GENERAL ATOMIC

GA-A14016

RADIOISOTOPE SPACE POWER GENERATOR ANNUAL REPORT

FOR THE PERIOD JULY 1, 1974
THROUGH JUNE 30, 1975

by

N. B. ELSNER, J. CHIN, and H. G. STALEY

Prepared under
Contract E(04-3)-167
Project Agreement No. 60
for the San Francisco Operations Office
U.S. Energy Research and Development Administration

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ABSTRACT

The Isotec Technology Program for FY-75 concentrated on materials development efforts in two areas: TPM-217 P-type material and SiGe technology.

TPM-217 P-type material is a 3M proprietary thermoelectric material whose principal components are Cu, Ag, and Se. The usefulness of TPM-217 P-type selenide in thermoelectric converters depends on its dimensional, electrical, and thermal stability at high temperature and its compatibility with other converter component materials in a low-pressure environment. Experimental efforts were directed toward determining (1) the vapor species above TPM-217 from 700° to 1100°C, (2) the weight loss rate for TPM-217 at 900°C in vacuo, and (3) the stability of TPM-217 material in contact with Mo, Fe, 316 stainless steel, and pyrocarbon.

The rate of vaporization for unprotected TPM-217 was of the order of 2.3×10^{-4} g/cm²-hr at 900°C. The major vapor species above TPM-217 at 1100°C was Se₂, comprising more than 90% of the gas monitored. Other vapor species included Cu, Ag, and CuSe. At 600°C the TPM-217 reacted with Fe and slightly with 316 stainless steel but showed no observable reaction with Mo and pyrocarbon.

The Si-Ge program is a continuation of the experimental work performed during FY-74. The development of coatings to suppress the vaporization of SiMo and SiGe continued. Techniques for applying ion-plated and chemical-vapor-deposited coatings of Si₃N₄ and (Si,Al)N alloys on SiMo were examined. Methods of controlling morphology and the chemical composition of these coatings were developed. Rates of vaporization for coated samples at 1100°C were measured.

Knudsen cell mass spectrometer and high-temperature evaporation rate measurements were made on commercially available Si_3N_4 to compare the results with those for vapor-deposited Si_3N_4 and Si_3N_4 -coated SiMo test samples. Weight loss rates for commercial Si_3N_4 samples were approximately the same as for stoichiometric Si_3N_4 vapor deposited on P-type SiMo. Steady-state weight loss rates for uncoated P-type SiMo controls were 10 to 100 times as high as for Si_3N_4 -coated P-type SiMo samples. Si_3N_4 -coated samples with excess Si had higher weight loss rates than similarly coated samples with stoichiometric Si_3N_4 .

Weight loss rates for (Si,Al)N-coated N-type SiMo samples were lower than for equivalent Si_3N_4 -coated N-type SiMo samples.

Knudsen cell evaluation of Si-SiGe-SiO₂ samples was completed. Single- and double-chamber Mo Knudsen cells containing Si and SiGe cubes were thermally aged at 1100°C in a vacuum ion-pumped furnace for 1300 hr. Specimen examination after thermal aging showed liquid Ge movement from SiGe to Si in experiments containing SiO₂ but not in experiments containing no SiO₂.

INTRODUCTION

General Atomic Company is conducting a two-part program for ERDA consisting of (1) an evaluation of TPM-217 P-type selenide thermoelectric material and (2) a continuation of a materials development program to improve the performance and useful life of the high-temperature Si-Ge thermopile.

The intent of the TPM-217 evaluation program is to seek ways of improving the reliability of TPM-217 and its compatibility with other materials at high temperatures in order to take advantage of its excellent thermoelectric properties. This evaluation will include microstructure, dimensional stability, material compatibility, and vaporization behavior at the proposed thermoelectric generator operating temperature of 900°C. This information will be used in future efforts to improve end cap joining and reduce vaporization degradation of the thermoelectric element.

The program on Si-Ge technology is continuing the search for methods of reducing degradation of the thermopile. Vaporization of Si and its reaction with the SiO_2 insulation are the major cause of generator degradation, while degradation due to liquid Ge is a possible secondary cause. Minimization of degradation due to vaporization is being sought through SiMo coating. Two objectives of the SiMo coating studies for the FY-75 program based on FY-74 results were (1) to produce and evaluate stoichiometric, low-temperature Si_3N_4 coatings for SiMo and (2) to produce and evaluate (Si,Al)N coatings for SiMo. The results will be compared with vaporization results for commercial Si_3N_4 to ensure adequate protection of the SiMo by the vapor-deposited Si_3N_4 coatings.

Experimental verification of proposed mechanisms for liquid Ge will also be sought. This information should provide guidelines for the selection of insulation materials which surround the thermoelectric couple.

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1. P-TYPE TPM-217 STUDIES

1.1. INTRODUCTION

The TPM-217 material studies were initiated by General Atomic Company (GA) in March 1975 when the material was received from 3M Company. The GA studies have been conducted along the following lines:

1. Vaporization characterization of the TPM-217 material. The goals of this task are to identify the species vaporizing and to determine the partial pressure of the species as a function of time and temperature.
2. Mesh-in-cap hot junction bonds. The PbTe-based thermoelectric alloys have demonstrated satisfactory performance in conjunction with the mesh-type bond (Ref. 1-1) and the goal of this task is to fabricate mesh-type joints utilizing TPM-217 materials.

The results obtained in both these tasks are discussed below.

1.2. BACKGROUND

P-type TPM-217 material sent to GA by 3M was in the form of bonded, partitioned thermoelectric elements. An as-received element, mounted and polished on cross section, is shown in Fig. 1-1. The as-received material is essentially three phase: the matrix, a Cu-colored phase, and a white-colored phase, which is Ag-rich. However, it is sometimes difficult to make a visual distinction between the Ag- and Cu-rich phases (see Fig. 1-2). The starting material for bonding is Se-rich (Ref. 1-2), and through the bonding processes the TPM-217 material is brought to a lower Se concentration by (1) vaporizing the excess Se and (2) reacting the TPM-217 with the

Fig. 1-1. Photomicrograph of an as-received, as-cast TPM-217 P-type material showing Ag- and Cu-rich phases

(a) (200X)

(b) (200X)

Fig. 1-2. Details of (a) Cu-rich and (b) Ag-rich phases in as-cast TPM-217 P-type material

braze alloy (Ag-28Cu) and the Cu cold pedestal. While the photomicrograph mosaic in Fig. 1-1 shows the Cu- and Ag-rich phases at the hot junctions of both partitions, these second phases are readily taken into solution and transported to the cold junctions of both partitions (Ref. 1-2).

1.3. VAPORIZATION CHARACTERIZATION

1.3.1. Mass Spectrometer Analyses

The mass spectrometric analyses of TPM-217 material were initially conducted in a graphite Knudsen cell but were subsequently repeated in a BN Knudsen cell. The results obtained in both analyses were quite similar, and the heats of vaporization of the species identified -- Ag, Se_2 , Cu, and CuSe -- are given in Table 1-1. The vapor pressure measurements of the identified species versus temperature are plotted in Fig. 1-3.

In the initial vaporization study utilizing the graphite Knudsen cell, a Cu-colored deposit was observed outside the cell after the run. How this Cu-colored deposit occurred is not known, but since Se readily wets graphite, it was postulated that somehow a Cu_xSe_z compound could migrate through the graphite cell. Based upon this anomalous behavior with the graphite cell, the analysis was repeated with a BN cell.

For the above analyses, the Knudsen cell was temperature and pressure calibrated by observing the melting point of Ag by taking advantage of the several-minute time lag for the Ag to go from solid to liquid. Thus, the thermocouple used for the Knudsen cell experiment was calibrated in the geometry and environment in which it was actually used.

