Chemomechanical Polishing of Silicon Carbide

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ABSTRACT

In an effort to improve silicon carbide (SiC) substrates surfaces prior to epitaxial growth, two chemomechanical polishing (CMP) techniques were investigated and the results were compared with a mechanical polishing procedure involving various grades of diamond paste. This work focused on silicon-terminated (0001) SiC surfaces. The two CMP techniques utilized (*i*) chromium oxide(III) abrasives and (*ii*) colloidal silica polishing slurry. The best surfaces were obtained after colloidal silica polishing under conditions that combined elevated temperatures (~55°C) with a high slurry alkalinity (pH > 10) and a high solute content. Cross-sectional transmission electron microscopy showed no observable subsurface damage, and atomic force microscopy showed a significant reduction in roughness compared to commercial diamond-polished wafers. Growth experiments following colloidal silica polishing yielded a much improved film surface morphology.

A pressing need in the development of SiC semiconductor technology is to improve the structural and surface quality of epitaxial films used in device fabrication. A flat and defect-free substrate surface is crucial for the epitaxial growth of thin films. Research on the epitaxial growth of 4H- and 6H-SiC has shown that process-induced defects on the substrate surface, such as scratches generated during lapping and polishing, are the primary contributors to unwanted polytype inclusions in the epi layer.[1-4]

Silicon carbide presents many challenges for wafer surface preparation because of its high hardness and remarkable chemical inertness. Existing surface polishing techniques for SiC can be categorized as purely mechanical, chemomechanical, or etching. Mechanical polishing of both poly- and single-crystalline SiC wafers primarily uses hard abrasives such as diamond polishing compounds mixed with water. Diamond abrasives achieve materials removal through plastic deformation, and thus unavoidably result in a hill-and-valley surface structure accompanied with a damaged (or strained) subsurface layer containing dislocations,[5] although the surface roughness and the subsurface damage can be reduced significantly with the use of submicron sized diamond abrasive particles.[6,7] In contrast, CMP techniques combine mechanical polishing with a chemical etching action, and can achieve truly defect-free surfaces. To the authors' knowledge, the only CMP process for SiC in the literature is a dry polishing process, reported by Kikuchi *et al.*,[8] utilizing 0.5 μm Cr_2O_3-impregnated acrylonitrile disks. These authors found an anisotropy in the polishing rate of 6H-SiC, with the rate of removal being significantly higher on the carbon-terminated ($000\bar{1}$) face where they obtained a defect-free surface. Generally, the carbon-terminated face of SiC is considered not as useful as the silicon-terminated (0001) face for device fabrication or as substrates for film growth. The third approach to preparing a smooth surface is by etching. Similar to CMP, etching can completely remove any subsurface damage resulting from prior mechanical polishing steps. A process which may have produced probably the best on-axis Si-terminated (0001) SiC surfaces so far has been recently reported by Owman *et al.*[9] These authors used an atmospheric-pressure hydrogen etch at 1550°C for 30 min and obtained a defect-free surface with regularly spaced steps of single 6H-SiC unit-cell height. An obvious disadvantage of a purely etching method, as compared to a CMP process, is that the former is not a global planarization technique. Etching removes a uniform layer of material from surface, and therefore cannot efficiently reduce long-range roughness. CMP reduces both local and long-range roughness with careful selection of polishing pad material. In this article, we report successful CMP polishing of the Si-terminated (0001) surface of SiC using concentrated colloidal silica slurries at high pH values and at elevated temperatures. This process can be integrated with the necessary dicing and polishing procedure in SiC wafer production. It may also be useful in the planarization of SiC-based very large scale integrated (VLSI) multilayer devices and SiC-based precision ultraviolet (UV)-laser optics with which a high-temperature hydrogen etch is incompatible.

