Ceramics are used in emerging MEMS technologies because of their diverse structural, chemical and functional properties and because innovative precursor-based processing is leading to low-cost and flexible approaches to manufacturing.

Ceramic MEMS

New Materials, Innovative Processing and Future Applications

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The genesis of microelectromechanical devices (MEMS) can be traced to silicon lithography,[1] which was invented for the microelectronics industry. Different crystallographic planes of silicon etch at different rates in different etchants. Among the first architectures to be created by exploiting this property of silicon was a heat sink with fins, on the microscale.

Complex MEMS with several moving parts are now constructed from silicon by multilayer lithographic and etching technologies. The emerging applications range from sensors and actuators[2,3] to entire systems. One of the most complex systems is a high-temperature microscale gas turbine[4] for power generation. It is known as a nanoturbine, because it generates only a few watts of power.

However, silicon is not a structural material. It has a fracture toughness of ~0.7 $\mathrm{MPa \cdot m^{1/2}}$, a softening temperature of 600°C and a high degree of reactivity to oxygen and water. Thus, the creation of many new, revolutionary MEMS systems requires that they be constructed from various materials, including ceramics.

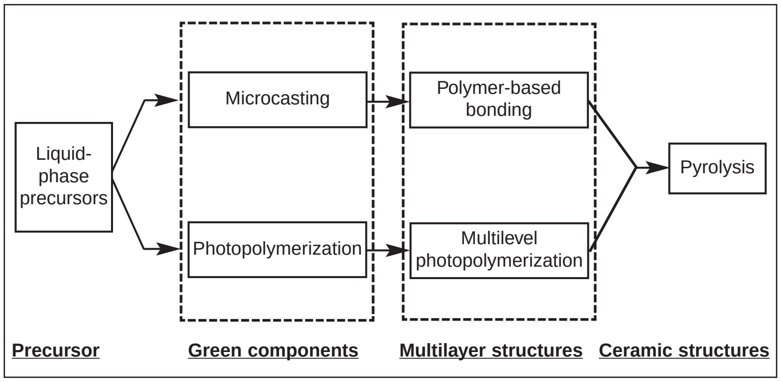
Several attributes of ceramics make them highly suitable for MEMS applications. The chemical inertness of ceramics makes them useful in biological applications. Ceramics resist corrosion at high temperatures, making them suitable for chemical engineering and microsensor applications in severe environments. The same attributes are vital in overcoming problems of friction and stiction in micromotorized systems.

The low density and high-temperature mechanical properties of ceramics makes them materials of choice for high-speed devices such as nanoturbines. Because ceramics are flaw-size sensitive, their strength and reliability can be expected to increase in small-scale applications.

Properties of Si-C-N as Compared to Other Silicon-Based Materials

Property	Si-C-N	SiC	Si_3N_4
Density (g/cm^3)	2.35	3.17	3.19
E modulus (GPa)	80–225	405	314
Poisson's ratio	0.17	0.14	0.24
CTE ($\times 10^{-6}$/K)	~3	3.8	2.5
Hardness (GPa)	25	30	28
Strength (MPa)	500–1200	418	700
Toughness (MPa·m$^{1/2}$)	3.5	4–6	5–8
Thermal shock FOM†	1100–5000	270	890

† strength/(E modulus·CTE).



Ceramic systems are fabricated from liquid precursors in two stages. First, the components are constructed to net shape by polymerization of the precursors stacked to create a 3-D green structure. Second, the assembly is pyrolyzed at 400–800°C in a controlled atmosphere to convert it to a ceramic. Two routes have been developed for net-shape polymerization—microcasting and stereo-photopolymerization.

MEMS technology can be used to integrate ceramics with semiconductors, metals and polymers to create systems that serve specific functions. This seamless connectivity between design, materials integration and manufacturing can create a new era for ceramic materials.

We present here another and perhaps most persuasive reason for pursuing ceramics for small-scale engineering—low-cost and reliable mass-scale manufacturing processes. In small-scale engineering, the green form of the net shape is prepared by microcasting a liquid ceramic precursor into a mold that has been prepared by conventional lithographic methods.

The precursor can be a chemical—for example, a metal organic—or it can be a slip. In the latter case, the microcasting process can be considered as a microversion of the conventional slip-casting process.