1.3.2. Comparison of Mass Spectrometric Data

The only other vaporization data on P-type TPM-217 have been obtained by 3M. In Ref. 1-3 they reported only the vapor species Se_2 ; however, in

TABLE 1-1
HEATS OF VAPORIZATION OF IDENTIFIED SPECIES IN TPM-217
(in kcal/mole)

Vapor Species	Graphite Knudsen Cell	BN Knudsen Cell
Ag	65.1 $\pm$ 1.0	62.0 $\pm$ 1.2
Se ₂	55.5 $\pm$ 1.2	58.6 $\pm$ 1.0
Cu	76.2 $\pm$ 0.6	77.1 $\pm$ 0.7
CuSe	87.0 $\pm$ 1.4	86.5 $\pm$ 1.2

Fig. 1-3. Vapor pressure of species identified in mass spectrometric analyses of TPM-217 versus temperature

subsequent unpublished studies additional species were identified. A comparison between the 3M and GA data is given below:

1. The vapor pressure of Se_2 as measured by GA and 3M is essentially the same.
2. The Ag vapor pressure over TPM-217 as measured by GA is the highest of any species, as shown in Fig. 1-4. Also plotted in this figure are the values measured by 3M, which are a factor of ~ 5 lower. This difference may be due to (1) differences in the material used by each investigator, (2) differences in calibration procedures, or (3) a combination of (1) and (2). The calibration curve for Ag derived by 3M is not in agreement with results reported by Hultgren (Ref. 1-4) or the National Bureau of Standards (Ref. 1-5).

It is important to note that the vapor pressure of Ag over TPM-217 is dependent upon the condition of the material. The material examined by GA contained a considerable amount of second phases which were either Ag- or Cu-rich. As revealed by discussions with 3M, these second phases are either taken into solution or driven to the cold end once the element is placed in a gradient and a current flows through the material for a short time. One measurement performed by 3M on single-phase material (all the Ag was supposedly in solution) yielded a vapor pressure of 1.5×10^{-6} Torr at 800°C , which is only a factor of 2 to 3 below that measured for two-phase material.

3. Both GA and 3M reported the same vapor pressure of Cu over TPM-217, i.e., the same as the pure metal.
4. GA detected CuSe and CuAg; 3M did not report detecting these compounds.

One cast and one vacuum-hot-pressed specimen were held at 900°C for a total of 368 hr. The rates of weight loss during the last 111 hr for

Fig. 1-4. Vapor pressure of Ag over TPM-217 versus temperature

cast and hot-pressed materials were 1.03×10^{-4} and 1.39×10^{-4} g/cm²-hr, respectively. While both alloys exhibit a large decrease in vaporization rate as a function of time, the weight loss rate is still appreciable. If the isothermal vaporization rate can be used as a guide, then the rate of vaporization must be reduced 2 to 3 orders of magnitude to make the TPM-217 material usable for 5-yr missions at 900°C.

1.3.3. Isothermal Vaporization

In addition to the mass spectrometric analyses, both cast and vacuum-hot-pressed samples were heated isothermally at 900°C in vacuum. The purpose of this test was to further characterize the TPM-217 material (e.g., morphological changes) with respect to preferential vaporization of any constituents and also to determine if surface enrichment occurred as a function of time.

In this test four samples were run at 900°C. Two of the samples were cast, and two were vacuum hot pressed at GA. The cast samples had been sliced and diced from the as-received thermoelectric elements supplied by 3M.

The weight loss data for the four specimens are given in Table 1-2. The visual change in the specimens as a function of time was significant. As can be seen in Fig. 1-5, pock marks or deep holes developed on the cast samples in a very nonuniform manner, whereas a crazing surface texture developed on the vacuum-hot-pressed samples (Fig. 1-6). Subsequent metallographic examination of a cast and a hot-pressed sample after 142 hr showed a porous network throughout both specimens and a complete absence of the Cu and Ag second phases that are normally observed in both the cast and the hot-pressed samples. On two of the samples, Cu whiskers were observed growing on the surface. The Cu whisker growth might have occurred because the Se₂ vapor pressure is much higher than that of Cu, and as the Se₂ is preferentially drawn off, Cu is enriched in the sample and readily diffuses to the area where the whisker is growing. Presumably, this

TABLE 1-2
RESULTS OF ISOTHERMAL VAPORIZATION TEST AT 900°C IN VACUUM

Sample	Time (hr)	Wt. Loss/Area (g/cm ²)	Wt. Loss/Area/Hr (g/cm ² /hr)
Cast			
A	70	0.0109	1.55×10^{-4}
	142	0.0205	1.44×10^{-4}
B	70	0.0110	1.57×10^{-4}
	142	0.0224	1.58×10^{-4}
Vacuum hot pressed			
A	70	0.0043	6.14×10^{-5}
	142	0.0125	8.80×10^{-5}
B	70	0.0159	2.27×10^{-4}
	142	0.0299	2.11×10^{-4}

Fig. 1-5. Cast TPM-217 material heated isothermally at 900°C in vacuum.
Note pock marks and holes

Fig. 1-6. Hot-pressed TPM-217 material heated at 900°C in vacuum. Note crazing surface texture.

whisker growth area is the coldest part of the sample. Microprobe analysis of these samples has not yet been performed.

1.4 JOINING

The mesh-in-cap type bond was initially developed for the Transit generator, and based upon its satisfactory performance in this generator, it was then modified into a more useful form for the ring converter segment. This segment is currently on test at Jet Propulsion Laboratories and is performing with a very low degradation rate of $\sim 0.2\%/1000$ hr (Ref. 1-1).

If the TPM-217 materials can be fabricated by powder metallurgy techniques, presumably mesh-in-cap type bonds can be utilized. However, the mesh-in-cap type bond also requires that the mesh and the end cap material be non-reactive with the thermoelectric material and possess a coefficient of thermal expansion that is not too different from the thermoelectric material being utilized. While the initial studies with TPM-217 have shown it is amenable to fabrication by powder metallurgy techniques, the qualification of a compatible end cap material is not expected to be an easily accomplished task. The work conducted thus far on developing a stable mesh-in-cap bond is described below.

1.4.1. Vacuum Hot Pressing (TPM-217 Cylinders Only, No Mesh or Cap)

As-received TPM-217 was separated from the Cu cold shoe pedestal and the W-25Re end caps and comminuted through 300 mesh. The conditions used for vacuum hot pressing N-type PbTe were satisfactory for fabricating dense TPM-217 cylinders. These conditions consisted of the following:

1. Maintaining vacuum up to 600°C .
2. Backfilling the system with H_2 at 600°C to reduce the surface oxides of the powder.
3. Reestablishing and maintaining vacuum and applying a load of 2000 psi at 600°C .

The microstructure of the vacuum-hot-pressed specimens is also three phase: the matrix, a Cu-colored phase, and a white-colored phase, which is Ag-rich. Microprobe analysis of several areas showed that the Cu-colored phase was predominantly Cu and the white phase was 75% to 85% Ag. As expected, these second phases were distributed evenly throughout the specimen.

1.4.2. Hot Joint Materials

As mentioned above, the end cap and mesh materials ideally should not only be non-reactive and immiscible with TPM-217 but should also have a similar thermal expansion. The materials W, W-25Re, and Mo have shown the best compatibility with TPM-217 (Ref. 1-2). Unfortunately, each of these materials has a very low thermal expansion that is approximately one-third that of TPM-217.

The high-temperature alloys that come the closest to TPM-217 in thermal expansion are the stainless steels and the Ni-base superalloys. The Fe-base ferritic alloys are ~60% lower in thermal expansion than TPM-217 and for this reason are not likely candidate materials.

In the initial compatibility studies at 600°C, the TPM-217 showed aggressive reaction with the Fe mesh but not with the pyrocarbon-coated Fe mesh (Fig. 1-7). Also, no reaction was observed with 316 stainless steel (Fig. 1-8) or Mo (Fig. 1-9). In short-time compatibility tests at 900°C (up to 24 hr), the pyrocarbon-coated Fe was not compatible. Apparently, the carbon coating was lost by dissolution in the Fe matrix. The 316 stainless steel exhibited a slight amount of chewing, while Mo and W-25Re showed little or no attack.

