Development of *β*-SiC from Graphite and Investigation of Preceramic Polymers Converted to *β*-SiC During Pyrolytic Bonding Processes of Graphite Components

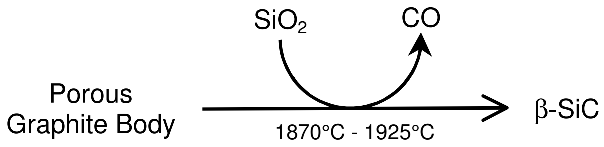
Analysis by Randy Lee for Poco Graphite, Decatur, TX, September, 1997

A series of experiments, processing trials and analytical evaluations were conducted to investigate the materials and process requirements for joining pre-fabricated ceramic components during the assembly of the company's primary products, large scale processing fixtures for the semiconductor wafer fab industry. Since these articles were required to withstand repeated exposures to high temperature, ionized gases and concentrated, hot mineral acids during end user applications, the company believed that the only material suitable for use within and throughout the fixture was limited to high purity silicon carbide (SiC). Thus, in the same regard, all material candidates chosen for bonding/joining options were also limited to SiC of very high purity (> 99.5%).

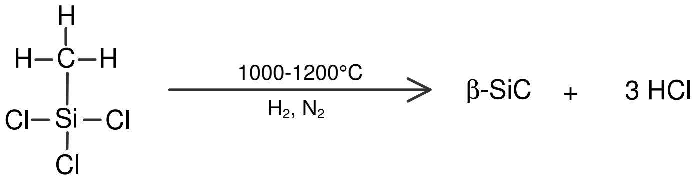
Three pre-ceramic adhesive material systems were evaluated along with a series of process variations which were implemented for each of the bonding process trials. Four separate furnace systems were utilized, but only one gave acceptable results during this initial phase of the project. It is not the intent of this essay to present an extended discussion of the details from those experiments. Rather, an abbreviated summary is given regarding the materials and processes that were investigated during those trial runs.

Background:

In contrast to the more conventional methods for ceramic fabrication, the company had previously acquired and developed the technology to convert porous graphite bodies into monolithic SiC through a high temperature gas-solid reduction reaction process within an electric arc furnace. The process utilizes sand (silica) particles, SiO_2, in a solid state thermal reaction that sacrifices carbon atoms within the porosity of the graphite substrate to produce silicon monoxide SiO, which then reacts with more carbon atoms in a second step solid-gas reaction, thus completing the conversion of hexagonal graphite into beta-SiC (CO is scrubbed from the system throughout).



As expected, the converted product is even more porous than the initial graphite substrate and must undergo subsequent processing to effectively seal the network of surface pores across the periphery of the SiC body. The method previously chosen by the company to accomplish this was Chemical Vapor Deposition (CVD) which slowly coats several mils of cubic β-SiC onto the surface. In this subject area, process research continues in efforts to define the relative degrees of deposition (CVD) vs infiltration (CVI) that are necessary to produce quality products. This ratio is dependent on the run conditions (primarily pressure and temperature) and was studied extensively in other project assignments but will not be dealt with here. However, the basic CVD/CVI reaction employed for this process utilized the SiC precursor, methyl trichlorosilane as the starting material, and resulted in about 2.0-2.5 mils coating thickness in a single 12 hour run.



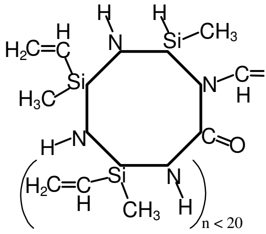
$$CH_3SiCl_3 \xrightarrow[H_2,\ N_2]{1000\text{-}1200^\circ C} \beta\text{-}SiC + 3\,HCl$$

MethylTrichloroSilane

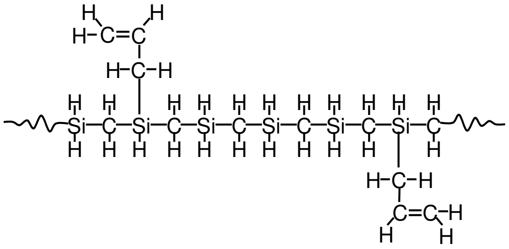
The discussion above serves as a brief overview for the processing of component substrates preceding and following the bonding/joining phase. The objective of this short report is quite limited and will only summarize the materials, processes and technologies that were related to the research conducted to investigate the joining and bonding of SiC components which had already been fabricated, but just prior to CVD/CVI processing. Since all processing takes place well below the transition point in which cubic beta SiC cubic is converted into the alpha rhombic form (~2500°C), the entire system (substrate, coating and joints) is expected to consist entirely of β-SiC. Previous X-ray diffraction studies have indeed shown this to be the case.

