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Chemical Mechanical Polishing of Cubic Silicon Carbide Films Grown on Si(100) Wafers

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This paper presents the results of a study to develop chemical mechanical polishing (CMP) processes for 3C-SiC films using commercial polishing pads in conjunction with basic colloidal SiO_2, acidic colloidal Al_2O_3, and near-neutral SiC slurries. The removal rate and surface roughness of the 3C-SiC surfaces were measured for the three slurries. The SiC-based slurry had the highest removal rate at 0.58 μm/h, while the colloidal SiO_2 slurry produced surfaces with the lowest average roughness at 15 Å. The removal rates of the Al_2O_3 slurries were found to be too low for practical applications. The surface chemistry and morphology of the as-deposited and polished 3C-SiC films were characterized using X-ray photoelectron spectroscopy and atomic force microscopy in order to gain insight into the physical and chemical mechanisms in the process.

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Excellent mechanical, electrical, and chemical properties coupled with advances in surface and bulk micromachining make SiC an important material for microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) with performance characteristics that cannot be achieved using Si.[1,2] For these applications, 3C-SiC is particularly attractive since it is the only SiC polytype that can be grown as single and polycrystalline thin films on Si substrates. 3C-SiC films are typically grown using high-temperature chemical vapor deposition (CVD) processes, but as-deposited films can be difficult to pattern into MEMS structures using lithographic techniques due to rough surface morphologies, which tend to increase with thickness. Excessive surface roughness is particularly problematic for NEMS structures, since it affects both the fabrication and the performance of the submicronmeter devices.[2]

To prepare rough SiC surfaces for microfabrication, several polishing techniques have been explored. These efforts include dry polishing using Cr_2O_3-impregnated acrylonitrile disks,[3] mechanical polishing with diamond-based slurries,[4,5] and chemical mechanical polishing (CMP) utilizing commercial silica slurries at room temperature and elevated temperatures (55°C).[5-8] These processes were developed specifically for 4H- and 6H-SiC wafers and epitaxial layers in the context of microelectronic devices. In what we believe to be the only paper on SiC polishing for MEMS applications, we reported on a SiC-based slurry optimized for the reduction of surface roughness on 3C-SiC films.[9] In that paper, the minimum achievable average surface roughness was 40 Å, an acceptable value for microlithography, but certainly not ideal for nanolithography.

This paper reports our effort to develop alkaline SiO_2, acidic Al_2O_3, and near-neutral SiC slurries to polish 3C-SiC films grown on Si(100) wafers with the goal of further reducing surface roughness. The removal rates and surface roughness reduction rates were compared for the three slurry types in order to determine the optimum conditions for SiC surface preparation. The chemical composition of the polished surfaces was studied using X-ray photoelectron spectroscopy (XPS) and the morphology of as-deposited and polished surfaces was characterized by atomic force microscopy (AFM).

Experimental

The samples used throughout the study were nominally 2 μm thick, single-crystal 3C-SiC films grown on 100 mm diam Si(100) wafers by atmospheric pressure chemical vapor deposition (APCVD) using an epitaxial growth system described in depth elsewhere.[10] The films were grown in an rf-induction heated reactor using a SiC-coated, graphite susceptor which was nearing the end of its usable lifetime, determined by an observable degradation of surface morphology in the as-deposited films, thus ensuring the production of rougher films to better facilitate the study of surface roughness reduction. The epitaxial growth process resulted in the production of 3C-SiC films with a 30% variation of thickness across each wafer. However, the reproducibility of the deposition process was quite high, with less than a 5% variation in average thickness from run to run, thus facilitating an accurate characterization of each polishing process in terms of removal rates and roughness reduction rates.

The polishing experiments were performed using a Struer's Pedamax-2 polishing system fitted with Rodel Suba IV polishing pads. The rotation speed of the wafer carrier was fixed in a counterclockwise direction, while the polishing pad was driven at 300 rpm in a clockwise direction. The polishing slurries were dispensed onto the spinning polishing pad at a rate of approximately 200 mL/min. The polishing pad was thoroughly brushed and rinsed after each polishing session to ensure complete removal of any slurry residue, thus minimizing the likelihood of cross contamination. A new pad was installed when the slurry type was changed. The adjustable loading force settings of the Pendamax-2 polishing tool were set at select values between 100 and 375 N for this study. The total polishing time for each sample was 30 min, with the process interrupted at 10 min intervals in order for surface roughness and film thickness data to be collected.