In subsequent studies, the alloys 316 stainless steel and Hastelloy X were preferentially enriched at the surface with Mo through preferential evaporation of the more volatile elements in both of the alloys. This

Fig. 1-7. Fe mesh uncoated (top) and coated (bottom) with pyrocarbon in a TPM-217 matrix. The pyrocarbon coating prevents the TPM-217 from chewing on the Fe mesh.

Fig. 1-8. Type 316 stainless steel mesh in a TPM-217 matrix. No chewing of the mesh was observed, and no new phases were formed.

Fig. 1-9. Mo mesh in a TPM-217 matrix. No chewing of the mesh was observed, and no new phases were formed.

enrichment was accomplished by holding the alloys at 1100°C in vacuum for 70 hr. The results of surface analysis of both alloys in the as-received and treated condition are given in Table 1-3. While this surface treatment did enrich the surface in Mo, it was not sufficient to prevent slight corrosive interaction with TPM-217.

1.4.3. Mesh-in-Cap Bonds

Several of the candidate materials were fabricated into conventional caps with the mesh material attached, and the caps were evaluated in the same vacuum-hot-pressing operation that was utilized in fabricating mesh-in-cap PbTe elements (Fig. 1-10). In most cases the TPM-217 flowed well and the filling of the mesh void area was complete. Copper extrusion and/or migration during the pressing operation was observed, and it might be necessary to perform the pressing operation in a slight temperature gradient (similar in fashion to the gradient bonding process utilized by 3M) to control the movement of the Cu.

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TABLE 1-3
CHEMICAL ANALYSIS^(a) OF SURFACE OF TWO ALLOYS AGED AT 1100°C FOR
70 HR AT 10⁻⁹ TORR

	Cr	Fe	Ni	Mo
Hastelloy X				
As-received	1,730	2,900	16,000	4,360
Vacuum treated				
Side 1	470	1,500	14,300	8,050
Side 2	675	1,650	14,500	7,200
316 stainless steel				
As-received	1,780	10,650	3,600	1,440
Vacuum treated				
Side 1	675	12,800	6,410	1,950
Side 2	740	13,075	5,850	1,800

(a) Analysis was performed by X-ray fluorescence, and values reported are in counts per second of the specific element.

Fig. 1-10. PbTe element fabrication sequence

2. SiGe AND SiMo TECHNOLOGY

This section describes the development of coatings to suppress the ratio of vaporization of P- and N-type SiMo and the weight loss rates which result from coating these materials. Also described are follow-up Knudsen cell experiments to clarify liquid Ge formation on SiGe in the presence or absence of SiO_2 .

2.1. Si_3N_4 AND (Si,Al)N COATINGS FOR SiGe AND SiMo LEGS

2.1.1. Si_3N_4 and (Si,Al)N Coating by Ion Plating

Ion plating is a vapor deposition process in which the substrate is negatively biased to start and sustain a glow discharge between an evaporating source and the substrate. The glow discharge partially ionizes atoms and molecules from the thermal evaporation. Ionized particles are accelerated toward the substrate by the electric field, and the resulting collision with the surface causes ion implantation (Refs. 2-1 through 2-4) and sometimes causes sputtering (Refs. 2-5, 2-6) of the substrate surface atoms.

Reactive ion plating combines the gas phase reactions of chemical vapor deposition (CVD) processes and electron beam vaporization of the evaporation process with the high-energy impingement of atoms of the sputtering process (Ref. 2-7). Reactive ion plating is thus CVD in which the reactive gas atoms and molecules are (1) introduced directly, (2) the result of evaporation of a source material, and (3) generated in an arc discharge. Activation of the reaction is enhanced by the acceleration of ionic species to the negatively biased substrate. Therefore, the deposition temperatures are lower than those in equivalent thermally activated processes.

Ion bombardment of the substrate before and during ion plating ensures continued contamination removal and production of active sites for deposition nucleation and growth (Ref. 2-8). However, this is not achieved without penalties, since carrier gases and gaseous contaminants are also ionized and driven into the substrate (Refs. 2-9, 2-10). Substrate geometry is a more serious problem. Very few electrode configurations are ideal for sustaining a glow discharge. Thus, current density, i.e., ion flux on the substrate, will be nonuniform. This means the rate of deposition and adhesion to the substrate can be nonuniform, resulting in nonuniform properties of the deposit (Ref. 2-11).

In spite of its shortcomings, ion plating is attractive for many low-temperature coating applications. One of these applications is the coating of Si_3N_4 or $(\text{Si},\text{Al})\text{N}$ on thermoelectric couples to improve the service lives of deep-space power sources. Previous work (Refs. 2-12 through 2-14) has shown Si_3N_4 to be effective in inhibiting electrical shorting and the rate of evaporation of SiGe and SiMo without any apparent reaction with them. Attempts were made to ion plate Si_3N_4 on P- and N-type SiMo . Silicon-rich coatings were made in this early work, but the coatings were still effective in lowering the rate of vaporization of SiMo .

During the period covered by this report, the morphology and chemical composition of ion-plated Si_3N_4 on SiMo as a function of process variables were studied in more detail to improve the effectiveness of the coating in lowering vaporization losses in thermal electric generators. In addition, an examination of $(\text{Si},\text{Al})\text{N}$ coatings was begun. The purpose of the AlN addition to Si_3N_4 is to minimize cracking and spalling of the Si_3N_4 coating due to differential thermal expansion between the SiMo and Si_3N_4 .

2.1.1.1. Deposition Parameters

Apparatus

The apparatus used for these depositions was custom built for GA by Airco Temescal (Fig. 2-1). Before each deposition trial, the system was

Fig. 2-1. Schematic diagram of ion-plating system

pumped down to less than 10^{-5} Torr, and the walls of the chamber were heated with $80^{\circ}\text{C}+$ water during the pump-down. After the warm wall pump-down, unheated tap water was run through the chamber walls, and the system was then pumped to less than 10^{-6} Torr. The evaporation source was remelted as required, and the substrate was sputter cleaned prior to each deposition.

Evaporation Source

The evaporation sources investigated were (1) arc-melted Si, (2) arc-melted Al, (3) arc-melted Si-Al alloys, and (4) hot-pressed Si_3N_4 prepared at GA or purchased from Norton Company. The electron beam source was fixed-focus from the lower chamber into the evaporation source through a slot in the upper chamber.

Early depositions were made with electron beam power inputs of 1.6 to 2.5 kW to the Si source. Uncontrolled splattering occurred with these power levels in spite of efforts to prevent it by (1) minimizing contamination by other elements and (2) eliminating pores from the Si. Splattering ceased after electron beam power inputs were limited to less than 1.4 kW. Splattering was not a problem when evaporating Al as it was with Si. An electron beam power of 3.2 kW could be used to melt Al without splattering.

Si_3N_4 sources were more difficult to control than Si sources. Rapid, variable effluence of volatiles from the subliming Si_3N_4 source occurred even at low (<0.6 kW) beam power. Since sublimation rather than melting eroded holes in the Si_3N_4 source, only a small fraction of the source was available for deposition, limiting the allowable deposition time. The source Si_3N_4 contained measurable concentrations of O_2 , Ag, Mn, Al, B, Cu, Fe, Ni, V, Mg, and Ti. Transfer of these contaminants to the deposit was unavoidable and thus limited the purity of these deposits.

Substrate

The substrates used in these deposition studies were N- and P-type SiMo, pyrocarbon, glass, and Al_2O_3 . The coatings on glass and Al_2O_3 were

used to determine coating rates, and pyrocarbon was used when a smooth, blemish-free surface was needed.

A 13.56-MHz, 1-kVA rf power supply was used to bias the substrate. By varying the bias on the substrate, some control of the substrate temperature could be obtained. The practical maximum substrate temperature from rf biasing was 500°C. Above this temperature, pitting of the substrate occurred. Nominal substrate temperatures used for these deposits were 100° to 300°C from bias power settings of 100 to 300 W.

Substrates were normally mounted on a flat, circular stainless steel support attached to the cathode of the rf power supply. The total surface area of the cathode and specimens was approximately 436 cm². The distance between the specimen and the electron beam source was 12.7 cm except for 14-cm specimen 6421-39, for which the distance was 15.2 cm.

