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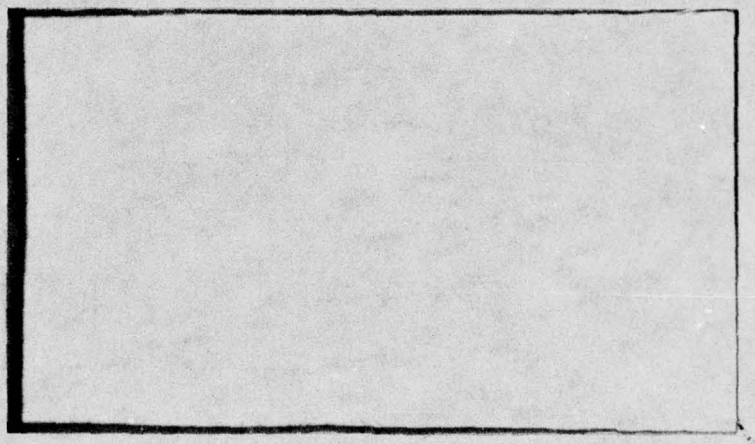

SCHOOL OF MATERIALS ENGINEERING

LEVEL II

12

(6) THE EFFECTS OF SUBSTRATE COMPOSITION ON THICK FILM CIRCUIT RELIABILITY.

(10) R. W. Vest

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Thick film resistors were prepared with and without AlSiMag 614 substrate dissolved in the resistor glass. The electrical characteristics of these devices were studied during sinter/anneal cycles up to 525°C. Two effects were identified, one which results in a slow decrease in resistance with time at the lower anneal temperatures and another which results in a more rapid increase in resistance at the higher anneal temperatures. The mechanisms of these effects are discussed in terms of changes in glass composition resulting from resistor - substrate interactions.

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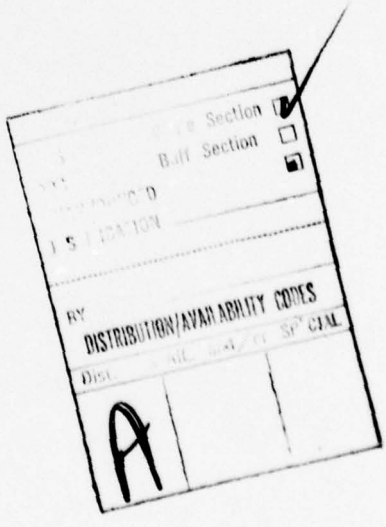
FORWARD

Research described in this report constitutes the first three months of effort under Contract No. N00019-78-C-0236 with the Naval Air Systems Command, Department of the Navy, under the technical cognizance of James Willis. The research was conducted in the Turner Laboratory for Electroceramics, School of Materials Engineering and School of Electrical Engineering, Purdue University, West Lafayette, Indiana 47907, under the direction of Professor R. W. Vest. Contributing to the project were Messrs. J. M. Himelick, P. Palanisamy and R. L. Reed.



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1. INTRODUCTION

The print and fire processing of thick film circuits ensures that there always will be some degree of chemical interaction between the film and the substrate, because all common substrate materials are soluble to some degree in the glasses used in thick film inks. This interaction is primarily responsible for the development of adhesion between the thick film and the substrate, but it also leads to changes in the composition of the glass with the net result that the physical properties of the glass will change. These changes in physical properties of the glass will result in modified kinetics for the various microstructure development processes and all electrical properties of the resistors are related to the microstructure.

The goal of this research program is to develop a sufficient level of understanding of the phenomena involved so that appropriate models can be developed. These models should lead to the writing of specifications for impurity limits and additive ranges for substrates, and to recommendations concerning glass composition and processing conditions.

