https://ntrs.nasa.gov/search.jsp?R=20030037184 2018-05-15T15:55:46+00:00Z

NASA/CR—2003-212198



Nanoporous Silicon Carbide for Nanoelectromechanical Systems Applications

T. Hossain, F. Khan, I. Adesida, P. Bohn, and T. Rittenhouse
University of Illinois at Urbana-Champaign, Urbana, Illinois

April 2003

The NASA STI Program Office . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.

- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.

- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at ***http://www.sti.nasa.gov***

- E-mail your question via the Internet to help@sti.nasa.gov

- Fax your question to the NASA Access Help Desk at 301–621–0134

- Telephone the NASA Access Help Desk at 301–621–0390

- Write to:
  NASA Access Help Desk
  NASA Center for AeroSpace Information
  7121 Standard Drive
  Hanover, MD 21076

NASA/CR—2003-212198



Nanoporous Silicon Carbide for Nanoelectromechanical Systems Applications

T. Hossain, F. Khan, I. Adesida, P. Bohn, and T. Rittenhouse
University of Illinois at Urbana-Champaign, Urbana, Illinois

Prepared under Grant NAG3–2661

National Aeronautics and
Space Administration

Glenn Research Center

April 2003

This report contains preliminary findings, subject to revision as analysis proceeds.

The Propulsion and Power Program at
NASA Glenn Research Center sponsored this work.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100

Available electronically at http://gltrs.grc.nasa.gov

Nanoporous Silicon Carbide For Nanoelectromechanical Systems Applications

T. Hossain, F. Khan, I. Adesida, P. Bohn, and T. Rittenhouse
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

A major goal of this project is to produce porous silicon carbide (PSiC) via an electroless process for eventual utilization in nanoscale sensing platforms. Results in the literature have shown a variety of porous morphologies in SiC produced in anodic cells. Therefore, predictability and reproducibility of porous structures are initial concerns. This work has concentrated on producing morphologies of known porosity, with particular attention paid toward producing the extremely high surface areas required for a porous flow sensor. We have conducted a parametric study of electroless etching conditions and characteristics of the resulting physical nanostructure and also investigated the relationship between morphology and materials properties. Further, we have investigated bulk etching of SiC using both photo-electrochemical etching and inductively-coupled-plasma reactive ion etching techniques.

I. Formation and Characterization of Porous SiC by electroless etching

a. Formation

Electroless etching is technically simple and inexpensive in comparison with anodic etching. However, several experimental parameters can be manipulated during electroless etching in order to produce the desired nanostructure. In this study, particular attention has been paid to the identity of the etchant, etchant concentrations, the polytype of the SiC wafer, the doping type and concentration in the wafer, the structural perfection of the SiC wafer, the presence of ultraviolet illumination during etching, and the presence of Pt as a catalyst during etching.

Previous work conducted in this laboratory suggested the feasibility of forming PSiC by an electroless process. An etchant composed of HF and H_2O_2 was found to produce porous gallium nitride (PGaN). When the thin PGaN layer was completely etched away, it was discovered that the SiC substrate had also become porous. Therefore, the HF:H_2O_2 etchant was initially chosen in this study for the electroless formation of PSiC. However, experiments quickly showed that pure SiC wafers were etched very inefficiently by the HF:H_2O_2 etchant. Thus, new chemical etchants were investigated.

Eventually, an etchant composed of a mixture of HF and $K_2S_2O_8$ was found to produce highly porous PSiC consistently. Two different concentration ratios are currently used to yield different porous morphologies. In the “concentrated HF” etchant,

a mixture of 14 M HF:0.075 M $S_2O_8^{2-}$ is used. The other etchant concentrations used ("dilute HF") are 0.50 M HF:0.15 M (saturated) $S_2O_8^{2-}$.

The resulting porous morphology in SiC is highly dependent upon the polytype of the initial SiC wafer. To date, two different polytypes of SiC have been investigated: 6H-SiC and 4H-SiC.

Because the energy of the holes available from $S_2O_8^{2-}$ reduction is not sufficient for direct injection into the valence band of SiC, ultraviolet irradiation is required during etching to form the porous morphology. In addition, sputtered Pt is necessary to catalyze the persulfate reduction and to act as a local cathode. The Pt areas also have the added benefit of acting as a sharp masking agent. Regions under the Pt remain unetched (Fig. 1), allowing for high-resolution patterning of porous structures.