Deposition Chamber Gases

Prior to each deposition, the ion plater chamber was filled with 99.999% ultra-high-purity Ar. The evaporation source was premelted in vacuo, and the substrate was sputter cleaned in 15-mTorr Ar. The gases used as a source for N were N₂, NH₃, and NH₃ + 1% SiH₄. All gases had a purity of 99.999+ or better. Nitrogen was used in the first trials but was abandoned when no Si₃N₄ could be detected in the deposit. All deposits were made by replacing the Ar in the chamber with the reactant gas and maintaining the chamber pressure at 12 ±3-mTorr Hg. Reactive gases and products were exhausted through the 5300 l/sec (for air), 10-in. oil diffusion pumping system.

2.1.1.2. Morphologies of Deposits. The deposits formed were all fine-grained columnar structures, and their morphologies bore little relationship to their chemical compositions. Some variations in the grain size of the deposits were noted, but these were more dependent on the composition of the substrate than on the chemistry of the gas mixtures used in these

experiments. Figure 2-2 shows the similarity of the deposits prepared from Si and Si-Al evaporation sources on P-type SiMo. Areas of surface-connected porosity are noticeable in the top view. These features were not evident in similar deposits on glass slides (Fig. 2-3). This porosity was thought to have resulted from outgassing of SiO from P-type SiMo. This hypothesis was reinforced when Knudsen cell mass spectrometer measurements showed that SiO was the only gas with a detectable partial pressure from P-type SiMo (Ref. 2-15) thermal outgassing examinations.

Side views of these deposits showed intergranular and transgranular fractures but generally good adhesion of the deposit to the substrate. Variations in substrate temperature between 100° and 300°C had no apparent effect on the morphology of the deposit. This is in agreement with the observations of Thornton (Ref. 2-16) and others (Refs. 2-17, 2-18) that morphology changes occur as a function of temperature and chamber pressure, although these changes are gradual and difficult to distinguish in a narrow temperature range below one-half the melting point of the deposit.

As seen in Fig. 2-4, despite the large apparent grain size, the deposits are composed of 0.2- to 0.6- μm grains which agglomerate into large columnar grains.

2.1.1.3. Stoichiometry of Deposits. The most difficult task in reactive ion plating is control of the stoichiometry of the deposit. This is especially true in the deposition of alloys such as (Si,Al)N. First, the evaporation rates for Al and Si are different when the Al and Si are heated with the same electron beam gun. Second, the activation energies, the reaction rates, and the free energies of formation of AlN and Si_3N_4 are different. Thus, the conditions for and the rates of deposition of AlN and Si_3N_4 are different. To sort out some of these differences, Si_3N_4 was separately deposited before attempting deposition of the (Si,Al)N alloys.

The stoichiometry of the deposits was determined by examining the deposits with an electron microprobe for Si, Al, N, O, and C. No assumptions were made as to how these elements might be combined in the deposits. The

(a)

(b)

(c)

(d)

Fig. 2-2. Morphological similarities between ion-plated, as-deposited (a) Si_3N_4 and (b) $(\text{Si},\text{Al})\text{N}$; (c) cross section of Si_3N_4 ; (d) cross section of $(\text{Si},\text{Al})\text{N}$

Fig. 2-3. SEM photomicrographs of Si_3N_4 deposited from Si and ammonia on (1) N-type SiMo (a,b) and simultaneously on a glass slide control (c) and (2) P-type SiMo (d,e) and simultaneously on a glass slide control (f). Substrates (a) and (d) were not outgassed; substrates (b) and (e) were outgassed for 200 hr at 1100°C and 10^{-9} Torr before Si_3N_4 deposits were made.

(a)

(b)

(c)

Fig. 2-4. SEM photomicrographs of an (Si,Al)N ion-plated deposit at three magnifications showing that the large grains are composed of very small grains

reliability of the microprobe measurement is considerably better for Si and Al than for O, N, or C. Therefore, the percent Si in the Si_3N_4 was taken as the best guide to stoichiometry in these compounds.

2.1.1.4. Si_3N_4 . Si_3N_4 was prepared from Si_3N_4 and Si evaporation sources, and the reactant gases were NH_3 and $\text{NH}_3 + 1\% \text{SiH}_4$. The Si_3N_4 evaporation source generated nearly stoichiometric Si for a Si_3N_4 deposit, but the O_2 concentration in the deposit was very high. Scanning electron microscope (SEM) examinations of these deposits showed that they contained a considerable number of irregular grains of the type generally associated with interference by contamination. This irregularity was not evident in deposits prepared from higher-purity Si evaporation sources.

Electron beam power into the Si evaporation source was the most sensitive process parameter in the reactive ion plating of Si_3N_4 . Figure 2-5 shows that the larger the electron beam power input to the Si source, the more Si-rich the deposit. Deposition rates for the Si-rich samples were 6200 to 7600 Å/min, and rates for the nearly stoichiometric Si_3N_4 deposits were 350 to 850 Å/min. Substrate temperature, gas composition, chamber pressure, and substrate bias variation had less effect on the stoichiometry of the deposit than the power input to the evaporation source. Oxygen and C were still major contaminants in these deposits in spite of efforts to minimize adsorbed moisture from the coating chamber interior. Attempts were made to examine the deposits with transmission electron diffraction patterns. As expected, these patterns could not be resolved because of the amorphous structure of the deposits.

2.1.1.5. (Si,Al)N Alloys. A compound deposited from an Al evaporation source with NH_3 and SiH_4 as reactive gases was mainly $\text{Al}_x\text{N}_y\text{O}_z$. Only during the last 6 min of the coating process did the coating contain some Si (Fig. 2-6). Metallographic and SEM photomicrographs reflected these changes in deposition composition (Fig. 2-7), and the conductive inner and outer layers are clearly distinguished in the SEM photomicrographs.

Fig. 2-5. Silicon in Si_3N_4 deposits as a function of electron beam power into an Si evaporation source

Fig. 2-6. Results of microprobe examinations across a fractured cross section of an (Si,Al)N ion-plated deposit prepared from Al evaporation and $\text{NH}_3 + 1\% \text{SiH}_4$ reactive gases

OUTER LAYER
 INTERMEDIATE LAYERS
 SUBSTRATE

(a)

OUTER COATING LAYER
 INTERMEDIATE LAYERS
 SUBSTRATE

(b)

Fig. 2-7. (a) SEM and (b) metallographic photomicrographs of a cross section of an (Si,Al)N ion-plated deposit prepared from Al

An attempt was made to deposit $(\text{Si}_3\text{N}_4)_x (\text{AlN})_y$ deposits from separate Si and Al evaporation sources. These deposits had nonuniform compositions from end to end on small samples. The composition of the deposit varied with the relative distances of the two evaporation sources from the deposit being analyzed. This situation could not be remedied in a fixed geometry system. For accurate control of the Si/Al ratio, a closely spaced, double evaporation source and a rotating substrate are needed. The double evaporation source was rejected in favor of a single premelted Si-Al evaporation source. It was recognized that the rates of evaporation for the Si and Al would be different, but for the purposes of these experiments, the Si/Al ratio of the final product was not preplanned. Therefore, the use of a single Si-Al alloy evaporation source was less troublesome than the use of a double evaporation source. Deposition rates for (Si,Al)N alloys were equivalent to those for Si_3N_4 deposits. The results of microprobe examinations of some of these deposits are given in Table 2-1.

Aluminum, Si, and N were co-deposited in these experiments. Oxygen was a contaminant in these deposits as it was in Si_3N_4 reactive ion plating deposition. The Al content of the deposit was only qualitatively related to the Al content of the evaporation source. The Si content of the deposits was not related to the Si in the evaporation source or the SiH_4 in the reactive gas.