Polishing slurries were created from the following baseline formulations: a colloidal SiO_2 slurry (SC-1) from Cabot Microelectronics; an Al_2O_3 slurry (Ultra-Sols) from Eminess Technologies; and a custom-prepared, SiC slurry made from an average size of 2.02 μm SiC powder dispersed in deionized water. For colloidal SiO_2-based polishing, custom formulations were made by diluting the baseline slurry with deionized water, thereby changing the slurry solid content. For this study, the solid content ranged from 1 to 15 wt %. The pH of the slurry was adjusted by adding appropriate amounts of KOH or HCl to the mixture, and ranged from 9 to 12, with the pH of the baseline slurry being 11. Like the SiO_2 slurries, customized acidic Al_2O_3 slurries were formulated by diluting the baseline Al_2O_3 slurry with deionized water and adjusting the pH by adding HCl or KOH. In this manner, slurries with a solid content of 5 to 15 wt % and a pH of 4 were created. Near neutral (a pH of 6 to 7) SiC slurries were made by mixing a fixed weight of SiC powder with various amounts of deionized water, yielding slurries with solid contents ranging from 1 to 9 wt %. Table I lists the physical properties of the abrasive particles contained in each of the slurries.

For the as-deposited 3C-SiC films, the thickness and the average surface roughness were measured at five equally spaced locations across each wafer, with the same points measured after each polishing time segment. Film thickness was measured using an optical

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Table I. The physical properties of abrasive particles in each slurry.

Abrasive particles	Density (g/cm^3)	Hardness Mohs	Hardness Knoop (kg/mm^2)
SiC	3.10	9.5	2500
SiO_2	2.67	7	820
Al_2O_3	3.98	9	2150

Table II. The atomic concentration at the surfaces of as-deposited and polished SiC surfaces.

	As-deposited	SiO_2 polished	SiC polished
C 1s	50.6	52.8	52.3
Si 2p	28.4	40.0	37.9
O 1s	20.9	7.2	9.8
Atomic ratio C/Si	1.78	1.32	1.38
Atomic ratio O/Si	0.74	0.18	0.26

reflectometer (Filmetrics F20)[11] and surface roughness was measured using a Dektak 3030ST stylus force profilometer.[9] For extremely rough as-deposited films, a light polish was initially performed in order to reduce the roughness to a level where optical thickness measurements could be made. The removal rate and surface roughness reduction rate were calculated by simply subtracting the measured values before and after polishing. The average removal rate was calculated by averaging the removal rate over the five locations on the wafer. The same method was used to determine the average roughness reduction rate.

Due to limitations associated with the stylus profilometer, an atomic force microscope (AFM, Digital Instrument Nanoscope Multimode III) was used to characterize the surface morphology of select 3C-SiC surfaces before and after the polishing experiments.[12] AFM measurements could not be performed at the intermediate steps, since such measurements would require the wafers to be diced into chips, thus rendering them unusable in the polishing tool. X-ray photoelectron spectroscopy (XPS) measurements were made on the same samples in a Perkin-Elmer 5500 XPS system, using a Al Kα line X-ray source at 1486.6 eV. The base pressure in the analysis chamber was around $\sim 10^{-9}$ Torr. The surface chemistry of SiC film was obtained by analyzing the shapes of the Si 2p, C 1s, and O 1s peaks. Sputter depth profiling using a 4 keV argon beam was sometimes performed to expose the bulk region of the samples in order to establish the baseline bulk concentrations of the various elements and an upper bound on the thickness of any near surface region.

