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THE FORMATION OF β SiC on Si

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β–SiC was formed on Si substrates in an horizontal, rf powered reactor. The reaction of Si with CH_4 was either directly at temperatures of 1200 – 1350°C or by a two step reaction in which CH_4 was first cracked at 900°C and then the deposited C reacted with Si at temperatures of 1200 – 1350°C. Important features of the study were the minimization of contaminants from susceptor and substrate support materials, removal of native oxides and a novel susceptor design. A rectangular, TaC coated Ta susceptor was used in conjunction with sapphire supports. Preheated He was used as a carrier gas. Growth characteristics and film structure are presented as a function of CH_4 concentration and substrate temperature.

Key words: β-SiC, methane-silicon reaction, susceptor design, substrate support.

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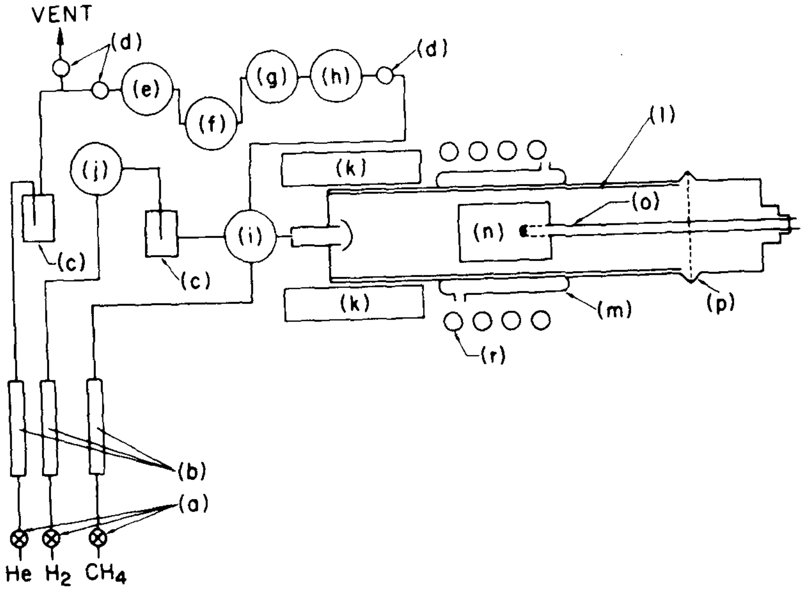
Introduction

The fabrication of crystallographically determined silicon nozzle arrays for non–impact printing applications has been described in the recent literature(1–4). Silicon nozzles are susceptible to chemical attack in certain types of inks and must therefore be passivated. Of the host of potential passivating films, oxides, nitrides, carbides, metals and alloys, deposited films appear less desirable than those formed via reactions involving the silicon surface, since they are more vulnerable to defects such as pinholes. Of the surface reaction types of films, silicon carbide appears most attractive because of its chemical inertness and mechanical hardness. The present study describes a method for the formation of silicon carbide layers via the thermodynamically favorable reaction of methane with silicon. An important aspect of the direct reaction of CH_4 with silicon involves the elimination of native silicon dioxide from the silicon surface, since the reaction of this oxide with methane to form SiC is extremely unfavorable thermodynamically. In the absence of such surface contamination, one would expect carbide formation to be self-limiting in thickness due to the impermeability of the material, and for dust particles to be of little concern since the gas phase reactant(s) could diffuse underneath them. Another important aspect of a carbiding method is the minimization of temperature gradients in the reactor. These can arise not only through reactor temperature inhomogeneities, but also because of the impingement of cold entrant gas on the substrates.

While a number of studies dealing with the general chemistry of the methane-silicon reaction have been reported on(5–8), none have been concerned directly with questions relating to overall system design, the impact of native oxide interference on the formation of passivating films and the effect of contaminants due to heating of the reactor components. The present report discusses the growth characteristics, film structure, and chemical properties of SiC formed in a system of novel susceptor design and describes a process for coverage of both sides of silicon substrates in a single thermal cycle.

