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# Silicon Carbide as a Material for Biomedical Microsystems

Christian A. Zorman

Department of Electrical Engineering and Computer Science  
Case Western Reserve University  
Cleveland, Ohio 44106 USA

**Abstract-** Silicon Carbide (SiC) is emerging as an enabling material for biomedical microsystems due to its unique combination of electrical, mechanical and chemical properties combined with its compatibility with Si micromachining techniques. This paper presents an overview of the latest advancements in this area including on-going research to develop SiC for biosensing, bio-microdevice packaging, bio-filtering, biomedical imaging and other related biomedical applications.

## I. INTRODUCTION

SiC is an attractive structural material for MEMS and NEMS applications due to its outstanding mechanical, chemical and electrical properties combined with its compatibility with Si micromachining techniques. Historical advancement of SiC for MEMS has focused on the development of single and polycrystalline SiC as a structural material for harsh environment applications, specifically environments where Si is not well suited, owing to its desirable and stable material properties over a very wide range of conditions. Such environments include those associated with high temperature ( $> 600^{\circ}\text{C}$ ), high wear, high radiation, and/or harsh chemicals. Properties that make SiC particularly well suited for such applications include a high electronic bandgap (2.9 to 3.2 eV), high hardness ( $2480 \text{ kg/mm}^2$ ), high resistance to chemical etching in acids and bases, and slow oxidation rates. SiC is also of interest for RF MEMS applications, where its inert surfaces resist stiction and its high Young's modulus ( $\sim 400 \text{ GPa}$ ) enables fabrication of mechanical resonators that can operate over a very wide frequency range, including the GHz range. Its chemical inertness, as well as its favorable mechanical properties, has stimulated interest in using SiC as a complementary material to Si for bioMEMS applications. This paper presents a selection of examples that illustrate recent developments in this area.

Crystalline SiC is a polymorphic material that is known to exist in over 100 distinct configurations known as polytypes. All polytypes share a common stoichiometric composition by not a common crystal structure. The base structure of crystalline SiC can be described as a chemically bonded bilayered tetrahedral comprised of three Si atoms and one carbon atom. The stacking sequences of the tetrahedra differentiate the polytypes. Currently only three

polytypes are technologically relevant since they are the only ones that can be produced as high quality substrates and/or thin films. Figure 1 shows the stacking sequence the two polytypes most commonly used in MEMS, namely 3C-SiC, which has a cubic structure and 6H-SiC which has a hexagonal structure. The hexagonal polytypes 6H-SiC and 4H-SiC the only polytypes that are commercially available as IC-grade wafers. High quality epitaxial films can be grown on these substrates. In contrast, 3C-SiC is not currently available as bulk substrates, but single crystalline films can be epitaxially grown directly on Si wafers despite a significant lattice mismatch ( $\sim 20\%$ ) owing to its zinc-blende crystal structure.

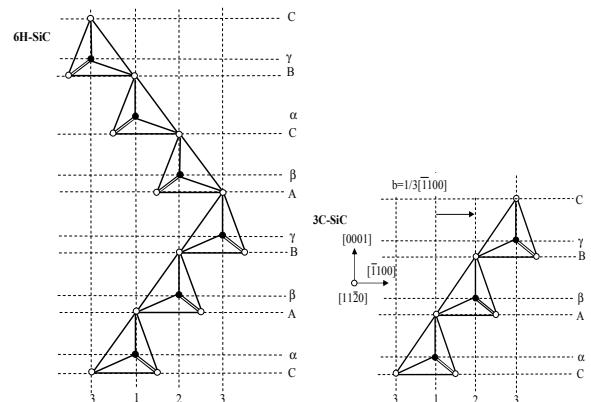


Fig. 1. The stacking sequence of the Si-C tetrahedral bilayer for SiC: (left) 6H-SiC, and (right) 3C-SiC.

## II. PROCESSING METHODS

### A. Thin Film Deposition Methods

Like Si, thin films of SiC can be deposited by a wide range of deposition techniques, the most common being atmospheric pressure chemical vapor deposition (APCVD), low pressure CVD (LPCVD), plasma enhanced chemical vapor deposition (PECVD) and sputtering. CVD is the most common general method to deposit SiC, due primarily to the wide range of microstructures that can be realized by this technique. Single crystalline 6H-SiC and 3C-SiC films are typically grown by either APCVD or LPCVD using reactors that closely resemble those used for Si epitaxy. Growth of 6H-SiC epitaxial films utilizes recipes not specifically for MEMS applications, but rather for high

temperature and high power devices. Silane ( $\text{SiH}_4$ ) and propane ( $\text{C}_3\text{H}_8$ ) are often used as Si- and C-containing precursors, and substrate temperatures exceed  $1450^\circ\text{C}$ . 3C-SiC films are grown in much the same manner, except that the deposition temperatures are limited to those below  $1360^\circ\text{C}$  as a result of the Si substrate, which has a melting temperature of  $\sim 1410^\circ\text{C}$ .

