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LPCVD Tungsten Deposition on Si-Ge Alloy

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The Radioiostopic Thermoelectric Generator (RTG), shown in Figure 1, consists of a heat source, an 80/20 Si-Ge thermopile, MIN-K insulation, and a stainless steel container. It was designed to deliver tens of mW for decades.

The thermopile consists of two channels, each containing 13 couples of alternate n/p doped wafers of 80/20 Si-Ge alloy. The wafers are glassed together to form the channels, and the channels subsequently glassed to form the thermopile as shown schematically in Figure 2. DC-diode-sputtered tungsten bridges the channel glass, interconnecting alternate wafers. Figure 3 shows the interconnect pattern. The channels are electrically connected in series.

Figures 4, 5, and 6 list the thermopile, 80/20 Si-Ge, and tungsten characteristics, respectively.

An important question is how to predict the operating lifetime of such a thermopile. If one plots the average resistance of the thermopile as a function of time at various operating temperatures, one gets the kind of plot shown in Figure 7. Initially, for a given operating temperature, the cold thermopile resistance is typically ~50 milli-ohms/contact. After a period of time (which is temperature dependent), the average resistance suddenly and rapidly increases. If that average resistance increases above a certain level, the generator will fail to deliver the required power. This "mean time to failure" decreases with increasing operating temperature.

The physical mechanism responsible for this phenomena appears to be due to diffusion of silicon into the tungsten interconnects. This process converts the tungsten film at the interface to a di-silicide resulting in voids in the Si-Ge just below the interface. The rapid increase in couple resistance is thus believed to be due to an increase in constriction resistance because of the loss of contact in the void regions.

If this diffusion model is correct, lifetime predictions as a function of operating temperature should be possible. An Arrhenius plot of the log mean time to failure (defined by the maximum tolerable thermopile resistance) as a function of 1/T is shown in Figure 8. The solid line is the least squares fit to the individual data points. The bars on the data points

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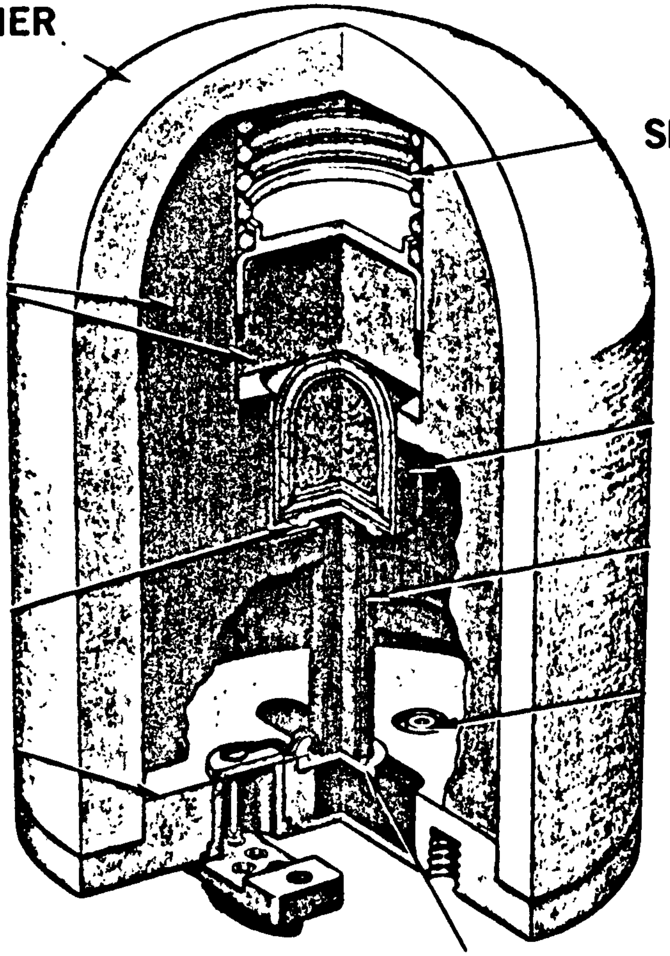
correspond to the minimum and maximum values for several samples. Figure 9 shows the mathematical relationship between the mean time to failure, temperature, and "activation energy" for the diffusion mechanism.

Based on this model, high temperature aging characteristics can be used to predict whether a given batch of thermopiles will meet the required lifetime criterion. A typical aging behavior of a DC-diode-sputtered thermopile is shown in Figure 10. Immediately after tungsten is sputtered onto the thermopile, the thermopile resistance is usually higher than required. A 550°C anneal for eight hours reduces the resistance to an acceptable level. Subsequent aging at 630°C results in the aging profile shown. If the thermopile fails between 15 and 80 hours, its aging characteristic fits the model, and we have confidence that it will meet the lifetime requirement.