Experimental Procedure

A schematic representation of the reaction train is shown in Fig. 1. The silicon substrates are reacted with preheated methane diluted with helium in an horizontal rf heated reactor. The methane is introduced into



a) metering valves

b) flow meters

c) Liquid N_2 trap

d) solenoid valves

e) Nb furnace (450°C)

f) Ti furnace (800°C)

g) Ti furnace (350°C)

h) Si furnace (1000°C)

i) mixing chamber

j) Pt furnace (450°C)

k) preheating furnace (650°C)

l) liner tube

m) wafer or N_2 cooling jacket

n) susceptor

o) thermocouple

p) 0-ring joint

r) R-F coil

Fig. 1 A Schematic Representation of the Reaction Train.

the system as a 0.6% mixture in helium (99.9999% purity), then diluted further with helium (99.995% purity). The diluent helium is purified using a liquid nitrogen trap followed by heated getters (Nb at 450°C, Ti at 800°C, Ti at 350°C, and Si at 1000°C in sequence). The diluted methane is then preheated in a quartz tube at 650°C prior to introduction into the reactor. With the susceptor discussed below, a silicon wafer can be heated at 1200°C in the purified He diluent gas for several hours with no detectable surface degradation. The silicon substrate to be carbided is supported on sapphire supports within a tantalum carbide coated tantalum susceptor which is in turn supported on sapphire skids as shown in Fig. 2. Power to the susceptor is provided by a 20kW, 300kHz Lepel generator$^{(9)}$ controlled by a fast cycle PID Eurotherm temperature controller$^{(10)}$. Temperature measurement is via a Pt-Pt10Rh thermocouple enclosed in a quartz tube lying adjacent to the substrate on the downstream side to prevent contamination of the silicon wafer.

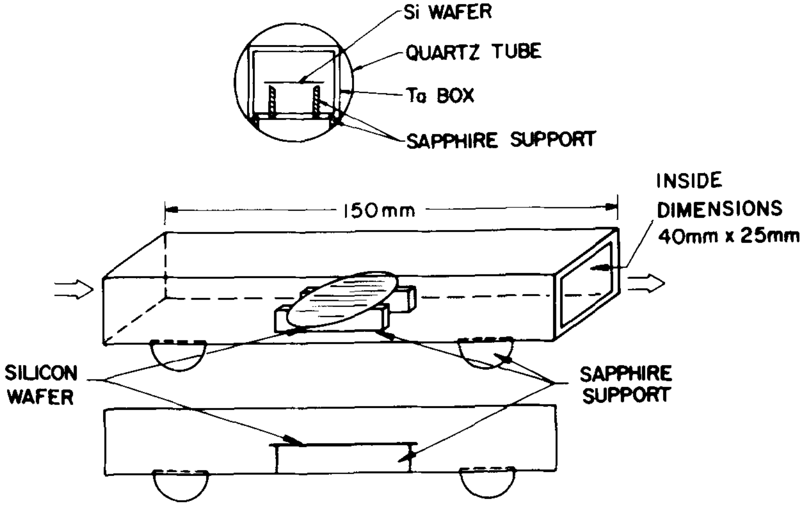


Fig. 2 Details of the Rectangular Susceptor and Sapphire Supports.

In the reaction temperature range examined (1200–1350°C), it was found that the presence of heated quartz parts in the system resulted in sufficient vaporization and subsequent reaction with the silicon to interfere severely with the process. The end result was always non–uniform, erratic carbiding of the silicon parts. Sapphire supports were therefore used to support the substrate as well as to isolate the hot susceptor from the quartz reaction chamber. The design of the susceptor, shown in Fig. 2, is rectangular in shape and open at both ends. The top and bottom are 6mm thick while the side walls are 3 mm thick. The tantalum pieces were annealed at the temperature of use, mechanically polished, then cleaned in trichloroethylene, acetone, deionized water, etched in "white etch" ($7HNO_3$:2HF), rinsed in deionized water, re-etched in a polishing solution ($5H_2SO_4$:$2HNO_3$:2HF), rinsed sequentially in deionized water and ethyl alcohol then dried with N_2. The parts are mated together via slots in the top and bottom piece. Prior to use, the susceptor was placed in the reactor, heated to 1300°C slowly (2 hrs) and treated in H_2 for 10 min to remove surface oxide. CH_4 in He (1.6×10^{-2} vol %) was then introduced into the system to form TaC on the Ta parts. The carbiding was conducted for 3 hrs. The system was then cooled to room temperature in a two hour time cycle.

