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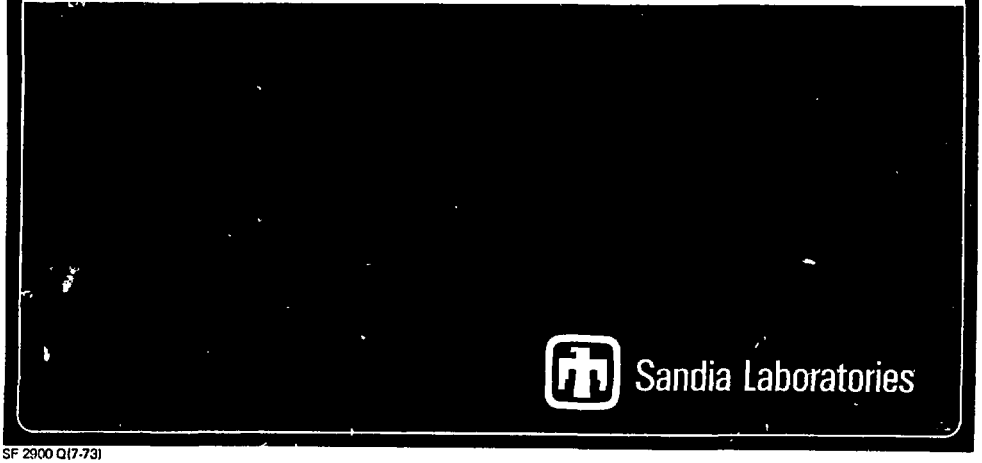

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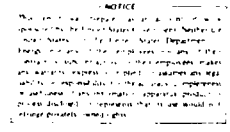
EFFECT OF HEAT TREATMENT ON THE ELECTRICAL RESISTANCE OF PHOTORESIST AS RELATED TO RADIOISOTOPIC THERMOELECTRIC GENERATOR AGING

Ralph T. Johnson, Jr.
Electronic Properties of Materials Division 5815
Sandia Laboratories
Albuquerque, New Mexico 87185

ABSTRACT

Photoresist is used in electrical contact definition and processing in radioisotopic thermoelectric generators. Inadequate removal of material during processing could lead to electrical shorting when exposed to the high temperature use environment. This effect has been simulated through studies of the electrical resistance of thin layers of photoresist (Kodak Metal Etch Resist) on glass (Corning 7052) with tungsten electrodes. Results show that both the photoresist and the glass contribute to the resistance. The glass resistance decreases with increasing temperature and becomes significant at high temperatures. Annealing studies on the photoresist show that the resistance of the photoresist decreases by over five orders of magnitude upon annealing to 500°C, with a corresponding decrease in activation energy from 0.27 eV (350°C anneal) to 0.10 eV (500°C anneal). Time dependent decreases in resistance of the photoresist were also measured for up to 8-9 days during high temperature anneals. Some electrolytic transport of tungsten may occur through the photoresist at high temperatures. Results are compared with data on thermoelectric generators and show that photoresist could cause the electrical aging (voltage degradation) problem observed in some generators.



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INTRODUCTION

Recently it was observed that some MC2730 Radioisotopic Thermoelectric Generators (1) produced on the production line at GEND exhibited a decrease in voltage output with time. This appears to be associated with an aging phenomena which was not present in the units produced by either the engineering development group at GEND or by the Sandia development shops. Examination of degrading units by Organization 2530 showed areas of contamination on the ends of the thermopiles which have electrical contacts. One possible source for the contamination was thought to be photoresist (2) which had not been removed during cleaning. This photoresist is used in contact definition and processing.

The purpose of our studies was to determine if inadequately removed photoresist could be a cause of electrical shorting. The photoresist is applied as a mixture of organic compounds and solvent. The resulting film has a high electrical resistance at room temperature. However, the operating temperature of the thermopile (300°C at the hot end) can produce charring and possible graphitization which would significantly decrease the resistance (3,4). These effects are examined in this report for thin layers of Kodak Metal Etch Resist (2,5) on Corning 7052 glass substrates with sputtered tungsten contacts. These materials were chosen because they were thought to simulate those used in the thermopile where shorting appeared to occur (i.e., between the thermopile channels separated by Corning 7052 glass - each channel

consists of stacks of SiGe elements with sputtered tungsten contacts). In our "idealized" configuration we did not attempt to match the actual thermopile geometry or processing.

Our experiments examine the electrical resistance of the photoresist to temperatures as high as 500°C. Although the thermopile operates at ∿300°C, the electrical experiments were extended to higher temperatures in order to investigate possible accelerated aging effects. The experiments have yielded information on the change in resistance and activation energy resulting from heat treatment and on time dependent variations in resistance at high temperature. The resistivity of the glass was also examined as well as effects associated with the possible migration of tungsten from the electrodes during heat treatment.