For comparison, Figures 11 and 12 show aging profiles for analogous LPCVD samples. In these samples, LPCVD was first selectively deposited to a thickness of 700 Angstroms at SNLA. Subsequently, additional tungsten was DC-diode-deposited at GEND to bridge the glass gap and complete the interconnect. As seen, the initial resistance prior to the 550°C anneal step is comparable to the post-anneal resistance of the production sputter sample. This is probably due to the lack of sputter damage at the interface of the LPCVD sample and/or substrate cleaning characteristic of the LPCVD process. The 630°C aging profiles for both samples appear to be headed to cross the resistance limit at or beyond the 80-hour point. In general, one whould think that crossover beyond the 80-hour point would imply a higher activation energy and hence a longer lifetime. That may be true. However, it would not fit the present aging model, and without many experiments to establish the same degree of confidence in a new model, the ultimate lifetime cannot be guaranteed.

In summary, LPCVD has a number of advantages. It is a simpler process than sputtering. It appears to be self-cleaning, a distinct advantage over the more surface-condition-sensitive sputtering process. LPCVD does not mechanically damage the surface as does sputtering, and this may be responsible for the low initial contact resistance observed. Finally, the aging profiles tend toward the high end of the acceptance window. This may imply a higher activation energy and a longer lifetime. However, more samples must be run to confirm lifetime predictions.