3C-SiC films are particularly well suited for MEMS applications due to the fact that single crystalline films can be grown directly on Si substrates. A commonly-used method to grow such films is based on two-step APCVD process first developed in the late 1980's [1] but later scaled up for 100 mm-diameter substrates [2]. The process utilizes  $\text{SiH}_4$  and  $\text{C}_3\text{H}_8$  as precursors, and  $\text{H}_2$  as a carrier gas. The growth temperature for single crystalline films ranges between  $1250^\circ\text{C}$  and  $1360^\circ\text{C}$ . To achieve such high temperatures, an induction-heated graphite susceptor is used to support the substrates. The process is initiated by etching contaminants from the wafer surface in  $\text{H}_2$  at  $1000^\circ\text{C}$  for several minutes in order to expose a single crystalline Si surface. The substrate is then cooled to below  $500^\circ\text{C}$ . The surface is converted to SiC by a process called carbonization, which is performed by exposing the wafer to a proper mixture of  $\text{H}_2$  and  $\text{C}_3\text{H}_8$  while heating the wafer to  $1280^\circ\text{C}$ . Full carbonization takes about 90s, after which a continuous film is formed and the reaction ceases. To sustain film growth,  $\text{SiH}_4$  is added to the  $\text{C}_3\text{H}_8/\text{H}_2$  mixture and flow rates are adjusted to achieve epitaxial growth.

Films grown using the aforementioned general procedure were among the first 3C-SiC to be used in MEMS structures. Some notable examples include micromechanical resonators [3], pressure sensors [4], and nanomechanical resonators [5]. It is worth noting that a 3C-SiC NEMS resonator was the first to demonstrate a fundamental resonant frequency that exceeded 1 GHz [6]. In addition to their outstanding mechanical properties, 3C-SiC films exhibit characteristics that make them attractive as a bioMEMS material. A study published in 2002 examined the biocompatibility of a set of MEMS materials which included Si,  $\text{Si}_3\text{N}_4$ ,  $\text{SiO}_2$ , SU-8, Ti, and 3C-SiC [23]. The materials were subjected to a baseline battery of ISO 10993 physicochemical and biocompatibility tests as well as commonly used procedures to sterilize medical implants. The tests included aqueous extraction tests, cytotoxicity tests, and tissue analysis after 1 week and 12 week implantations. The analysis showed that 3C-SiC was both biocompatible (within the confines of the tests) and impervious to surface damage during sterilization.

Unlike single crystalline 3C-SiC, polycrystalline 3C-SiC, hereafter referred to simply as poly-SiC, can be deposited on sacrificial films such as  $\text{SiO}_2$  and polysilicon, thus enabling surface micromachining with a complexity that is comparable with polysilicon surface micromachining [7]. In fact, a wide range of micromachined structures, such as lateral resonators, flow sensors, capacitive pressure sensors, micromotors, and microbridge resonators can be fabricated using the deposition, patterning, etching and sacrificial release techniques commonly used in polysilicon surface micromachining. Like polysilicon, poly-SiC films can be

deposited on large-area wafers (150 mm-diam.) in large scale, LPCVD furnaces capable of holding up to 100 wafers per run [8]. Two general approaches that differ primarily by the precursor have been to deposit poly-SiC films for MEMS applications in large-scale furnaces. Modeled after the aforementioned APCVD method to deposit single crystalline 3C-SiC, a dual-precursor approach that uses dichlorosilane ( $\text{Si}_2\text{H}_2\text{Cl}_2$ ) and acetylene ( $\text{C}_2\text{H}_2$ ) as Si- and C-containing precursors has been developed. N-type conductivity is achieved by way of *in-situ* doping using  $\text{NH}_4$ . Films are generally deposited at temperatures between  $800^\circ\text{C}$  and  $900^\circ\text{C}$ . Residual stresses, which can be problematic in poly-SiC deposited at such high temperatures, can be controlled during the deposition process by proper selection of precursor flow rates or deposition pressure, with nearly stress-free films achievable under proper conditions [9]. Figure 2 shows the relationship between deposition pressure and residual stress for films deposited using the dual precursor approach. A single Si- and C-containing precursor known as disilobutane (DSB) has also been used to deposit poly-SiC films for MEMS applications [10]. Like the dual precursor approach, films are generally deposited at temperatures between  $800^\circ\text{C}$  and  $900^\circ\text{C}$ , and can be doped using  $\text{NH}_4$ . The as-deposited films are generally tensile, but annealing can be used to convert the stress to compressive.

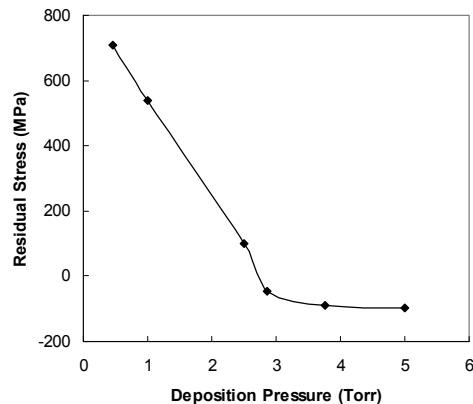


Fig. 2. Residual stress versus deposition pressure for undoped poly-SiC films deposited using the dual precursor approach [9].

Single crystalline and polycrystalline SiC films generally exhibit n-type conductivity due to incorporation of nitrogen (a shallow donor in SiC) during the deposition process. In fact, in spite of its large electronic bandgap, it is very challenging to even grow semi-insulating SiC due to the fact that nitrogen is a common contaminant in the deposition systems as well as the non-semiconductor grade precursor gases (i.e.,  $\text{C}_2\text{H}_2$ ) that are commonly used carbon sources. Amorphous SiC films (a-SiC), on the other hand, are generally electrically insulating, and thus complement their single- and polycrystalline counterparts. The insulating character of these films comes about by the amorphous microstructure as well as the low deposition temperatures associated with processes used to deposit the films. The low deposition processes do not provide enough energy to efficiently activate dopants, even nitrogen.

