

THERMIONIC EMISSION FROM MICROFABRICATED SILICON-CARBIDE FILAMENTS

J.-H. Lee¹, I. Bargatin¹, J. Provine¹, W. A. Clay², J. W. Schwede²,
F. Liu³, R. Maboudian³, N. A. Melosh⁴, Z.-X. Shen², and R.T. Howe¹

¹Department of Electrical Engineering, Stanford University, Stanford, California 94305

²Department of Physics, Stanford University

³Department of Chemical Engineering, University of California, Berkeley, California 94720

⁴Department of Materials Science and Engineering, Stanford University

Abstract: We have measured thermionic emission from microfabricated 3C silicon carbide filaments. When the filaments were heated resistively, the emitted current grew approximately exponentially with the applied heating power, consistent with the thermionic emission mechanism. Using photoemission, we have also determined the work function of cesiated 3C-SiC to be approximately 1.65 eV at room temperature. These measurements demonstrate the potential of SiC for electron emission applications and, in particular, for microfabricated thermionic energy converters.

Keywords: thermionic emission, silicon carbide, thermionic energy conversion

INTRODUCTION

Silicon carbide (SiC) is an attractive material for electronic devices operating at high temperatures and high power. The three most common SiC polymorphs (3C, 4H, and 6H) have relatively large bandgaps and are chemically and thermally stable, with thermal decomposition temperatures of over 2500°C. The recent development of SiC surface micromachining has allowed fabrication and testing of polycrystalline 3C SiC (poly-SiC) MEMS devices that operate at temperatures of 1000°C or higher [1,2,3]. This paper reports on the design and fabrication of suspended microfilaments made of polycrystalline 3C-SiC and measurement of thermionic emission from these structures. Previously, thermionic emission from SiC was reported only for bulk samples [4].

FABRICATION

The filament structures consisted of five microbridges connected in parallel, shown in Fig. 1. Individual filaments are 100 μm wide and 300 nm thick, with lengths varying between 1 and 4 mm. The filaments are anchored on 1mm x 1mm SiC pads, to which aluminum wires were bonded directly.

Figure 2 outlines the single mask fabrication process. We started with a 100mm-diameter wafer composed of a top layer of 300-nm-thick polycrystalline 3C-SiC (n-doped with nitrogen,

780 Ω per square sheet resistance, 280 MPa tensile residual stress) [5], a 1 μm-thick buried SiO₂ layer, and the silicon substrate.

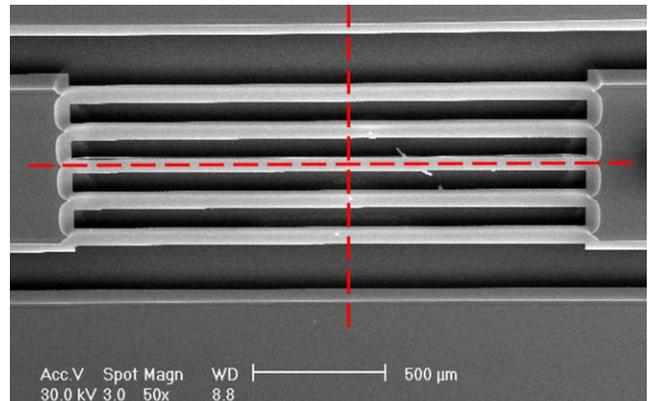


Fig. 1: Scanning electron micrograph (45 degree angle) of a fabricated filament structure with all filaments intact. Vertical and horizontal dashed red lines indicate the positions of the transverse and longitudinal cross sections shown in Fig. 2.

Next, a 400-nm-thick low-temperature oxide (LTO) was deposited at 400°C to act as the hard mask during reactive ion etching of SiC layer, and patterned using transparency-mask photolithography and C₂F₆-based reactive ion etching. The exposed silicon carbide layer was then anisotropically etched using a mixed Cl₂ and HBr-based chemistry [6]. After stripping of the photoresist and the wet etch of the residual oxide layers, the exposed Si substrate was isotropically etched in XeF₂. Finally, the newly exposed oxide

on the bottom side of the filaments was etched with vapor HF. Many of the released filaments broke due to their small thickness, large lateral dimensions, and the tensile residual stress in the SiC layer.