EXPERIMENTAL

The sample experimental configuration for the photoresist experiments is shown in Figure 1. Standard Corning 7052 glass was used as the substrate. The glass separating the thermopile channels in radioisotopic thermoelectric generators is of the same composition but is obtained from a glass powder (frit) which is heat treated to produce a bond between the channels. Tungsten electrodes were sputtered on to the glass surface and were ∿2 cm in length and were spaced ∿1 cm apart. Photoresist was applied using standard spinning techniques (2). Thicknesses were estimated to be ∿1 um. Electrical contact was made to the tungsten electrodes using spring-loaded leads. The sample was mounted between tantalum heater strips in an oil pumped, liquid

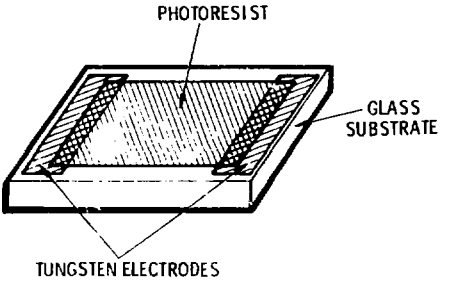

Figure 1. Sample configuration for electrical resistance measurements of photoresist on glass.

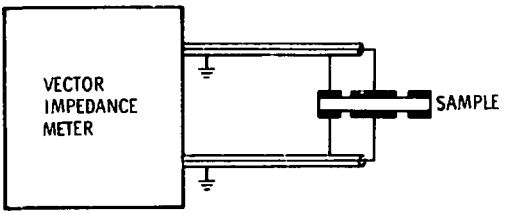

Figure 2. Sample electrode configuration and experimental arrangement for determination of the bulk resistivity of the glass using ac techniques.

nitrogen trapped vacuum system operating at $\sim 10^{-7}$ torr. Generally, the sample was held at each temperature setting for 15-30 min before the data were recorded. A Keithley 616 electrometer was used for making two-terminal dc resistance measurements.

The electrical resistance of the Corning 7052 glass was determined using two different experimental configurations. The resistance of the glass substrate was determined using the sample arrangement of Figure 1 with no photoresist applied. DC resistance measurements were made as in the photoresist experiments. The resistivity of the glass was determined using the experimental arrangement of Figure 2. With this configuration tungsten electrodes were sputtered on opposite faces of the glass sample. A guard ring configuration was used as previously described (6) to minimize surface leakage currents. This helped ensure that properties of the bulk glass were measured. The measurements were made using both a dc technique and an ac technique and frequency analysis method previously described (6,7). The same sample heating arrangement and vacuum environment were used as in the photoresist experiment.

RESULTS

Temperature Dependence

The temperature dependence of the resistivity of the glass is given in Figure 3. Data are given for the experimental configuration of Figure 1 (open circles) with no photoresist and for the bulk resistivity arrangement of Figure 2 (open and closed triangles). The overlap of the data in the higher

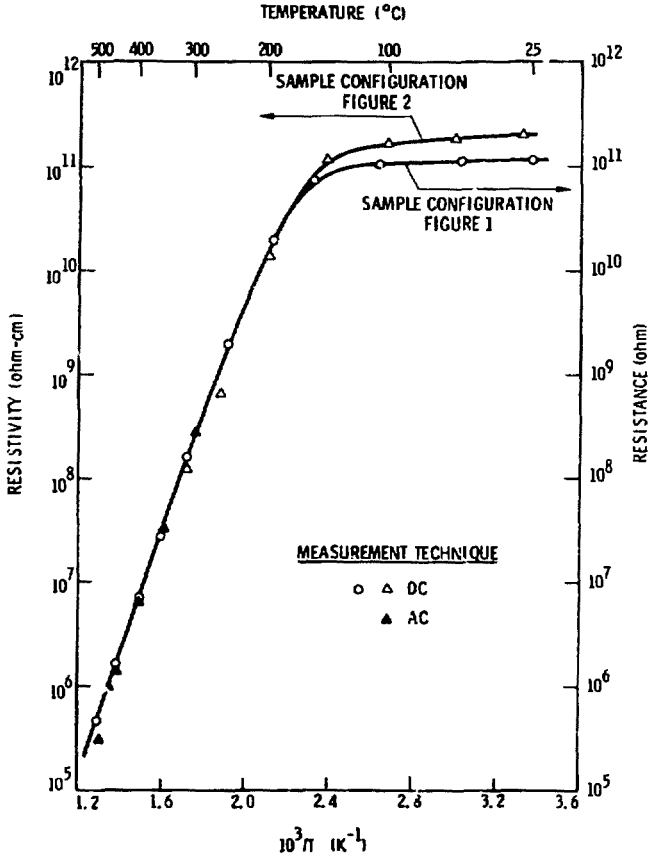

Figure 3. Temperature dependence of (a) the resistance of the glass using the sample configuration of Figure 1 (with no photoresist and (b) the bulk resistivity of the glass using the experimental arrangement of Figure 2.