Amorphous SiC films are generally deposited either by

plasma enhanced chemical vapor deposition or sputtering. PECVD is arguably the more popular of the two techniques owing at least in part to its use in depositing amorphous Si, SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> films. The most common precursor gas system for a-SiC is the SiH<sub>4</sub>/CH<sub>4</sub> system. Several groups have demonstrated MEMS structures from films deposited using this precursor system. Examples include rf switches [11] and accelerometers [12]. Like poly-SiC, single precursor gases that contain both Si and C are also effective source gases for a-SiC films. When hydrogen-containing source gases are used, the resulting films are generally hydrogenated, and therefore more accurately designated as a-SiC:H films. Typical deposition temperatures are in the 300°C to 400°C range.

Amorphous SiC films deposited by PECVD generally exhibit a very wide range of residual stress that have a strong dependence on deposition conditions. Figure 3 is a plot of residual stress versus annealing time for an a-SiC:H film deposited using the single precursor trimethylsilane [13]. The as-deposited film exhibits a high compressive residual stress. A modest annealing temperature of 450°C for a short duration (~10 min) is more than sufficient to change the nature of the stress from compressive to tensile. Additional annealing increases the tensile stress up to a certain value before leveling off. This behavior is advantageous for MEMS structures since the stress in a particular structure can be controlled by an easy-to-execute post deposition processing step. The annealing temperature is Si-IC compatible, and within the acceptable range for a group of temperature tolerant polymers including polyimide. A similar behavior has been observed for films deposited using the SiH<sub>4</sub>/CH<sub>4</sub> precursor system [14].

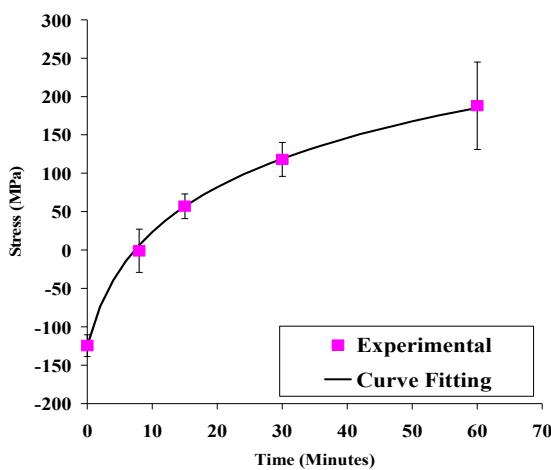


Fig. 3. Residual stress versus annealing time for an a-SiC:H film deposited using trimethylsilane and annealed at 450°C [13].

Sputtering may also be used to deposit a-SiC films. In contrast to films deposited by PECVD, sputtering of SiC films is often performed on unheated or modestly-heated substrates. As with PECVD films, the residual stresses in sputter-deposited SiC films exhibit a wide range of process-dependent values. It has been observed however that films with moderate tensile stress (~ 200MPa) can be deposited without the need for a post-deposition anneal. Films can be deposited both by DC sputtering if a conductive target is

used, or RF sputtering when the target is semi-insulating. Films can also be deposited by reactive sputtering of a Si target in the presence of a carbon-containing gas. Sputtered SiC films are generally conformal in nature, making them particularly well suited as a protective surface coating. That being said, free-standing MEMS structures, such as the microbridges shown in Fig. 4 can also be fabricated using conventional micromachining techniques.

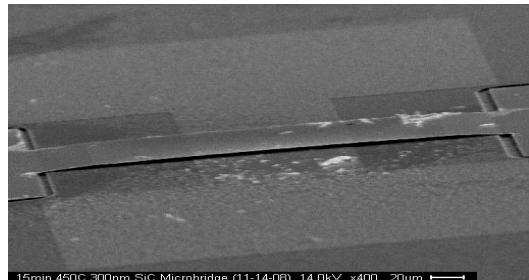


Fig. 4. Doubly-clamped, microbridge switch fabricated from a sputter-deposited a-SiC film.

#### B. Micromachining Methods

As stated previously, micromachining of SiC films leverages heavily on the techniques common to Si micromachining. With the exception of bulk anisotropic etching, techniques developed for Si bulk micromachining, including photoelectrochemical etching, deep reactive ion etching, and laser micromachining can be adapted for SiC albeit typically with slower removal rates. Thin single crystalline and poly-SiC structures deposited directly onto (100) Si wafers can also be fabricated by anisotropic Si wet etching. Surface micromachining of SiC thin films can be performed in much the same way as done for polysilicon. Early work in this area focused on thin film micromolding as a means to pattern the SiC structural films [15], however advances in selective reactive ion etching [16] have enabled surface micromachining of SiC to follow directly from polysilicon. In fact, poly-SiC surface micromachining is even more flexible than polysilicon surface micromachining in that while both processes can utilize SiO<sub>2</sub> as a sacrificial layer, poly-SiC surface micromachining can also be performed using polysilicon as a sacrificial layer. In fact, a four-structural layer poly-SiC surface micromachining process analogous to the polysilicon MUMPS process was first demonstrated nearly a decade ago [7]. Wafer bonding of SiC is also performed in much the same manner as Si wafer bonding, except that a thin deposited SiO<sub>2</sub> film is required as an interfacial bonding layer [17].