The present discussion, however, is limited to the fabrication of a new class of ceramics, silicon carbonitrides (Si-C-N), directly from liquid precursors, called polysilazanes. Our work is conducted using the commercial precursor Ceraset (Honeywell Inc., Fort Washington, Pa.).

The work reported here can be extended to many ceramics—structural, piezoelectric, optical and superconducting—because metal organic precursors for most, if not all, of these ceramics are now commercially available.

Si-C-N are predominantly amorphous ceramics.[5] They are composed of silicon, carbon and nitrogen such that there is some free carbon. Therefore, in general, Si-C-N can be written as $SiC \cdot nSi_3N_4 \cdot xC$. The apparent glass transition temperature of these covalent glasses is ~1500°C, and it increases to 1800°C[6] with the addition of boron.

The oxidation resistance of Si-C-N compares favorably with that of pure chemically vapor deposited (CVD) SiC. The high strength and low modulus of Si-C-N gives them a high figure-of-merit value for thermal shock resistance.

The processing route for Si-C-N renders it suitable for low-cost, mass-scale fabrication of MEMS. The process consists of essentially two steps.

- The liquid precursor is cast into a net shape and cross-linked (thermally or with an initiator) to create a rigid polymer.
- The free-standing forms are pyrolyzed at 400–900°C under a controlled atmosphere, yielding components made of Si-C-N.

Even though the maximum processing temperature is <1000°C, the service temperature of the Si-C-N components can be 1500–1800°C. Many components can be produced in a single batch using microlithographic methods. This process is much less expensive and much more flexible than the CVD process that is used to make devices from SiC.

The microcasting process for fabrication of Si-C-N MEMS from Ceraset precursor was developed at the University of Colorado at Boulder under a contract from DARPA. Potential applications in high-temperature systems, such as micropower generation,[7] were sought.

Another unique feature of the Boulder work is to design and build MEMS devices to measure the fundamental material properties of Si-C-N. This approach has educational and fundamental missions. Scientifically, it focuses attention on Si-C-N properties and their variability in small-scale structures. Educationally, it focuses on a powerful way to teach students MEMS device technology and fundamental materials science.

Green Body Fabrication of MEMS

There are two ways to fabricate green MEMS structures: microcasting and photopolymerization. Components also can be bonded in the green state to construct 3-D devices.

The microcasting process uses photolithographic techniques to create a microsized mold, into which liquid precursor is cast and solidified. Two types of molds have been developed for microcasting—those made from a photoresist and those made from a metal foil.

Photoresist as mold. SU-8 photoresist[1] (MicroChem Corp., Santa Clara, Calif.) is an epoxy-type photoresist[8] based on EPON SU-8 resin. The molds are produced by standard UV lithography. This mold is particularly suitable for producing high-aspect-ratio structures having straight vertical sidewalls. Another advantage of SU-8 is that it decomposes while the Si-C-N is being pyrolyzed and, thus, the process becomes a lost-mold technique.[11, 12]

The procedure consists of spinning the photoresist onto a substrate—a silicon wafer—to produce a layer of uniform thickness, which depends on the spin speed. The photoresist is lithographically patterned and developed. The liquid precursor is spun onto this surface so that it fills the mold cavities.

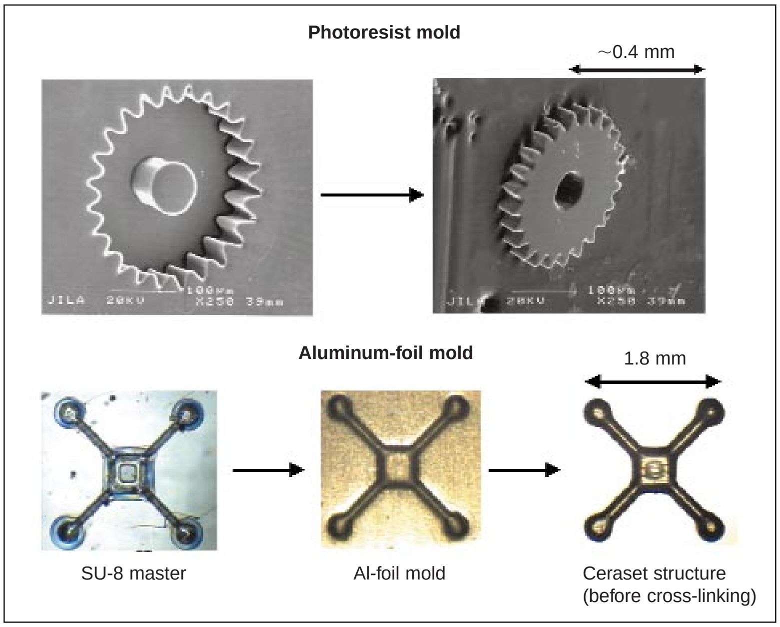
The entire assembly is thermally set. The wafer is polished to remove the thin overlying Ceraset layer that covers the entire wafer. The structure is cross-linked under isostatic pressure and pyrolyzed. The SU-8 decomposes during pyrolysis, freeing the Si-C-N part.

