THIRD QUARTERLY REPORT

ON

BONDING LARGE AREA SILICON WAFERS

CONTRACT NO. 952022

PREPARED FOR

JET PROPULSION LABORATORY
4800 Oak Grove Drive
Pasadena, California 91103

APR 1968

PREPARED BY

MOTOROLA INC.
SEMICONDUCTOR PRODUCTS DIVISION
5005 E. McDowell Road
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ABSTRACT

Results obtained on the initial studies on the use of low temperature diffusion bonding techniques for the bonding of large area silicon substrates to heat sinks are described. Liquid-solid and solid-solid diffusion bonding systems are described. Both homo- and heterotype bonds are possible with each diffusion system. Two-inch diameter silicon wafers have been bonded to molybdenum utilizing a gold-indium liquid-solid diffusion technique. Also silver-gold solid-solid diffusion bonds have been successfully made. The development of a computer program for stress analysis is nearing completion. An analytical solution based upon superposition techniques has been developed during this period to enable this analysis. An attempt to bond 0.62-inch diameter silicon wafers to tungsten utilizing a molten solder technique based upon aluminum-silicon eutectic solder failed due to rupture of either the solder bond or the silicon body. The thermal conductivities of eutectic aluminum-silicon and tin-lead alloys have been determined.

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SECTION I

1.0 INTRODUCTION

This report describes work performed during the third 3-month period of an 18-month program on the development of techniques for reliably bonding large area silicon single crystals to suitable heat sinks. The purpose is to enable bonding of silicon single crystals greater than 10,000 square mils and approaching 2 inches in diameter to excellent heat sinks in a manner which does not damage the silicon or alter the electrical properties of semiconductor devices constructed therein. The system, which should not degrade under repeated thermal shock, is to be applied to the packaging of large scale integrated circuit devices.

Phase one of this program is a study of the basic properties of potential bonding materials and the development of analytical techniques which will determine the materials and processes to be evaluated on early large area bonding experiments.

Diffusion bonding methods appear most attractive for bonding silicon to heat sinks since high temperature melting solder materials possessing desirable mechanical properties can be employed by these methods at low temperatures. This relatively low temperature process enables the use of such solders without introducing excessive strains caused by differences in thermal expansion coefficients which would otherwise occur if molten solder methods were used. Initial results with these methods are described in subsection 2.1.

Described in subsection 2.2 is an analytical solution for determining the stresses introduced in bonded members due to differences in thermal expansion coefficients, elastic properties, temperature excursion and geometries which has been developed during this period.

Attempts to bond 0.62-inch diameter silicon to tungsten with molten eutectic aluminum-silicon solders are described in subsection 2.3.

A method for determining the thermal conductivity of material has been established, and results are reported in subsection 2.4 on the thermal conductivity of eutectic aluminum-silicon and lead-tin alloys.

SECTION II

2.0 TECHNICAL DISCUSSION

2.1 DIFFUSION BONDING

To bond large area silicon to heat sinks it is becoming apparent that nonstandard bonding techniques must be employed. This is because:

(1) Low temperature bonding must be invoked to minimize stress due to the disparity of thermal expansion coefficients between silicon and heat sink materials.

(2) Hard solders with elevated melting points must be employed. They must possess high elastic limits to prevent embrittlement due to work hardening of the solder.

An attractive solution of this apparent dichotomy is to employ diffusion bonding techniques wherein the bond can be made at relatively low temperatures, but the resultant bonding material will possess desirable mechanical properties and will melt only at temperatures in excess of the bonding temperature. The diffusion process is a particularly attractive bonding method for joining silicon to a heat sink since thin films of metals can be employed as the bonding material requiring relatively short times for the diffusion process to become complete.

During this report period two basic classes of diffusion bonds have received initial study with encouraging results obtained with each method. These are discussed in the following two subsections.

2.1.1 Liquid-Solid Diffusion Bonds

Low melting point metals in the group, mercury, gallium, indium, lead and tin generally form refractory binary alloys with metals in the group, silver, gold, copper, magnesium, and lead.

Table I indicates those binary couples of potential usefulness for this purpose.