Micromachining of a-SiC films less restrictive than poly-SiC owing to its compatibility with temperature sensitive materials. Amorphous SiC films have long been used as etch masks for Si anisotropic etching due to their chemical inertness. As such, free standing structures of a-SiC can easily be rendered. Surface micromachining can be performed using a wide variety of substrate materials including SiO<sub>2</sub> and polyimide [18]. Unlike its crystalline counterparts, direct bonding of a-SiC surfaces to Si substrates has been demonstrated [19]. Like Si, oxygen plasma treatment of a-SiC surfaces enables bonding at substrate temperatures as low as 150°C. Much like Si<sub>3</sub>N<sub>4</sub>,

the insulating qualities of a-SiC enable the fabrication of metal-based MEMS structures on SiC-based mechanical supports, such as the rf switches reported in Ref. 11.

### III. SiC FOR BIOMEDICAL MICRODEVICES

#### A. Crystalline SiC

Use of single crystalline SiC for biomedical microdevice applications can largely be segmented into two distinct groups: (1) device fabricated from bulk 6H-SiC substrates, and (2) devices fabricated from epitaxial 3C-SiC films grown on Si wafers. Devices fabricated from bulk 6H-SiC wafers capitalize on the outstanding mechanical durability of the bulk substrate, the chemical inertness of the 6H-SiC surface and the availability of high-quality wafer substrates. Recently, a study was conducted to evaluate the mechanical and tribological characteristics of bulk SiC for use in orthopedic implants [20]. In this case, the hardness, coefficient of friction and scratch resistance of 6H-SiC was compared to commonly-used orthopedic materials, such as CoCrMo, Ti-6Al-4V, and stainless steel. The study concluded that SiC outperforms these materials in all categories. Devices fabricated from epitaxial 3C-SiC films leverage the ability to grow high quality films on inexpensive, micromachinable Si substrates, which is not possible in 6H-SiC. This approach works particularly well in situations where the Si substrate can provide suitable mechanical support.

As mentioned previously, electrochemical etching can be used to etch SiC substrates. Under conditions similar to those used to form porous Si from bulk Si substrates, porous SiC structures can be formed from 6H-SiC wafers. The pore size and porosity of the resulting structures offers the potential to use porous SiC in biofiltration applications. In 2004, Rosenbloom, et al., described the development of porous SiC membranes for use as protein filters [21]. The filters consist of suspended membranes fabricated from n-type and p-type 6H-SiC substrates. The etching was performed in a HF/5% ethanol solution. The p-type substrates required no illumination while the n-type substrates required UV illumination via a 350W lamp in order to create the electron-hole pairs required for etching. Free-standing, porous structures ranging in thickness from 20 to 110  $\mu\text{m}$  were fabricated using the procedures outlined in the paper.

Although the porosity of the membranes could not be evaluated quantitatively, membranes evaluated using solutions containing proteins ranging in molecular weight from 17000 to 80000 Daltons were able to pass proteins of up to 29000 Daltons and were able to exclude proteins in excess of 45000 Daltons, corresponding to molecular diameters of less than 4.7 nm and 5.0 nm, respectively. Moreover, the porous SiC membranes exhibited lower protein absorption as compared to commercially available polymer-based membranes specifically designed for protein absorption, indicating the potential for SiC membranes in biofiltering applications.

6H-SiC substrates have also been used as the principal mechanical support material for microprobe-based sensors. MEMS-based microprobe for biosensing applications are

currently the subject of intense research due to the promise of achieving high functionality in a minimally-invasive form factor when using MEMS technology. A typical probe may consist of a thin shank that supports multiple, chemically-sensitive thin film metallic electrodes. A common material for the shank is Si; however, concerns over the electrical and mechanical properties of these structures currently limit their applicability. To address these issues and to extend the utility of MEMS-based probe technology, Gabriel, et al., report on the development of a 6H-SiC needle-based microprobe for organ monitoring during transplantation [22]. The sensor consists of a semi-insulating 6H-SiC wafer on which a 1.5  $\mu\text{m}$ -thick  $\text{SiO}_2$  film is deposited by PECVD. Ti/Pt microelectrodes are then fabricated on top of the  $\text{SiO}_2$  film. A thin (300/700 nm-thick)  $\text{SiO}_2/\text{Si}_3\text{N}_4$  multilayer is deposited by PECVD to passivate the structure. Reactive ion etching is used to open windows to the Pt electrodes and a dicing saw is used to fashion the substrate into microneedles that measure roughly 15 mm in length and 1 mm in width. Si probes of similar design and dimensions were also fabricated for side-by-side comparisons.

Both SiC and Si microneedle probes were subjected to a battery of electrical and mechanical testing. In particular, impedance testing was performed in physiological saline solutions at frequencies ranging between 10 Hz and 1 MHz and mechanical load testing was performed using a nanoindenter to vertically deflect microneedles that were anchored to a rigid substrate. The paper reports that the 6H-SiC microneedle probes exhibited a 4X higher modulus of rupture and a 10X higher range in practical operating frequency as compared with similarly designed Si probes. The higher modulus of rupture value is likely due to the increased fracture strength of SiC as compared with Si and the improved electrical performance is due to its higher intrinsic resistivity as a result of its higher electronic bandgap.

In applications where bulk SiC structures are not required but SiC surfaces are desired, 3C-SiC films provide a convenient and low-cost alternative to 6H-SiC. One of the earliest 3C-SiC MEMS structures to be fabricated was the free-standing membrane. Such structures typically range in thickness from several hundred nm to several microns depending on the application. The membranes are extremely durable, with a 1x1mm<sup>2</sup>, 2  $\mu\text{m}$ -thick membrane able to withstand applied pressures of well over 100 PSI without breaking. Such strong membranes offer opportunities to utilize 3C-SiC films in a variety of applications, most notably micromachined pressure sensors. Such pressure sensors would have to incorporate membranes that are biocompatible and yet exhibit antifouling characteristics to be practical for long-term implant applications. As mentioned previously, Kotzar et al., showed that 3C-SiC films are biocompatible [23], a conclusion that was also reached by Coletti et. al., [24], who found that mammalian cell proliferation was greater on 3C-SiC surfaces than on Si surfaces. This finding suggests that although SiC is chemically inert, surface treatments will be required to suppress biofouling on exposed transducer elements made from SiC.