Previously reported studies [1, 2] under this program have primarily concentrated on the magnitude of the effects resulting from chemical interaction between a thick film resistor and a ceramic substrate. The rates of dissolution of two substrates, 96% Al_2O_3 (AlSiMag 614) and 99.5% Al_2O_3 (AlSiMag 772), in two lead borosilicate glasses (63 w/o PbO-25w/o-B_2O_3-12w/oSiO_2 and 70w/o PbO - 20w/o B_2O_3 - 10w/oSiO_2) were measured at various temperatures. The rate limiting steps for each substrate-glass system were determined in all appropriate temperature ranges, and analytical equations were developed to predict the substrate recession as a

function of time and temperature for thick film resistors. Studies of the influence of substrate constituents dissolved in the glass on the electrical properties of the resistors showed a significant effect on both sheet resistance and temperature coefficient of resistance. The sheet resistance increased and the TCR decreased as the amount of substrate dissolved in the resistor glass increased for the same processing conditions.

2. SINTER/ANNEAL STUDIES

2.1 Purpose

In order to study the influence of dissolved substrate on the electrical properties of thick film resistors a technique was developed [2] for printing and firing resistors made with glasses containing varying amounts of dissolved substrate on platinum foil so that no further change in resistor glass composition occurred during processing. The resistors were approximately 125 μm thick after removal from the platinum foil, and it was desirable to provide some form of mechanical support. It was also desirable to remove residual stresses which may have developed due to the mismatch in thermal expansion between platinum and the resistor glass. The procedure developed to accomplish these two goals was to place the resistor on an appropriate substrate and raise the temperature to slightly below the softening point of the glass where the residual stresses would be annealed out and the resistors would sinter to the substrate. However, it was determined [2] that the electrical properties of resistors made from both standard glass and glass with varying amounts of dissolved substrate changed irreversibly during the sinter/anneal process. The experiments described in this section were designed to monitor the resistance as a function of time at various elevated temperatures in order to determine the precise changes which were occurring and to develop an insight concerning the cause(s) of these changes.

2.2 Experimental

Two thick film formulations were prepared containing 5 w/o RuO_2 relative to glass. One formulation contained the standard 63-25-12 glass frit while the other contained a glass frit made from the 63-25-12 com-

position plus 10 w/o dissolved AlSiMag 614 substrate. Resistors were made from these formulations by screen printing and firing on platinum foil as previously described [2]. After removing the resistors from the platinum foil, areas for four electrical contacts were prepared by lightly abrading the appropriate areas of the surface using an airabrasive unit with Al_2O_3 abrasive. Platinum electrodes were rf sputtered onto these areas through an appropriate mask, and platinum lead wires were attached to the electroded areas of each resistor using a conducting epoxy. The resistors were then placed on AlSiMag 614 substrates and loaded one at a time in a push-rod furnace. The current leads from the resistor were connected in series with a standard resistor and a constant current source. Device current was monitored across the standard resistor and device voltage at the inner (voltage) terminals. The device voltage, which was directly proportional to resistance, was recorded as a function of time, and a digital volt meter was used when greater accuracy than that provided by the strip chart recorder was required.

The resistance of each device was measured at room temperature and then the temperature was increased to 125°C and resistance measured again. These two values permitted the calculation of the hot TCR prior to elevated temperature exposure. After the 125°C reading, the sample was raised to the desired maximum temperature for that run (425°, 450°, 475°, 500°, or 525°C). After 15 minutes at temperature the sample was immediately withdrawn to 125°C. After reaching thermal equilibrium at 125°C, the resistance was recorded and the sample returned to room temperature for final reading. By following this procedure, each run provided a hot TCR before and after high temperature exposure in addition to a continuous recording

of resistance during the thermal treatment. This procedure was followed for each sample with the initial maximum temperature of 425°C, and repeated at successively higher temperatures for each device until it had sintered onto the substrate.

2.3 Results

Several trends were observed from the collection of data obtained for both standard and substrate glass resistors. These trends were repeatable from one device to the next at each temperature. Even devices which had seen higher temperatures in their prior thermal history repeated the behavior at the lower temperatures during subsequent runs. The behavior at each of the five test temperatures will be discussed individually.