To compare the effect of different polishing media on the Si-terminated (0001) face of SiC, three abrasive/cloth combinations were chosen for the study. Mechanical polishing was performed using diamond paste applied on Struers DP-DUR polishing cloths with deionized water as lubricant. In the first of the two CMP procedures performed, suspended chromium oxide polishing abrasives were used on the Buehler Microcloth polishing cloth. This process used deionized water as lubricant and was therefore different from the dry process reported by Kikuchi *et al.*[8] The second CMP procedure was performed using Rodel colloidal silica polishing slurries on Rodel 750 pads (Rodel, Inc., Newark, DE 19713). The substrates used here were commercial SiC wafers of either 4H or 6H polytypes produced by one of the sublimation techniques, *e.g.*, Acheson or the modified Lely process. The size of these pieces ranged from about 30 to 130 mm^2 and the thickness ranged from 0.260 to 0.330 mm. The C-terminated faces of these samples were mounted on a precision-polished quartz carrier disk of 83 mm diam and the disk was placed on the vacuum chuck of a Logitech PP5 polishing jig (Struers, Inc., Westlake, OH 44145). The PP5 jig was then put on a rotating disk mounted on a Logitech PM2A single station precision polishing machine (Struers, Inc.) All removal rates reported below were measured when a 15 N force was applied on the carrier plate at a rotation speed of 30 rpm for the rotating disk on the PM2A. The area being polished in each cycle was kept constant at ~100 to 130 mm^2 by mounting several small pieces symmetrically about the center of the quartz carrier plate. New pads were always prewetted with deionized water. No pad conditioning/reconditioning was otherwise performed during each polishing session.

Nomarski differential interference contrast (NDIC) microscopy and atomic force microscopy (AFM) observations were carried out to determine the surface quality. In addition, cross-sectional transmission electron microscopy (XTEM) was used to examine the extent of subsurface damage on well-polished samples. AFM imaging was performed using a Digital Instruments Dimension 3000 operated in the tapping mode. XTEM observations were performed on a Philips CM20 microscope working at 200 kV. Chemical vapor deposition (CVD) was carried out on as-received and repolished commercial wafers to assess the improvement in epi layer quality brought about by the CMP procedure.

Removal rate measurements are tabulated in Table I. In the Table, "no action" means unimproved surfaces with measured removal rates below 0.5 μm after polishing sessions of at least 8 h in duration (*i.e.*, <60 nm/h). By "minimal," we mean clearly improved surfaces with a removal rate of less than 60 nm/h. The best results were achieved with Nalco 2350 (Rodel, Inc.) at 1:2 strength (further dilution may still be adequate although a slower removal rate is expected). The slurry, preheated to 40 to 55°C, was introduced on the polishing pad which was heated with an infrared lamp to maintain a temperature of ~55°C. The slurry feeding rate was not critical to the success of the process but generally should be kept at an adequate, stable rate to prevent the pad from becoming too dry. Due to limitations with our equipment, we did not recirculate the slurry, and therefore the impact of changing pH during polishing could not be determined.

NDIC micrographs taken before and after the colloidal silica polishing are compared in Fig. 1. While it was easy to find a high density of hairline scratches randomly distributed on all as-received SiC surfaces, the repolished surfaces were featureless. It was impossible to find the correct focus on the surface polished by this new process without resorting to focusing aids such as residual

Table I. Comparison of surface material removal rates by the different polishing media.

Polishing medium	Removal rate	Comments
Diamond paste (particle size = 1 μm)	2 to 2.25 μm/h	Optically shiny, <50 nm subsurface damage zone; occasional 70 nm defects
Cr_2O_3 slurry (particle size = 1 μm)	Si-face: No action C-face: 3 to 3.6 μm/h	Si-face: severe scratching C-face: optically shiny
Colloidal silica (particle size = 59 to 70 nm) 25 w/o SiO_2, slurry feed = 500 ml/h	1. pH 8.5, RT: No action 2. pH 10, RT: minimal 3. pH 11, RT: <0.1 μm/h 4. pH 8.5, 55°C: No action 5. pH 10, 55°C: <0.1 μm/h 6. pH 11, 55°C: <0.2 μm/h	RT = room temperature Featureless surface and no observable subsurface damage for processes 5 and 6