In addition to its outstanding mechanical properties, 3C-SiC thin films have unique optical properties that may play a significant role in developing new techniques for biomedical imaging. In conventional optical microscopy the spatial resolution is limited to one-half of the illuminating wavelength due to diffraction effects. To resolve features well below this limit, a technique known as near-field scanning optical microscopy (NSOM) has recently emerged. NSOM utilizes an optical detector that is placed very close ( $\sim$  few nm) to a sample in order to detect evanescent fields that are located in that region. These evanescent fields carry spatial information about the object being probed. Under proper conditions, NSOM probes are able to achieve resolutions on the order of  $1/20^{\text{th}}$  of the illuminating wavelength, making them particularly well suited for nanoscale imaging. NSOM is potentially a very powerful tool for biological imaging except that the requirement that the probe be placed in very close proximity to the sample means significantly hampers the ability to use the probe to image biological specimens in fluidic environments. As a first step to addressing this limitation, Taubner, et al., report the successful development of a 3C-SiC based superlens for NSOM [25]. Superlenses are constructed from materials that exhibit a negative permittivity. Such materials can be configured so that evanescent waves associated with the image side of the lens are detectable on the probe side. The permittivity in 3C-SiC is a negative value for an incident wavelength of  $11\text{ }\mu\text{m}$ .

The superlens consists of a free-standing, 440 nm-thick 3C-SiC film that was epitaxially grown on a (100) Si substrate. The membrane was fabricated by anisotropic Si etching. On both sides of the 3C-SiC membrane, a 220 nm-thick SiO<sub>2</sub> film was deposited by PECVD. The net result of this construction was to create a thin film superlens structure that displaced the NSOM probe by a distance of at least 880 nm from the specimen being examined. In order to demonstrate the superlensing effect a thin Au film was deposited on the membrane surface opposite the NSOM probe. The Au film was patterned into circular features ranging in diameter from 540 nm to 1200 nm. At an incident wavelength of  $9.25\text{ }\mu\text{m}$ , no image was detected by the NSOM probe. At  $11\text{ }\mu\text{m}$ , images from the 540 nm-diameter structures could be resolved, corresponding to a resolution of  $1/20^{\text{th}}$  of the incident wavelength as expected for direct NSOM imaging of the patterned Au structures without the superlens. This demonstration shows that the superlens enables significant displacement of the probe from the sample being imaged without significant loss of resolution. Presumably, a 3C-SiC superlens could be incorporated into the structure of a microfluidic device to enable in-situ NSOM imaging of biological samples.

#### B. Amorphous SiC

In terms of biomedical microdevice development, amorphous SiC has by far the longest track record of any SiC microstructure. Early work focused on developing amorphous hydrogenated SiC (a-SiC:H) films as corrosion resistant coatings for Ti alloy-based orthopedic implants [26]. By the mid 1990's a-SiC had been explored as a coating material for Ta, stainless-steel and other metallic

coronary stents [27, 28]. In these cases, it was hoped that the surface properties of SiC would improve the hemocompatibility of the stent structure. However, clinical trial data indicate that while the SiC coatings cause no adverse effects, they did not seem to provide any significant advantage either [29].

Recent interest in a-SiC has focused on its use as a coating material for implantable microsystems requiring hermetic sealing. The rationale behind such an approach is based on the fact that SiC is an excellent diffusion barrier material. In fact, a-SiC was identified by the IC community as a possible low-k intermetal dielectric material for devices utilizing Cu metallization in part because of its potential to protect Si transistor structure from the deleterious effects of Cu incorporation. Some of the earliest work in the development of a-SiC as a dielectric coating material for biomedical implants was performed by Cogan, et al., [30]. In this study, a-SiC films were deposited using SiH<sub>4</sub> and CH<sub>4</sub> as precursors on Pt and Ir microwire electrodes as well as Si and quartz substrates and subjected to a battery of tests to evaluate the dielectric properties, chemical stability and biocompatibility. Leakage current measurements performed in PBS solution at  $37^{\circ}\text{C}$  on wires coated with  $\sim 600$  nm-thick films showed leakage currents of  $5 \times 10^{-13}\text{ A}$  for films deposited at  $400^{\circ}\text{C}$ . Leakage currents increased to  $6.5 \times 10^{-13}\text{ A}$  for 1  $\mu\text{m}$ -thick films deposited at  $200^{\circ}\text{C}$ . Chemical dissolution rates in PBS at  $37^{\circ}\text{C}$  and  $90^{\circ}\text{C}$  were evaluated for the a-SiC films on Si substrates as well as control specimens consisting of LPCVD Si<sub>3</sub>N<sub>4</sub> coated Si wafers. It was found that the dissolution rates for the nitride films were 0.4 nm/day and 2 nm/hr at  $37^{\circ}\text{C}$  and  $90^{\circ}\text{C}$ , respectively. In contrast, the a-SiC films were chemically stable at  $37^{\circ}\text{C}$  and dissolved at only 0.1 nm/hr at  $90^{\circ}\text{C}$ . SiC-coated quartz discs were implanted into the subcutaneous region of New Zealand White rabbits to determine the inflammatory response of tissue upon exposure to SiC. As compared to silicone and quartz control specimens, no inflammatory response was observed.