Results and Discussion

As-deposited APCVD 3C-SiC films.—Figure 1 is a representative AFM micrograph of the roughest section of an as-deposited, 2 μm thick 3C-SiC film. This micrograph shows an undulant surface that is characteristic of the as-deposited films. Stylus profilometry indicates that the average roughness of the as-deposited films is about 930 Å, making them ideal specimens for polishing studies. The surface of the unpolished 3C-SiC films consists of Si, C, and O, with the O content at 20.9 atom %, as determined by XPS. Such a high content of O at the surface is not surprising since a thin stable oxide film can be formed on untreated SiC surfaces. The O content decreases to a constant value of less than 1 atom % at a depth of about 20 Å below the surface as determined by XPS sputter depth profiling, indicative of a thin oxide that formed either at the end of the film growth process or upon exposure to atmosphere. The sputter depth profiling confirmed that the SiC films were stoichiometric. A summary of the XPS results from the unpolished, as well as polished samples, is presented in Table II.

3C-SiC films polished with the SiC slurries.—As stated previously, the baseline SiC slurry consisted of 2.02 μm sized SiC powder mixed with deionized water, resulting in near-neutral (pH around 6) polishing slurries with a SiC solid content ranging from 1 to 9 wt %. Figure 2 shows the relationship between the average removal rate and slurry solid content for these SiC-based slurries. The relationship is generally linear, with a removal rate of 96 Å/min or 0.58 μm/h for the 9 wt % slurry, the limit of our study. In contrast, the roughness reduction rate actually decreased as the slurry solid content was increased, with the highest rate being 11.5 Å/min for the 1.5 wt % slurry and the lowest being 4.3 Å/min for the 9 wt % slurry. Given the abrasive nature of SiC powders, it is likely that the high solid content SiC slurries produce a higher density of polishing-induced scratches and other surface defects than the low solid content slurries, thus resulting in lower than expected roughness reduction rates. Figure 3 is a plot of removal rate *vs.* loading force for a slurry solid content of 1.5 wt %. The data indicate that the removal rate of increases with increasing loading force in a manner consistent with Preston's equation[13]

$$R \sim FVA^{-1}$$

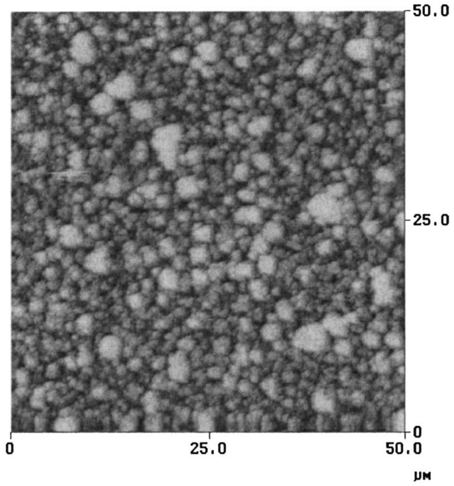

Figure 1. Typical AFM surface morphology from the roughest section of an as-deposited 3C-SiC film. The average surface roughness is 930 Å.

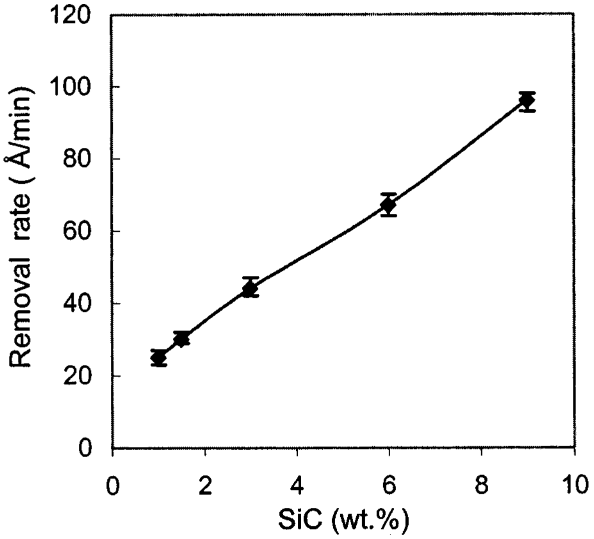

Figure 2. Removal rate *vs.* solid content for a SiC slurry with an average particle size of 2.02 μm and a polishing force of 360 N.