temperature region is only fortuitous since both resistance data (Figure 1) and bulk resistivity data (Figure 2) are given. The bulk resistivity data taken in the temperature range $\lesssim$350°C were measured using dc techniques whereas at higher temperatures it was necessary to use ac techniques to avoid polarization effects. Results indicated that at temperatures below 300-350°C conduction is principally electronic in nature, whereas at higher temperatures conduction is mixed with transport via both ionic and electronic carriers. DC polarization measurements at 400°C indicated that the ionic contribution to the current is >75% of the total current at 400°C.

The photoresist (on the glass) temperature dependence of resistance is given in Figure 4. The sample configuration for these experiments was that of Figure 1. In the first temperature cycle the resistance was measured from 25 to 350°C. The resistance below ~150°C (~$10^{11}\Omega$) was that of the glass substance. [Data for the glass (from Figure 3) are also shown.] Above ~250°C significant time dependent resistance variations (associated with the photoresist) were observed, as indicated by the arrows. The sample was cooled to room temperature (~25°C) following each cycle to high temperature. With each succeeding experiment (temperature cycle) the sample was cycled to a higher temperature (with the exception that the sample was cycled twice to 450°C). This produced a decrease in both the magnitude of the resistance and the activation energy in the lower temperature region. These changes are

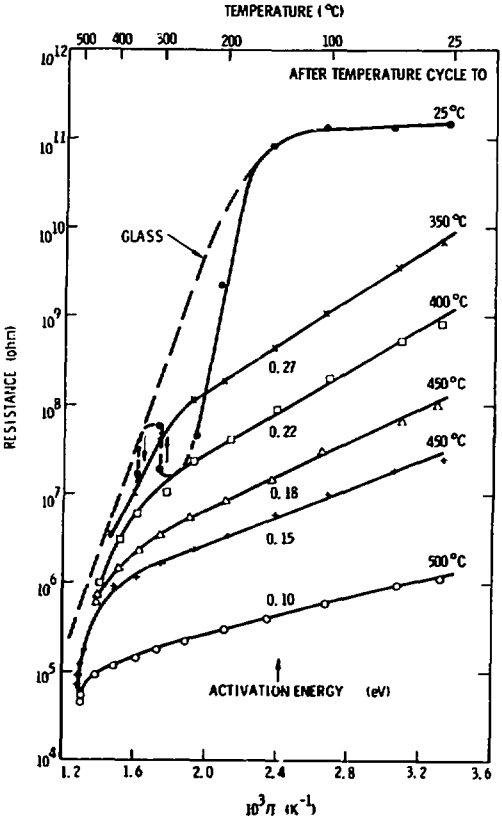

Figure 4. Temperature dependence of the resistance of the photoresist on the glass substrate (Figure 1 configuration). Data for the glass substrate are given by the dashed line. Results show that both the magnitude of the resistance and the activation energy of the photoresist decreases with annealing (cycling to high temperature).

associated with the photoresist. At high temperatures, the resistance approached that of the glass substrate.

Time Dependence

During each temperature cycle in Figure 4 the sample was held at the highest temperature setting for periods of 2-10 h. Time dependent resistance variations were observed, with the resistance decreasing with time. Results at several anneal temperatures are shown in Figure 5. The data at 400°C were recorded first, followed by the experiments at 450 and 500°C. Similar experiments were pursued on another photoresist sample at 450°C for a period of 8-9 days. These results are given in Figure 6 and show that the resistance changes occur over very long periods of time.

Electrolytic Conduction

During the high temperature anneal experiments a dc potential was applied to the photoresist samples. Visual examination of the samples after the anneal showed considerable discoloration extending from one of the tungsten electrodes into the photoresist. X-ray fluorescense and ion beam analysis (low energy ion backscattering and secondary ion mass spectrometry) of the discolored photoresist indicated the presence of tungsten as well as other impurities. Results suggested that tungsten from the electrodes may be transported through the photoresist under the influence of an electric field. Such electrolytic conduction is known to occur in a number of organic systems at high temperatures (8).