425°C

Figure 1 shows typical behavior of the resistance at temperature relative to the resistance at 125°C as a function of time for the standard glass and substrate glass resistors at 425°C. The standard glass devices showed an increase in resistance by about 20% relative to the value at 125°C during the first 4 minutes and then a slow decrease in resistance until the end of the anneal period (15 minutes). At 125°C after the anneal the resistance was always within ± 1% of its value at 125°C before the anneal. The substrate glass resistors showed an initial decrease of approximately 10% in resistance during the first minute of heating from 125°C, and then a rapid increase for the next 3 minutes to a value approximately 35% greater than the value at 125°C. This increase was then followed by a slow decrease throughout the duration of the anneal. At 125°C after the anneal the substrate glass devices returned to a resistance

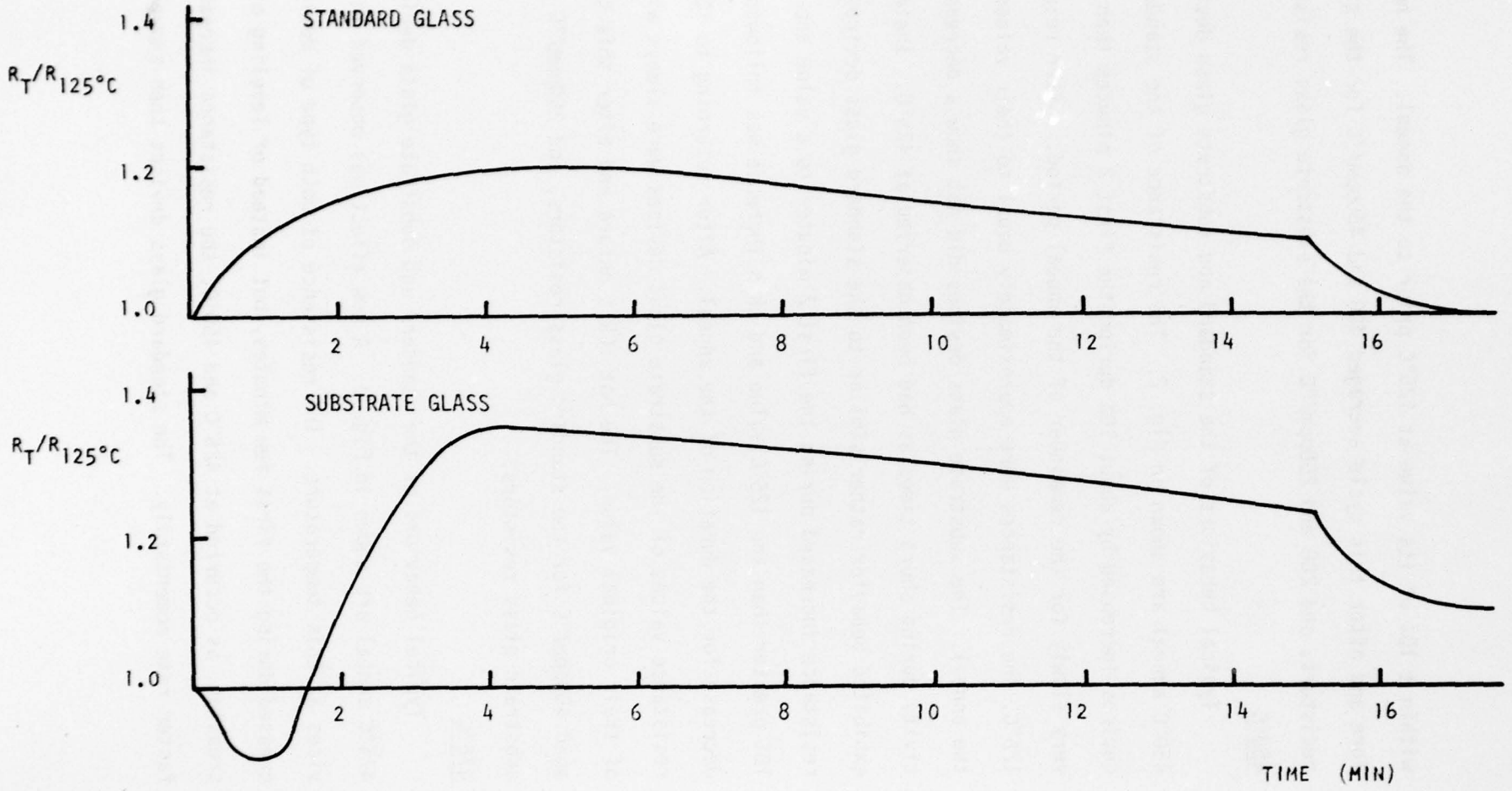

Figure 1. Relative Resistance During 425°C Anneal

within ± 10% of its value at 125°C prior to the anneal. The hot TCR's before and after this cycle averaged 400 and 450ppm/°C for the standard glass resistors, and 200 and 250ppm/°C for the substrate glass resistors.

450°C

Typical behaviors of the standard and substrate glass devices during 450°C anneal are shown in Fig. 2. The resistance of the standard glass devices increased by about 10% during the first 2 minutes then decreased very slowly for the remainder of the anneal period. After returning to 125°C, the resistances were approximately equal to their values prior to the anneal. The substrate glass devices did not show a decreasing resistivity during short times as had been observed at 425°C. Instead, they exhibited behavior rather similar to the standard glass devices. The resistance increased during the first 2 minutes to a value approximately 10% greater than the 125°C value and this increase was followed by a slow decrease for the duration of the anneal. After returning to 125°C the resistance values of the substrate glass devices were always within ± 5% of their original value. The hot TCR's before and after this cycle averaged 400ppm/°C for the standard glass resistors, and 250ppm/°C for the substrate glass resistors.

475°C

Typical behaviors of the standard and substrate glass devices during 475°C anneal are shown in Fig. 3. A new effect was observed in both devices at this temperature. The resistance of both type of devices increased during the first few minutes, but instead of leveling off or decreasing, as occurred at 425°C and 450°C, the resistance increased at a faster rate momentarily. The standard glass devices then showed a slowly