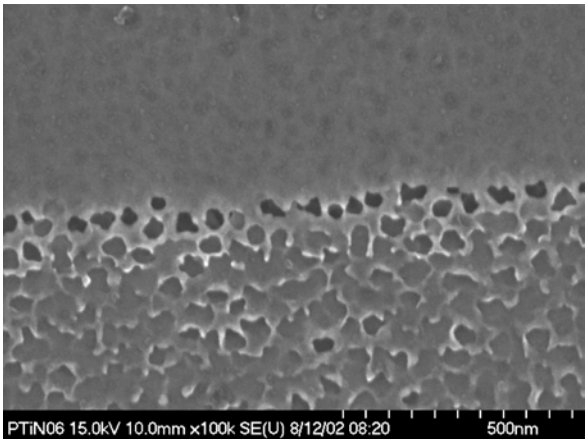


Figure 1. Plan view SEM image of a porous region (bottom of photo) next to unetched planar surface (top of photo) that was coated with 100 Å Pt prior to initiating the etching process.

n-doped 6H-SiC. For short etch times (~10 min) with the concentrated HF etchant, a ridged porous morphology results (Fig. 2). For longer etch times (~60 min) with the concentrated HF etchant, strong porosity results that is still restricted to the top surface layer (Fig. 3). For short (~10 min) etch times with the dilute HF etchant, morphologies similar to figure 2 result. However, for long (~60 min) etch times with the dilute HF etchant, spongelike morphologies result that can extend deep (>100 μm) into the wafer (Figs. 4 and 5).

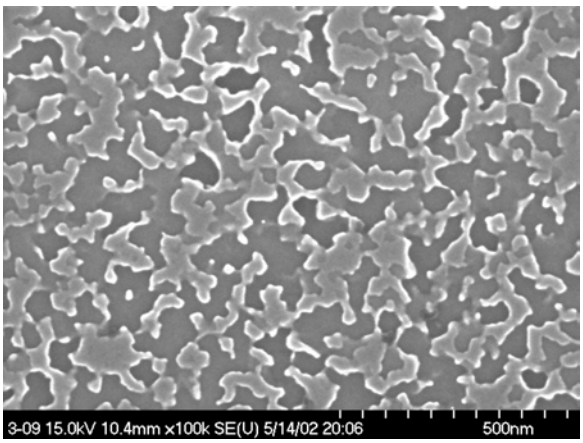


Figure 2. Plan view SEM showing the ridged porous structure resulting from short etch times in 6H-SiC wafers with either concentrated or dilute HF etchant.

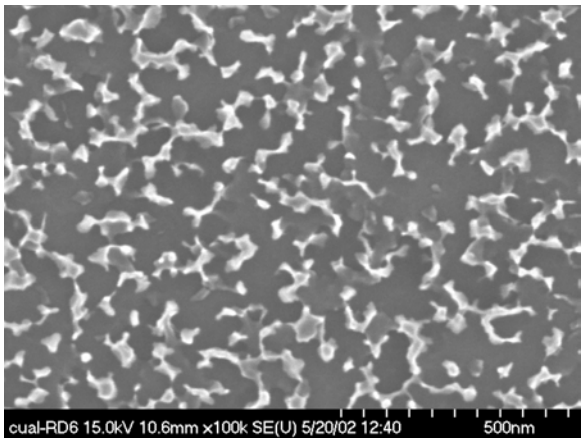


Figure 3. Plan view SEM image showing the strong planar porosity (restricted to top surface layer) that results from etching 6H-SiC in the concentrated HF etchant for long etch times.

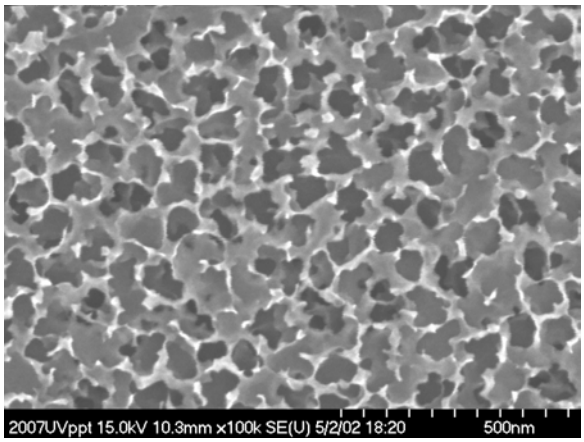
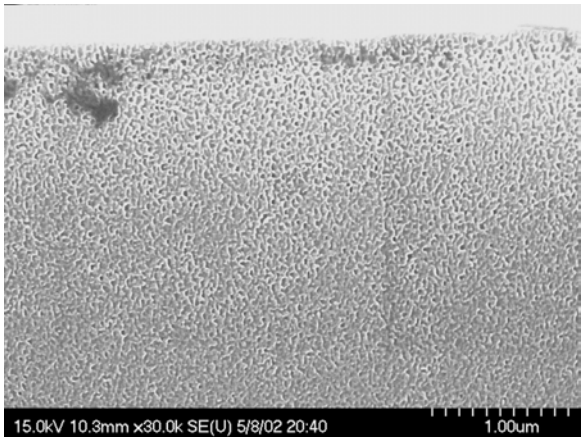


Figure 4. Plan view SEM image showing the spongelike porosity that results from etching 6H-SiC in dilute HF etchant for long etch times.