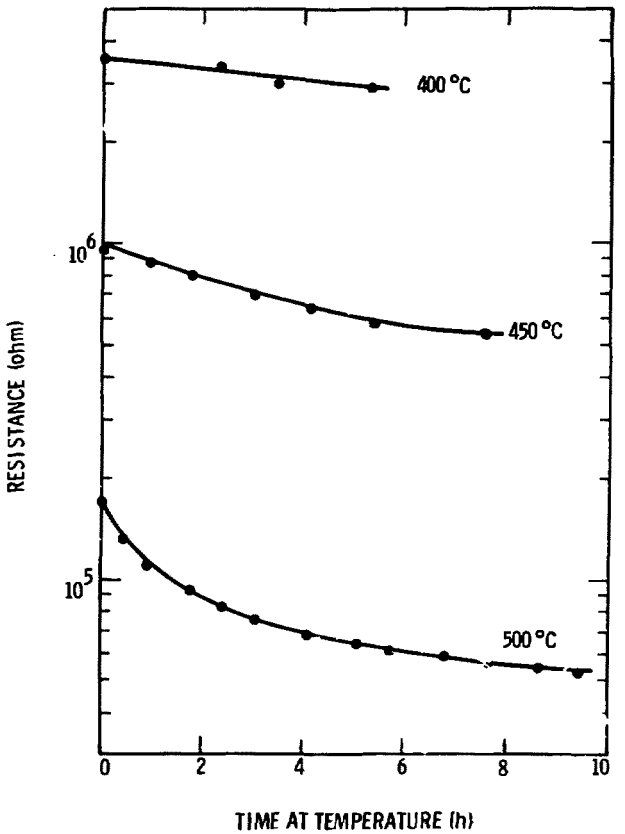

Figure 5. Time dependence of the resistance of the photoresist (Figure 1 configuration) at selected annealing temperatures.

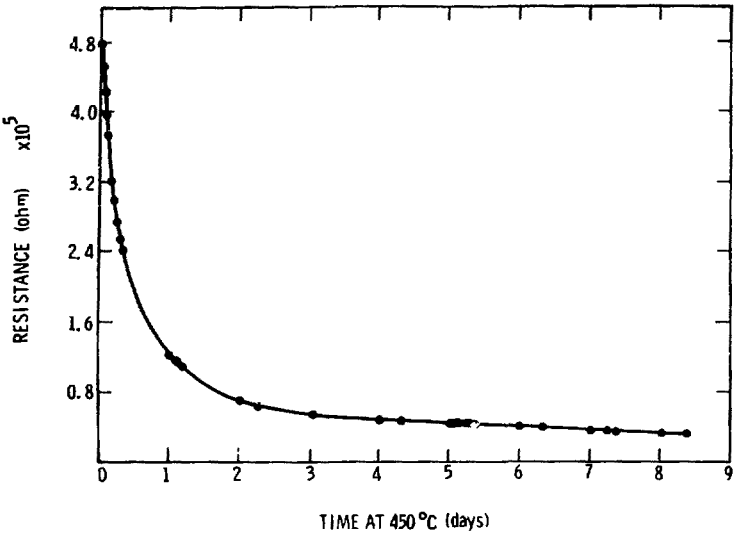

Figure 6. Time dependence of the resistance of the photoresist (Figure 1 configuration) at 450°C over a period of 8-9 days.

COMPARISON WITH RADIOISOTOPIC THERMOELECTRIC GENERATOR

The electrical aging and shorting characteristics of some radioisotopic thermoelectric generators have been examined by W. R. Abel (9). Measurements of a shorted region across the two thermopile elements in one generator gave a resistance of $\sim 10^{4}\,\Omega$ at 300°C with an activation energy of ~0.32 eV. The shorted region had dimensions which were estimated to be ~0.4 cm in width and $\sim 10^{-2}$ cm in length (the approximate distance between channels). Assuming a thickness of ~1 μm this gives a resistivity of ~40 Ω-cm at 300°C for the shorted region. It is of

interest to compare this with the photoresist data in Figure 4 for the 500°C anneal. This anneal accelerated the aging of the photoresist and is thought to approximate the aging situation in the radioisotopic generator. The results in Figure 4 give an activation energy of 0.10 eV for the 500°C anneal with a resistivity of ∿28 Ω-cm at 300°C assuming a photoresist thickness of ∿1 μm. This magnitude of resistivity compares very favorably with that estimated for the electrical shorts in the radioisotopic thermoelectric generator; however, the activation energies are considerably different. This may indicate that either the conduction mechanisms in the shorted region and in the photoresist may be different or the photoresist may not be the cause of the problem. A difference in conduction mechanisms might occur due to the electrolytic transport of tungsten into the photoresist. In the generator the distance between the thermopile channels is $\sim 10^{-2}$ cm whereas in the photoresist experiment (Figure 1) the distance between tungsten electrodes was ∿1 cm. In the photoresist experiment, tungsten had not completely diffused and bridged the electrodes, whereas it may have done so in the generator which was tested for the short. More experiments would be needed to determine the extent to which these effects might affect the activation energy.