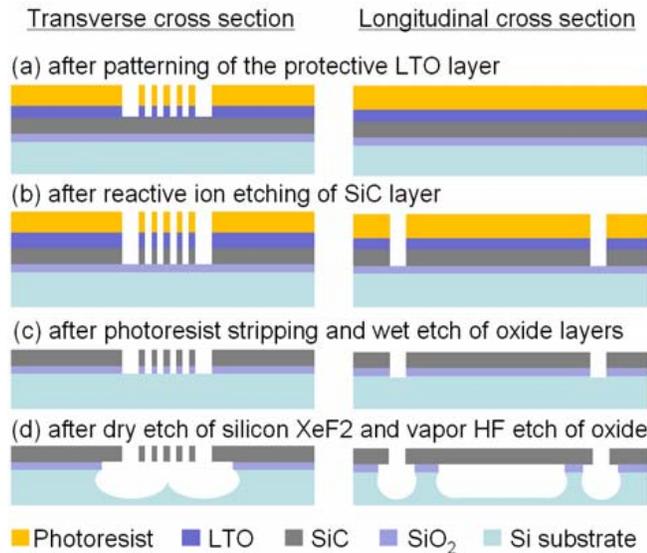


Fig. 2: Schematic cross-sectional views (not to scale) outlining the fabrication process.

EXPERIMENTAL

After fabrication, the sample was wire-bonded and mounted on a teflon sample holder (Fig. 3) in a high-vacuum chamber ($P < 10^{-6}$ Torr). One side of the filaments was electrically grounded and a slowly increasing voltage was applied stepwise to the other side. At the typical applied voltages (20–30V), the filaments glowed bright yellow.

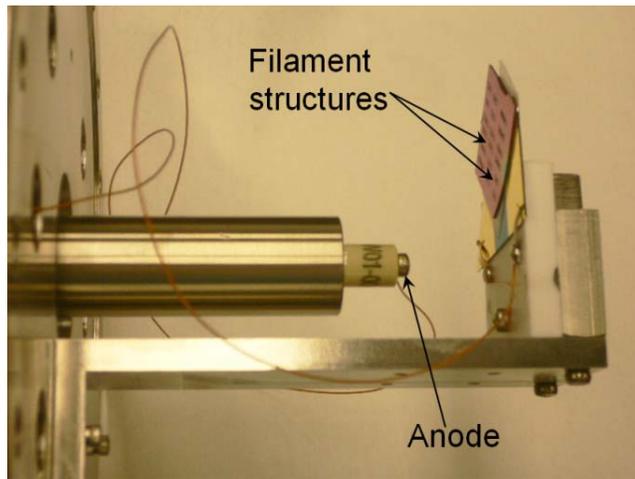


Fig. 3: Photograph of the vacuum sample holder.

The anode was positioned a few centimeters from the filament and electrically biased at +200V

with respect to ground to collect most of the thermionically emitted electrons. The field emission current was negligible for the filament-anode distances and voltages used.

Figure 4 shows the measured anode current versus the applied resistive heating power for a structure with only two intact 1-mm-long bridging filaments. The exponential rise in the current with the heating power strongly supports the thermionic nature of the measured anode current.

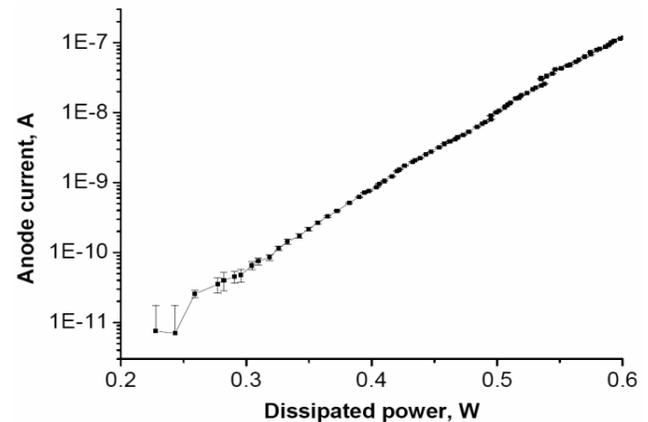


Fig. 4: Measured thermionic emission current versus the Joule power dissipated in the filaments.