A disadvantage of the photoresist-as-mold technique is that the photoresist and the ceramic precursor are both organic. They can react with one another under the wide range of temperatures and environments to which the assembly is subjected during pyrolysis.

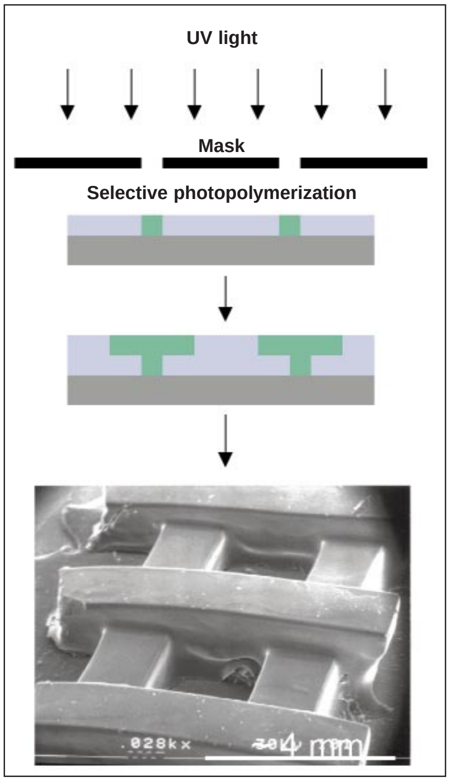
These reactions are difficult to identify and control, which creates uncertainty in the manufacturing process. The metal-mold process avoids this disadvantage.[13]

Metal as mold. A positive structure—i.e., a die—is fabricated on a silicon wafer using the SU-8 photoresist method. The die is used to emboss a thin aluminum foil with the micromold cavity structure. The foil is supported underneath by plasticine during the forging process.

The ceramic precursor is cast into the aluminum micromold, and a



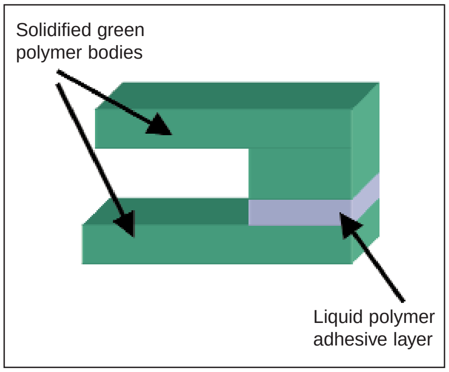
Two approaches for microcasting, i.e., the fabrication of green but rigid polymeric components. The photoresist method was used to fabricate the gear (shown here in its ceramic form, after pyrolysis). The metal-mold method—where the mold cavity is embossed into aluminum foil that is peeled away after casting and solidifying the precursor—was used to fabricate the other part.



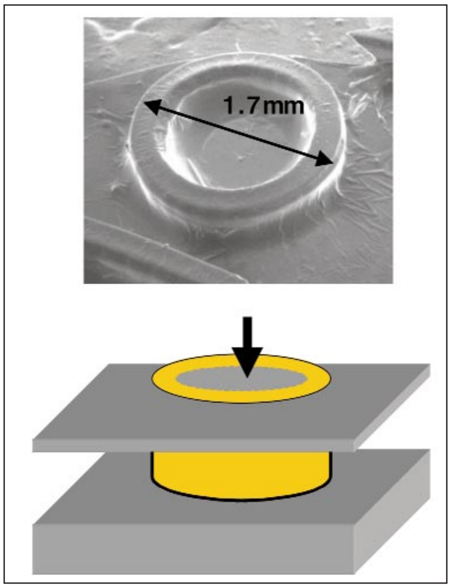
In the photopolymerization process, a layer of precursor, supported on a solid substrate, is cross-linked to a shape through a noncontact mask using UV radiation. A multilayer structure is constructed by successive exposure of liquid layers of the precursor, as shown in the two-layer example made using Ceraset and dimethoxy-2-phenyl acetophenone (DMPA; Igracure 651, Aldrich Chemical, Milwaukee, Wis.) as the initiator. The initiator and primary and secondary cleavage produce methyl radicals that catalyze the cross-linking process.

piece of NaCl crystal is placed over the surface of the casting. The crystal serves as a rigid substrate for further handling of the microcasting. The assembly is thermally set in an oven to solidify the precursor.