Microprobe examinations of cross sections of these deposits showed them to be generally uniform in composition from the substrate to the coating exterior. Thus, these deposits were unlike the deposit from an Al source with NH_3 and SiH_4 reactive gases. There were no obvious changes in electrical conductance from the substrate to the outer coating edge, as determined by SEM photomicrographs. This again reflects a uniform distribution of elements in the deposits.

2.1.1.6. Discussion of Si_3N_4 and (Si,Al)N Ion Plating. Co-deposition of Si, Al, and N by reactive ion plating can be achieved. The morphology of the deposits is related less to the chemistry of the deposit than to the

TABLE 2-1
MICROPROBE EXAMINATION OF Si_3N_4 , AlN , AND $(\text{Si},\text{Al})\text{N}$ DEPOSITS

Sample No.	Evaporation Source	Reactant Gas	Electron Beam Gun Power (kW)	Substrate Bias (W)	Concentration (%)				
					Si	Al	N	O	C
6421-113	Si_3N_4 ^(a)	$\text{NH}_3 + 1\% \text{SiH}_4$	0.2	150 to 250	55 to 70	0	9 to 15	12 to 25	0.5 to 5
6421-39	Si	$\text{NH}_3 + 1\% \text{SiH}_4$	1.6 to 1.8	300	67	0	12	NA ^(b)	NA
6421-107	Si	$\text{NH}_3 + 1\% \text{SiH}_4$	1.4 to 1.6	300	76	0	0	18	1
6421-111	Si	NH_3	1.6 to 1.8	300	75 to 90	0	0 to 14	1 to 14	2 to 3
6421-115	Si	NH_3	0.8	100	58	0	30	5	5
6421-123	Si	NH_3	0.8	100	61	0	31	5	1 to 2
6421-109	Al	$\text{NH}_3 + 1\% \text{SiH}_4$	3.0 to 3.2	300	0 to 8	48 to 69	14 to 32	12 to 19	0
6421-81	Si ^(c)		1.2 to 1.3	300 to 500	47	10	12	NA	NA
	Al ^(c)	$\text{NH}_3 + 1\% \text{SiH}_4$	1.6						
6421-125	99 Si + 1 Al	NH_3	0.8 to 0.9	110	55 to 65	13	15	10	0
6421-101	99 Si + 1 Al	$\text{NH}_3 + 1\% \text{SiH}_4$	1.4 to 1.6	300	52 to 54	17	24 to 25	0 to 10	0
6421-105	99 Si + 1 Al ^(d)	$\text{NH}_3 + 1\% \text{SiH}_4$	1.4 to 1.6	300	62 to 65	5	19	5 to 10	0
6421-87	99 Si + 1 Al	$\text{NH}_3 + 1\% \text{SiH}_4$	1.4	350	60	0 ^(e)	40	NA	NA
6421-83	90 Si + 10 Al	$\text{NH}_3 + 1\% \text{SiH}_4$	1.4 to 1.6	300	38	23	9	NA	NA
6421-85	90 Si + 10 Al	$\text{NH}_3 + 1\% \text{SiH}_4$	1.8	300	40	22	25 to 30	NA	NA

(a) Norton hot-pressed Si_3N_4 .

(b) NA = not available.

(c) Two electron beam sources used.

(d) Same melt as used in 6421-101, with 1/2% Al added to make up for Al loss.

(e) Spots of Al detected containing <1% to 25% Al.

temperature of the substrate being coated. In the temperature region investigated in this study, all deposits were columnar with a fine-grained substructure. The resulting amorphous structure could not be resolved with electron diffraction patterns.

Control of the Si, Al, and N concentrations in the final product is the most difficult task in the reactive ion plating process. When the rate of evaporation of Si or Al is very high relative to the active N in the system, the deposit is Si- or Al-rich. When the evaporation rate of Al or Si is kept low, the composition of the deposit approaches that of stoichiometric Si_3N_4 or AlN. It is known from glow discharge studies that less than 10% of the atoms in the discharge are ionized. Thus, most of the Si or Al atoms are absorbed non-ionized on the substrate. Slowing the rate of evaporation increases the probability of a physically adsorbed Si or Al atom reacting with an activated N atom or ion before it is encapsulated by other adsorbing Si or Al atoms.

Si-Al-N alloys can be deposited in NH_3 or $\text{NH}_3 + \text{SiH}_4$ gas mixtures from separate Si and Al evaporating sources or a single Si-Al evaporating source. Single-source evaporation is practical for the eutectic mixture containing 11.7% Si and 88.3% Al. For other ratios, double evaporation sources should be used for (Si,Al)N deposition. (Si,Al)N can also be prepared from evaporating Al in a reactive gas mixture of $\text{NH}_3 + \text{SiH}_4$. Oxygen, C, and other trace contaminants in the coating system are readily incorporated in the deposit. Thus, there is reason to believe Si-Al-O-N compounds are major components of these deposits. In coating systems where large cold wall surfaces and heat shields exist, O is difficult to avoid.

2.1.1.7. Summary of Si_3N_4 and (Si,Al)N Ion Plating Trials

1. Reactive ion plating offers a low-temperature means of depositing Si_3N_4 and (Si,Al)N alloys on thermoelectric elements.
2. Control of alloy composition is mainly through control of rates of evaporation of the metal atoms in a pressure-limited ion plater system.

3. Adhesion of Si_3N_4 and (Si,Al)N alloys on SiMo, glass, pyrocarbon, and Al_2O_3 was good owing to continuous sputter cleaning of the substrate and bias potential acceleration of ions into the substrate.
4. Morphologies of reactive ion-plated Si_3N_4 and (Si,Al)N deposits are comparable to morphologies of deposits prepared by reactive sputtering and reactive evaporation.
5. Deposition rates for reactive ion-plated Si_3N_4 and (Si,Al)N deposits are comparable to those for high-temperature CVD processes.

2.1.2. Si_3N_4 and (Si,Al)N Coating by CVD

Chemical vapor deposition is a thermally activated process which has been used to apply Si_3N_4 to a variety of substrates (Refs. 2-19 through 2-22). This process was evaluated as a means of eventually applying (Si,Al)N coatings on thermoelectric couples. Si_3N_4 was deposited to permit evaluation of CVD processes and comparison of CVD Si_3N_4 -coated SiMo with previously ion-plated SiMo.

2.1.2.1. CVD Apparatus. The apparatus for chemical vapor depositions was built with GA funds. It is now being used to deposit Si_3N_4 coatings in the present program and is being modified to deposit (Si,Al)N alloys.

Design features enable flexibility in coating types and reaction conditions. Figure 2-8 is a photograph of the gas control panel and reaction chamber housing. Figure 2-9 shows the quartz tube reaction chamber surrounded by the water-cooled induction heating coil. Not shown is the high-vacuum system which allows the system to be pumped down and outgassed before each deposition. Deposits can be made at any pressure from 10^{-5} Torr to 1 atm and at any temperature from ambient to 2000°C.

Fig. 2-8. CVD reaction chamber showing induction coil and gas inlet

Fig. 2-9. Gas control panel and reaction chamber housing for CVD apparatus

The present system (Fig. 2-10) provides capability for using H_2 , He, Ar, NH_3 , SiH_4 , and mixtures of $SiH_4 + N_2$ or $SiH_4 + NH_3$. In addition, a system for depositing AlN from $AlCl_3$ and NH_3 is being added. The control panel allows for a wide variation in flow rates and pressures; thus, a wide range of gas mixtures is available for experimentation. Substrate temperatures are controlled by means of a variable power 30-kW motor generator. Temperatures are monitored with an optical pyrometer and a Pt-Pt/10% Rh thermocouple in contact with the substrate material.

Gas flow over the substrate is controlled in two ways: (1) the reactant gases enter the top of the reactant chamber and are guided around a deflector plate, which prevents streaming and improves gas mixing; and (2) the substrate sample, deflector, and ceramic mounting pedestal are rotated, thus reducing the probability of uneven coating if the reactant gases are not adequately mixed.

System pressures are monitored with a thermocouple gauge, an ionization gauge, and an MITS Baratron absolute pressure monitor. The latter is arranged to monitor the reactant chamber pressure, which may be varied by changing reactant gas inlet flow rates and gas product outlet exhaust rates.