Disussion:

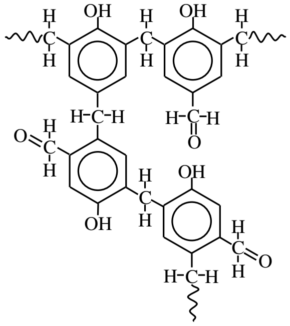
In the past, Poco has conducted many investigations into the use of phenolic resin and a reaction bonding precursor. This report examines the use of newer materials classified as preceramic polymers or resins. There are several developmental polymers on the market, which are advertised as pre-ceramic precursors. The two materials evaluated for this study were the SiC precursors, Ceraset from Dupont's Lanxide division, and Allyl HydridoPolyCarboSilane, or AHPCS, which is produced in limited quantities by Starfire systems. Both systems are sold as viscous, solvent-dilutable thermosetting resins which are suitable for adhesive formulation and undergo crosslinking via peroxide-initiated free radical reactions during cure. A third system evaluated was based on the more common phenol-formadehyde (phenolic) resin and is not actually a precursor for SiC until elemental Si is properly incorporated into the system which ultimately undergoes a 'reaction bonding' process.



Vinyl Ureasilazane
Oligomer (Ceraset)

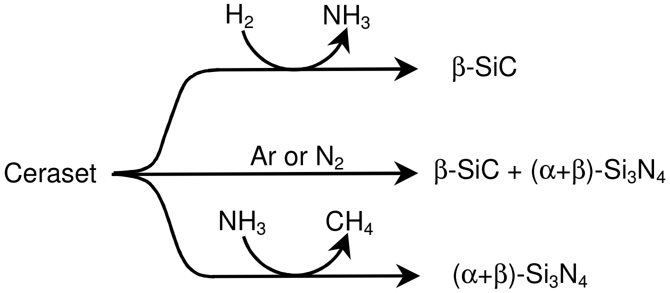


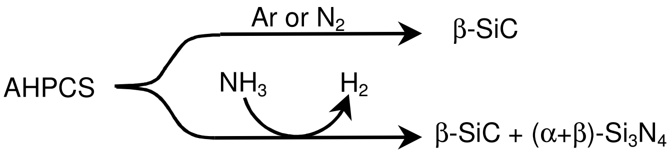
Allyl HydridoPolyCarboSilane

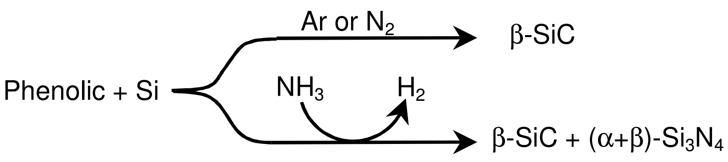


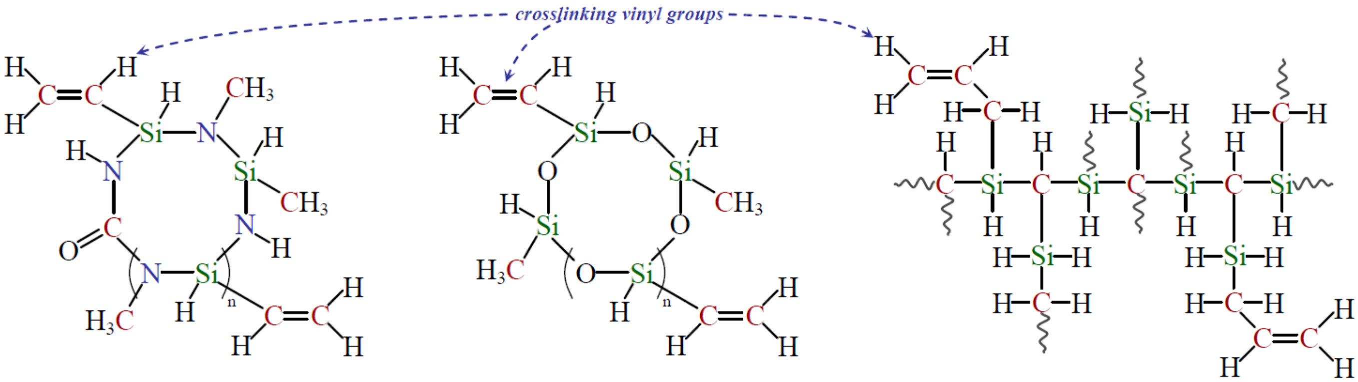
Phenol-Formadehyde
(Phenolic) Prepolymer