TABLE I

	Ag	Au	Cu	Mg	Pb
Ga	x	x	x	x	
Hg	x	x		x	x
In	x	x	x	x	x
Pb		x			
Sn	x	x	x	x	x

The phase diagram of gold-indium presented in Figure 1 is typical of the phase diagrams of the binary systems of Table I. Here it is seen that pure indium melts at 155°C. When a thin layer of indium is deposited onto a thin layer of gold, the indium will melt and flow at temperatures above 155°C. If the layered gold-indium is allowed to remain at elevated temperatures, the gold diffuses into the indium and the indium diffuses into the gold to eventually form, depending upon the relative amounts of the two components, a single-phase solid solution of indium in gold, or a two-phase system. The melting point of the final solder composition (when the indium is below 66.6 atomic percent) is in excess of 451°C. The limiting temperature then for this solder, when employed for bonding silicon, is the gold-silicon eutectic temperature of 370°C.

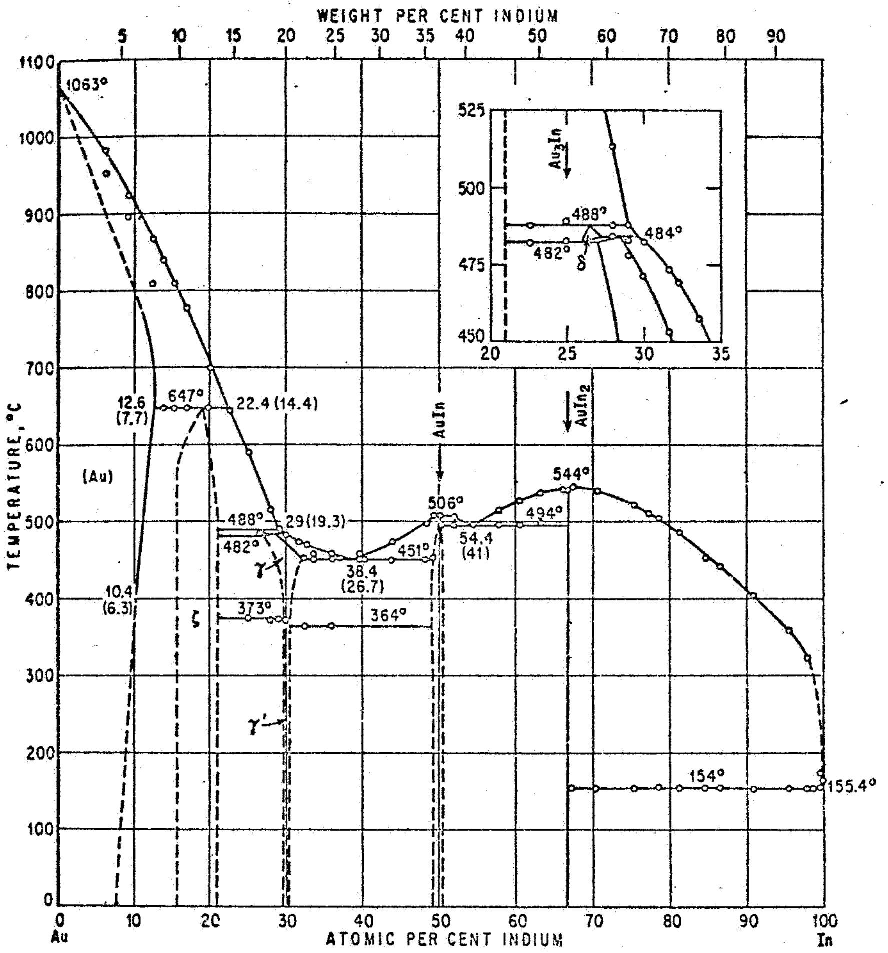

Figure 1. Phase Diagram for Gold-Indium

If the time is limited, preventing the diffusion process from reaching equilibrium, then all possible phases indicated in the phase diagram with compositions varying from 100 percent gold to 100 percent indium are to be expected. As shown in the diagram of Figure 1, five intermediate phases exist below 364°C. These are:

Au_4In (ζ) at 80% atomic Au
Au_3In at 75% atomic Au
Au_9In_4 (γ) at 69.2% atomic Au
AuIn at 50% atomic Au
$AuIn_2$ at 33.3 atomic Au.