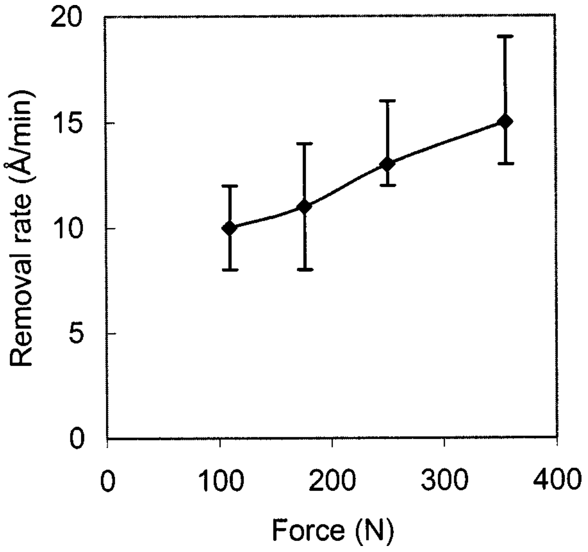

Figure 3. Removal rate *vs.* polishing force for a 1.5 wt % SiC slurry.

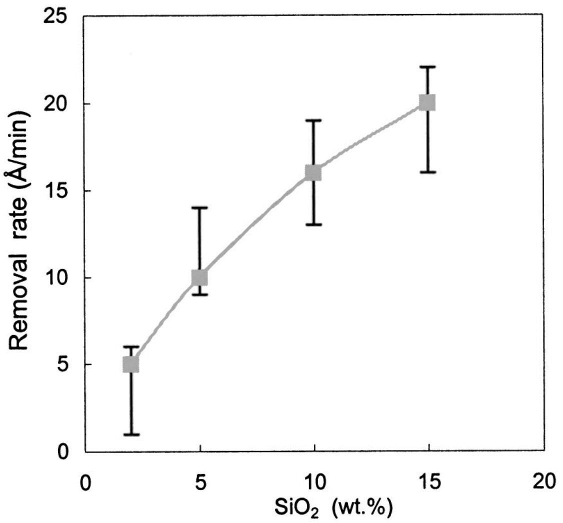

Figure 5. Removal rate *vs.* solid content for a SiO_2 slurry with a pH of 10.4 and a polishing force of 360 N.

where R is the removal rate, F is the normal force, A is the area of contact, and V is the pad velocity. An increase in removal rate with an increase in loading force can be attributed to the formation and migration of a hydrated surface layer, which is enhanced at high pressures (loading forces).[14] An additional set of samples was polished using a 1.5 wt % slurry heated to 55°C. No measurable change in roughness reduction and removal rate as compared with a similar room temperature slurry was observed. Figure 4 shows an AFM micrograph of a 3C-SiC surface after being polished at room temperature with a 1.5 wt % SiC slurry and a loading force of 360 N for 30 min. In comparison with the AFM micrograph from the as-deposited sample shown Fig. 1, the surface appears to be nearly featureless, having an average roughness of only 25 Å.

3C-SiC films polished with the SC-1 SiO_2 slurries.—Since SiC powders suitable for polishing slurries are only available in relatively large particle sizes, it is difficult to obtain defect-free SiC surfaces with an average surface roughness below 10 Å using SiC-based slurries. However, commercially available SiO_2-based slurries using relatively soft SiO_2 abrasives with a particle aggregate size of only about 1000 Å are an attractive alternative for SiC polishing, especially if the high pH values facilitate a chemical component to the removal process. It was for these reasons that Cabot Microelectronics SC-1 colloidal silica polishing slurry was selected for this study. Figure 5 shows the effect of SiO_2 solid contents in the SC-1 slurry on the removal rate of 3C-SiC. At a constant pH, the removal rate of 3C-SiC increases with increasing SiO_2 content. This effect is consistent with the observations made for SiC-based slurries described previously. Although the removal rate behavior is similar to the SiC slurries, the magnitude of the removal rate is much lower for the SiO_2 slurry at equivalent solid concentrations, an observation consistent with the hardness differences of SiO_2 and SiC. With respect to pH, an increase in the pH for alkaline slurries results in an increase in the removal rate, from a low average of 2 Å/min for a pH of 9 to a high average of 12 Å/min for a pH of 12 as shown in Fig. 6. Acidic slurries could not be formulated because colloidal SiO_2 in SC-1 slurries is not stable at low pH values. Figure 7 shows an AFM micrograph of a 3C-SiC surface after being polished at room temperature with a 10 wt % SiO_2-based slurry and a pH of 11.4 for 30 min. For this sample, the average surface roughness was 15 Å.