Hsu, et al., [31] has recently extended the use of a-SiC as a protective coating for Si-based implantable devices. The technology driver for this research is an integrated, Si-based microneedle electrode array known as the Utah Probe. This probe is a three-dimensional structure consisting of a  $10 \times 10$  array of tapered silicon posts that are micromachined into the thickness of a Si substrate. Each post supports Ti/Pt/Ir electrodes that provide the electrical interface to nerve tissue. The packaged probe is integrated with Si-based IC's using a range of conventional packaging approaches that are customized for this particular application. Wireless telemetry systems for data and power are also included. The inclusion of on-board electronics necessitates the use of hermetic coatings to protect moisture-sensitive components as well as to prevent out-diffusion of device material. Along these lines, Hsu, et al., have developed PECVD-based a-SiC:H coatings for encapsulation. For initial development, the films were deposited on Si and oxide-coated Si wafers using SiH<sub>4</sub> and CH<sub>4</sub> as precursors and H<sub>2</sub> as a dilution gas. Substrate temperatures ranged from  $150^{\circ}\text{C}$  to  $275^{\circ}\text{C}$ . Film stress was

found to range from -130 MPa to -328 MPa depending on deposition conditions. A 650 nm-thick film deposited at 200°C survived soak testing in PSB for a 6 week period. Interdigitated Ti/Pt electrode structures were coated with a 650 nm-thick a-SiC:H film deposited at 200°C and subjected to impedance spectroscopy testing in Ringer's solution at 37°C for a 6 month period. The frequency range for this test was 1 Hz to 100 kHz. It was found that the impedance remained constant over the testing period, ranging from  $1 \times 10^8 \Omega$  at 1 Hz to  $\sim 1 \times 10^4 \Omega$  at 100 kHz, indicating that the film has superior moisture barrier properties, since moisture penetration would significantly decrease the impedance at any given frequency. A recent paper by this group describes the use of a-SiC coatings applied to fully integrated assemblies [32]. The SiC coatings act with a parylene thin film to provide protection from moisture intrusion. The SiC film acts as an impermeable passivation layer while the parylene overcoat provides additional protection and biocompatibility. The assembly includes epoxy-based underfill material to fill the space between the IC chip and the microneedle array which are electrically joined by flip-chip bonding. The researchers report that the underfill epoxy was compatible with the moderately high deposition temperature used for the a-SiC:H coatings even though the deposition temperatures were close to the degradation temperature of the epoxy. Moreover, the materials remained compatible after autoclave-based sterilization.

Use of a-SiC thin films as protective coatings is not limited to metallic wires and Si-based devices; in fact the low deposition temperatures associated with a-SiC suggest that these films may be well suited for hermetic sealing of polymer-based electrode structures. Polymeric substrates are very attractive for implantable microdevices due to their inherent mechanical flexibility. Micromachining techniques for several popular polymers, including polyimide, liquid crystal polymer, parylene and PDMS, have advanced to the point where device structures, such as neural electrode arrays, are routinely fabricated from these materials. These structures are generally suitable for acute testing; however the moisture absorption rates of these polymers require the integration of hermetic materials for long term implant applications. To make these polymer substrates better suited for long term implant applications, we have been exploring means to apply a-SiC barrier coatings directly to polymer surfaces. Our first attempts have focused on polyimide, owing to its stability at moderately high temperatures [33]. Figure 5 is an optical photograph of a peripheral nerve electrode made from polyimide and coated with a thin a-SiC layer. The electrode structure consists of eight Pt thin film contacts, a long interconnect segment, and a contact pad region designed to mate with a commercially available flex connector. This particular device is designed for acute testing, but subsequent designs will replace the flex connector interface with a section to mount ASICs. The top surface in this particular device is coated with a thin ( $\sim 500$  nm-thick) a-SiC:H film deposited by PECVD using the SiH<sub>4</sub>/CH<sub>4</sub> precursor system. The deposition temperature was 300°C. Reactive ion etching using a CF<sub>4</sub>/O<sub>2</sub> plasma and

photoresist as an etch mask was used to open windows through the SiC coating to the Pt contacts. The film adheres well to the polyimide substrate as well as the Pt metallization, even when the device is mechanically deformed. Some cracking was observed in regions that span the thin Pt traces, presumably due to excessive residual stress. Research is ongoing to develop means to relieve the residual stress as well as to evaluate the effectiveness of the a-SiC:H films as moisture barrier coatings when applied to polyimide surfaces.



Fig. 5. Optical photograph of a polyimide-based peripheral nerve electrode coated with a thin a-SiC film [33].

In anticipation that a-SiC coatings will be used to encapsulate implantable wireless microsystems, we have initiated a study to evaluate the effect of such coatings on the performance of microfabricated antennas [34]. Figure 6 is representative data of the measured return loss for a dual frequency, co-planar waveguide-fed, folded slot antenna with and without a protective a-SiC coating. In this case, the antenna consisted of Au metallization on an alumina substrate, selected primarily for convenience. The SiC coating was 450 nm thick deposited by the process used to coat the aforementioned peripheral nerve electrodes. Both coated and uncoated antennas exhibited a return loss better than -15dB at 5 and 7 GHz. The gain of both the coated and uncoated antennas was 3 dB. The durability of the SiC coating was assessed by immersing the coated antenna in Au etchant for 24 hrs. Testing after immersion showed no discernable difference in performance.