2.1.2.2. CVD Experiments. (Si,Al)N coatings are expected to be made at temperatures other than those ideal for Si_3N_4 alone. Thus, the variation in the CVD Si_3N_4 deposit with temperature must be known. Toward this end, Si_3N_4 deposits were made from 1000° to $1400^\circ C$. The conditions for the depositions are given in Table 2-2. The results of SEM examinations performed thus far can be seen in Figs. 2-11 through 2-14. The appearance of the as-deposited CVD Si_3N_4 surfaces is similar to that of lower-temperature ion-plated deposits, but a fractured cross section of the coating (Figs. 2-13 and 2-14) shows transgranular fracture and none of the columnar grain structure of the low-temperature coatings. Microprobe examinations indicated that the deposits contained 60% Si and 40% N; both the Si and N were uniformly distributed (Fig. 2-15). The effect of temperature on CVD Si_3N_4 deposits can be summarized as follows:

Fig. 2-10. Schematic diagram of the GA CVD apparatus

TABLE 2-2
CVD Si_3N_4 DEPOSITION PARAMETERS

Sample No.	Substrate Temperature ($^{\circ}\text{C}$)	He (cm^3/min)	H_2 (cm^3/min)	N Gas (cm^3/min)	NH_3 (cm^3/min)	Coating Time (min)	Deposition Chamber Pressure (Torr)	Remarks
6834-5	900	--	840	2360	110	40	40	Very thin coating
6834-7	900	1700	1200	100 ^(a)	400	240	250	
6834-9	1030	1550	840	1150	--	120	100	Pore-free, uniform deposit
6834-11	1030	1550	840	1150 ^(a)	--	60	60	
6834-15	1000	1550	840	1150	--	45	50	
6834-17	1030	1550	840	1150	--	120	60	
6834-19	1030	1620	500	1000	--	60	40	
6834-31	1300	1550	840	1150	--	90	100	
6834-33	1200	1550	840	1150	--	90	100	
6834-35	1200	1550	840	1150	--	90	40	
6834-31H	1400	1550	840	1150	--	90	100	Substrate holder for 6834-31

^(a) SiH_4 gas used instead of N gas.

(a)

(b)

Fig. 2-11. CVD Si_3N_4 deposited from NH_3 , SiH_4 , H_2 , and He gas mixtures at (a) 1030°C (sample 6834-11) and (b) 1200°C (sample 6834-33). Both samples are shown at 1500X.

(a)

(b)

Fig. 2-12. CVD Si₃N₄ deposited from NH₃, SiH₄, H₂, and He gas mixtures at (a) 1300°C (sample 6834-3, 400X) and (b) 1400°C (sample 6834-31, 1500X)

Fig. 2-13. Scanning electron photomicrographs of Si_3N_4 on pyrocarbon from deposition run 6834-9:
(a) cross view (400X) and (b) plan view (400X)

Fig. 2-14. Scanning electron photomicrographs of Si_3N_4 on pyrocarbon from deposition run 6834-9:
(a) cross view (1500X) and (b) plan view (1500X)

Fig. 2-15. Results of microprobe scans for (a) Si and (b) N from Si_3N_4 deposition run 6834-7

1. Above 1300°C, CVD Si_3N_4 deposits are faceted, a strong indicator that recrystallization and grain growth are occurring.
2. Below 1300°C, CVD Si_3N_4 deposits are rounded, showing limited adsorbed reactant atom mobility.
3. Hillocks and whiskers seen in higher-temperature deposits (Fig. 2-16) are probably due to low reactant gas concentration at the higher temperatures. This indicates the need for increased SiH_4 and NH_3 gas flows at higher deposition temperatures.

2.1.2.3. (Si,Al)N Pre-Deposition Experiments. The first step in CVD (Si,Al)N coating development was to determine if Si_3N_4 and AlN would co-deposit in a CVD system. The experiment was set up as shown in Fig. 2-17. A small sample of Al was placed in the center of a smooth-surface pyrocarbon disk. Helium at 3000 cm^3/min and $\text{N}_2 + 1\% \text{SiH}_4$ gas flowing at 1000 cm^3/min were used in the deposition.

According to Long and Foster (Ref. 2-23) the reaction of N with Al metal is exothermic, producing the AlN. The Si from SiH_4 is available to react with N atoms either from the thermal decomposition of N or from the decomposition of N resulting from its reaction with Al. Thus, the reaction should generate (Si,Al)N deposits if the temperature is high enough.

The temperature selected for this deposition was 1000°C. The total run time was 65 min. Microprobe examinations of the Al with the outer coating removed and the pyrocarbon surface around the Al were made after the coating was completed. The results of these examinations are shown in Fig. 2-18 and may be summarized as follows:

1. Aluminum and Si-N compounds will co-deposit in the same CVD system.
2. Aluminum reacting with N is exothermic and will wet a pyrocarbon surface and spread. Vapor transport of AlN from the Al-N_2 reaction is not apparent.

Fig. 2-16. Si_3N_4 whiskers grown on sample 6834-31H (800X). The 1400°C faceted deposit changes to random, rounded agglomerates in the cooled region above the main deposit.

Fig. 2-17. Experimental arrangement for trial co-deposition of (Si,Al)N alloy

2-29

The chemical composition of the resulting deposit was Al, 15% to 18%; Si, 23% to 28%; N, 50% to 55% as determined by microprobe examinations. The apparatus for this deposition is shown in Fig. 2-19. The aluminum chloride formation was separately controlled to approximately 400° to 500°C.

2.2. RATES OF EVAPORATION

The sole purpose of coating N-type SiMo and P-type SiMo in these experiments was to inhibit their rates of evaporation in a space power thermoelectric generator. The thermoelectric environment was partially simulated by testing samples at 1100°C in an ion-pumped system capable of $<10^{-9}$ Torr pressures. Experiments reported in the last annual report (Ref. 2-24) showed the rates of vaporization for uncoated N- and P-type SiMo were over 6 times as high as those for Si_3N_4 -coated samples prepared at that time. Rates of evaporation for Si_3N_4 -coated N-type SiMo were 2 to 3 times as large as for equivalent Si_3N_4 -coated samples. Further, all coatings prepared at that time were hyperstoichiometric in Si.

2.2.1. Si_3N_4 Stoichiometry

Silicon and N concentrations in Si_3N_4 deposits were determined in microprobe examinations. When compared with the conditions of deposition (Fig. 2-5), the results imply a smooth dependence of the Si/N ratio in ion

of surfaces of Al (outer surface removed) and pyrocarbon after 1000°C in a N₂ + 1% SiH₄ and He gas mixture

2.2.2. Evaporation Rate Measurements

It has recently become obvious that the GA calculated weight loss rates place too much emphasis on the initial sample weight loss. Weight loss rates given in GA reports are calculated as the average weight loss rates from the start of thermal anneals to the point the data are taken. To determine what difference this makes, cumulative weight loss for recent Si_3N_4 -coated P-type SiMo was plotted as a function of time (see Figs. 2-21 and 2-22). As expected, the data show rapid weight losses at less than 400 hr. After 400 hr at 1100°C , all samples show a steady-state weight loss rate for the duration of the tests. These steady-state weight loss rates were calculated and are given in Table 2-3.

The weight loss rates for uncoated P-type SiMo are nearly identical to those previously reported, since initial weight loss rates for these samples are not as significant as for coated samples. Weight loss rates for Si_3N_4 -coated P-type SiMo containing hyperstoichiometric Si are 4.7 to $5.2 \times 10^{-7} \text{ g/cm}^2\text{-hr}$, which are 1/2 to 1/3 of the rates previously reported. The steady-state weight loss rates for stoichiometric Si_3N_4 -coated P-type SiMo are 4.1 to $33.0 \times 10^{-8} \text{ g/cm}^2\text{-hr}$, which are again 1/2 to 1/3 of the average weight loss rates reported previously using initial high weight loss data.