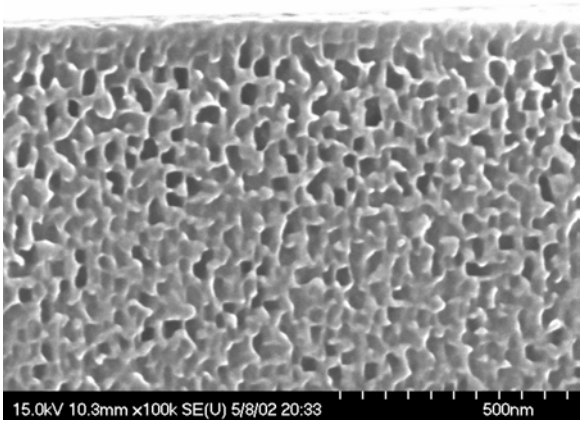


Figure 5. Cross-sectional views of the spongelike morphology in 6H-SiC that has been etched with the dilute HF etchant for long times. The top surface of the wafer is at the top of each photo.

At this point in time, the depth of the porous layer into the wafer is still difficult to control. Current results indicate that the structural perfection of the SiC starting material plays a major role in how deep the pores propagate into the wafer. However, dislocations, micropipes, stacking faults, etc. appear to vary greatly across the face of commercially-available 2" SiC wafers. Initial X-ray diffraction (XRD) experiments have been conducted to link crystallographic perfection of the starting material with resulting porous morphology.

n-doped 4H-SiC. The 4H polytype of SiC yields a distinctly different morphology when exposed to the same etchant conditions as the 6H wafer. Unfortunately, predictability of morphology for the 4H polytype is much poorer than that for the 6H-SiC. The resulting morphology appears fairly independent of the concentration of etchants used. For short etch times (~10 min) a ridged porous structure similar to the 6H polytype is obtained in 4H wafers (*cf.* Fig. 2). For longer etch times (~60 minutes), 4H wafers often yield a cellular structure with nanofingers, but a highly porous spongelike structure may also be obtained (Fig. 6).

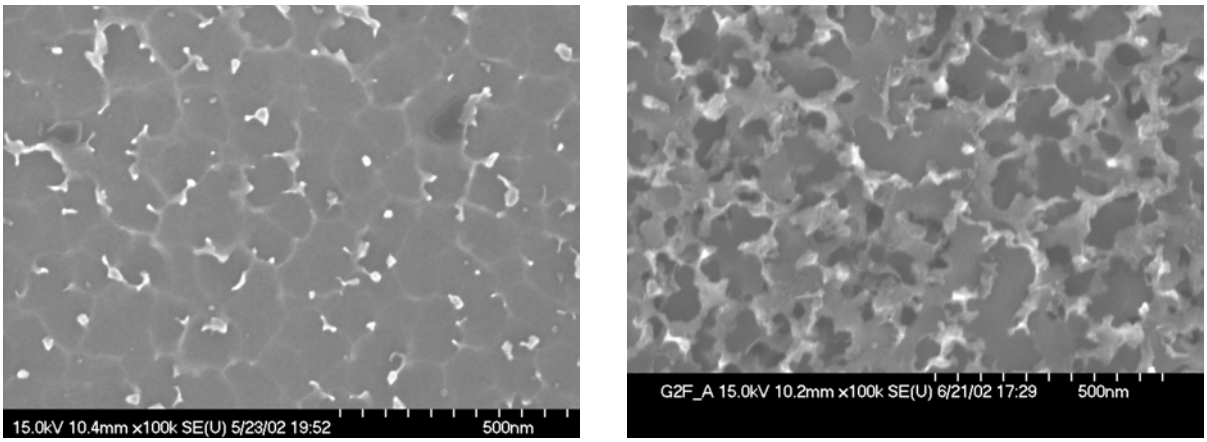


Figure 6. Plan view SEM images showing the different morphologies that can develop when 4H-SiC is etched for long times (~60 min) in either the concentrated or dilute HF etchant. In the left photo, a cellular structure with fingers has developed, while in the right photo a more spongelike morphology has formed.

In the 4H wafers etched to date, no submerged porosity has been achieved. The etchant has only formed a surface layer of pores ≤ 25 nm deep. For this reason, electroless etching of 6H polytype wafers will initially be investigated further for the development of high surface area sensor applications.

In addition, electroless etching has not resulted in porous structures for either semi-insulating 6H-SiC or p-doped 4H-SiC. The surface of these wafers remains primarily planar. The $HF/S_2O_8^{2-}$ etchant does, however, decorate the dislocations, micropipes, and scratches on the surface of the wafer.