The widths of these phases, all of which exist during the process of reaching solid state equilibrium, are inversely a function of the rate of diffusion of indium or gold through the phase. Since little information is available concerning the mechanical and thermal properties of the intermetallic phases, initial studies were directed toward establishing the time at various temperatures required to establish the α phase (solid solution if In in Au) as a function of solder thicknesses.

It is emphasized that these hard solders can be used to bond silicon to substrates at relatively low temperatures employing solid state diffusion to form the alloy from its layered thin film constituents. The temperature employed is determined by the thickness of the solder film, the composition of the alloy to be formed and the amount of time available for the diffusion process. The advantage of selecting one of the alloy components to be a low melting material when pure is to enable a liquid phase to form at low temperatures where it can flow and wet two surfaces to aid in the elimination of voids which otherwise may arise due to slight surface irregularities.

2.1.1.1 Experimental Results

Bonds were made between silicon and molybdenum or tungsten heat sinks during this report period in the following manner:

The silicon was prepared by

(1) Backside buffered etch with HF to remove any silicon dioxide film just prior to step 2.

(2) Vacuum deposit 0.3 micron of gold on the back of the silicon wafer.

(3) Alloy the gold to the silicon by raising the gold-silicon couple to 400°C in N_2 or forming gas to form a near eutectic alloy composition. This provides intimate contact between the gold and silicon resulting in good adherence. The wafer is then quenched from the alloying temperature to room temperature to form highly dispersed and tiny silicon crystallites distributed throughout the gold. The quench enhances adherence of an electroplated gold to the eutectic alloy.

(4) Electroplate gold onto the gold-silicon eutectic to a thickness of 0.35 mil.

The molybdenum or tungsten substrate is prepared by the following steps:

(1) Flatten the substrate by a lapping procedure to obtain a smooth surface.

(2) Electroplate a gold film 0.35 mil thick onto the molybdenum or tungsten substrate.

(3) Anneal the gold film at 1000°C in hydrogen for 1 hour to enhance adherence between the gold and the substrate.

(4) Electroplate an indium film to a thickness determined by the desired resultant alloy composition and the total amount of gold present on both the substrate and the silicon wafer.

The silicon is then clamped under pressure to the indium- and gold-plated substrate and placed into a furnace where it is heated at the desired temperature under a forming gas ambient. After a short heating period, the clamp may be removed, if desired, and the bonded silicon returned to the furnace to complete the diffusion process.

To reduce stress due to the difference in thermal expansion coefficients between silicon and the heat-sink member, it is desirable to form the bond at the lowest temperature possible. To take advantage of the liquid phase for the elimination of voids, this temperature initially should be in excess of the melting temperature of the lowest melting element comprising the alloy. A second constraint on the temperature is the time required for the desired diffusion to take place. If the diffusion has not proceeded to completion, all of the phases from pure gold, through the liquidus indium-rich composition can exist. At present it is not known whether the intermediate phases possess sufficient strength for bonding. Efforts to form a single phase solid solution of indium in gold therefore have initially been made.

Figure 2 presents a photomicrograph of an angle cross section through a gold-indium diffusion bond between silicon and molybdenum which was made in the manner described above. Using 3.13 percent by weight indium, the diffusion was permitted to take place for 2 hours at 300°C. The bond thickness is about 0.715 mil