colloidal silica particles deliberately left on the surface. AFM data showed a significant reduction in the surface roughness: from 2 nm rms on the best commercially available surfaces prior to the treatment to 0.5 nm rms after this treatment (Fig. 2). This number also represents an order of magnitude reduction in surface roughness compared to that achieved by the Cr_2O_3 dry polishing. Bright field (BF) and weak-beam dark-field (WBDF) XTEM micrographs showed no evidence of subsurface damage on the colloidal silica polished samples (Fig. 3). Further evidence of quality improvement came from CVD growth studies performed on the same wafer before treatment and after treatment. As shown in Fig. 4, the reduction in observable morphological defects was significant.

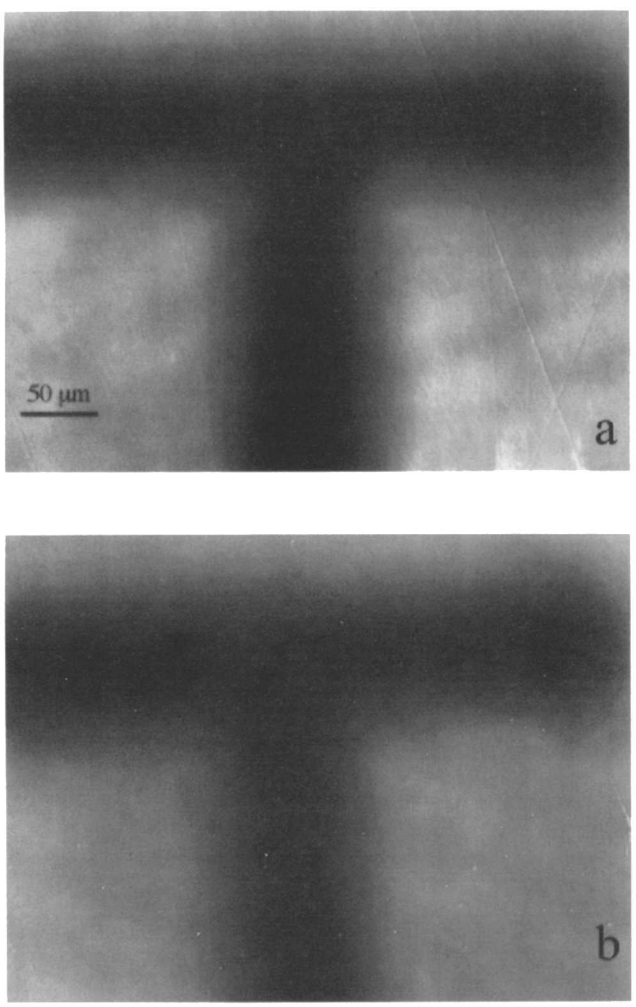

Fig. 1. NDIC images of a commercial 4H-SiC wafer: (a) as-received, showing clearly visible scratches on its (0001) surface; (b) the same area after CMP repolishing showing a featureless surface except for the residual silica particles which were left on the surface to act as focusing aids. The letter "T" was laser-inscribed on the back of the transparent wafer which serves as a location marker.

CMP using colloidal silica has been employed since the mid-1960s for obtaining defect-free surfaces on silicon wafers. However, due to the very large differences in the bonding energies and mechanical properties between silicon and silicon carbide, there are no reports so far on using this common polishing medium on silicon carbide.

