SiC Surface Preparation by Hydrogen Cleaning for High-Temperature, High-Power Device Integration

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Abstract

A hydrogen etch process has been developed that effectively converts rough, oxide-contaminated Silicon Carbide (SiC) surfaces into smooth, clean surfaces with atomic steps. In order to create novel, robust, high-power, high-frequency devices based on wide bandgap SiC, a well controlled, clean, and atomically smooth substrate surface is necessary. Silicon carbide wafers received from commercial vendors contain scratches, micropipes, oxides, and other containments that can impede the growth of thin films. A hydrogen furnace has been designed and custom built that can heat the SiC up to 2000°C in a controlled mixture of hydrogen and argon. The furnace produces atomic steps, as seen by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), on both the silicon and carbon face. In addition, Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) scans show negligible oxygen and no evidence of graphitic carbon on the surface. By varying Ar/H_2 flow ratios, operating windows that avoid hydrogen over-etching and still remove the surface contaminants have been determined. The final surface, suspected to be hydrogen-terminated, has been demonstrated to be stable for 24 hours in laboratory air.

Introduction

Integrating wide bandgap semiconductors with functional thin films is driven by the need to develop high-power, high-frequency, robust devices, capable of operating in high-temperature environments where silicon-based devices are inadequate. One potential wide bandgap semiconductor is silicon carbide (SiC), whose properties are compared to silicon's properties in Table 1. Commercially available SiC, from vendors including Cree, Intrinsic, Dow Corning, and II-VI, contain an oxide layer a few monolayers thick and surface scratches, which are remnants of mechanical polishing. Types of surface preparation or cleaning methods for SiC described in the literature include hot-wall CVD, quartz-tube furnace, and hydrogen plasma.[4,6,7] In all of these techniques, a heated SiC surface is exposed to some form of hydrogen due to the demonstrated capability of hydrogen species to form volatile hydrides and etch both oxides and silicon. Although morphological results of the various surface preparation methods are frequently presented, chemical composition studies of these surfaces are few,[2,5] and do not compare different surface preparation methods.

One of the goals of our laboratory is to investigate nucleation and growth mechanism of functional oxides on SiC substrates for high-power, high-frequency devices as well as for novel multifunctional devices. To effectively study nucleation and growth, it is necessary to produce well-characterized, smooth SiC surfaces with atomic steps and minimal oxygen contamination. In order to accomplish this, a relatively inexpensive and versatile bench top apparatus has been built and the impacts of its processing parameters on morphology and

chemistry have been studied. In addition, the SiC surface after several different cleaning methods has been compared.

Table 1: Comparison of select semiconducting properties of silicon and silicon carbide. Silicon carbide's wide bandgap, high electric breakdown field, and high thermal conductivity relative to silicon, make SiC a promising material for high-power, robust devices.

Property	**Si**	**6H-SiC**
Bandgap (eV)	1.12	3.03
Structure	Cubic (diamond)	Hexagonal
Lattice spacing (Å)	a = 5.43	a = 3.08 c = 15.12
Electric breakdown field (kV/cm)	300	2500
Thermal conductivity (W/cm K)	1.5	4.9
Saturated electron drift velocity (cm/sec)	$1x10^{17}$	$2x10^{17}$

Experimental

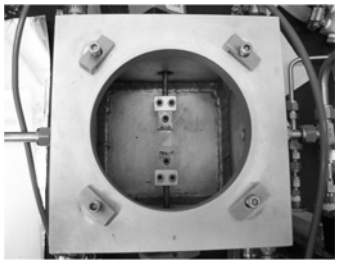
Commercially available hydrogen furnaces can cost as much as $70,000 and occupy a large amount of floor space.[8] Modeled after work by Ramachandran et al.[3] and with consultation with Randy Feestra of Carnegie Mellon University, we designed and built a "hydrogen furnace" that can fit on a bench top and costs under $3,000. The custom hydrogen furnace shown in Figure 1 allows precise control over the substrate temperature, total gas flow rate, and Ar/H_2 gas flow ratios.

The main chamber of the furnace consists of an aluminum box (7.5 x 7.5 x 7.5 in^3) with integrated water cooling. Attached to the top of the box is a stainless steel cylinder with a quartz glass viewport for temperature measurement using an optical pyrometer. On two opposite sides, are the inlets and outlets for high purity Ar and H_2 process gasses. On the inlet side, each gas feed has a separate flowmeter for both total flow and gas ratio control. On the outlet side, a custom built burner is lit to burn excess H_2 in the outlet gas. A power supply provides up to 115 amps to a piece of 0.001 inch thick tantalum (Ta) foil clamped between the two power feedthroughs. The SiC sample rests on this foil (see Figure 1b). The temperature is controlled by the amount of current passing through the Ta foil.