The silicon substrates were "chem-mech" polished, (100), p type, 5Ω cm, float zone material. Prior to loading into the reactor, the substrates were etched in buffered HF, rinsed in deionized water and dried. A wafer was loaded into the susceptor, the system was flushed with helium and heated to 1250°C in a helium ambient atmosphere. It was kept at temperature for 10 min to remove native oxide, Eq. 1(11). This procedure was found to be much more effective than treatment with hydrogen at elevated temperatures since the latter always

$$Si(s) + Si0_2(s) \xrightarrow{>1000^\circ C} 2\ Si0(g) \qquad (1)$$

resulted in surfaces with degraded smoothness. Silicon carbide was then formed using one of the two reaction sequences outlined in Fig. 3. Both processes gave acceptable results. In essence the first process (Fig. 3a) is a single stage one in which the CH_4 is reacted directly with the silicon in the temperature range 1200–1300°C. The second process (Fig. 3b) is a two stage one in which carbon is first deposited on the silicon at 900°C and reacted subsequently with it at the higher temperatures. The data in this paper are all for the simpler one step process.

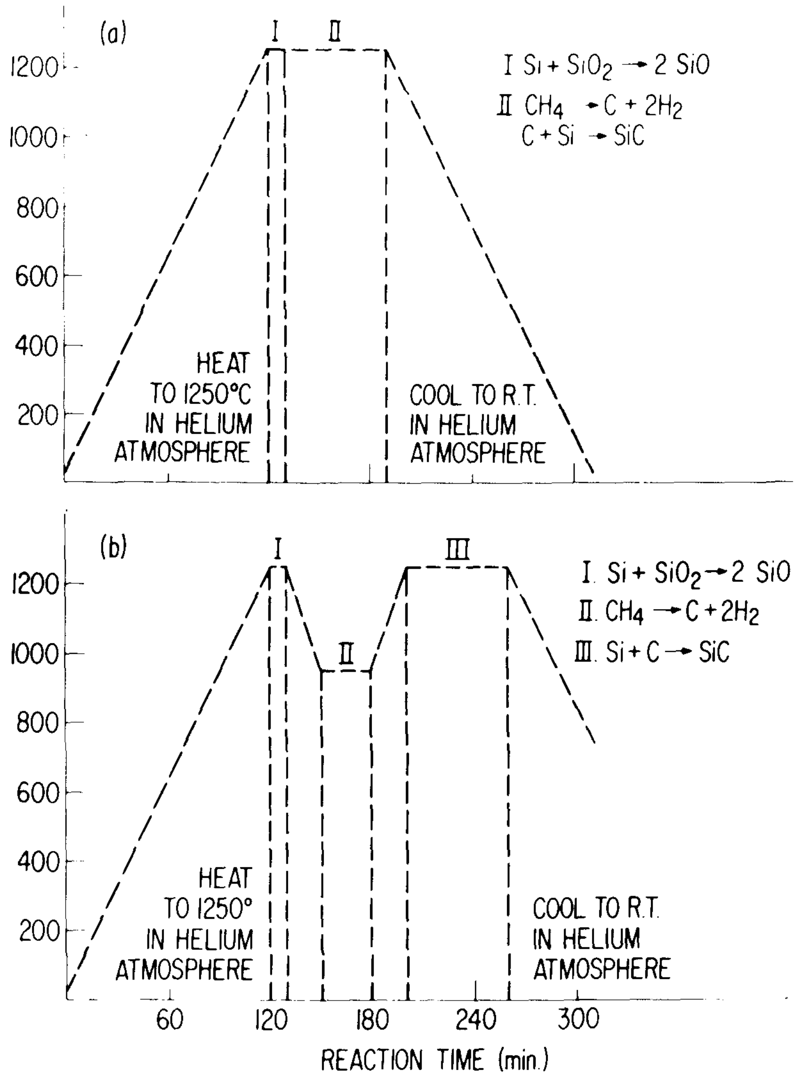


Fig. 3 Outlines of the Two Reaction Sequences.

Results and Discussion

Susceptor Design

As mentioned earlier, susceptor material and design are critical in obtaining uniform, defect free coatings because system outgassing and/or volatilization interferes with the reaction. Graphite susceptors and silicon carbide coated graphite susceptors were examined extensively, and in all cases, to varying degrees, caused degradation of the silicon surfaces when silicon control wafers were heated in purified helium for required times at required temperatures. Silicon and tungsten coated graphite were also examined and these always cracked at the carbiding temperatures. Tantalum silicide coated tantalum was examined(12) and found acceptable, except that the parts could not be cleaned of deposited carbon without damaging the silicide. Pure tantalum susceptors(13, 14) worked also, except that they became carbided in use, but not as uniformly as when carbided prior to use.