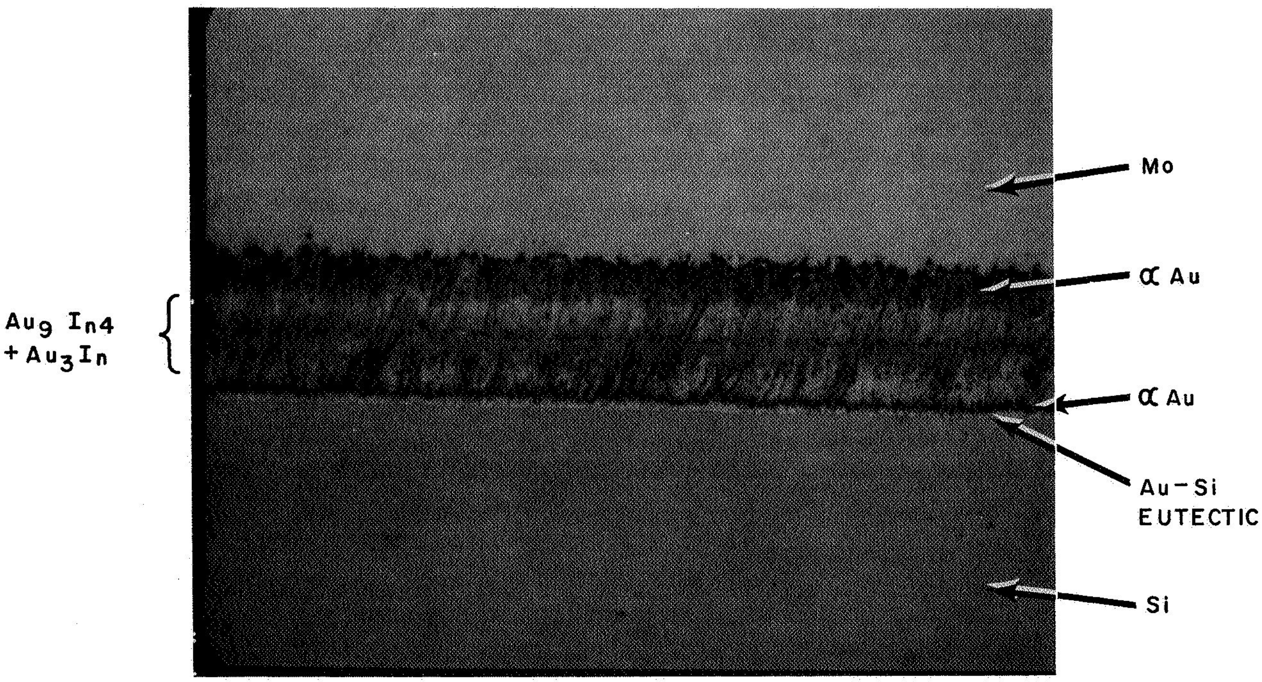

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Figure 2. Angle Cross Section Through Au-In Diffusion Bond Between Mo and Si (3.1% wt In)

thick. In this sample, the thickness of the gold plated on the molybdenum was excessive, and that plated onto the silicon was insufficient.

Figure 3 shows a photomicrograph of a similar cross section where 9.5 percent by weight indium was employed. The bond was formed at 300°C for 2 hours in forming gas. As in Figure 2, no voids are observable.

Initially, problems in developing proper clamping techniques were experienced. However, success has been achieved in bonding 2-inch diameter silicon wafers, 8 mils thick, to molybdenum substrates using Au-In diffusion bonding at 200°C.

A modification of the liquid-solid diffusion bonding technique has been very briefly explored where a gold-plated body is bonded to a second body which was plated by silver and then gold to form a Body A-gold-indium-silver-Body B diffusion bond. Other combinations of materials are of interest and will be explored in the next report period.

2.1.2 Solid-Solid Diffusion Bonds

The possibility of the formation of mechanically weak intermetallics when using the liquid-solid type of diffusion bond has led to the investigation of solid-solid diffusion bonding systems. These may be homo- or heterobonds between metals possessing relatively high self-diffusion or interdiffusion coefficients. Homodiffusion bonds are most attractive since there is no possibility for the formation of undesirable intermetallics. Thus, Au-Au, Cu-Cu, Ag-Ag, Sn-Sn, and Pb-Pb diffusion bonds will be the subject of extensive investigation.