A comparison of thermoelectric generator output was made using calculations based on the photoresist time dependent resistance data (Figure 6) and actual aging data on a generator

with photoresist. The aging behavior of a generator was simulated using a unit prepared under carefully controlled, thought to be "ideal," conditions (9). The photoresist was not removed after the photolithographic process (2). This left photoresist on the tungsten electrodes and on the sides of the thermopile, bridging the thermopile channels over a distance of ∿0.4 cm. The distance between channels was $\sim 10^{-2}$ cm. To accelerate aging the generator was stored at a temperature of 150°C. This put the hot junction at ∿450°C. The variation (decrease) in the open circuit voltage as a function of time at 450°C (hot junction) is given in Figure 7. The decrease in open circuit voltage with time is very similar to that observed in the "bad" units which led to this investigation. The calculation of the effect of shorting on the open circuit voltage of a generator using the photoresist data from Figure 6 was made utilizing the equivalent circuit of Figure 8. The nominal voltage from a unit is 5.3 V. The internal impedance which includes the SiGe resistance and the tungsten interconnections is ∿130 Ω. The time dependent shorting resistance R was taken to be that of the photoresist (Figure 6) with the appropriate geometric correction ($\sim 5 \times 10^{-2}$). The open circuit voltage calculated from these data is given as the open circles in Figure 7. Results show that the calculated values are in very good agreement with the measured open circuit voltage from the generator with photoresist. The agreement is probably fortuitous, especially considering the estimates made for the area of the

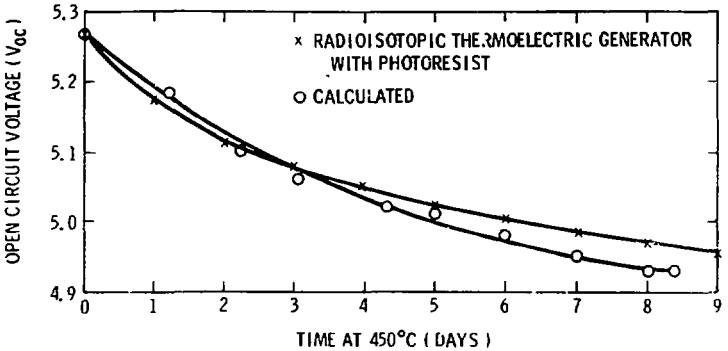

Figure 7. Time dependent variations in the open circuit voltage of a radioisotopic thermoelectric generator with photoresist (purposely not removed after the photolithographic process) with the hot junction at 450°C. Results are seen to compare favorably with the calculated valves obtained using the equivalent circuit of Figure 8 and the photoresist resistance variation data in Figure 6 with an appropriate geometry correction (see text).

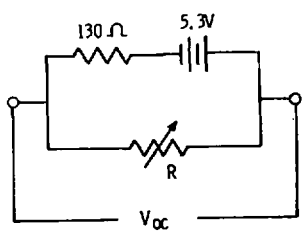

Figure 8. Equivalent circuit for a radioisotopic thermoelectric generator with a variable shorting resistance, R. Voc is the open circuit voltage.

shorted region. Nevertheless, these results do show that the photoresist could cause time dependent voltage decreases which are very similar to those observed in some radioisotopic thermoelectric generators.

CONCLUSIONS

The magnitude of the photoresist resistance as well as the time dependent resistance variations are consistent with the suggestion that inadequately removed photoresist could cause the electrical shorting problem observed in some radioisotopic thermoelectric generators. The resistance activation energy, however, does not fit this supposition. This could be due to effects associated with diffusion of tungsten from the electrodes which could change the conduction mechanism.

It is also certainly possible that the photoresist may not be the cause of the generator aging problem. Other organic contaminants would be expected to have similar electrical characteristics at high temperature (3). There is evidence (9) that thermopiles which have been exposed to organics from contaminated thermal insulation exhibit similar aging characteristics.

Although there are several possible explanations for the aging behavior, it can definitely be concluded from the work reported here that photoresist can cause voltage degradation similar to that observed in some radioisotopic thermoelectric generators. Every effort should be made to ensure that this source of contamination be removed during processing.

ACKNOWLEDGEMENTS

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