For supporting the wafers, quartz knife edges were tried and found to be unacceptable. At the points of contact with the silicon, the reaction depicted in Eq. 1 ensued. This prevented complete carbiding of the surface and resulted in the formation of blotchy carbide films. Sapphire supports did not cause deterioration of the surfaces prior to or during carbiding, and enabled both exposed surfaces of the silicon wafers to be coated uniformly. The box design of the susceptor provided a very uniform temperature environment which was found to be essential in obtaining coatings of uniform thickness. Even with this design, however, it was important to use preheated gases to prevent front to back temperature gradients in the susceptor.

Growth Characteristics

The growth of SiC was examined as a function of deposition time, deposition temperature and CH_4 concentrations. In Fig. 4 is shown the SiC film thickness, as a function of deposition time at four different CH_4 concentrations. The reaction temperature was 1250°C and the linear gas stream velocity, referenced to room temperature, was kept constant at

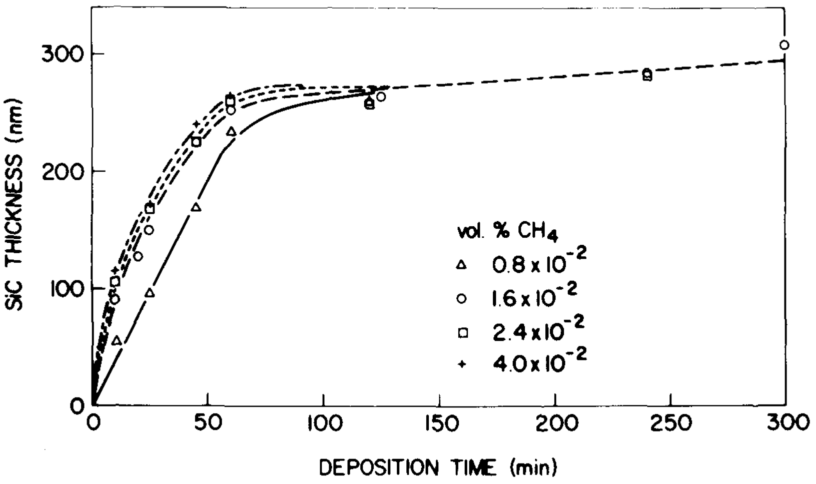


Fig. 4 SiC Film Thickness (nm) as a Function of Deposition Time (min) at Four Different CH_4 Concentrations.

4 cm/sec. The gas flow conditions and CH_4 concentrations studied are shown in Table I. It can be seen that the film thickness increases rapidly up to 60 min Beyond this time, the SiC growth proceeds at a much slower rate. At about 260 nm of SiC and after approximately 120 min of growth time, the thickness achieved appears to become insensitive to the concentration of CH_4.

A carbon layer was observed to be present on the grown SiC film after approximately 60 min of reaction time for the three lower CH_4 concentrations. In the case of the highest CH_4 concentration used, 4 x 10^{-2} vol %, a carbon layer was seen after 20 min of reaction. Samples containing such carbon layers were examined with x-ray diffraction which showed them to be graphite. In those experiments where graphite was formed, SiC thickness measurements were made after removing the carbon layer by oxidation in air at 650°C. All other films (those without carbon) were clear, smooth and shiny as grown.

TABLE I

Gas Flow Conditions for SiC Formation

(Cross Sectional Area of Reaction Chamber = 37 cm^2)

(Linear Gas Stream Velocity = 4 cm/sec)

He Flow Rate liters/min	CH_4–He Mixture liters/min	Total Flow Rate liters/min	CH_4 Concentration vol % x 10^2
9.150	0.125	9.275	0.8
9.025	0.250	9.275	1.6
8.90	0.375	9.275	2.4
8.65	0.625	9.275	4.0

In the present study, at the lowest CH_4 concentration employed, 0.8 x 10^{-2} vol % (curve a, Fig. 4), the growth rate appears to be linear up to approximately 60 min. If the data of Fig. 4 is replotted so that the square of SiC thickness is plotted as a function of deposition time (Fig. 5), it is seen that, except for the lowest CH_4 concentration, the plot is linear indicating parabolic (diffusion controlled) growth kinetics. Finally, after 60 min, the growth rate drops to a lower value and follows some other reaction mechanism. This final low growth rate stage may be governed by the reaction of Si with a solid phase of carbon, rather than freshly cracked CH_4. It was observed that during a "two step reaction" in which CH_4 is first cracked at 900°C and the Si reacted at an elevated temperature, the formation of SiC is appreciably slower than in the "one step reaction."