While uncured AHPCS basically consists of linear polymer chains, Ceraset exhibits a tertiary-type structure that is not actually cyclic as it appears, and should probably be classified as an oligomer rather than a polymer. The crosslinking process for Ceraset and AHPCS is best accomplished by the application of heat during cure (after addition of the peroxide initiator). Free radical reactions between segments form crosslinks via double bonds with the vinyl and allyl side groups along these molecules. In general, phenolic resins are alcoholic mixtures containing partially polymerized phenol-formadehyde products that become hardened during elevated heat curing via advanced condensation reactions between phenols, aldehydes and growing polymers. Crosslinking occurs 'isotropically' since links are formed in all directions producing a very hard plastic. Each reaction produces a water molecule, and since the resin is typically diluted with 25-30% isopropanol, the final cured product is quite porous (unless cured under high pressure). Atmospheric or vacuum pyrolysis of phenolic bonds gives a highly porous charred product which is required for the subsequent reaction bonding process.



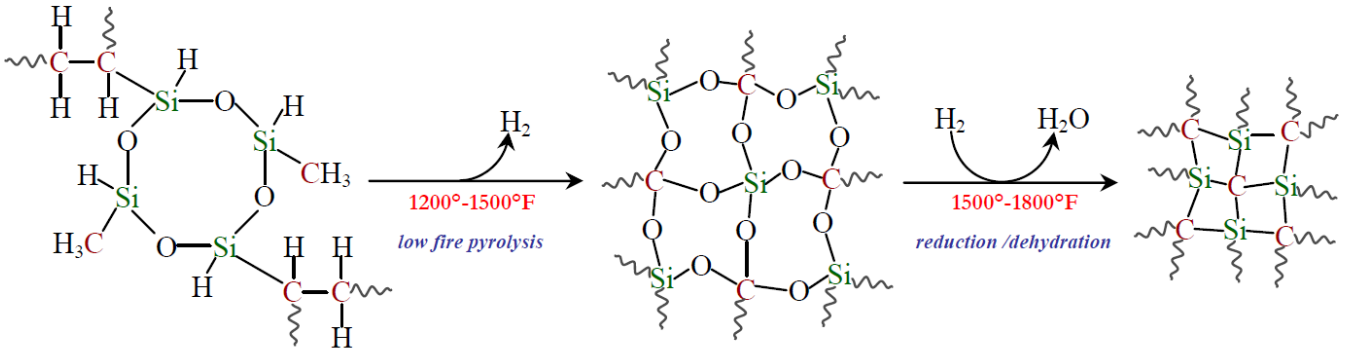






Urea Silazane Oligomer Unit Silicon Oxycarbide (Siloxane) Oligomer Unit Branched Carbosilane Polymer Segment

Crosslinking sites for monomers of Ceraset (Urea Silazane), analogous Siloxane and AHPCS monomers.



Crosslinked Siloxane Resin Glassy Silicon Oxycarbide Ceramic Glassy a-SiC Ceramic

Example of conversion of cured siloxane polymer through its glassy phase prior to conversion into the β-SiC crystalline structure.

– Amorphous (Glassy) a-SiC:

This unusual form of SiC is uniquely derived from pre-ceramic polymers (including the carbosilanes, silazanes and siloxanes) and is stable up to about 2000°-2200°F when it begins to crystallize (into β-SiC). The SMP-10 pre-ceramic polymer backbone consists of an alternating carbon-silicon sequence with pendant allyl (propenyl) side groups which incorporate unsaturation into the structure permitting curing/crosslinking (via free radical addition) to harden the polymer resin prior to pyrolysis. Carbosilane units solidify into a glassy structure, analogous to the glassy carbons derived from thermosetting organic polymers. There is not much information available concerning the material science of a-SiC since it is a rather new form of SiC.