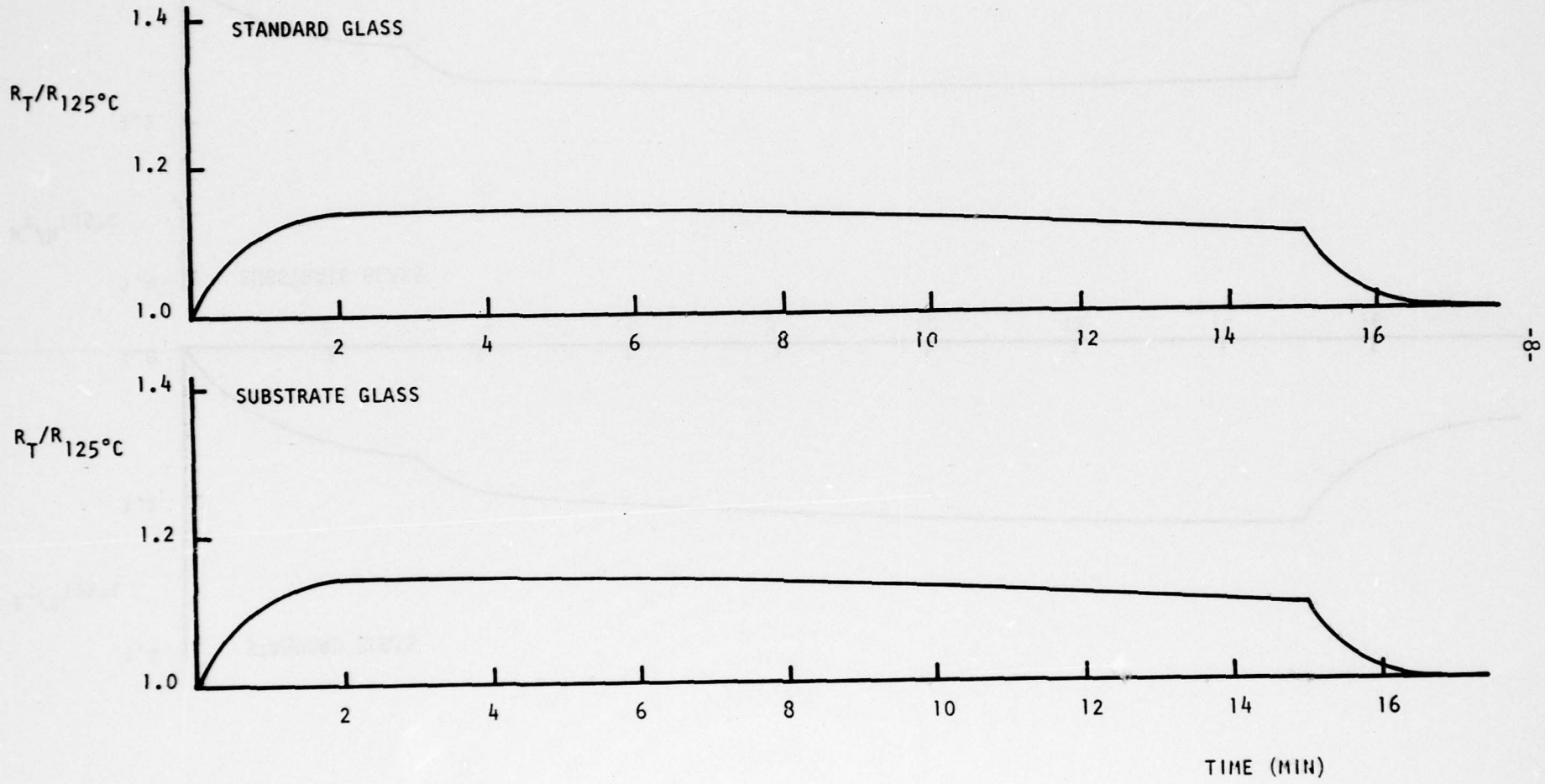

Figure 2. Relative Resistance During 450°C Anneal

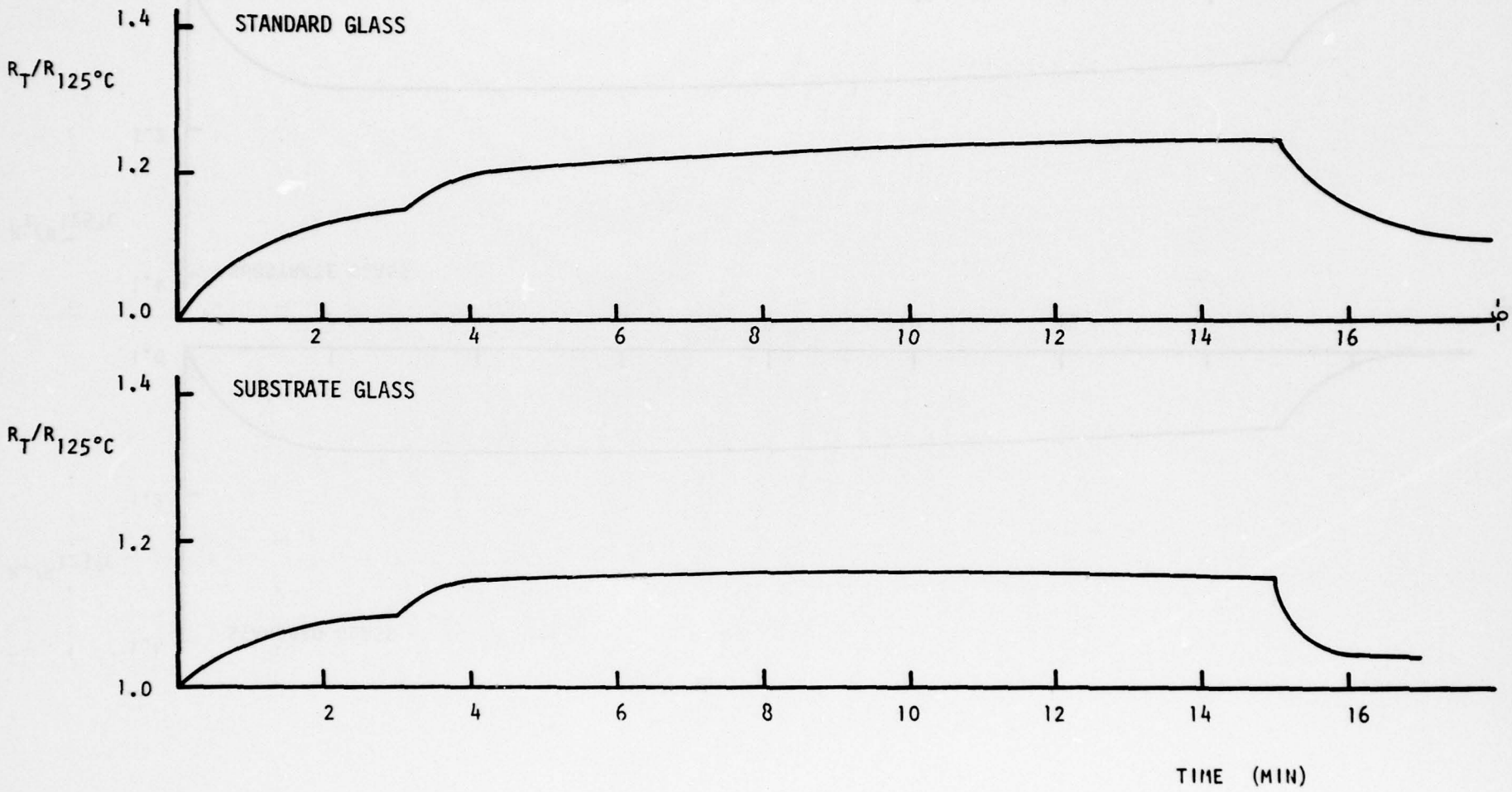

Figure 3. Relative Resistance During 475°C Anneal

increasing resistance while the resistance of the substrate glass devices remained constant until the end of the anneal period. When both standard and substrate glass devices were returned to 125°C after the anneal they were always higher in resistance by 5 - 10% relative to the 125°C value prior to the anneal. The hot TCR's before and after this cycle averaged 400 and 450ppm/°C for the standard glass resistors, and 250 and 300ppm/°C for the substrate glass resistors.

500°C

Typical behavior of the standard and substrate glass devices during 500°C anneal are shown in Fig. 4. After an initial increase in resistance, both devices increased at a faster rate momentarily, which was the same effect observed at 475°C. After this momentary rapid increase, the resistance increased linearly throughout the remainder of the anneal cycle. At the end of the 15 minute anneal the standard glass devices had increased by 45 - 50% whereas the substrate glass devices had increased by 30 - 35%. On returning to 125°C all samples were higher in resistance than the 125°C value prior to the anneal by 10 - 20%. It was observed that the standard glass resistors had sintered to the substrate during this time-temperature processing. The hot TCR's before and after this cycle averaged 400 and 350ppm/°C for the standard glass resistors, and 250 and 200ppm/°C for the substrate glass resistors.