The resistance of the device remained constant at 1.1 k Ω over the entire range of applied power in Fig. 4. After reaching the maximum power of approximately 0.6W, both the thermionic and the filament currents started to drift lower, indicating structural degradation of the filaments. One of the filaments fractured after cooling to room temperature. Similar structural degradation at high temperatures was observed with other filament structures, at similar maximum thermionic currents. The failure is probably caused by thermal stresses since, during the heating, the filaments visibly buckled away from the substrate, due to substantial differential thermal expansion. In future designs, we plan to incorporate stress-relief structures to alleviate this problem. We are also modifying the setup and device design to directly measure the filament temperature, which will allow us to determine the thermionic work function and the Richardson-Dushman constant. The authors are aware of only one previous measurement of thermionic emission from SiC in Ref. [4]. The measurements were performed on bulk polycrystalline SiC produced by reactive

sintering, and the work function was found to vary between 3.8 and 4.7 eV [4].

Cesium is frequently used as a coating that can substantially lower the work function of thermionic emitters. For example, a cesium coating of approximately one monolayer can lower the work function of tungsten thermionic emitters from approximately 4 eV to 1.6 eV [7]. We have not yet measured thermionic emission from cesiated silicon carbide devices; however, we have measured the work function of cesiated silicon carbide using photoemission at room temperature.

Figure 5 shows the measured photoemission yield. For these measurements, we have used an unprocessed piece of the original silicon carbide wafer, described in the fabrication section. Cesium was evaporated on the sample while continuously monitoring the photoemission current produced by the white light of a Xe lamp. The evaporation was stopped when the measured photocurrent reached a maximum and just started to decrease. This activation procedure is standard in photoemission studies and typically results in the maximum lowering of the work function and a cesium coating approximately one monolayer thick.

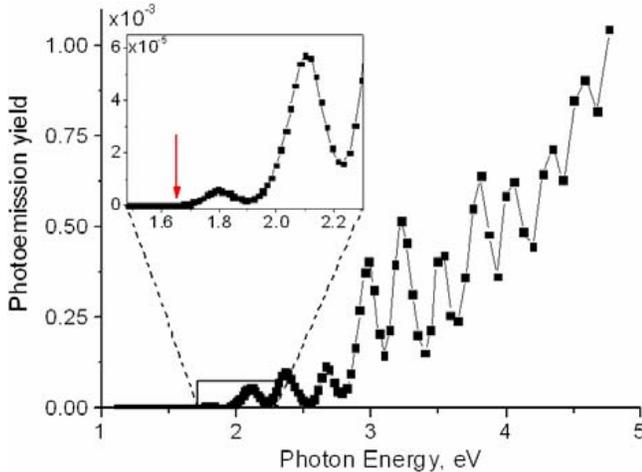


Fig. 5: Measured photoemission yield of a cesiated SiC sample. The inset zooms in on the section of the graph around the photoemission threshold (indicated by the red arrow).

The prominent oscillations in the photoemission yield are caused by the interference of the incident light inside the SiC and buried oxide layers. The positions of the photoemission yield maxima and minima agree with the predictions of a simple thin-film-stack model. The photoemission yield

goes to zero at the photon energy of approximately 1.65 eV, which corresponds to the work function of the cesiated SiC surface at room temperature. This value compares favorably to the work function of cesiated tungsten (~1.6 eV).

THERMIONIC ENERGY CONVERSION

We are interested in the thermionic emission properties of SiC because it is a promising material for building a microfabricated thermionic energy converter (TEC) [7]. TECs are unique heat engines that convert heat directly to electricity at very high temperatures, typically $> 1000^{\circ}\text{C}$ (see Fig. 6). The high operating temperatures on both sides of the converter make TECs suitable as topping cycles [8] in, for example, solar-thermal power generation.

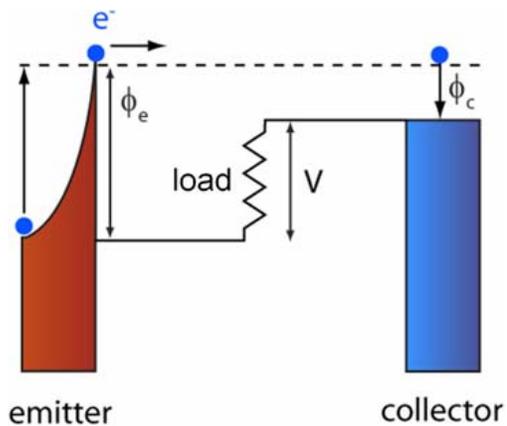


Fig. 6: Schematic of a thermionic energy converter. The hot cathode (emitter) and the cooler anode (collector) are separated by a vacuum gap. If the cathode is hot enough, the electrons can overcome the energy barrier of the cathode work function and escape into the vacuum gap. The electrons then condense on the collector and return to the cathode through the load, performing useful work.