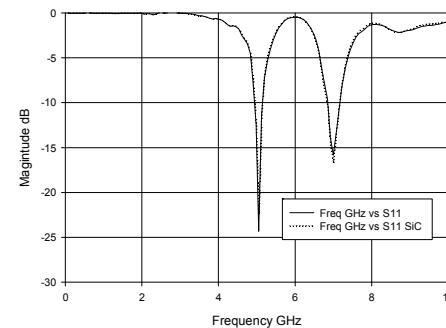


Fig. 6. Measured return loss of SiC coated and uncoated dual frequency folded slot antennas [34].

### III. CONCLUSIONS

Silicon carbide, now widely accepted as a material for harsh environment MEMS, is beginning to gain favor in the biomedical microdevice community for its potential as a structural and packaging material. Owing to its unique combination of electrical, mechanical, chemical and optical properties, SiC is positioned to have additional positive impact in the development of microdevice technologies, especially as thin film deposition techniques and the requisite micromachining techniques continue to advance. Of particular importance will be the development of

processing techniques that make SiC compatible with polymeric and other temperature-sensitive substrates that are likely to be used in next-generation biomedical microdevices.

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#### REFERENCES

- [1] S. Nishino, J.A. Powell, and H. Will, "Production of large-area single-crystal wafers of cubic SiC for semiconductor devices", *Appl. Phys Lett.*, vol. 42, pp. 460-462, 1983.
- [2] C.A. Zorman, A.J. Fleischman, A.S. Dews, M. Mehregany, C. Jacob, S. Nishino, and P. Pirouz, "Epitaxial growth of 3C-SiC films on 4 in. diam (100) silicon wafers by atmospheric pressure chemical vapor deposition", *J. Appl. Phys.*, vol. 78, pp. 5136-5138, 1995.
- [3] W.C. Chang, and C.A. Zorman, "Determination of Young's moduli of 3C (110) single crystal and (111) polycrystalline silicon carbide from operating frequencies", *J. Mater Sci.*, vol 43, pp. 4512-4517, 2008.
- [4] D.J. Young, J. Du, C.A. Zorman, and W.H. Ko, "High Temperature Single Crystal 3C-SiC Capacitive Pressure Sensor", *IEEE Sen. Journal*, vol. 4, pp. 464-470, 2004.
- [5] Y.T. Yang, K. L. Ekinci, X.M.H. Huang, L.M. Schiavone, C.A. Zorman, M. Mehregany, and M.L. Roukes, "Monocrystalline Silicon Carbide NEMS", *Appl. Phys. Lett.*, vol. 78, pp. 162-164, 2001.
- [6] X.M.H. Huang, C.A. Zorman, M. Mehregany, and M.L. Roukes, "Microwave-Frequency Nanoelectromechanical Systems", *Nature*, vol. 421, pg. 496, 2003.
- [7] X. Song, S. Rajgopal, J.M. Melzak, C.A. Zorman, and M. Mehregany, "Development of a multilayer SiC surface micromachining process with capabilities and design rules comparable with conventional polysilicon surface micromachining", *Mat. Sci. Forum*, vol. 389-393, pp. 755-758, 2001.
- [8] C.A. Zorman, S. Rajgopal, X.A. Fu, R. Jezeski, J. Melzak, M. Mehregany, "Deposition of polycrystalline 3C-SiC films on 100 mm diameter (100) Si wafers in a large-volume LPCVD furnace", *Electrochem. and Solid State Lett.*, vol. 5, pp. G99-G101, 2002.
- [9] X. Fu, R. Jezeski, C.A. Zorman and M. Mehregany, "The Use of Deposition Pressure to Control the Residual Stress in Polycrystalline SiC Films", *Appl. Phys. Lett.*, vol. 84, pp. 341-343, 2004.
- [10] C.R. Stoldt, C. Carraro, W.R. Ashurst, D. Gao, R.T. Howe and R. Maboudian, "A low-temperature CVD process for silicon carbide MEMS" *Sens Actuators A*, vol 97/98, pp. 410-415, 2002.
- [11] R. J. Parro, M.C. Scardelletti, N.C. Varajay, S. Zimmerman, and C.A. Zorman, "Amorphous SiC as a structural layer in microbridge based RF MEMS switches for use in software defined radio" *Solid State Electron.*, vol 52, pp. 1647-1651, 2008.
- [12] L.S. Pakula, H. Yang, and P.J. French, "A CMOS compatible SiC accelerometer", *Proc. IEEE Sens. Conf. Toronto*, pp. 761-764 2003.
- [13] J. Du, N. Singh, J. Summers and C.A. Zorman, "Development of PECVD SiC for MEMS using Trimethylsilane as the Precursor", *Mat. Res. Soc. Symp. Proc.*, vol. 919, pp. 283-288
- [14] J.B. Summers, M.C. Scardelletti, R. Parro, and C.A. Zorman, "Development of Amorphous SiC for MEMS-based Microbridges", *Proceedings - SPIE MEMS/MOEMS Comp. and Apps. IV*, San Jose CA, January 22-23, 2007, vol. 6464, pp. 64640H-1 to H-12
- [15] A.A. Yasseen, C.A. Zorman and M. Mehregany, "Surface micromachining of polycrystalline SiC films using microfabricated molds of SiO<sub>2</sub> and polysilicon", *J. of Microelectromech. Sys.*, vol. 8, pp. 237-242, 1999.
- [16] D. Gao, R.T. Howe, and R. Maboudian, "High-selectivity etching of polycrystalline 3C-SiC films using HBr-based transformer coupled plasma" *Appl. Phys. Lett.*, vol 82, pp. 1742-1744, 2003.