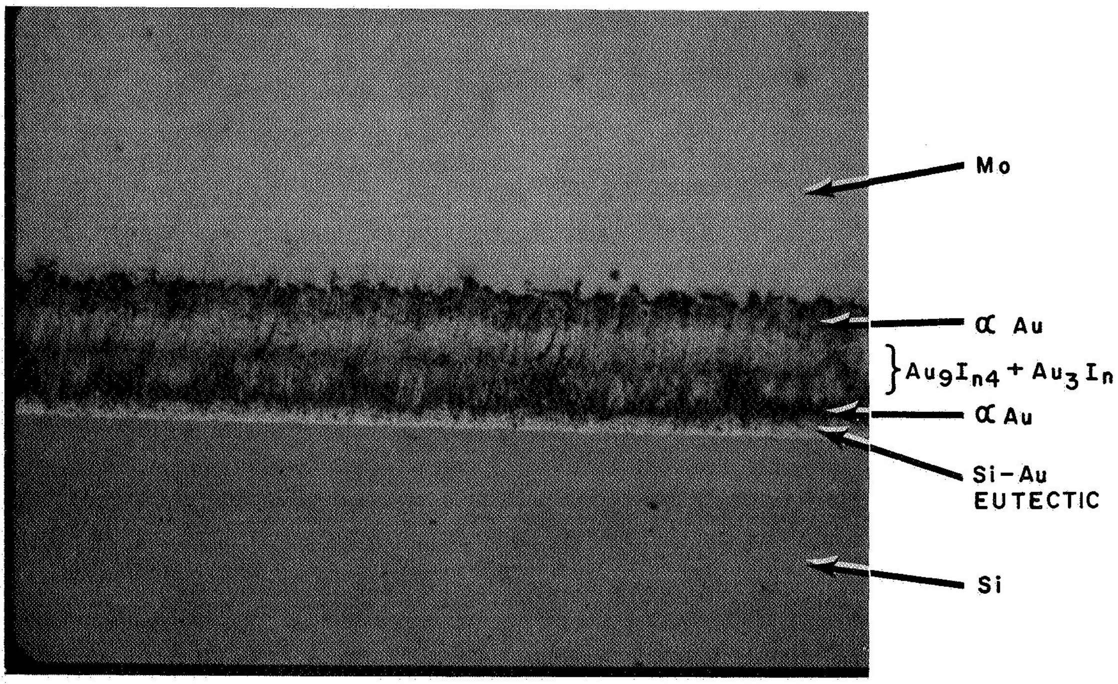

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Figure 3. Angle Cross Section Through Au-In Diffusion Bond Between Mo and Si (9.5% wt In)

Hetero-solid-solid bonds are also attractive possibilities when the couple does not form intermetallics. Such a couple is silver-gold which, as shown in the phase diagram of Figure 4, forms a continuous series of solid solutions. Also, couples which form eutectic type alloys plus regions of mutual solid solubility, such as silver-copper whose phase diagram is presented in Figure 5, are excellent candidates for hetero-solid-solid diffusion bonds.

During this report period diffusion bonds have been made using the silver-gold system producing excellent bonds which, in spite of the relatively rough surfaces, appeared void free. This is attributed to the fact that both the silver and the gold were sufficiently soft to enable flow of these materials, when clamped together, to fill any voids which might have occurred due to nonplanar surfaces.

Hetero-solid-solid diffusion bonds of interest are presented in Table II along with the lowest melting temperature of possible alloys. Great differences in the diffusion coefficients of A into B and B into A should be avoided to reduce the possibility of void growth by the Kirkendall effect.

TABLE II

Possible Heterosystem	Solid-Solid Diffusion Bonds, Min. Temperature (°C)
Ag-Au	960
Ag-Cu	979
Au-Cu	889
Au-Ni	950
Cu-Ni	1083
Pb-Sn	183