Based on the removal mechanism of colloidal silica on (111) silicon surfaces proposed by Pietsch *et al.*[10,11] and others[12] it is speculated that an oxidation process is also occurring during the colloidal silica CMP of SiC. Each silicon atom on the (0001) surface of SiC is strongly bonded to three underlying carbon atoms and has one unsatisfied (dangling) bond pointing outward. These dangling bonds are often eliminated by reconstruction where neighboring atoms form surface (polymeric) bonds, or, alternatively, they may be compensated by foreign atoms (*e.g.*, oxygen or hydrogen) which usually segregate at the free surface. The alkaline solution contains OH^- groups which induce a dipole and weaken the Si-C bonds; in addition, they allow the H_2O or the dissolved oxygen in the slurry to attack the Si surface bonds and form SiO_2. Subsequently, the top Si-C bilayer at the surface (with the overlaying oxide layers) is polished away by the mechanical grinding action of the silica particles, and a new Si-terminated surface is exposed. This process could then be repeated to further remove Si-C bilayers from the surface.

A proper balance between the speed of mechanical abrasion and chemical etching rate is probably critical to the success of

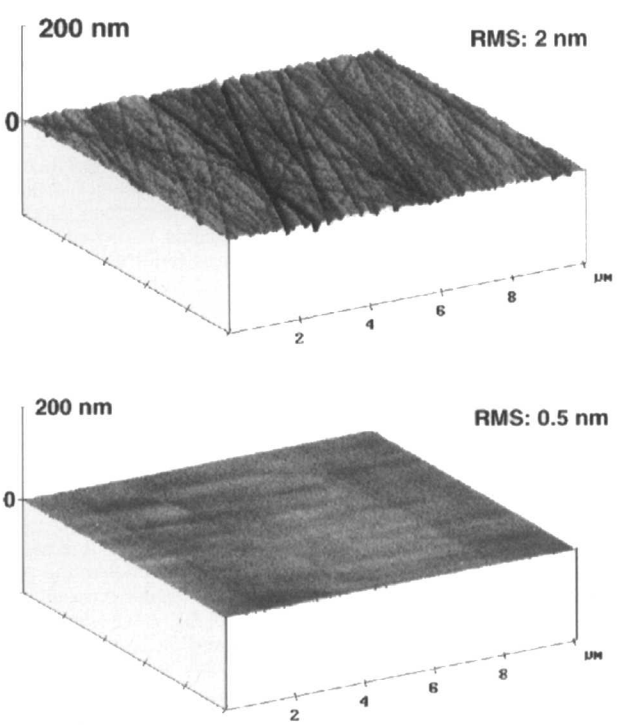

Fig. 2. AFM images of (0001) SiC surfaces showing effectiveness of colloidal silica CMP: (a, top) as-received commercial 4H-SiC wafer; (b, bottom) same area after CMP repolishing.