Because the high surface area characteristic of porous materials is one of the drivers for their application in sensing platforms, the specific surface area of SiC will be an important parameter in applications such as flow-sensing in the interior of high-temperature combustion chambers. Although there is wide variation with the specific processing conditions, literature results for porous silicon (PSi) indicate surface areas of approximately 100 m^2/g. Surface areas for several PSiC samples formed in this work were measured via BET isotherms and were *ca.* 50 m^2/g.

b. Optical Characterization of Porous SiC

Various optical properties of PSiC have been investigated in this study. In the literature, porous silicon has shown a blue-shifting of its photoluminescence after the formation of a porous nanostructure. In light of this, cathodoluminescence (CL) and photoluminescence (PL) studies were conducted to look for similar changes in luminescence. Also, Raman studies were conducted in order to characterize the porous morphology, as has been reported in the literature for porous silicon.

Cathodoluminescence was conducted to explore the possibility that the bandgap of PSiC would be blue-shifted and intensified, as it is in PGaN, possibly leading to efficient blue or ultraviolet emitters. However, results of this study have shown that no blue-shifting of the peak CL occurs for either porous 6H-SiC or porous 4H-SiC. Furthermore, porous 6H-SiC shows only slightly more intense CL emission, while porous 4H-SiC shows slightly less intense CL emission as compared to the bulk substrate.

Some sensing modalities have been proposed in which sensing is based on the reduction of PL emission upon immersion in the test medium. PL investigations in this study have yielded results similar to literature reports from anodically-etched PSiC. PL from the bandgap region of wavelengths does not appear to intensify in the porous samples. Changes in the PL in this region of the spectrum are apparently due to local changes in the doping, defects, etc., and are unrelated to the development of porous morphology.

PL from the broad visible peak (500-700 nm) of porous 6H-SiC appears to red-shift slightly (up to 20 nm) and become more intense in the porous samples. Intensity increases of 3x are common. The largest increases in PL intensity are derived from the band at 486 nm. The PL at this wavelength increases as the porosity of the sample increases. PL increases of 50x are achievable via electroless etching of SiC (Fig. 7).

Raman investigations were conducted in an attempt to quantify the degree of porosity non-destructively. In a porous structure, the lattice symmetry is disrupted and coupling of phonon states with different **K** values occurs, leading to a broadening and shift in the location of the Raman bands. Previous work has shown that the longitudinal optic (LO) mode of PSi tends to broaden asymmetrically and red-shift as nanostructures