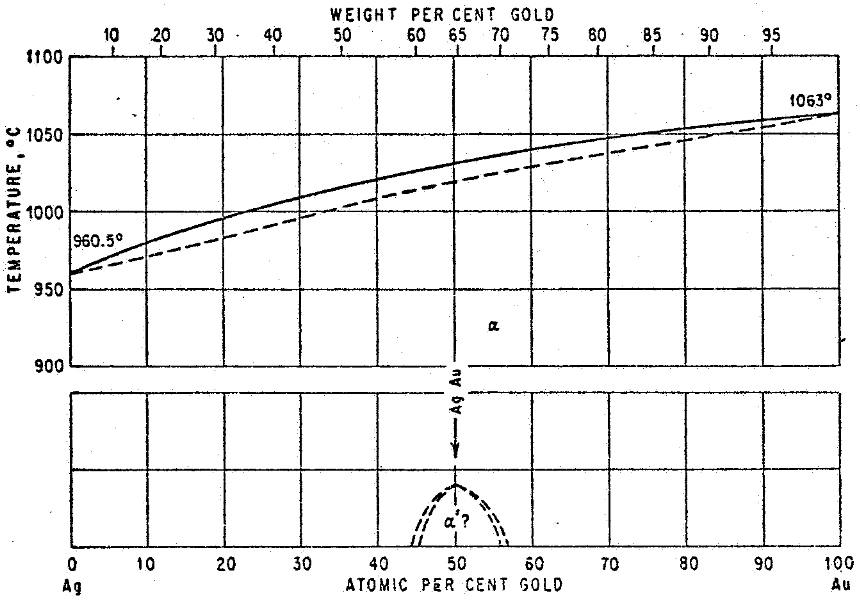

Figure 4. Silver-Gold Constitution Diagram

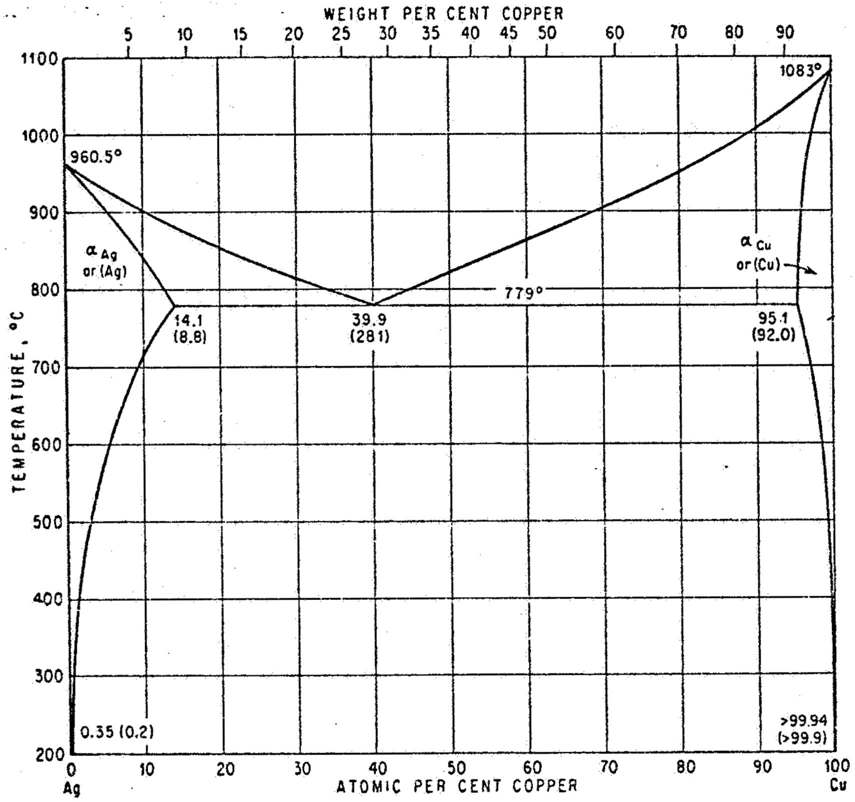

Figure 5. Silver-Copper Constitution Diagram

2.2 STRESS ANALYSIS

Additional work on the numerical solution for determining the stress in joined bodies resulting from the disparity of thermal expansion coefficients has indicated that the method described in the previous report is too sensitive to the choice of numerical approximations to the differential equations to obtain meaningful results. Accordingly, an analytical solution, as described in this section, was initiated to determine the resultant stresses in the axial, radial and hoop directions as well as the shear stress. The method employed is to determine these stresses under four stress conditions applied to assure that the stress at the surface of the body is zero. The sum of the various stresses for each condition will yield the desired solution. The method, therefore, is one of superposition.

2.2.1 Solution I

Two cylindrical bodies, as depicted in Figure 1, of differing materials are allowed to experience a thermal excursion prior to being joined. Each cylinder is allowed to expand unconstrained according to its thermal expansion coefficient with the residual stress being equal to zero.