The low weight loss rate for sample 6834-19 of $4.1 \times 10^{-8} \text{ g/cm}^2\text{-hr}$ is not fully understood. Weight loss rates for other stoichiometric Si_3N_4 coatings on P-type SiMo are nearly the same whether the coatings were ion plated or CVD. A very encouraging trend can be seen in all the data. None of the weight loss rates are as high as for uncoated samples once steady-state weight loss occurs. This is true for the longest tests conducted thus far, which have exceeded 4000 hr. Weight loss rates for uncoated P-type SiMo controls remain 5 to 20 times as high as those for Si_3N_4 -coated samples.

Fig. 2-21. Cumulative weight loss per unit area for Si_3N_4 -coated P-type SiMo containing hyperstoichiometric Si as a function of time at 1100°C and 10^{-9} Torr

Fig. 2-22. Cumulative weight loss per unit area for Si₃N₄-coated P-type SiMo as a function of time at 1100°C and 10⁻⁹ Torr

TABLE 2-3
STEADY-STATE WEIGHT LOSS RATE FOR Si_xN_y -COATED P-TYPE SiMo AT
1100°C AND 10^{-9} TORR

Sample No.	Deposition Technique	Percent Si in Coating	Steady-State Weight Loss Rate (g/cm ² -hr)
6114-105	Uncoated P-type SiMo		$9.4 \times 10^{-6(a)}$
6114-87	Uncoated P-type SiMo		2.2×10^{-6}
6114-102	Ion plated	79	4.9×10^{-7}
6114-85	Ion plated	>60	5.2×10^{-7}
6114-100	Ion plated	76	4.7×10^{-7}
6114-140	Ion plated	60	3.3×10^{-7}
6834-17A	CVD	60	2.0×10^{-7}
6834-17B	CVD	60	3.2×10^{-7}
6834-19	CVD	60	4.1×10^{-8}

(a) Results were too high to show in figures. This calculation was made from data after steady-state weight loss.

2.2.3. AlN Addition

The primary reasons for adding Al to Si were (1) to tie up residual oxygen in the form of Si-Al-O-N (Sialon) (Refs. 2-25 through 2-28) and (2) to provide a better thermal expansion match between the Si-Mo substrates and the protective nitride coating.

No assumptions regarding the formation of Sialon can be made from the limited data obtained thus far in (Si,Al)N deposition. No attempts were made in the first depositions to control the Si/Al ratio other than to vary the concentration of Al in the SiAl evaporation source. It is obvious from the SiAl phase diagram that the composition of the melt and hence of the vaporizing liquid will change during the SiAl evaporation.

In spite of problems encountered in the co-deposition of ion-plated Si_3N_4 and AlN, some positive results were noted. First, the intergranular bonding appears improved in the Al-containing deposits. The evidence for this is transgranular fracture of grains rather than the intergranular failure noted in comparable Si_3N_4 ion-plated deposits. Second, the rate of evaporation was lower for (Si,Al)N-coated N-type SiMo than for equivalent (Si_3N_4) -coated N-type SiMo specimens (Table 2-4, Figs. 2-23 and 2-24). This result, if sustained in future experiments, will provide a third reason for adding Al to Si_3N_4 .

2.2.4. Commercial Si_3N_4

The rates of vaporization for commercial Si_3N_4 were established for the following reasons: (1) to determine what volatile products one might expect from the vaporization of commercial Si_3N_4 proposed for use in thermoelectric generators, (2) to determine vaporization rates for Si_3N_4 independent of SiMo and SiGe, and (3) to determine the effect of manufacturing processes on the rates of vaporization of commercial Si_3N_4 .

TABLE 2-4
STEADY-STATE WEIGHT LOSS RATE FOR ION-PLATED
(Si,Al)N ALLOYS

Sample Numbers	Surface Area (cm ²)	Electron Beam Source Composition (%)		Steady-State Weight Loss Rate (g/cm ² -hr)
		Si	Al	
6114-113	13.06	90	10	6.4×10^{-7}
6114-115	2.38	90	10	6.4×10^{-7}
6114-117	2.41	90	10	6.4×10^{-7}
6114-119 ^(a)	2.37	90	10	5.3×10^{-7}
6114-121	2.36	99	1	4.8×10^{-7}
6114-98	2.27	N-type SiMo control (uncoated)		7.33×10^{-6}

^(a) Annealed at 1100°C after Knudsen cell examination at 1100°C.

Fig. 2-23. Weight loss rate of (Si,Al)N-coated N-type SiMo at 1100°C and 10^{-9} Torr compared with weight loss rates for uncoated and Si₃N₄-coated N-type SiMo

Fig. 2-24. Cumulative weight loss for (Si,Al)N deposits

The results of emission spectrometer examination of several commercially available Si_3N_4 samples are shown in Table 2-5. A sample of Si_3N_4 -SiC from Norton is included for comparison. The high concentrations of some of the impurities were expected. MgO , $\text{Al}_2\text{O}_3\text{ZnO}_2$, and similar oxides are used as sintering aids in Si_3N_4 densification. Tungsten is used in fine powder preparation before sintering, and W balls are used to grind the powder.

Knudsen cell equilibrium vapor pressures were measured for several Si_3N_4 samples. The results of these examinations are summarized in Table 2-6. The results show that alkali metal release predominates below 1000°C . Above this temperature Mg and SiO are the principal vapor species.

A plot of VT, which is related to the total gas pressure, versus $0.1/T$ (Fig. 2-25) shows two slopes to the vaporization curve for Norton hot-pressed Si_3N_4 , which intersect about 1000°C . Based on the Knudsen cell partial pressure measurements, this gas at 1400°C is 67% Mg; 25% SiO; 7.5% a mixture of Na, Mn, Al, and Fe; and only 0.37% Si. These results show clearly that the decomposition of Norton hot-pressed Si_3N_4 is related to the metallic contaminants and O in Si_3N_4 and is not due to the decomposition of Si_3N_4 into Si and N_2 .

Evaporation rates for these materials were determined by heating them in an ion-pumped vacuum furnace to 1100°C and periodically removing the samples for visual examinations and to determine weight loss. Pressures were maintained below 10^{-8} Torr during the thermal aging. Weight loss rates versus time at temperature in these furnaces are shown in Fig. 2-26. The results show that the reaction-bonded Si_3N_4 has a much higher rate of evaporation than hot-pressed samples.

2.3. SiO_2/SiGe COMPATIBILITY TESTS: LIQUID Ge FORMATION

Early experimental results (Ref. 2-29) suggested the formation of liquid Ge through an intermediate reaction with SiO_2 as follows:

TABLE 2-5
ELEMENT CONCENTRATION^(a) IN Si_3N_4 SAMPLES
(in ppm)

Sample	Ag	Mn	Al	B	Cu	Ni	V	Mg	Ti	Cr	Nb	Fe	Mo	Ba	Ca	Co	Ta	W	Zr
5192-21 SiC, Norton Crystar NC 400	200	40	1000	80	80	400	200	40	200			800							
5192-19B Si_3N_4 hot-pressed NC 132	10	800	1000	60	80	100	200	10^4	600	600	100	4000	80	60	1000	2000	1000	10^4	
5192-19C SiC Norton NC 400	200	40	800	80	100	400	100	60	100			4000	10						
5192-19D SiC Ceradyne 146A		40	10^4	40	100	200	400	60	600			800		80		2000		10^4	
5192-19E SiC Ceradyne 146I		40	10^4	4000	40	40	20	60	200			800	10	80					
5192-19G Si_3N_4 -SiC Norton NC 33		800	6000		80	400	400	10^4	600	800	200	600		60		4000	1000	10^4	
5192-24 Si_3N_4 Ceradyne			10^3	40	200	6000	80		600	200		10^3	60		10^3				10^3

^(a) Determined by emission spectrometer examination.