– Crystalline (Beta) β-SiC:

When a-SiC is subjected to higher pyrolysis temperatures (greater than about 2000°-2200°F, depending on time exposure), the glassy structure rearranges into a facecentered cubic configuration designated as β-SiC. This process of crystallization causes volumetric shrinkage which opens up most of the previously closed voids and creates additional porosity – all open to the outside. The bulk density is reflective of the openness exhibited by the porosity. This value/range has been independently determined and also confirmed by Starfire scientists (inventors of the AHPCS polymer).

Experimental Summary:

The hardened or cured (crosslinked) forms of both the Ceraset and AHPCS are converted directly into ceramic upon firing (pyrolysis). The resulting composition is heavily dependent upon the type of atmosphere employed. When small pieces of silicon metal were placed near pre-pyrolyzed joints previously bonded using phenolic resin (filled with SiC particles), Si-rich SiC joins were formed. This is due to capillary infiltration of molten Si into the pores of the charred phenolic joint during the final pyrolytic conversion step. Due to the presence of elemental Si which remains in the product after firing, reaction bonded joints are not expected to be a viable approached to the production of trouble-free, high purity joints. As depicted in the reaction chart above, the gas/atmosphere composition plays an important role in the final composition of the joint. Ceraset, which contains carbon, silicon and nitrogen, can be made to produce bonds containing only SiC when H_2 is employed to extract the nitrogen from system, or bonds containing mixtures of SiC and Si_3N_4 with an inert gas, or exclusively Si_3N_4 when ammonia is the predominant gas used in the firing process. The other two systems contain only carbon as the primary atomic species and nitrogen must be forced into the structure during the conversion process. In might be noted that EDX analysis conducted on test samples throughout the study indicated that N_2 atmospheres had no effect on the nitrogen make-up in the final product even when firing temperatures of 2200°C were employed.

Over eighty independent trial runs were conducted examining coupon pairs bonded with each of the three adhesive systems. Coupon substrates were taken directly from the company's graphite-to-SiC conversion process but prior to CVD coating. In all, a host of relevant parameters and conditions were evaluated including:

(1) Pre-cure resin staging
(2) Various forms, sources and particle sizes of SiC and C as fillers
(3) Varying filler levels from 50% to 70%
(4) Various atmosphere gas mixtures and concentrations (flow rates) from 10 cfh to 40 cfh
(5) Varying vacuum and pressure from 0.5 torr to 10 psig
(6) Embedment of samples in calcined coke particles vs direct exposure to flowing gasses
(7) Variations in peak temperature from 1200°C to 2200°C
(8) Variations in temperature ramp rate and hold points from 3°C/min to 10°C/m
(9) Low temp firing (sintering) followed by higher temp post-firing typically from 1000°C-1200°C to 1600°C-2200°C
(10) Firing in (a) large production pyrolytic carbon CVD chamber furnace, (b) large production SIC CVD chamber furnace, (c) small laboratory sintering furnace and (d) large production graphitizing tube furnace

A fundamental point of conclusion is the following:

The graphitizing furnace produced the only acceptable results (mechanically) and it is recommended that the causes for inadequate joint formation in the other furnaces be further investigated. All three adhesive systems gave passing results in this furnace (joints were stronger than the substrate).

Based on the fundamental point given above, the following conclusions can stated:

(a) Resin staging, particle sources or loading levels have no effect on ultimate joint mechanical quality but only serve as methods to modify the adhesive viscosity (or paste consistency) during the initial bonding step.
(b) Gas flow composition has a definite effect on final joint composition and possibly performance of the joint as noted above. Variations in flow rate had no effect as well as pyrolysis in coke particles.
(c) Pressure appears to have little or no effect on joint characteristics as long as positive gas flow pressure is maintained throughout the run. As expected, vacuum runs produced weak, porous joints.
(d) Peak firing temperature and ramp rate had no effect on joint quality except that run below about 1400°C contained an appreciable amount of oxygen in the joints (perhaps silicon oxycarbide) that was reduced to the 1-2% level when post-fired at higher temperatures (> 1600°C).

Crossectional EDX and mechanical tests were conducted throughout, but none of those results will be given here. A representative analysis by EDX for all three bonding systems processed through the graphitizing furnace in N_2 to 2200°C was 54-56% Si, 42-44% C, 1-2% O.

References: Product literature and phone discussions with personnel from Starfire (AHCPS) and Dupont (Ceraset).

All illustrations, reactions and technical descriptions are the handiwork
and interpretation of the author except where noted .