2.2.2 Solution II

Radial stress is then applied to the circumference of both cylindrical bodies to bring their two radii equal. The stress applied is that which results in equal work being done on each body to bring them a common radius. This is depicted in Figure 2. Under this condition

$$\sigma_z = \tau_{rz} = 0$$

$\sigma_\theta = \sigma_r = \sigma_1$ for material No. 1

$\sigma_\theta = \sigma_r = \sigma_2$ for material No. 2

where

σ_z = is the normal strain in the z direction

σ_r = is the radial stress

σ_θ = is the hoop stress

σ_1 and σ_2 are the applied radial stress at the circumferences of the two bodies.

2.2.3 Solution III

The two bodies are joined together and are then subjected to an applied radial stress at the circumference which is equal and opposite to the stresses applied in the previous case. This condition is depicted in Figure 3. The solution becomes

$$\sigma_r = \frac{\partial}{\partial z}\left[\nu\nabla^2\phi - \frac{\partial^2\phi}{\partial r^2}\right]$$

$$\sigma_z = \frac{\partial}{\partial z}\left[(2-\nu)\ \nabla^2\phi - \frac{\partial^2\phi}{\partial z^2}\right]$$

$$\sigma_\phi = \frac{\partial}{\partial z}\left[\nu\nabla^2\phi - \frac{1}{r}\frac{\partial\phi}{\partial r}\right]$$

$$\tau_{rz} = \frac{\partial}{\partial r}\left[(1-\nu)\ \nabla^2 \phi - \frac{\partial \phi^2}{\partial z^2}\right]$$

$$\phi = \sin k\ z \left[a_o J_o\ (ikr) + a_1(ikr)J_1(ikr)\right]$$

where τ_{rz} is shear stress and ν is Poisson's ratio for the materials involved. The step function σ_r at the circumference is expanded in a Fourier cosine series and the solution becomes a series consisting of the Fourier series and modified Bessel functions of the first kind.

The solution leaves small residual stresses (σ_z) at the ends of the cylinder which must be eliminated if accurate results are to be obtained.

2.2.4 Solution IV

Figure 4 depicts the residual stress induced by Solution III. This must be corrected to obtain more precise results. A solution that satisfies the equations of equilibrium for this case is:

$$\sigma_z = f(z) * A_z(r)$$

$$\tau_{rz} = \frac{-f'(z)}{k} * A_{rz}(r)$$

$$\sigma_r = \frac{-f''(z)}{k^2} * A_r(r)$$

$$\sigma_\phi = \frac{-f''(z)}{k^2} * A_\phi(r)$$

where the A's are the portions of Solutions III that are functions of r. The boundary conditions on f′(z) are

$f'(z) = 0$ at $z = 0,1$

$f'(z)$ = maximum at the material interface.

2.2.5 Final Solution

The final stresses are obtained by adding the stresses in each solution.

For example:

$$\tau_{rz} = \tau_{rz_I} + \tau_{rz_{II}} + \tau_{rz_{III}} + \tau_{rz_{IV}}$$

A similar procedure is employed to determine all of the remaining stresses.

2.2.6 Current Status

Solutions I and II are readily determined. A computer program has been generated for obtaining Solution III. It remains to determine a satisfactory fit for the residual σ_z at the ends of the cylinder in Solution III for use in Solution IV. This step must be done in each individual case. During this next reporting period, solutions will be generated to determine the stresses which exist between silicon and typical heat sink materials as a function of the dimensions of the members and temperature excursions to which they will be subjected.

2.3 ALUMINUM-SILICON ALLOY SOLDER

The aluminum-silicon alloy eutectic is an interesting solder for semiconductor devices mainly because one of its constituents is silicon and forms naturally when an aluminum film deposited on silicon is heated to the eutectic melting point of near 577°C. At this temperature, sufficient silicon dissolves into the aluminum to form the eutectic composition.

Devices constructed with aluminum metallization naturally cannot utilize this alloy solder because similar alloying reactions would take place at the various ohmic contacts. Also, at this temperature there is a very rapid reaction between aluminum and silicon dioxide, wherein the aluminum reduces SiO_2 to form Al_2O_3 and Si. However, recently developed metallization techniques utilizing platinum silicide, titanium, platinum and gold--the so-called "beam lead metallization" developed by the Bell Telephone Laboratories--will enable the use of temperatures required for this bond.