CONTAINER
SPRING
MIN-K
INSULATION
HEAT SOURCE
THERMOPILE
INSULATOR
TUBULATION
BASE PLATE
INSULATOR

r̄tg

Figure 1

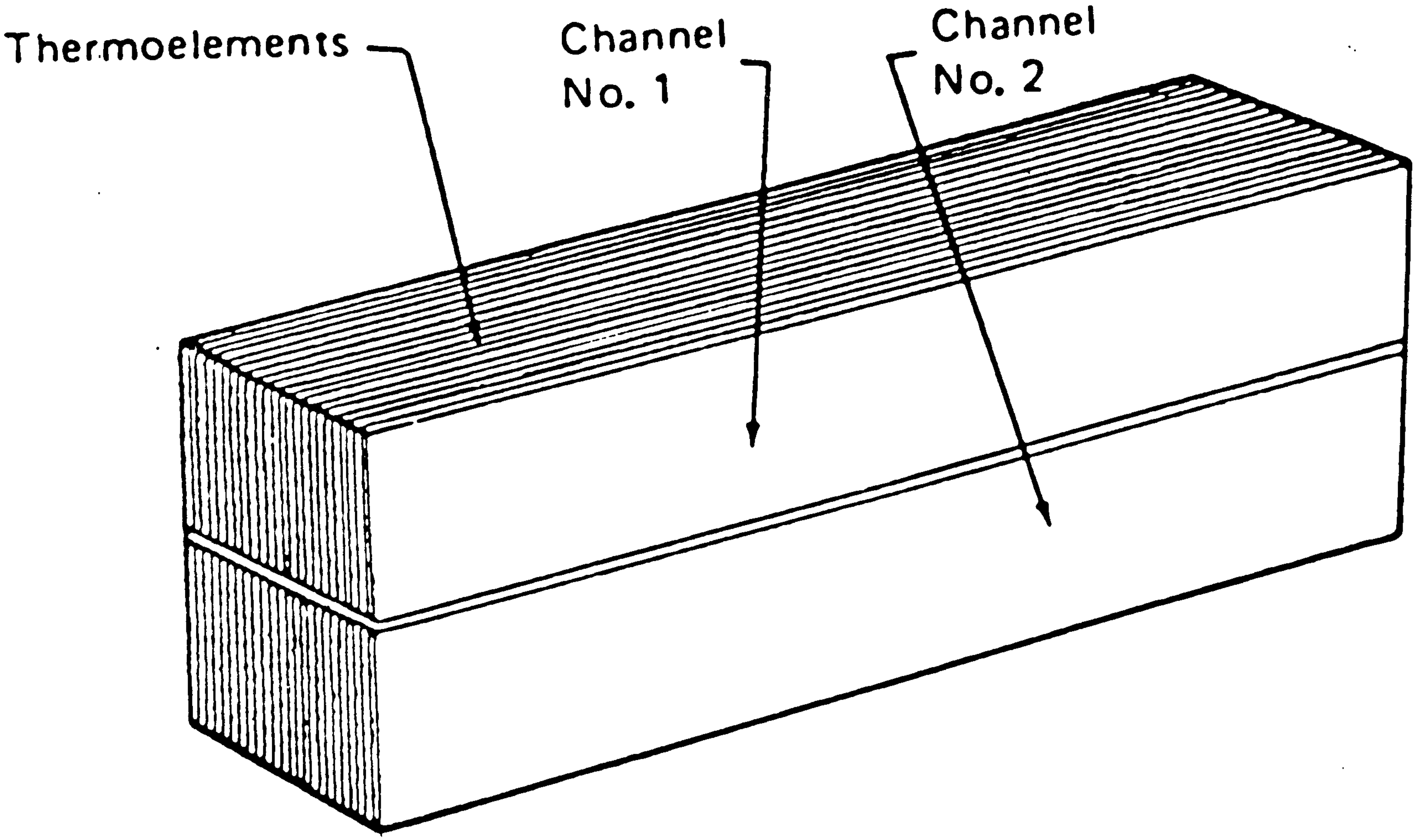
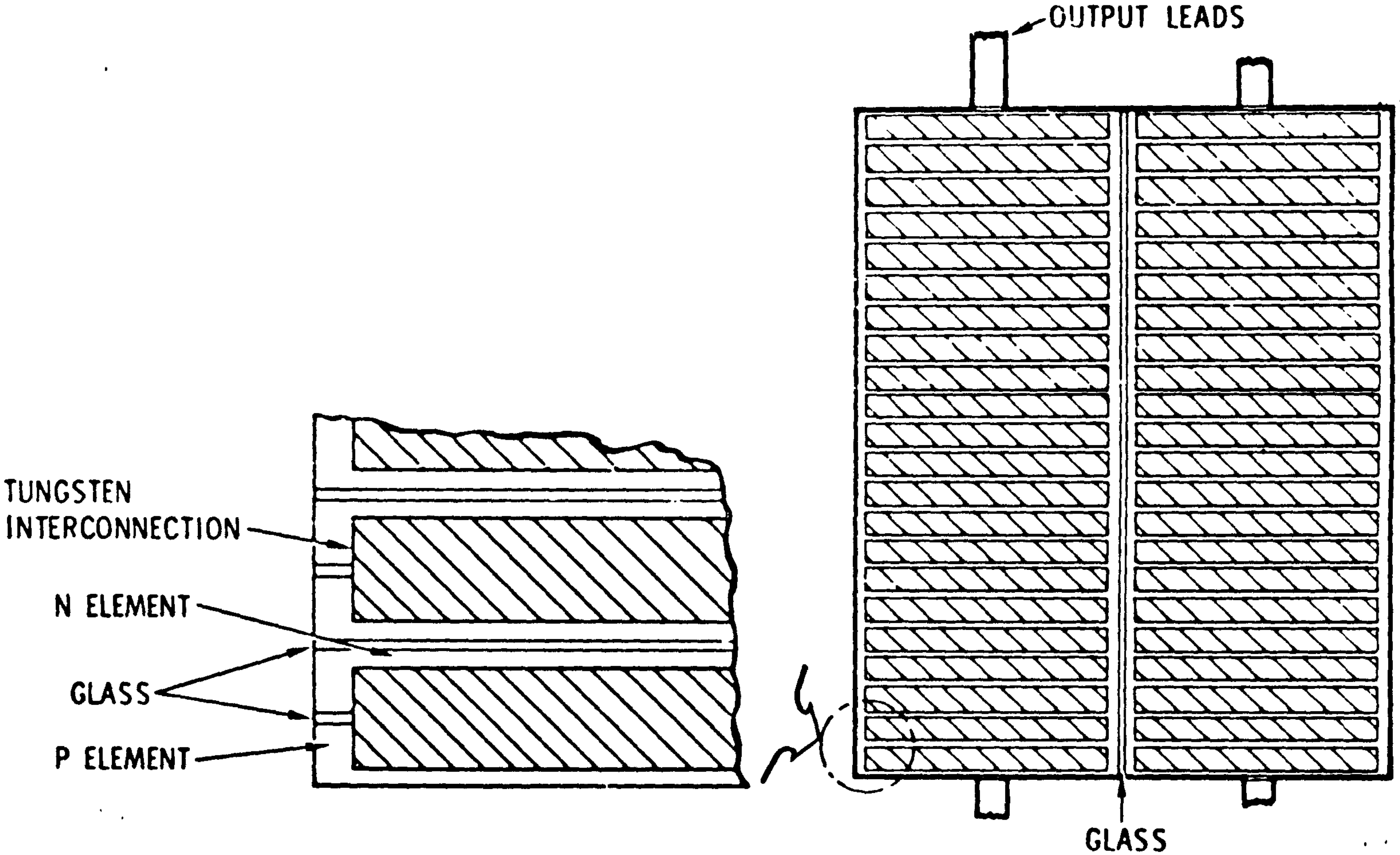