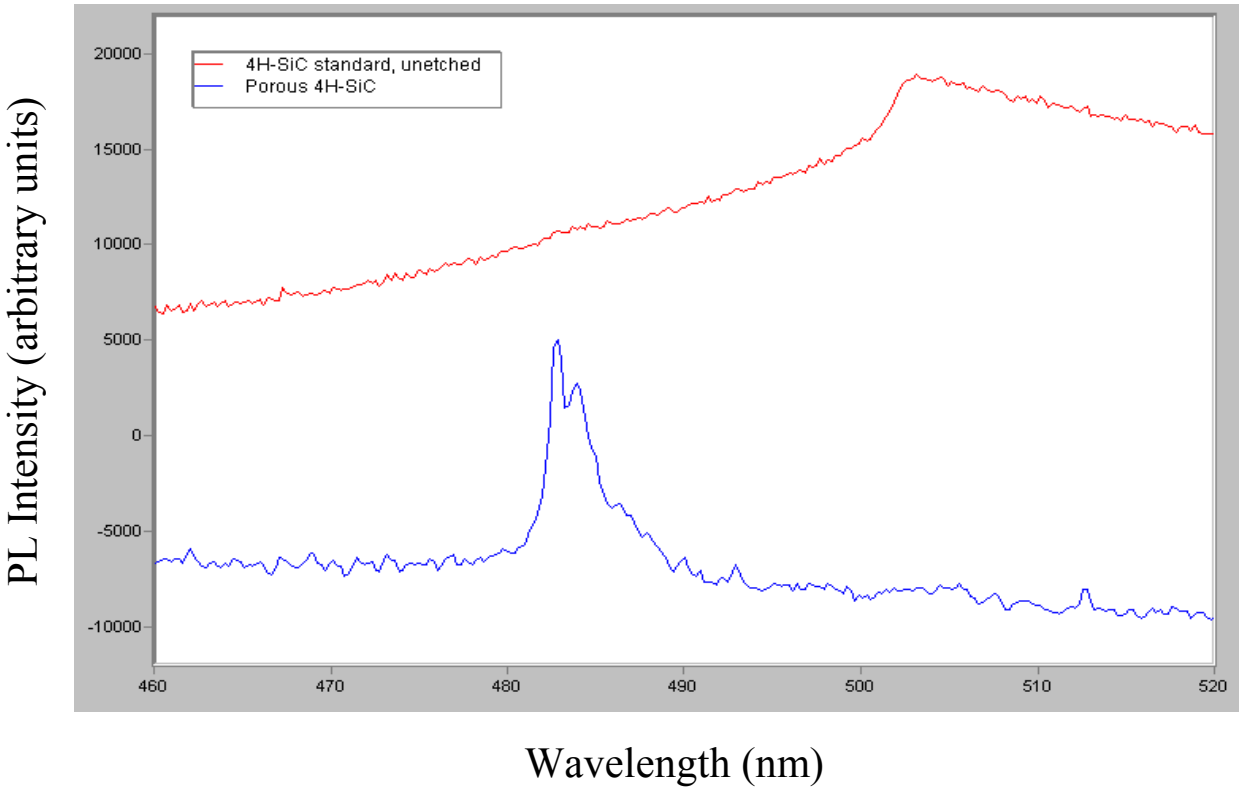


Figure 7. Photoluminescence spectrum demonstrating the increase in intensity of PL emission centered at 486 nm as a result of porous morphology. The top spectrum is from an unetched piece of 4H-SiC wafer; the bottom spectrum is from a piece of the same 4H-SiC wafer that has been etched in the concentrated HF etchant for one hour, resulting in a spongelike porosity.

are formed. However, in the literature, there are no reports of similar red-shifts in the location of the LO mode in PSiC formed via anodic etching. Likewise, in the electroless etching used to form the PSiC in this work, the LO mode was not found to shift with the development of porosity. In addition, the LO mode does not exhibit any significant broadening as the structure becomes porous. These results point to the extreme stability of PSiC, and indicate that the porous layer does not introduce significant strain to the wafer.

II. Bulk Etching of 6H-SiC

In the fabrication of some types of sensors, it is necessary to perform bulk etching to form thin films directly or to etch isotropically for eventual release of thin films. We have initiated investigations of both wet and dry etching of SiC for these applications.

a. Wet Etching

In this study, the experiments were carried out on single-crystal n-type 6H-SiC wafers. A two-layer metal film of Ti(100A) followed by Pt.(2200A) was used as an etch mask and the etch patterns were defined photolithograpically using a lift-of process. The SiC sample was place into a Teflon electrochemical cell, along with a Pt wire counter electrode and a saturated calomel reference electrode. Dilute HF was employed as an etching solution. The SiC sample was illuminated by UV light for an hour and was biased at different voltages. The UV light was focused down to a 2 cm^2 spot with a power density of 125 mW/cm^2. The schematic drawing of the PEC etching system is shown in Figure 8.

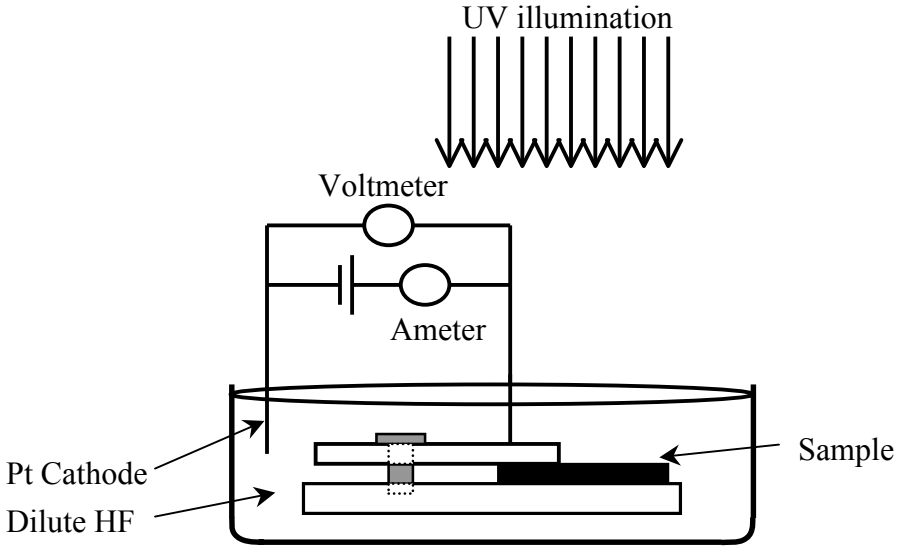


Figure 8. Schematic of etching apparatus

As indicated above, the etching process consisted of two-steps. The SiC sample was first anodized to form a deep porous layer and the layer was subsequently removed by thermal oxidation followed by an HF dip. To illustrate the two-step etching, SEM studies were performed before and after the anodized layer was oxidized and etched off. The surface of the anodized SiC became porous as shown in Fig. 9, however, we have not studied the porosity engendered by anodic etching at this point. The anodized PSiC samples were thermally oxidized in a steam ambient for 4 hours at 1150 ^0C.