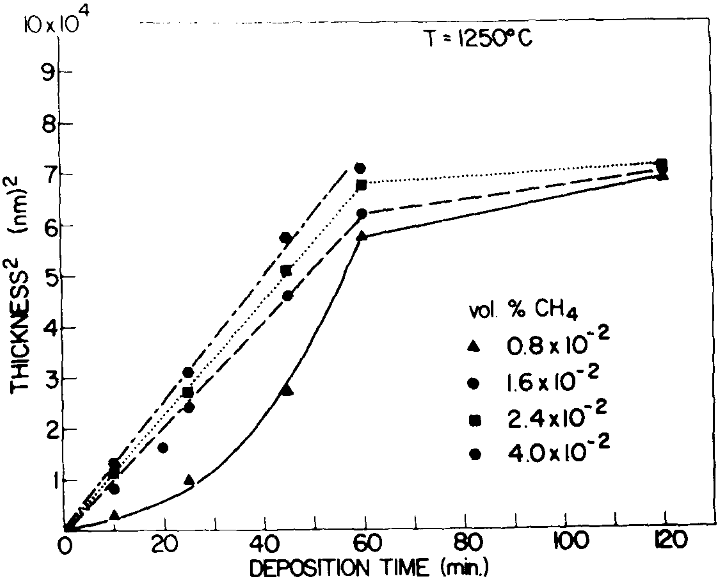


Fig. 5 SiC Film Thickness Squared (nm^2) as a Function of Deposition Time (min).

The SiC growth rate dependence on deposition temperature at three CH_4 concentrations and a constant growth time of 10 min is shown in Fig. 6. The growth rate (nm SiC/min) is plotted on a log scale as a function of 1/T. It can be seen that the activation energy, for which there is limited data, is different at each concentration. The trend, for which the authors have no explanation, is that the activation energy increases with decreasing CH_4 concentration. The values for the activation energy range from 15.9 kcal/mole at 0.8×10^{-2} vol % to 7.3 kcal/mole at 2.4×10^{-2} vol %.

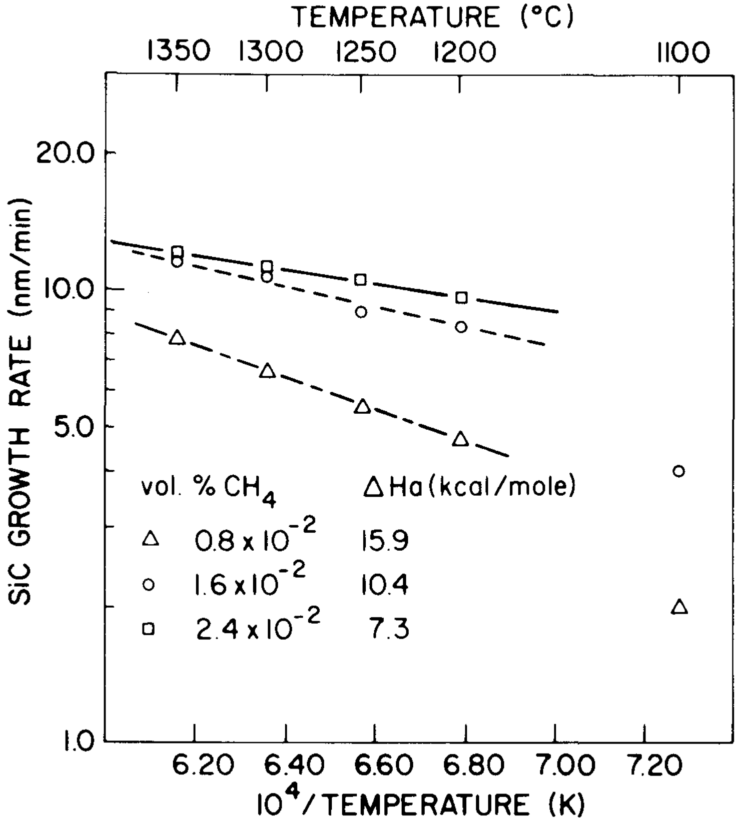


Fig. 6 Log of SiC Growth Rate (nm/min) as a Function of 1/T (K).