The potential advantages of thermionic converters with micron-scale vacuum gaps between the anode and the cathode have been known for many years [7], but they remained technically infeasible due to the limitations of traditional machining. Recently, at least two groups have demonstrated microfabricated thermionic converters with micron-scale gaps [9,10]. However, they faced significant challenges of structural and chemical stability under extreme operating temperatures and the need for excellent thermal isolation between the anode and cathode.

As a result, conversion efficiencies were extremely low.

These problems may be alleviated by the recent discoveries of materials with very low work functions. For example, Nemanich, *et al.*, have shown that phosphorus-doped diamond films can have effective work functions of the order of 1 eV [11]. In addition, a number of methods have been developed for introducing cesium and other alkali elements into microfabricated cavities (see, *e.g.*, Ref. [12]). There are many known materials that exhibit very low work functions when coated with cesium and oxygen.

The availability of such low work function materials may lead to microfabricated TECs that operate at moderately high temperatures: 1000°C cathode temperature instead of 1500-2500°C typical of the past TEC designs, improving the conversion efficiencies and expanding the range of potential applications.

CONCLUSION

We have measured thermionic emission from microfabricated 3C-SiC filaments. We have also measured the work function of cesiated n-doped 3C-SiC using photoemission. These measurements demonstrate that polycrystalline 3C-SiC is a promising material for electron emission applications. In particular, it can be used in future microfabricated thermionic energy converters.

This work was supported by DARPA and Robert Bosch LLC, Palo Alto, California through the Center on Interfacial Engineering in Microelectromechanical Systems (grant number HR0011-06-0049, Dr. D.L. Polla, Program Manager).

REFERENCES

- [1] Chen L, Mehreghany M, 2007 Exploring Silicon Carbide for Thermal Infrared Radiators *Technical Digest IEEE SENSORS 2007 (Atlanta, GA, October 28-31, 2007)* 620-623
- [2] Knobloch A J, Saia R, Durocher K, Subramanian K 2007 Experimental Study of a Novel Silicon Carbide MEMS Ignition Device *Technical Digest TRANSDUCERS & EUROSENSORS 2007 (Lyon, France, June 10-14, 2007)* 2167-2170
- [3] Wijesundara M B J, Walther D C, Stoldt C R, Fu K, Gao D, Carraro C, Maboudian R, Pisano A P 2003 Low Temperature CVD SiC Coated Si Microcomponents for Reduced Scale Engines *Proceedings of ASME International Mechanical Engineering Congress and R&D Expo (Washington D.C., November 15-22, 2003)* 173-180
- [4] Gnesin G G, Oleinik G S, Okhremchuk L N, Podehrynyaeva I A, Fomenko V S 1970 Work function of polycrystalline silicon carbide *High Temperature* **8** 623-626
- [5] Liu F, Carraro C, Maboudian R 2009 manuscript in preparation
- [6] Gao D, Howe R T, Maboudian R 2003 High-selectivity etching of polycrystalline 3C-SiC films using HBr-based transformer coupled plasma *Appl. Phys. Lett.* **82** 1742-1744
- [7] Hatsopoulos G N, Gyftopoulos E P 1973 *Thermionic Energy Conversion, Vol. 1* (Cambridge, Mass., MIT Press)
- [8] Moyzhes B Y, Geballe T H 2005 The thermionic energy converter as a topping cycle for more efficient heat engines—new triode designs with a longitudinal magnetic field *J. Phys. D: Appl. Phys.* **38** 782
- [9] King D B, Sadwick L P, Wernsman B R 2003, Microminiature Thermionic Converters, US Patent 6,509,669
- [10] Zhang C, Najafi K, Bernal L P, Washabaugh B D 2003 Micro Combustion-Thermionic Power Generation: Feasibility, Design, and Initial Results *Technical Digest TRANSDUCERS'03 (Boston, Mass., June 8-12, 2003)* 40-44
- [11] Koeck F A M, Nemanich R J, Lazea A, Haenen K 2009 Thermionic electron emission from low work-function phosphorus doped diamond films *Diam. Rel. Mater.* **18** 789
- [12] Liew L.-A., Moreland J, Gerginov V 2007 Wafer-level filling of microfabricated atomic vapor cells based on thin-film deposition and photolysis of cesium azide, *Appl. Phys. Lett.* **90** 114106