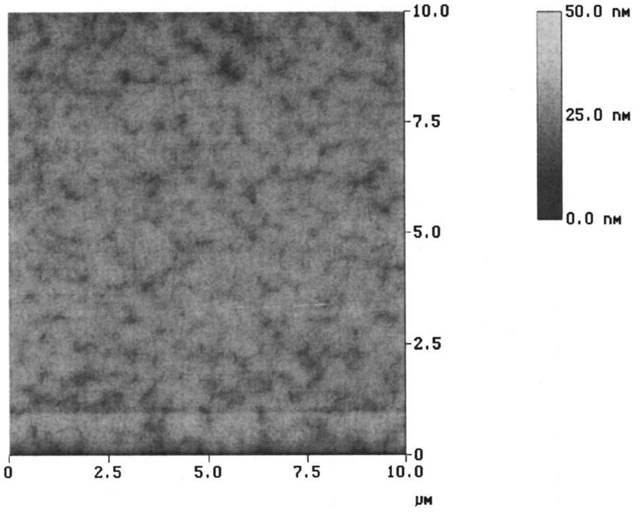

Figure 4. AFM micrograph of a 3C-SiC film polished with a SiC slurry. The average surface roughness is 25 Å.

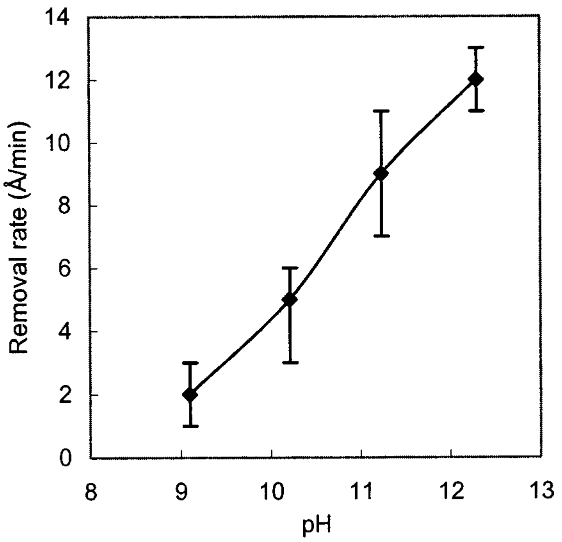

Figure 6. Removal rate *vs.* pH for a SiO_2 slurry with a solid content of 6 wt % and a polishing force of 360 N.

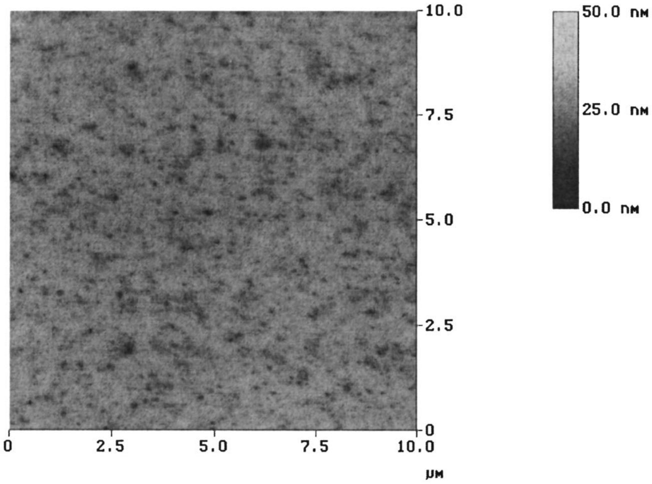

Figure 7. AFM micrograph of a 3C-SiC surface polished with a SiO_2 slurry. The average surface roughness is 15 Å.