The 6H-SiC substrates, produced by BandGap Technologies Inc., were 0.8° off-axis, showed the expected scratches from mechanical polishing, and had an oxygen content between 8% and 16% depending on the substrate orientation, carbon or silicon respectively. The SiC substrates used in this study were degreased in a series of heated solvents, including trichloroethylene, acetone, and methanol, prior to insertion into the furnace. The SiC $(000\bar{1})$ was then placed on top of the tantalum foil which is secured between two copper clamps and connected to the power leads. For each experiment, the furnace was purged with high purity argon for 10 minutes before heating the substrate. Hydrogen was then introduced and the two gas flow rates were set. Both gas flow rates were controlled using manually controlled gas flow meters. Once the desired flow rates were established, current was sent through the tantalum foil by a Sorensen DCR 20-115B power supply. By varying the current, the substrate was

(a)

(b)



(c)

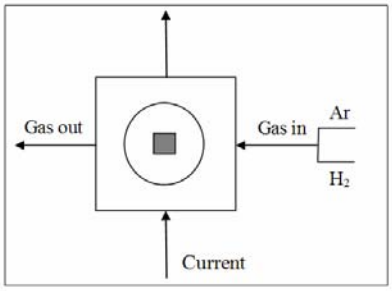


Figure 1: Photographs and schematic illustration of the custom built hydrogen furnace. (a) The glass viewport allows temperature monitoring with an optical pyrometer, and water cooling in the aluminum walls prevents overheating of the box. (b) High-power feedthroughs have copper clamps on the ends that hold a piece of Ta foil on which the substrate rests. (c) Schematic of the top view in (b) showing the flow of the gases across the heated substrate.

resistively heated to temperatures up to 2000^{o}C, which was measured using a two-color Omegascope OS3750 pyrometer. In all experiments discussed below, the SiC substrate was held at 1800^{o}C for one hour, with heating and cooling rates of approximately 100^{o}C every 30 seconds. Although reaching and maintaining the substrate temperature was consistent within 10°C from run to run, precise control over the heating and cooling rates was difficult due to the resolution of the power supply (5 amps). The sample was cooled under the same processing flow rates of hydrogen and argon. After cleaning, x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) was performed in a UHV chamber with a base pressure of 2x10^{-9} Torr. A PHI 15-110A CMA was used for AES and a PHI 10-360-4-015 Hemispherical analyzer was used for XPS. The x-ray source was a PHI 04-173-0-077 Mg/Al dual anode and all data was collected using the Al anode (1486.6 eV). A Hitatchi S-4700 CFE field emission scanning electron microscope and a Digital Instruments Dimension 2000 scanning probe microscope were used to observe the impact of processing conditions on surface morphology.

Preliminary Results and Discussion

A temperature of 1800°C was determined to be most effective, by XPS analysis, in removing oxygen from the surface in a reasonable amount of time. This temperature is consistent with the temperature range (1600°C to 1800°C) used in other hydrogen cleaning methods of surface preparation.[3,4,6,7] In the current investigation, XPS and AES are being used to determine the affects of flow rates and flow ratios on the bonding information and surface chemistry of the SiC substrate.

Pure hydrogen flowing at 11 lpm successfully reduced the oxide layer to less than 0.5 monolayer (ML) and removed the polishing scratches from the surface. Both AES and XPS analysis confirm the removal of surface oxide, and AES peak shapes show distinctly more SiC-like silicon and carbon peaks. However, AFM images showed “wavy” step edges, suggesting over etching of the surface. By adding up to 50% argon by volume to the flowing gas, the over-

etching was reduced and the desired straight atomic step-edge morphology was produced with a RMS roughness of 0.193 nm.

Although current studies are still underway, preliminary results suggest the oxygen content remaining on the surface after treatment in the furnace is influenced by both the amount of hydrogen exposed to the surface as well as a combination of the Ar/H_2 ratio and total flow rate. A minimum hydrogen flow rate of approximately 5 lpm of hydrogen is needed to significantly reduce surface oxygen. When the Ar/H_2 ratio is between of 1.5 to 2.0 and H_2 flow above 5 lpm, trends in surface composition suggest a balance between the kinetics of the hydrogen etching reactions and the mass transport of hydrogen to the surface. The processing window affects the (0001) and $(000\bar{1})$ orientations differently. This is consistent with the literature that shows different reactivities of the carbon and silicon surfaces.[1] This also presents an opportunity to more completely understand the different chemical activities of the surfaces through analysis of the impact of processing parameters.

Conclusions and Continuing Work:

The hydrogen furnace consistently produces atomically stepped surfaces without scratches from mechanical polishing and with less than 0.5 ML of oxygen on the surface by flowing argon and hydrogen gas (Ar/H_2 = 0.3, H_2 = 7.7 lpm) over the SiC substrate heated to 1800°C. The custom bench top device fits easily in a hood, cost less than $3,000, and is more successful in removing surface oxygen than the other methods tested. The impact of both Ar/H_2 ratio and total flow rate is currently being investigated to provide insights on etching mechanism that may help understand the chemical differences between the carbon and silicon face orientations. The chemistry difference between the two orientations is also being investigated, and the most recent results will be presented.

Acknowledgements

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