During this report period, silicon wafers 8 mils thick and 0.625 inch in diameter were brazed to aluminum-clad tungsten substrates 0.875 inch in diameter and 0.078 inch thick. The process involved the vacuum deposition of aluminum onto both the silicon and the tungsten, clamping the members together and heating in a forming gas ambient at 600°C.

In general, the forces generated upon cooling due to the differences in the expansion coefficients of the silicon and tungsten, which are generated during the temperature excursion from the freezing point of the solder at 577°C to room temperature, resulted in failure of either the solder bond or the silicon.

When the computer program as discussed in subsection 2.2 is finalized to enable calculation of the forces generated as a function of the geometry of these two bodies, it is planned to explore this system further. The geometry limitations imposed on the members by their expansion coefficients, elastic modulii, and yield strengths will be determined.

2.4 THERMAL CONDUCTIVITY MEASUREMENTS

The Colora Messtecknik G.m.b.H. of Germany thermal conductometer has been installed, calibrated, and initial measurements have been made on solder alloys.

2.4.1 Al-Si Eutectic Solder

Aluminum-silicon alloy forms a eutectic at 11.3 percent atomic silicon which melts at 577°C. This alloy is used extensively for bonding silicon wafers to aluminum-clad molybdenum. It is therefore of interest to measure the thermal conductivity of this solder material.

Three samples of the Al-Si eutectic were obtained from Alloys Unlimited Inc. of Melville, New York, in the form of right cylinders 1 inch high by 0.65 inch in diameter. The thermal conductivity for these samples was determined to be

Sample A	0.183 cal/cm second°C
Sample B	0.210 cal/cm second°C
Sample C	0.194 cal/cm second°C
Average	0.196 cal/cm second°C

This is small compared to a value of 0.53 cal/cm sec°C for pure aluminum and is identical to the published thermal conductivity of silicon.

2.4.2 Pb-Sn Eutectic Solder

The eutectic lead-tin alloy is commonly used for a solder in electronic equipment. This alloy contains 26.1 percent atomic (38.1 percent weight) lead and melts at 183°C. Three sample cylinders of this material were obtained from Alloys Unlimited Inc. having dimensions of 1-inch height by 0.65-inch diameter. The thermal conductivity for these samples was determined to be:

Sample A	0.099 cal/cm second°C
Sample B	0.094 cal/cm second°C
Sample C	0.099 cal/cm second°C
Average	0.097 cal/cm second°C

This value compares to values listed of 0.083 cal/cm sec°C for lead and 0.157 cal/cm sec°C for tin.

In the future, thermal conductivities of alloy solders developed on this program will be determined.

SECTION III

3.0 CONCLUSIONS

Diffusion bonding techniques using either liquid-solid or solid-solid methods appear very encouraging for bonding large area silicon wafers to suitable heat sinks. Both homo- and heterobonds using these methods must be further explored to select the most suitable materials and to finalize a reproducible process. The successes in bonding 2-inch diameter silicon wafers to heat sinks must be further evaluated by thermal cycling, thermal shock and thermal conductivity measurements.

The analytical solution for determining stresses in bonded members is proceeding quite well, and it is anticipated that a computer program will be finalized early in the next report period. The analysis of stress between silicon and several heat sink materials will then be made as a function of the geometry of the bodies and their temperature excursions.

Attempts to bond 0.62-inch diameter silicon to tungsten with a molten aluminum-silicon eutectic alloy failed due to excessive stresses introduced when cooling from the alloy melting point of 577°C to room temperature. This system will be subjected to the above-described stress analysis program to determine geometry constraints which must be applied if a reliable bond is to be achieved.

Techniques have been developed for measuring the thermal conductivity of solder alloys. These techniques will be extended during the next report period to measure the thermal conductivity from a silicon surface through a bond to the outside surface of a heat sink. It is desirable to know the extent of possible interfacial thermal barriers between the solder and silicon or solder and the heat sink.

SECTION IV

4.0 NEW TECHNOLOGY

No reportable items of new technology have been developed under this contract.