As with the SiC slurries, experiments conducted with heated SiO_2-based slurries showed no measurable differences when compared with equivalent room temperature slurries, an observation that differs from the results reported in Ref. 6 for 6H-SiC polishing.

3C-SiC films polished with the Al_2O_3 slurries.—Acidic Al_2O_3 slurries formulated with two different particle sizes (690 and 2800 Å) were used to polish SiC films. Figure 8 shows that an increase in solid contents and particle size results in an increase in removal rate. In general, the polishing rates of Al_2O_3 slurries were found to be much lower than basic SiO_2 slurries for the same abrasive contents. As shown in Table I, the hardness of Al_2O_3 is much higher than that of SiO_2, but only slightly lower than that of SiC. Based on hardness and particle size alone, it might be expected that the polishing rate of Al_2O_3 slurries would be much higher than SiO_2 slurries for the same solid contents. This result, however, suggests that the alkaline nature of the SiO_2 slurries plays a major role in SiC polishing. Due to the low removal rates, no further studies with Al_2O_3-polished slurries were performed.

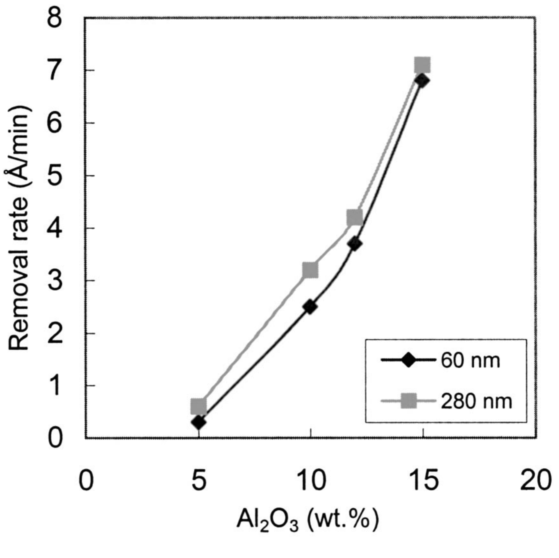

Figure 8. Removal rate *vs.* solid content for a Al_2O_3 slurry with a pH of 4 and a loading force of 360 N.

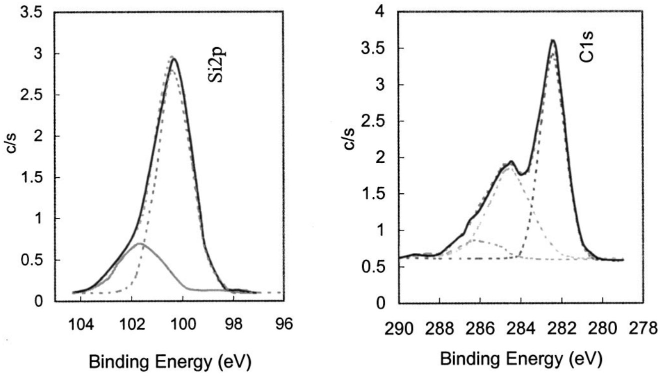

Figure 9. Si 2p and C 1s XPS peaks from a 3C-SiC surface after being polished with a SiC slurry.

XPS analysis of the polished 3C-SiC films.—XPS was used to examine SiC surfaces polished using the SiO_2- and SiC-based slurries. Table II lists the atomic concentration of C, Si, and O on the as-deposited and polished surfaces with SiO_2- and SiC-based slurries. For the polished samples, the specimens were loaded into the analysis chamber immediately after concluding the final 20 min polishing step. Oxygen was found on the surface of all samples, with the concentration being highest on the as-deposited films (23%) and lowest on the sample polished with the SiO_2 slurry (7.2%). These observations contrast with XPS studies on Si_3N_4, where the percentage of atomic O on Si_3N_4 surfaces is higher for polished films than for as-deposited samples.[12,15] In all cases, the concentration of O decreased to about 1% at a depth of approximately 30 Å beneath the surface, suggesting that the enhanced oxygen concentration at the surface was related to a thin surface oxide layer. The surface of one sample was re-examined one week after the polishing experiments were concluded. It was verified that oxygen concentration had not increased, implying that the oxide on the polished SiC surfaces were formed as a result of the polishing step, not simply exposure to atmosphere.