Film Structure

The grown films were found to be β-SiC. The results obtained in the present study show that in the case of films approximately 40 nm thick, the crystallinity depends on the deposition temperature and Si surface quality. Thin single crystal films (~ 40 nm) were obtained at the highest growth temperature (1350°C), while films grown at the lower temperatures were polycrystalline.

The average grain size for thick films (~ 100 nm) as a function of deposition temperature is shown in Fig. 7. The grain size was determined using TEM on samples that were prepared by etching away the Si from the backside of the wafer with white etch. When the substrate temperature was uniform, excellent grain size uniformity was obtained. It was observed that the SiC nucleates initially at dislocations and it was at these sites that the largest grains were found.

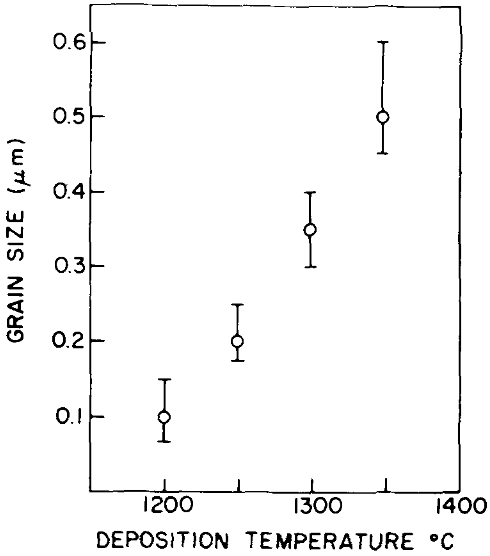


Fig. 7 The Grain Size (μm) Distribution for thick Films (~ 100nm) as a Function of Deposition Temperature (°C).

Optical Properties

The real part of the index of refraction, n, as measured by ellipsometry, was found to be 2.66–2.68 at 546.1 nm and 2.72 at 720 nm. N. W. Thibault(15) reported the index for β–SiC as close to 2.63 and for α–SiC (at 546.1 nm) as 2.66.

Film Thickness Measurements

Several methods for measuring SiC film thickness have been described in the literature but difficulties, for a variety of reasons, were experienced. These techniques for thickness measurements are discussed below, as are problems associated with them.

1. IR Absorption – This method was reported on by Spitzer et al.(3) and Mogab(16). The SiC film structure (grain size) influences the absorption of the film which can cause an error of as much as 100%.

2. Ellipsometry – This technique can be used only for excellent quality films. Layers which are smooth, uniform and free from carbon deposits will give good results, all other layers gave unsatisfactory results.

3. SEM Measurements – Graul and Wagner(6) report that the thickness of the layer was measured by cleaving followed by measurement using scanning electron microscopy. It was observed in the present study that an error of as much as 50% could result because of the difficulty in determining the Si–SiC interface in good quality films. It was found that the electron beam reflects from Si and SiC in a like manner.

4. IBM Film Thickness Analyser – A prototype of the IBM automatic Film Thickness Analyser was used successfully for most of the samples that were thicker than 55 nm. The reproducibility of the measurements were found to be ± 2.5 nm. The results correlated well with data obtained using the Tolansky multiple beam interferometer and were also comparable to thickness determination obtained via nuclear back scattering measurements

Chemical and Mechanical Properties

Si wafers coated with SiC were exposed for 24 hrs to white etch ($7ml\ HNO_3{:}2ml\ HF$) or 50% NaOH solutions at room temperature. The films were found to be impervious to attack and no changes were observed after the etch treatments. The films were also pinhole free and had excellent adhesion to the substrates. There was no evidence of cracking due to thermal stressing, either as formed or after a liquid nitrogen quench.

Conclusions

The motivation for this study was to achieve high quality, ultra smooth SiC layers on Si nozzle arrays. The main effort was spent in examining the growth and system parameters. The surface smoothness and film quality improved when the various sources of impurities were eliminated from the system by the use of proper susceptor design and material for the susceptor and support. It was also observed that the use of a He ambient atmosphere instead of the commonly used hydrogen ambient improved the surface structure.

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