The aluminum foil is peeled away, leaving behind the solid precursor part on the salt crystal. The part is released from the crystal by quick immersion in deionized water. The free-standing microcomponent can be bonded to other microcomponents to create 3D structures, which are pyrolyzed to ceramic MEMS.



Individual cast components can be bonded in the polymer state using the liquid precursor as an adhesive. The process can be used to construct multilayer 3-D structures.



The first phase of a pressure transducer constructed by bonding a Si-C-N ring to a Si-C-N membrane and measuring the deflection of the membrane in response to a point-compression load. The deflection in the second stage is measured by a change in the capacitance between the membrane and the rigid substrate.

Photopolymerization

Photopolymerization is an alternative route to create solid polymer structures from a liquid precursor.[14] The process is conducted at room temperature. A photoinitiator is added to the precursor, which catalyzes polymerization of the precursor upon exposure to UV light.

Shapes are constructed by exposing a layer of the precursor through a noncontact mask. The liquid precursor is supported on a substrate. Silicon, Teflon and salt crystals have been successfully used for this purpose.

Multilayer structures can be created in-situ by successive exposure to several layers, one over the other, each layer having its own geometry. Conceptually, the process is similar to the free-form rapid-prototyping method, and it is called stereo-photolithography. This process has the potential of yielding free-standing green structures of complex shape.

Fundamental technological issues are related to the resolution of the structures in the vertical plane, because the UV radiation scatters into the liquid. The activated photoinitiator has a finite diffusion distance, creating uncertainty in the edge resolution of the solid structure. The exposure time also can affect the efficiency of the stereo-photolithographic process.

3-D Structures

Useful MEMS almost always require the construction of 3-D structures. In the polymer process, the 3-D structures are assembled in the green state, prior to pyrolysis. Stereo-photolithography is one way to construct 3-D structures. Another way is to create multilayer structures by bonding two or more green parts using a layer of liquid precursor as the adhesive. Ceraset is an effective bonding adhesive of cross-linked polymer components.

Several MEMS devices have been made using stereo-photolithography. It also is feasible to incorporate metallic interlayers into the green state using screen-printing. This is similar to the approach used in the fabrication of multilayer ceramic substrates for electronic packaging.

Pyrolysis

The final step in the fabrication of Si-C-N MEMS is pyrolysis of the green-state polymer structure in a controlled atmosphere by gradually heating from 400 to 900°C. The pyrolysis converts the organic material to an inorganic, covalent glass that is highly refractory. The glass remains stable up to 1800°C. Si-C-N also exhibits outstanding creep and oxidation resistance.

The volatile molecular species released and the associated weight change during pyrolysis have been measured. The absolute density of the material increases from ~1–1.2 g/cm^3 in the green state to 1.9–2.4 g/cm^3 in the ceramic state, with a weight loss of 15–20 wt%. The linear shrinkage during pyrolysis ranges from 15 to 20%.

The small dimensions of MEMS preclude the development of cracks during pyrolysis. Crack-free specimens have been obtained, where the smallest dimension of the component—e.g,. the thickness dimension of a disk shape—is <300 μm.

Three Si-C-N devices have been fabricated—a pressure transducer, an electrostatic actuator and a combustion chamber.[9] These devices have been chosen to demonstrate technologically significant applications of high-temperature MEMS and to demonstrate that MEMS can be used to measure fundamental materials-science properties of Si-C-N.

Pressure Transducer. The Si-C-N pressure transducer consists of a membrane supported on a circular ring. The membrane deflects in response to an applied load or pressure. The membrane–ring assembly is fabricated by bonding a ring structure to a flat membrane, both made of Si-C-N polymer, and it is pyrolyzed.

A mechanical response of the membrane—applied load versus displacement—is obtained using a microhardness tester, which gives a linear relationship between the load and the displacement. The work in progress is to create a capacitor between the flexible membrane and the rigid substrate and measure the deflection of the membrane by the change in the capacitance of the device.