Deconvolution of Si 2p, C 1s, and O 1s XPS peaks was performed to identify the chemical components of the surface oxide layer. Figure 9 and 10 show the deconvolution of Si 2p peak and C 1s peak of 3C-SiC samples polished using SiC and SiO_2 slurries, and Table III lists the percentages of chemical components on the as-deposited and polished SiC surfaces. The binding energies associated with the Si 2p and C1s peaks are in good agreement with work previously published for oxidized SiC.[16-18] There is an obvious Si-C-O component for 3C-SiC surfaces polished using both SiC and SiO_2 slurries. The data suggest that the polishing processes resulted

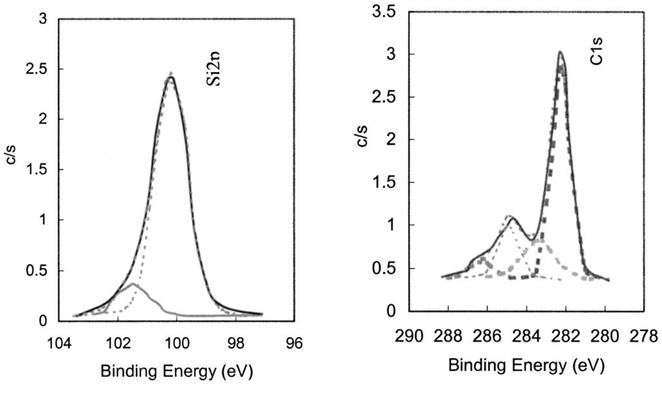

Figure 10. Si 2p and C 1s XPS peaks from a 3C-SiC surface after being polished with a SiO_2 slurry.

Table III. The atomic concentration and chemical composition at the surface of as-deposited and polished SiC films as determined by XPS.

		As-deposited	SC-1 polished	SiC polished
Si 2p	Si-Si	0	0.51	0
	SiC	52.44	88.81	77.99
	Si-C-O	47.56	10.68	22.01
C 1s	SiC	31.59	58.23	50.35
	$Si_4C_{4-x}O_2$	0	18.54	0
	$Si_4C_4O_4$	36.35	17.37	41.89
	C-O	30.63	5.86	7.66
	COOH	1.43	0	0.09

in the formation of $Si_4C_4O_4$ and $Si_4C_{4-x}O_2$ at the surface, with a thickness in the range of 10 to 30 Å as determined by argon sputtering. This finding is consistent with the reports from other studies,[3,19] that also showed that wet and dry polishing of SiC involves the formation and removal of a surface oxide. For the case of abrasive-free wet polishing, it has been shown that the polishing rate of polycrystalline SiC using cast iron plates and Si_3N_4 pads with oxidizing solutions depends on the type of oxidant used in the solution.[19] Likewise, dry polishing of 6H-SiC with Cr_2O_3-impregnated acrylonitrile disks results in the oxidation of 6H-SiC surfaces.[3] Our findings offer further support that the formation of a surface oxide is an important component in an effective SiC polishing process.

Conclusions

Basic colloidal SiO_2, acidic colloidal Al_2O_3, and near-neutral SiC slurries were used to polish 3C-SiC deposited by APCVD. SiC slurries have the highest polishing rates, followed by SiO_2 slurries and Al_2O_3 slurries. Colloidal SiO_2 slurries produce surfaces with the lowest surface roughness. For all slurries, an increase in the abrasive content produces an increase in the polishing rate. The polishing rate of the Al_2O_3 slurries was found to be too low for practical applications. For both SiC and SiO_2-based slurries, XPS analysis of the surfaces indicates that a surface oxide is formed during the process, which is then removed as the process continues.

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