TABLE 2-6
RESULTS OF KNUDSEN CELL EXAMINATIONS OF HEATED COMMERCIAL Si_3N_4
(in ppm)

Temp (°C)	Al	Mn	Fe	K	Mg	Na	Ca	Si	SiO	SiS
Ceradyne Hot-Pressed Si_3N_4 (Sample 5192-24)										
975						3.6×10^{-8}				
1000						3.4×10^{-8}				
1200	1.9×10^{-9}	4.0×10^{-8}	1.1×10^{-8}	--	2.7×10^{-6}	3.6×10^{-8}	--	--	1.6×10^{-7}	2.2×10^{-7}
Norton Reaction-Bonded Si_3N_4 (Sample 5192-25A)										
1000						1.5×10^{-7}				
1200	1.0×10^{-8}	9.6×10^{-8}	9.7×10^{-9}	1.9×10^{-7}	3.0×10^{-8}	6.8×10^{-7}	--	--	--	6.5×10^{-9}
Norton Hot-Pressed Si_3N_4 with Y_2O_3 (Sample 5192-29)										
950						2.7×10^{-7}				
1000	--	2.0×10^{-8}	--	1.7×10^{-8}	--	8.4×10^{-8}	--	--	6.2×10^{-8}	5.6×10^{-9}
1200	3.3×10^{-8}	1.0×10^{-7}	1.9×10^{-9}	2.4×10^{-9}	6.0×10^{-9}	1.8×10^{-8}	7.6×10^{-8}	--	--	--
1400	7.9×10^{-9}	1.6×10^{-7}	4.4×10^{-8}	3.1×10^{-8}	8.0×10^{-8}	1.2×10^{-7}	1.1×10^{-6}	--	4.5×10^{-6}	2.2×10^{-8}

Fig. 2-25. CO and/or N₂ pressure increase with temperature for Norton hot-pressed Si₃N₄

Fig. 2-26. Rate of evaporation for commercial Si_3N_4 samples and a Si_3N_4 -SiC sample at 1100°C and 10^{-9} Torr

The free energy of these reactions is positive and thus the reactions will not occur unless the products are continuously removed, requiring an equilibrium adjustment in the partial pressures of reactants and products. To determine if these reactions are probable, a series of Knudsen cell experiments were set up as shown in Fig. 2-27, and it was found that liquid Ge was indeed generated. The generation of liquid Ge in this experiment is in agreement with experiments previously performed using the mass spectrometer.

For uniformity, all cells were made from the same Mo bar. The completed cells were solvent cleaned and outgassed before the Si and SiGe samples were placed in them. The SiGe was made from RCA hot-pressed material, and the Si was commercially pure, cast material. Samples were annealed at 1100°C in a 10^{-9} Torr vacuum ion-pumped system. Samples were removed periodically for weight measurements and observations. Figures 2-28 through 2-32 show photomacrographs of the test samples after 1301 hr at temperature.

SiGe alone (Test 1) and Si + SiGe (Test 2) showed little, if any, interaction or redistribution of Ge from SiGe to Si or from one side of SiGe to another in the single-chamber Knudsen cell tests. SiGe samples in the double-chamber Knudsen cell tests (Tests 3 and 4) showed major surface feature changes. Liquid Ge accumulation was very prominent at the bottom of the SiGe sample in Chamber 1 of Test 4, while the SiGe sample in Test 3 showed Ge enrichment, although not the amount shown in Test 4. Results of microprobe examinations are shown in Figs. 2-33 through 2-36. It is clear from these results that quartz in the system caused movement of Ge to the surface of the SiGe samples and to the Si samples where Ge was not present at the beginning of the experiment. When quartz was absent from the system, Ge did not move from SiGe to Si in the system.

SINGLE CHAMBER
KNUDSEN CELL TEST 1

SMALL HOLE IN CELL

SINGLE CHAMBER
KNUDSEN CELL TEST 2

DOUBLE CHAMBER
KNUDSEN CELL TEST 3

SAMPLE THAT
SHOWED CON-
SIDERABLE
LIQUID Ge

DOUBLE CHAMBER
KNUDSEN CELL TEST 4

Fig. 2-27. Knudsen cell experiments

(a)

(b)

Fig. 2-28. Photomicrographs of (a) side and (b) bottom of SiGe cube in a single-chamber Knudsen cell after 1301 hr at 1100°C and 10^{-9} Torr

(a)

(b)

(c)

(d)

Fig. 2-29. Photomicrographs of (a) side and (b) bottom of SiGe cube and (c) side and (d) bottom of Si cube in a single-chamber Mo Knudsen cell after 1301 hr at 1100°C and 10^{-9} Torr

(a)

(b)

(c)

(d)

Fig. 2-30. Photomicrographs of (a) side and (b) bottom of SiGe cube in one side of a double-chamber Mo Knudsen cell containing quartz and (c) side and (d) bottom of Si cube in second side of Knudsen cell after 1301 hr at 1100°C and 10^{-9} Torr

(a)

(b)

Fig. 2-31. Photomicrographs of (a) side and (b) bottom of SiGe cube in one side of a double-chamber Mo Knudsen cell after 1301 hr at 1100°C and 10^{-9} Torr

(a)

(b)

(c)

(d)

Fig. 2-32. Photomicrographs of (a) side and (b) bottom of SiGe cube and (c) side and (d) bottom of Si cube in second side of a double-chamber Mo Knudsen cell separated from the first chamber by Astro Quartz after 1301 hr at 1100°C and 10^{-9} Torr

Fig. 2-33. SiGe in single-chamber Knudsen cell after 1300 hr at 1100°C and 10^{-9} Torr

Fig. 2-34. Results of microprobe examination of SiGe and Si in a single-chamber Knudsen cell after 1300 hr at 1100°C and 10^{-9} Torr

Fig. 2-35. Results of microprobe examination of SiGe and Si in a double-chamber Knudsen cell separated by quartz wool after 1300 hr at 1100°C and 10^{-9} Torr

Fig. 2-36. Results of microprobe examination of SiGe and Si in a double-chamber Knudsen cell separated by quartz after 1300 hr at 1100°C and 10^{-9} Torr

Quartz added to the reactants caused a significant change in the weight loss rate versus time plots. Weight loss rates were higher with annealing time in these samples and lower with time in the single-chamber Knudsen cell tests. Weight loss rates are summarized in Fig. 2-37. Loose quartz fibers were observed on some of the samples in Tests 3 and 4. These fibers were not readily removed. They were observed in the first postannealing examination after 57 hr at 1100°C. The number of fibers per sample did not appear to increase or decrease as the test progressed. Their presence does not alter the fact that weight loss rates were higher in tests containing SiO₂ than in those without SiO₂, since weight loss measurements were the difference between annealed weights and time zero weights (i.e., when there were no observed quartz fibers).

The results of Knudsen cell examinations for Ge movement in the system can be summarized as follows:

1. Very little movement of Ge occurs in SiGe samples heated to 1100°C at 10⁻⁹ Torr for 1300 hr in an Mo Knudsen cell. SiGe remains stable with no evidence of phase separations when annealed in the absence of SiO₂ in the system.
2. Without the presence of SiO₂, the rate of evaporation of Si and SiGe steadily decreases. This decrease probably reflects a decrease in adsorbed contaminants and residual SiO₂ and SiO in the samples.
3. Movement of Ge from SiGe to Si does not occur if gas phase reactions do not occur which will enhance this movement.
4. Considerable movement of Ge from SiGe samples to Si samples occurs when SiO₂ is included within an Mo Knudsen cell heated at 1100°C and 10⁻⁹ Torr.

Fig. 2-37. Weight loss rates determined in Knudsen cell experiments containing SiGe and Si at 1100°C, with and without quartz in the system

5. SiGe samples become unstable in the presence of SiO_2 . Liquid Ge is generated and flows to the bottom of the SiGe cube. The rates of evaporation of SiGe and Si increase. These changes are predicted by the reactions:

where SiO is continually being removed and liquid Ge is being deposited.

Further evidence for these reactions was provided by the summary weight loss measurements for these experiments (Fig. 2-37). Here, the Knudsen cell experiments containing SiO_2 , SiGe, and Si show much higher weight losses, i.e., loss of gaseous products, than equivalent experiments with SiO_2 .

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