- [17] K. N. Vinod, C.A. Zorman, A. Yasseen, and M. Mehregany, "Fabrication of low defect density 3C-SiC on SiO<sub>2</sub> structures using wafer bonding techniques", *J. Electron. Mat.* vol. 27, pp. L17-L20, 1998.
- [18] A. Bagolini, L. Pakula, T.L.M. Scholtes, H.T.M. Pham, P.J. French, and P.M. Sarro, "Polyimide sacrificial layer and novel materials for post-processing surface micromachining" *J. Micromech. Microeng.* vol. 12, pp 385-389, 2002.
- [19] J. Du and C.A. Zorman, "A Low Temperature a-SiC/Si Direct Bonding Process for MEMS/NEMS", *Technical Digest - 14<sup>th</sup> International Conference on Solid State Sensors, Actuators and Microsystems (Transducers 2007)*, Lyon France, June 9-14, 2007, pp. 2075-2078.
- [20] X. Li, X. Wang, R. Bondokov, J. Morris, Y.H. An, and T.S. Sundarshan, "Micro/Nanoscale Mechanical and Tribological Characterization of SiC for Orthopedic Applications", *J. Biomed. Mat. Res. B*, vol 72, pp 353-361, 2005
- [21] A.J. Rosenbloom, D.M. Sipe, Y. Shishkin, Y. Ke, R.P. Devaty, and W.J. Choyke, "Nanoporous SiC: A candidate semi-permeable material for biomedical applications", *Biomed. Microdevices*, vol 6, pp. 261-267, 2004.
- [22] G. Gabriel, I. Erill, J. Caro, R. Gomez, D. Riera, R. Villa, and P. Godignon, "Manufacturing and full characterization of silicon carbide-based multi-sensor micro-probes for biomedical applications", *Microelect. Journal*, vol. 38, pp. 406-415, 2007.
- [23] G. Kotzar, M. Freas, P. Abel, A. Fleischman, S. Roy, C. Zorman J.M. Moran, and J. Melzak,, "Evaluation of MEMS Materials of Construction for Implantable Medical Devices", *Biomaterials*, vol. 23, pp. 2737-2750, (2002).
- [24] C. Coletti, M.J. Jaroszeski, A. Pallaoro, A.M. Hoff, S. Iannotta, and S.E. Saddow, "Biocompatibility and wettability of crystalline SiC and Si surfaces", *Proc. 29<sup>th</sup> Annual International Conf. of the IEEE EBMS*, Lyon France, August 23-26, 2007, pp. 5849-5852.
- [25] T. Taubner, D. Korobkin, Y. Urzhumov, G. Shvets, and R. Hillenbrand, "Near-field Microscopy Through a SiC Superlens", *Science*, vol 313, pg. 1595, 2006.
- [26] C. Sella, J. Lecoeur, Y. Sampeur, and P. Catania, "Corrosion resistance of amorphous hydrogenated SiC and diamond-like coatings deposited by rf plasma-enhanced chemical vapor deposition", *Surf. Coat. Tech.*, vol. 60, pp. 577-583, (1993).
- [27] M. Amon, S. Winkler, A. Dekker, A. Bolz, C. Mittermayer, and M. Schaldach, "Introduction of a new coronary stent with enhanced rediopacity and hemocompatibility", *Proc. Annual Conf. IEEE EMBS*, vol 17, pp. 107-108, (1995).
- [28] M. Amon, A. Bolz, M. Schaldach, "Improvement of stenting therapy with a silicon carbide coated tantalum stent", *J. Mat. Sci.: Mat. Med.*, vol. 7, pp. 273-278, (1996).
- [29] O. Bertrand, R. Sipehia, R. Mongrain, J. Rodes, J.-C. Tardif, L. Bilodeau, G. Cote, M.G. Bourassa, "Biocompatibility Aspects of New Stent Technology", *J. Amer. Coll. Card.*, vol. 32, pp. 562-571, (1998).
- [30] S.F. Cogan, D.J. Edell, A.A. Guzelian, Y.P. Liu, and R. Edell, "Plasma-enhanced chemical vapor deposited silicon carbide as an implantable dielectric coating", *J. Biomat. Res A*, vol. 67, 856-867, 2003.
- [31] J.-M. Hsu, P. Tathireddy, L. Rieth, A.R. Norman, and F. Soltzbacher, "Characterization of a-SiC:H thin films as an encapsulation material for integrated silicon based neural interface devices", *Thin Solid Films*, vol. 516, pp. 34-41, 2007.
- [32] S. Kim, R. Bhandari, M. Klein, S. Negi, L. Rieth, P. Tathireddy, M. Toepper, H. Oppermann, and F. Soltzbacher, "Integrated wireless neural interface based on the Utah electrode array", *Biomed. Microdevices*, in press.
- [33] A. Hess, J. Du, R. Parro, J. Dunning and C.A. Zorman, "PECVD Silicon Carbide as a Thin Film Packaging Material for Microfabricated Neural Electrodes", *Mat. Res. Soc. Symp. Proc.*, vol. 1009E, paper # 1009-U04-03, 2007.
- [34] M. Scardelletti, N. Varajay, D. Oldham and C.A. Zorman, "Silicon Carbide as a Chemically-resistant Thin Film Packaging Technology for Microfabricated Antennas", *Proc. - 2006 IEEE Wireless Microwave Tech. Conf.*, Clearwater FL, December 4-5, 2006, paper number FC-5.