was repeated at least once.

The RRs were determined using a Filmetrics® F20 analyzer, which measured the thickness of the films before and after polishing, at 16 points across the diameter of the wafer. The wafer was aligned to a notch during every measurement such that the same points were measured before and after polish. The difference in the thickness of the film before and after polish was used to calculate RR. The standard deviation of the RR was also determined using these data. The RRs thus obtained, are reported in the units of nm h^{-1}, to be consistent with previous reports on this topic. The pre-polish and post-polish surface characteristics (RMS roughness, maximum peak-to-valley distance, etc.) of the films were measured using a Horizon non-contact optical profilometer (Burleigh Instruments, Inc.) and atomic force microscopy (AFM, Thermomicroscopes Autoprobe M5, in the tapping mode).