Electrostatic Actuator. We have constructed the first parallel-plate piston microactuator fabricated using a polymer-derived ceramic. The four-flexured structure was fabricated using photopolymerization. Gold was deposited on one side of the Si-C-N part for electrical conductivity.

An Al_2O_3 substrate—a common material used in MEMS and electronic-packaging prototyping—was patterned with electrical traces. Indium solder was deposited on select bonding pads, using masking and lift-off techniques. The Si-C-N structure was attached to the substrate using an in-house-developed flip-chip bonding process so that the Si-C-N was suspended 3 mm above the address electrode.

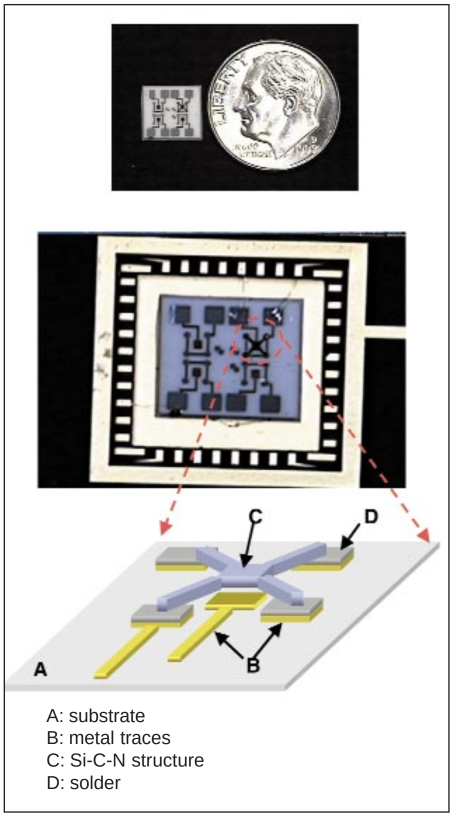
The entire assembly was placed into a ceramic dual-in-line package for electrical testing, which consisted of applying voltage between the Si-C-N and the address electrode and measuring the plate deflection under a laser interferometric microscope. The result agreed well with the parabolic relationship predicted by electromechanical analysis.

The actuator is being developed for experimental temperatures up to 1600°C so that the internal friction behavior and the glass transition of the Si-C-N ceramic as a function of frequency and temperature can be determined.

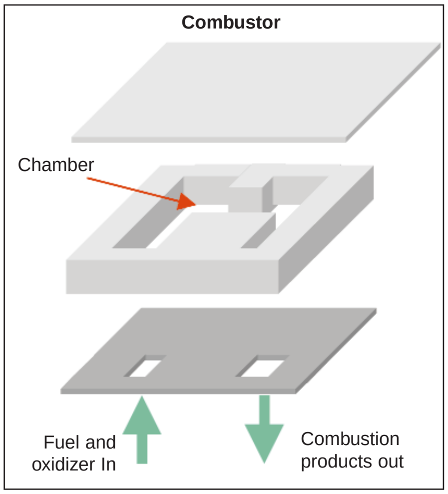
The fabrication of MEMS from a high-temperature ceramic material and its successful integration with existing MEMS technologies—such as flip-chip bonding and electronics-packaging processes—opens the way for applications where the special structural, chemical and functional properties of ceramics can create new technologies.

The high-temperature MEMS actuator can be used in micromirror arrays[10] for high-power laser communications. Mirrors made from polysilicon cannot withstand the temperatures generated by even moderate optical power densities.

Combustion Chamber. The combustion chamber consists of three layers—floor, walls and lid. Fuel and oxidizer enter the chamber through an inlet port in the floor and proceed through



MEMS made from Si-C-N to measure fundamental mechanical properties of Si-C-N. This configuration is being developed to determine the internal friction behavior at high temperature. Results show the measurement of Young's modulus at room temperature by plotting the Si-C-N electrode against the applied voltage.



Design of a combustor with inlet and outlet ports and vertical-wall chamber structure for combustion. First prototype has been constructed and high-temperature testing is being conducted.

a mazelike series of walls within the reaction chamber. The byproducts exit the chamber through the outlet port. The chamber is constructed using photopolymerization in three layers—floor, wall structure and lid—that are bonded in the green state and pyrolyzed. ■

Acknowledgments

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