Figure 2



ID THERMOELEMENT CONFIGURATION

Figure 3

THERMOPILE CHARACTERISTICS

* 80% Si   20% Ge
* N Doped with 2×10^{19} Atoms Phosphorus/cm^3
* P Doped with 2×10^{19} Atoms Boron/cm^3
* 26 Couples 2 Wafers 0.23 mm x 3.1 mm x 25.4 mm

Figure 4

80/20 Si–Ge

COMBINED SEEBECK COEFFICIENT	α	~ 500 μV/°C
RESISTIVITIES	ρ_n	~ 5.0 mΩ–cm
	ρ_p	~ 5.7 mΩ–cm
HALL MOBILITY	μ	~ 45 cm^2/V–sec

Figure 5

TUNGSTEN FILM

DEPOSITION – DC DIODE SPUTTERED

THICKNESS – 1–3μm

RESISTIVITY ~ 35μΩ–cm

Figure 6

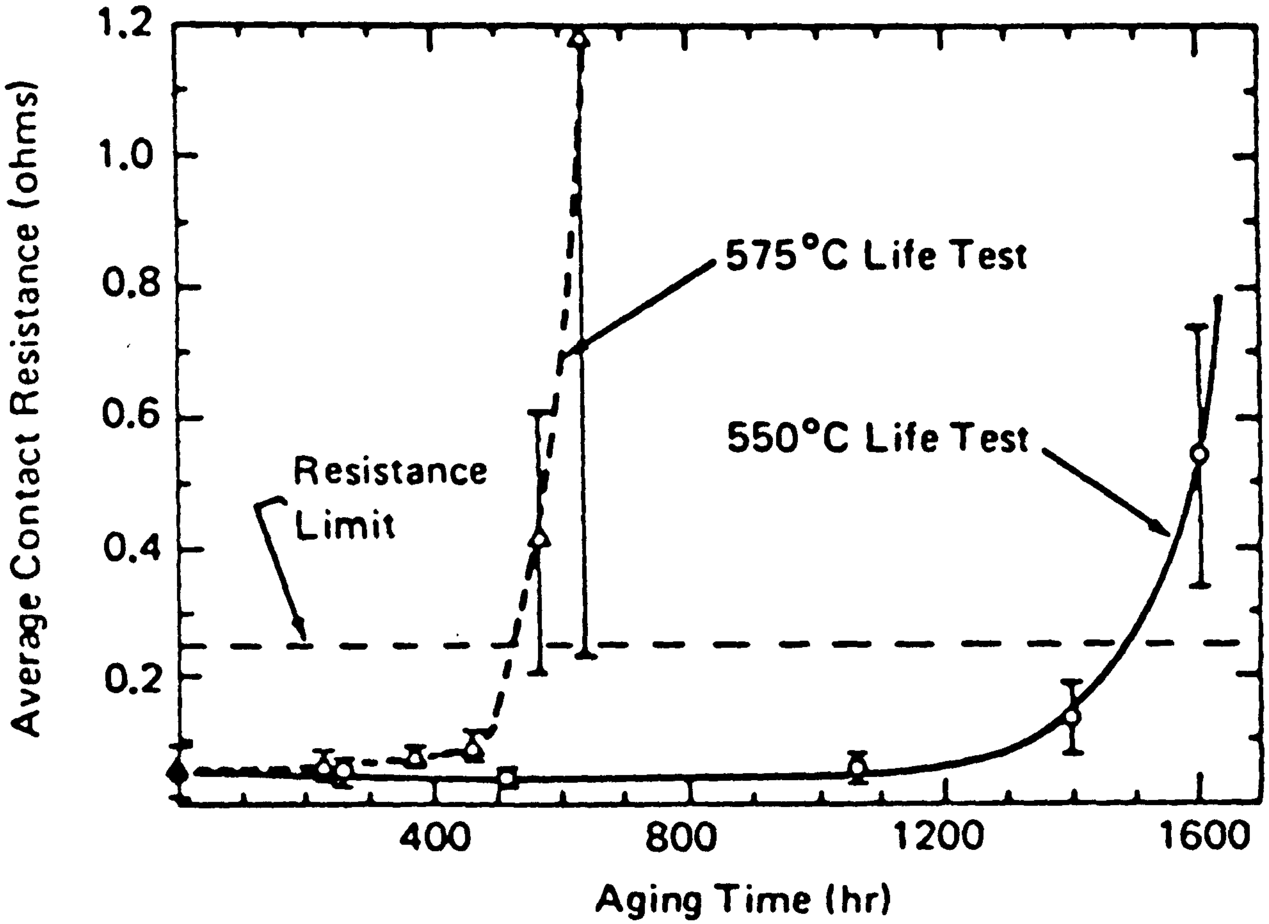
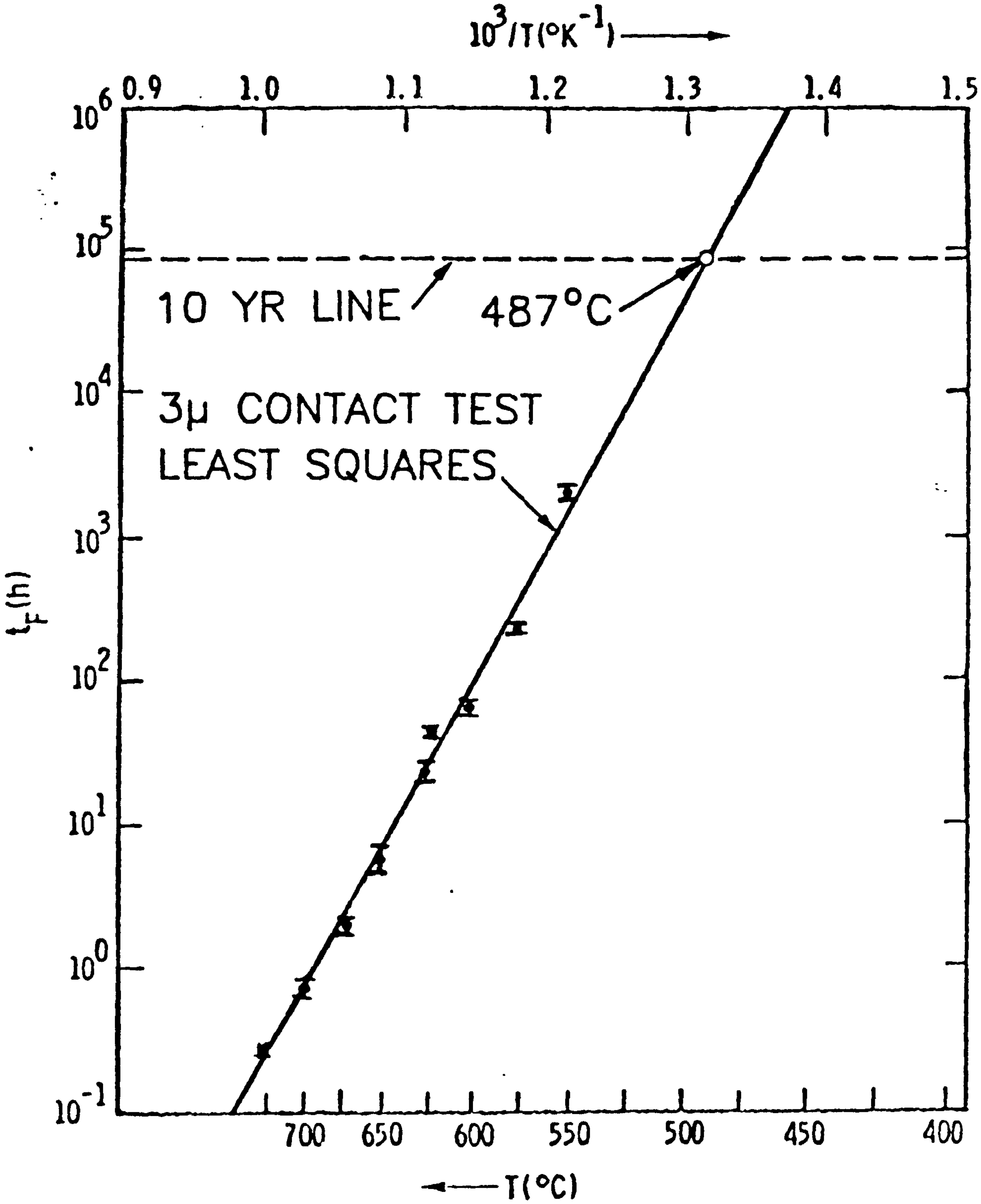