Under these conditions, SiC oxidized to form SiO_2. A short HF dip removed the oxide and produced etched features as shown in Fig. 10.

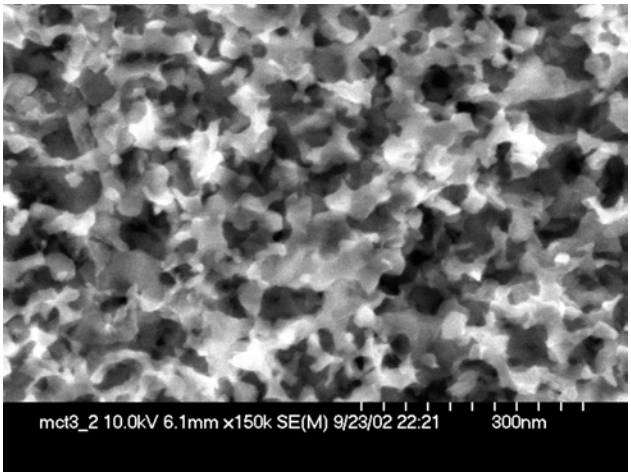


Figure 9. Anodized SiC surface (After PEC etch)



Figure 10a. SiC etch profile at 3.2mA (3.13 μm etch depth)

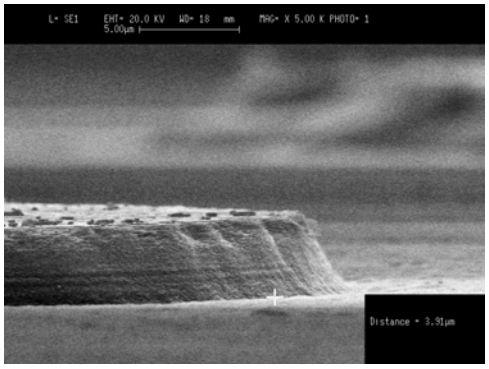


Figure 10b. SiC etch profile at 4.2mA (3.91 μm etch depth)

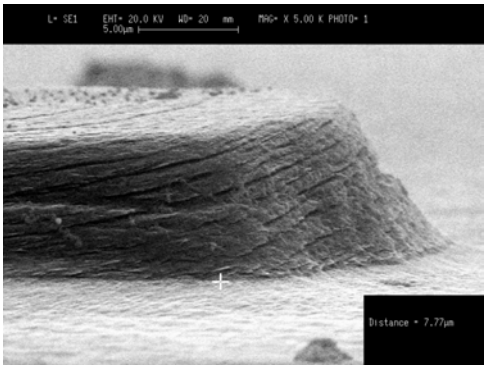


Figure 10c. SiC etch profile at 6.1mA (7.77 μm etch depth)

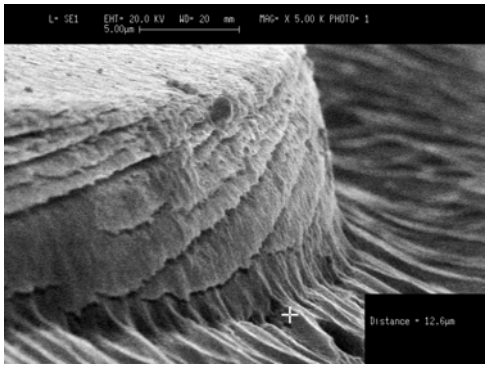


Figure 10d. SiC etch profile at 7.4mA (12.6 μm etch depth)

The maximum etch rate obtained was approximately 2000A/min. Etch depth as a function of etch current is presented in Fig. 11. It showed etch depth increased significantly with etch current. Further increases in etch current (bias) will be investigated.

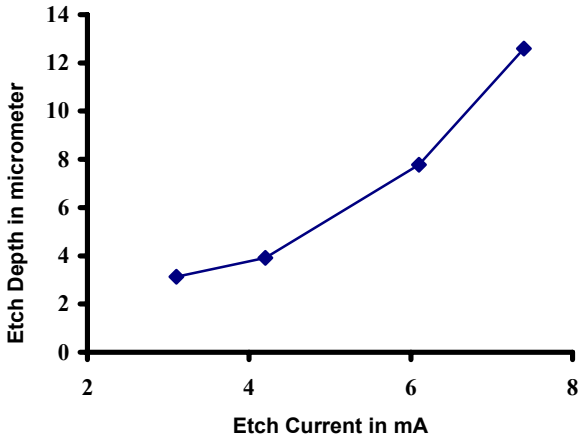


Figure 11. Etch depth as a function of etch current

b. Dry Etching

Owing to its inert chemical nature and high bond energy, SiC substrates are resistant to common wet chemical etchants, making dry etching studies necessary for the fabrication of free suspending SiC cantilevers. This makes it essential to do comprehensive studies on etching characterization of SiC to find etching conditions suitable for various device fabrication needs. For example we need highly anisotropic etching to define the dimensions, length, width and thickness of the SiC cantilever. On the other hand we need isotropic etching condition to undercut the SiC to form the self-suspending cantilever.