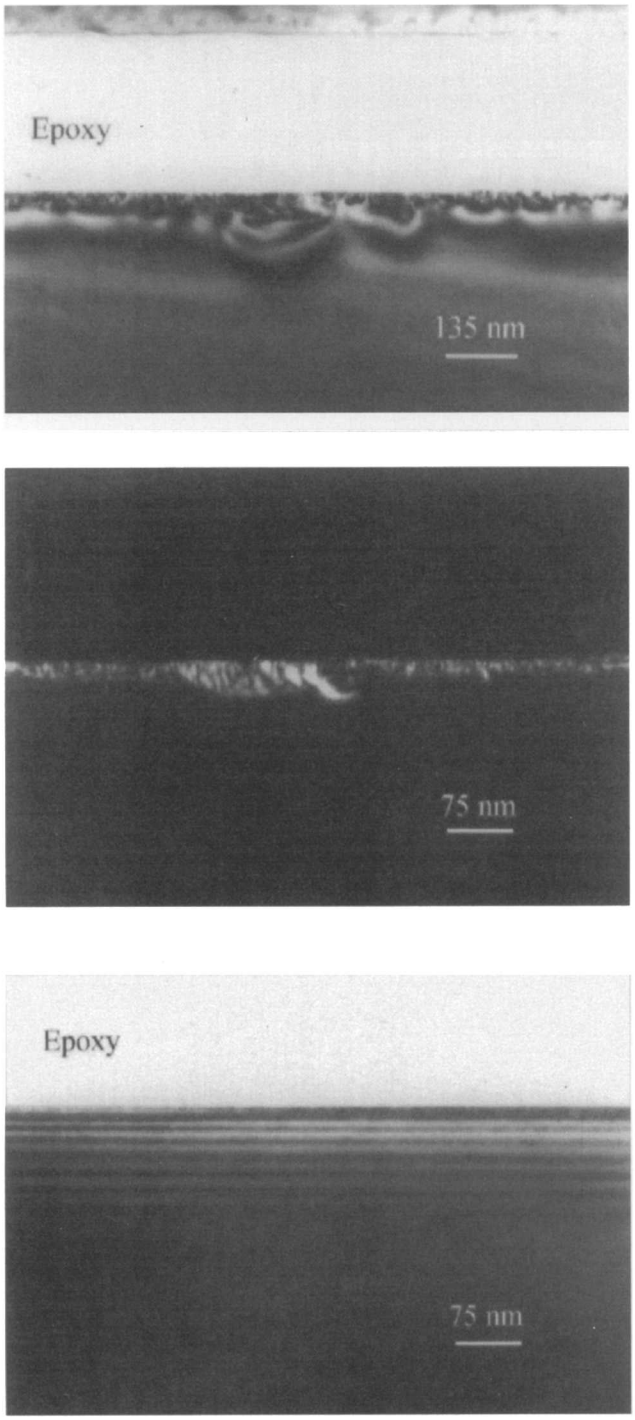

Fig. 3. (a, top) Bright-field (BF) XTEM micrograph showing the extent of subsurface damage after a 1 μm diamond polishing procedure. The strain contrast exaggerates the size of the damaged zone; (b, middle) Weak-beam dark-field (WBDF) image of the same area where the depth of the damaged zone is about 50 nm; (c, bottom) BF XTEM micrograph of the wafer following a Nalco-2350 polish under optimum conditions. No subsurface damage could be observed under BF or WBDF imaging conditions on the entire electron-transparent region of the sample.

CMP on SiC. If the rate of chemical reaction is not fast enough, mechanical action results in subsurface damage and a very slow removal rate. A higher pH value increases chemical reaction rate by increasing the concentration of the OH^- groups which weaken the Si-C bonds. Also, since chemical reactions are thermally activated processes and generally obey the Arrhenius relationship, increasing the slurry temperature and/or the temperature at the pad surface is also an effective means of enhancing the chemical etching.

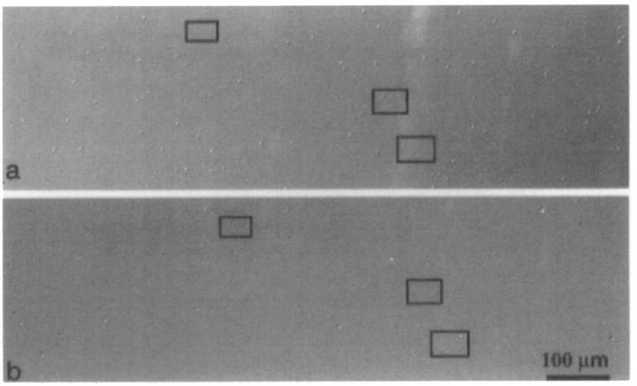

Fig. 4. (a) NDIC images of the same area of a 6H-SiC sample with two different epi layers (a) first epi layer on an as-received surface, (b) second epilayer, after the first epi layer was removed by diamond polishing followed by CMP. Boxes indicate defects common to both epi layers (probably due to dislocations in the bulk crystal).

In summary, we have demonstrated a CMP process on the Si-terminated face of SiC to produce a low-defect surface. The successful application of this process requires concentrated colloidal silica slurry at temperatures higher than 55°C and a pH value higher than 10. The polishing rate should allow the removal of any subsurface damage caused by a prior 1 μm diamond stock removal step in ~30 min. Further optimization of this process can be expected under other polishing conditions and proper selection of slurry/pad combinations. However, much work is still needed to understand the microscopic mechanism of this polishing process.

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