1.2
1.0
0.8
0.6
0.4
0.2
Average Contact Resistance (ohms)
575°C Life Test
550°C Life Test
Resistance Limit
400
800
1200
1600
Aging Time (hr)

Figure 7



FAILURE TIME VS TEMPERATURE DATA FOR LIFE TESTS WITH 3μm CONTACT SAMPLES

Figure 8

$$\text{Log } t_F = A(10^3/T) + B$$

t_F = average time to failure

T = absolute temperature

$$t_F = t_{F_0} \exp(Q/RT)$$

t_{F_0} = constant

R = universal gas constant

Q = activation energy

$$Q(\text{kcal/mole}) = 4.58\ A(^{o}K)$$

$$Q \sim 75(\text{kcal/mole})$$

Figure 9

ANNEAL AND AGING PROFILES

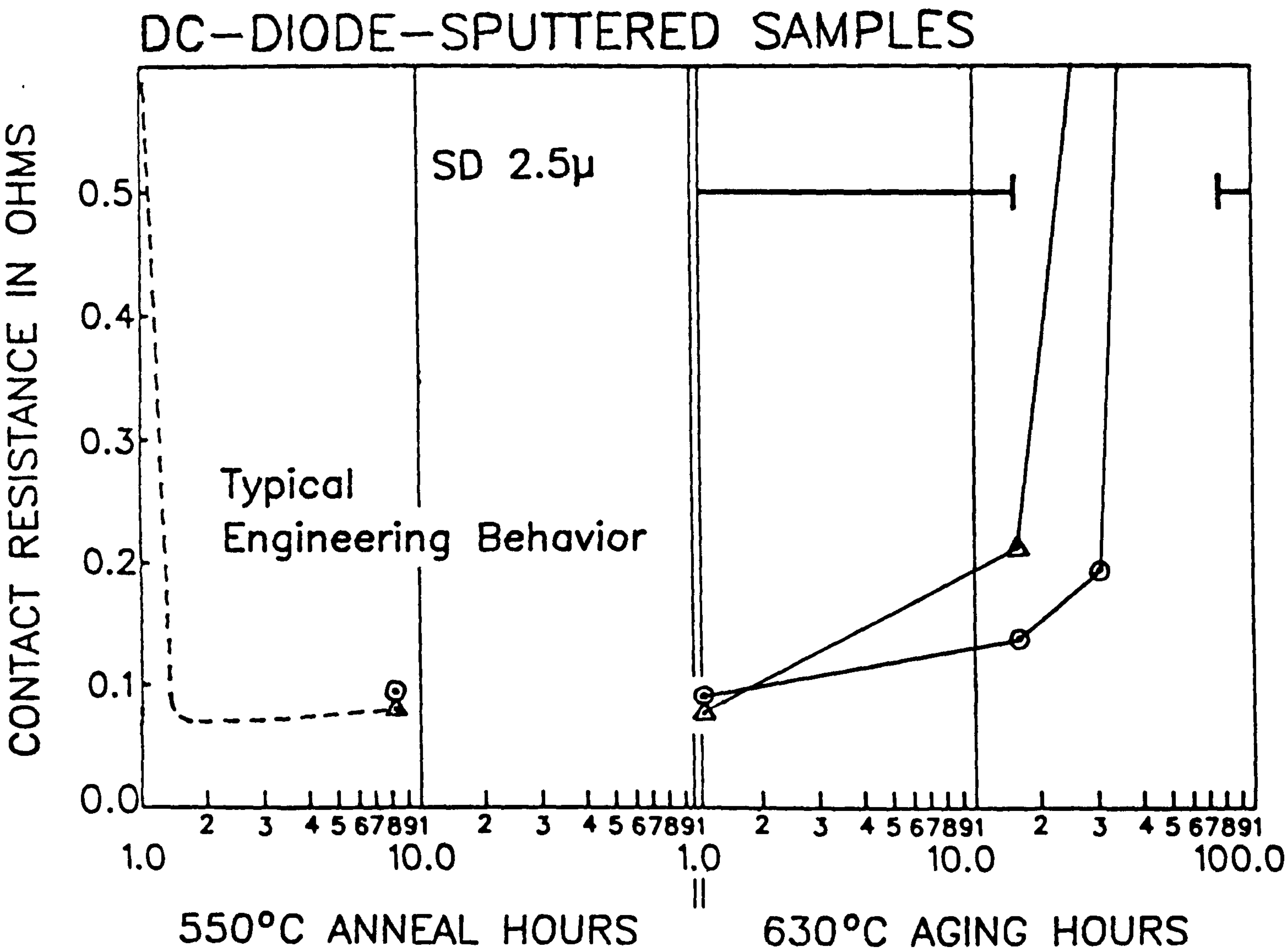


Figure 10

ANNEAL AND AGING PROFILES

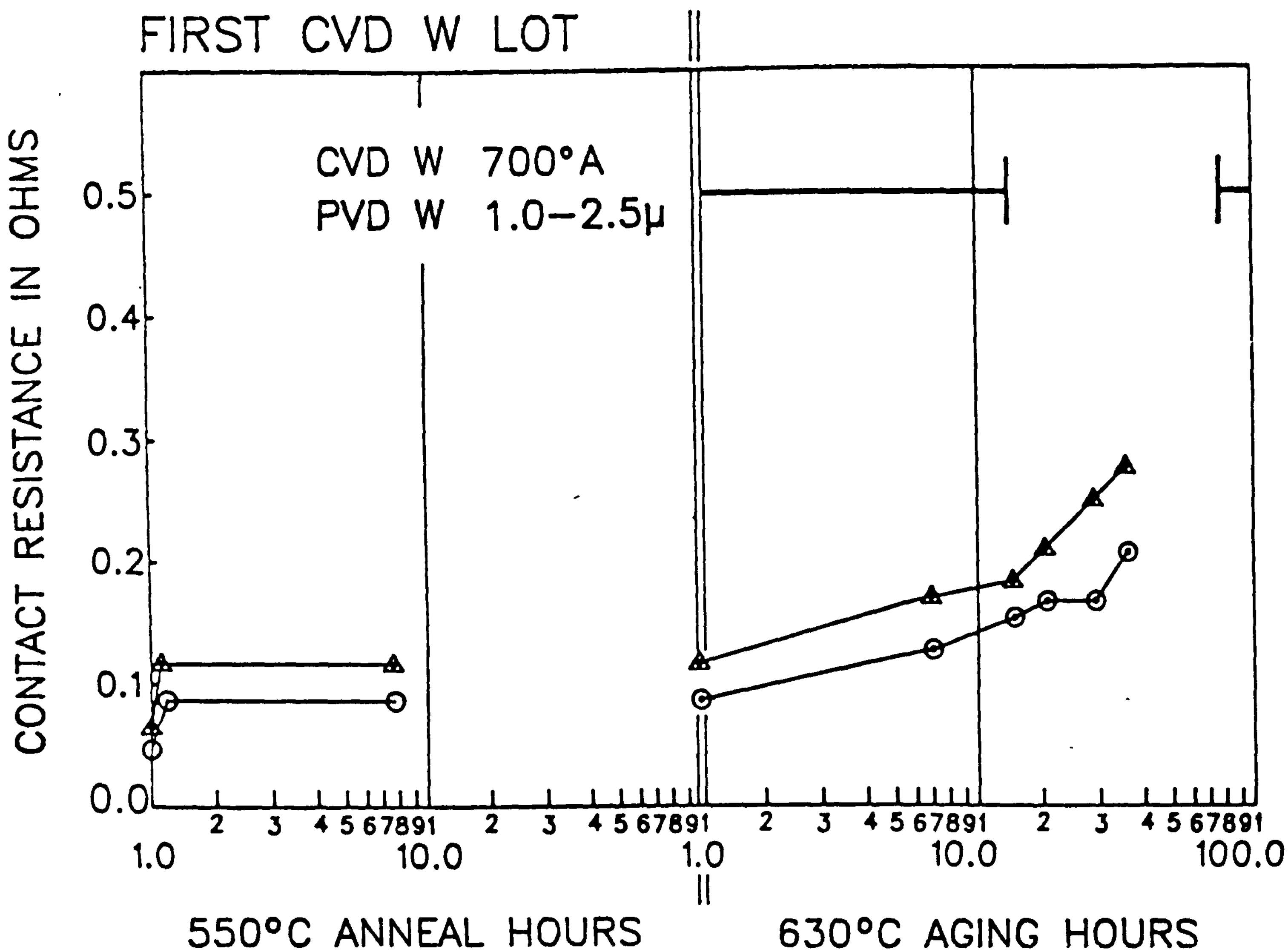


Figure 11

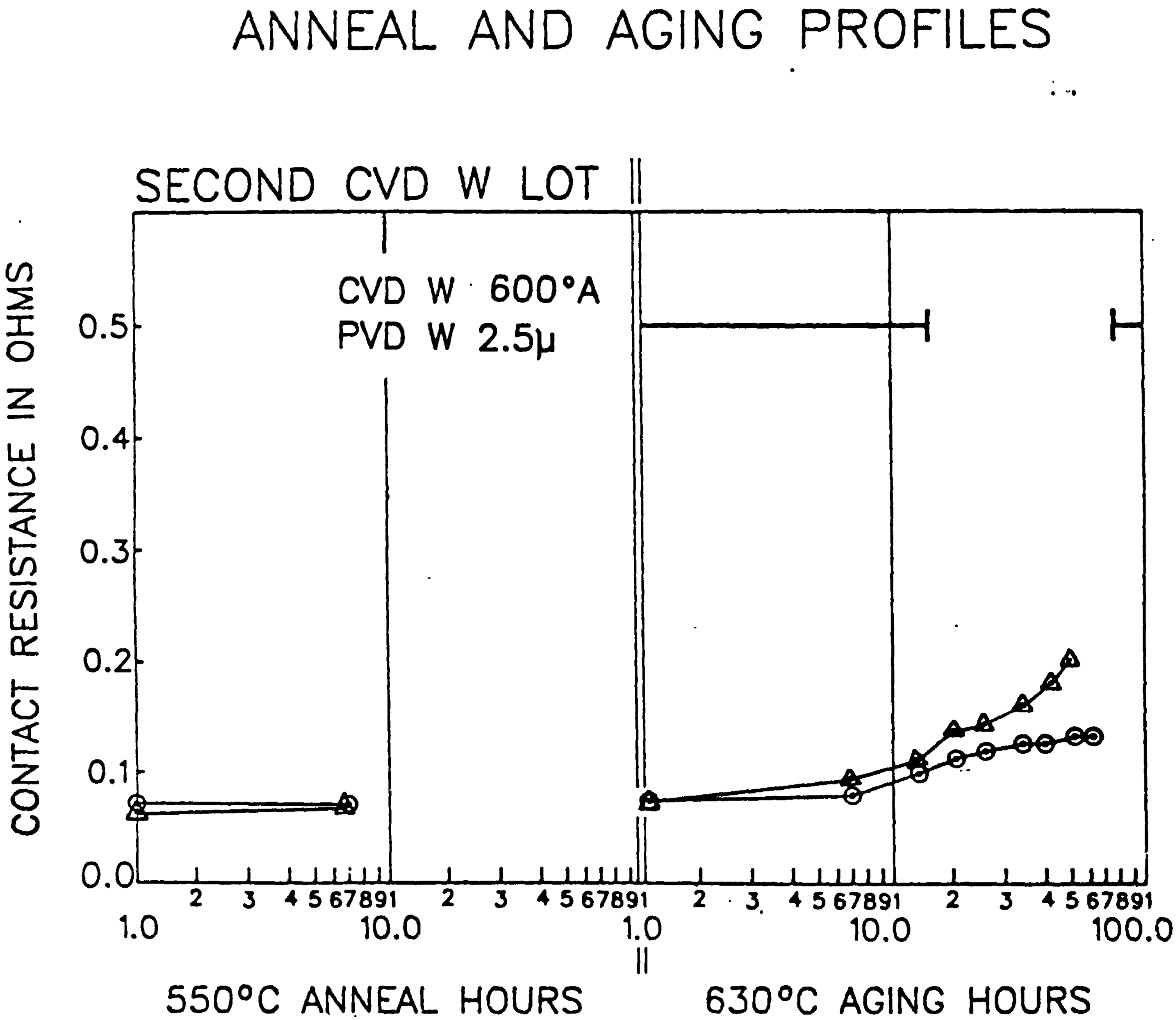

ANNEAL AND AGING PROFILES
SECOND CVD W LOT
CVD W 600°A
PVD W 2.5μ
CONTACT RESISTANCE IN OHMS
0.0
0.1
0.2
0.3
0.4
0.5
1.0
10.0
1.0
10.0
100.0
550°C ANNEAL HOURS
630°C AGING HOURS

Figure 12

APPARENT LPCVD ADVANTAGES

* SIMPLE PROCESS

* SELF-CLEANING

* LACK OF SPUTTERING DAMAGE
  LOW INITIAL CONTACT RESISTANCE

* HIGHER ACTIVATION ENERGY
  (MODEL TO BE CONFIRMED)

Figure 13