Dry etching techniques mostly depend on plasma assisted etching. Plasma assisted etching proceeds via a combination of physical and chemical mechanisms. The dominant mechanism is usually determined by the choice of partial pressure ratio of the reactive or inert gases. It is also affected by other accompanying plasma conditions. In the case of inductively coupled plasma reactive ion etching (ICP-RIE), these would be gas flow rates, chamber pressure, bias voltage and ICP coil power. By using different combinations of the above mentioned conditions the substrate can be etched by (a) physical sputtering – purely physical removal of the material by energetic ions of the gas molecules; (b) chemical plasma etching – neutral radicals formed in the plasma reacting with the substrate to form volatile compounds; (c) ion enhanced chemical etching – energetic ions either damage the surface to enhance the rate of

surface chemical reactions or they help enhance the removal of the chemical by-products from the surface. Etching conditions in which physical sputtering mechanisms or ion enhanced chemical etching is dominant tend to be anisotropic. While etching conditions in which chemical plasma etching is dominant are isotropic in nature.

We have extensively studied ICP-RIE etching conditions for SiC. Figure 12 shows etch rate of SiC with respect to chamber pressure for different ICP coil powers using SF_6/O_2 gas chemistry. Increasing pressure increases the density of reactive species present in the chamber. However, it also decreases the mean free path, thereby affecting the energy with which the ions impinge on the substrate and the average lifetime of the ions before they recombine. Increasing the ICP coil power increases the density and the energy of the ions overcoming the reduction in etch rate due to the reduced mean free path and lifetime of the ions. Keeping the bias voltage value at –300 V, when the ICP coil power was increased from 500 to 900 W, the optimum chamber pressure increased from 4 to 8 mT. At –300 V bias voltage, 900 W ICP coil power, and 8 mT chamber pressure, an etch rate of 1.05 μm was achieved for SF_6/O_2 gas mixture. This is the highest etch rate achieved for SiC using a commercial ICP-RIE system.

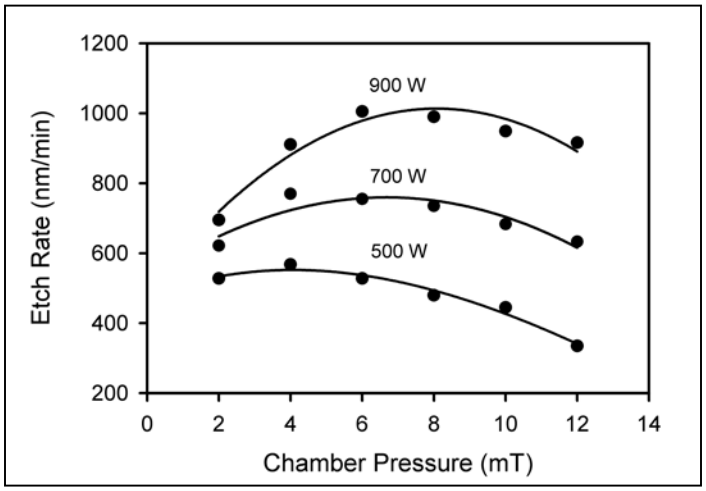


Figure 12. Etch rate of SiC vs. pressure

Figure 13 shows the proposed fabrication sequence for the self-suspending SiC cantilever. It will begin with deposition of Indium-Tin-Oxide (ITO) mask pattern on the SiC wafer followed by anisotropically etching SiC. Next, a thin film of ITO will be sputtered over the entire wafer. We will then blanket etch the SiC wafer to etch back the ITO mask. The last step would be to isotropically etch SiC to release the free standing cantilever.

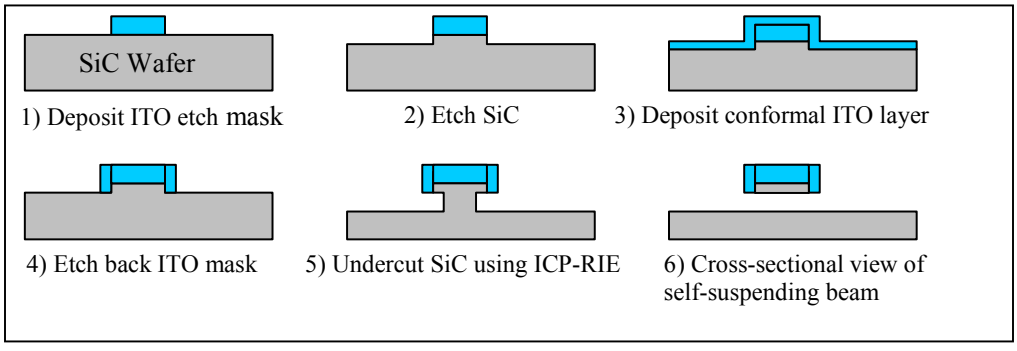


Figure 13. Process for achieving self-suspended SiC films by dry etching

Presently we are optimizing the dry-etching process to undercut SiC. Figure 14 shows an undercut SiC structure using Ni mask. The structure was undercut by 2.6 μm in 150 minutes giving an undercut rate in excess of 1 μm/hr. Conditions to achieve high undercut rate will be investigated.

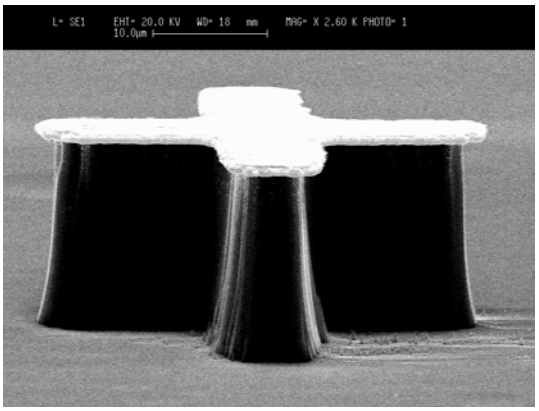


Figure 14. SiC etched using ICP-RIE in SF_6 showing undercut.

III. Summary

Several key accomplishments have been achieved during FY02 for this grant, including:

- determination of an electroless etchant and conditions capable of producing PSiC
- demonstration of precise patterning of the porous morphology
- quantification of surface area; results have been obtained with PSiC that are comparable to that of the more mature porous silicon technology
- characterization of PL and Raman for various porous morphologies, serving as a basis for nanoelectromechanical systems investigations
- bulk etching of SiC using electrochemical etching, oxidation, and HF dip
- characterization of ICP-RIE etching of SiC for high undercut etch rate

Most importantly for the objectives of this project, the high surface areas necessary for a sensor application have been demonstrated. Also, as anticipated PSiC has proven to be a very robust material, an important consideration for the Aerospace Propulsion and Power Program.

Program for Year 2 of the proposal are:

- Develop nanoporous SiC formation by metal-assisted electroless chemical etching in nonaqueous solution, and explore the achievable range of structures by this process.
- Explore the formation of nanoporous SiC/metal composites by *in situ* metal assisted etching and deposition.
- Studies of lateral patterning to determine relationship between etching conditions and spatial resolution.
- Create cantilevers by using dopant selective etching by undercutting and freeing cantilevers using the PEC method and/or dry etching method. Investigate resolution limits by using electron-beam defined lines for the porous SiC cantilevers. Delineate possible sensor fabrication process.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 2003	Annual Contractor Report

4. TITLE AND SUBTITLE

Nanoporous Silicon Carbide for Nanoelectromechanical Systems Applications

5. FUNDING NUMBERS

WU–708–87–23–00
NAG3–2661

6. AUTHOR(S)

T. Hossain, F. Khan, I. Adesida, P. Bohn, and T. Rittenhouse

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

8. PERFORMING ORGANIZATION REPORT NUMBER

E–13801

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, DC 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA CR—2003-212198

11. SUPPLEMENTARY NOTES

Project Manager, Michael Lienhard, Instrumentation and Controls Division, NASA Glenn Research Center, organization code 5510, 216–433–8932.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category: 25 Distribution: Nonstandard

Available electronically at http://gltrs.grc.nasa.gov

This publication is available from the NASA Center for AeroSpace Information, 301–621–0390.

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

A major goal of this project is to produce porous silicon carbide (PSiC) via an electroless process for eventual utilization in nanoscale sensing platforms. Results in the literature have shown a variety of porous morphologies in SiC produced in anodic cells. Therefore, predictability and reproducibility of porous structures are initial concerns. This work has concentrated on producing morphologies of known porosity, with particular attention paid toward producing the extremely high surface areas required for a porous flow sensor. We have conducted a parametric study of electroless etching conditions and characteristics of the resulting physical nanostructure and also investigated the relationship between morphology and materials properties. Further, we have investigated bulk etching of SiC using both photo-electrochemical etching and inductively-coupled-plasma reactive ion etching techniques.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Nanotechnology; Nanoporous; Silicon carbide; NEMS	18
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	