525°C

Since the standard glass resistors sintered to the substrate at 500°C, only substrate glass devices were run at 525°C; typical behavior is shown in Fig. 5. These devices exhibited the same characteristics as at 500°C but the linear increase in resistance was much faster than the rate at

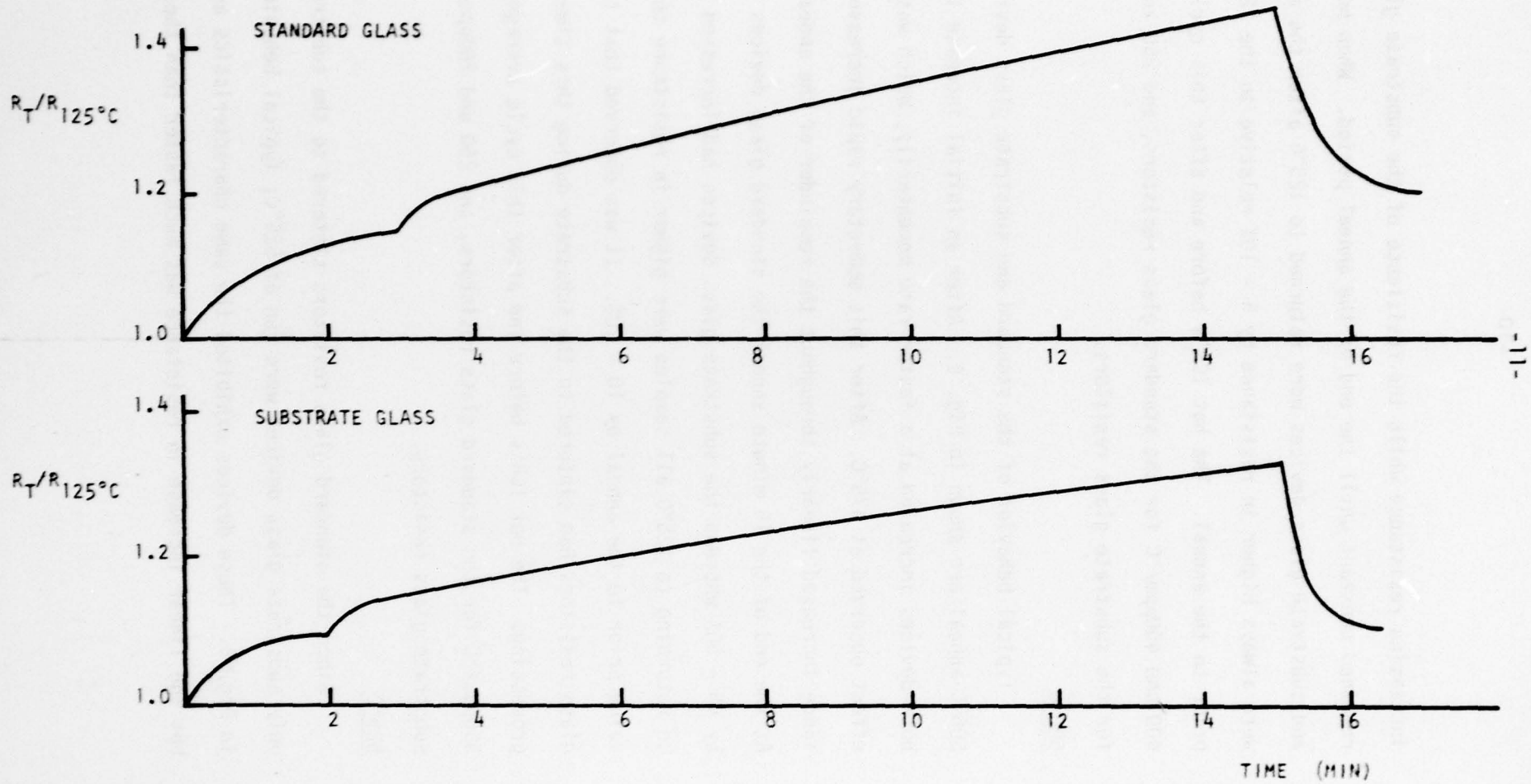

Figure 4. Relative Resistance During 500°C Anneal

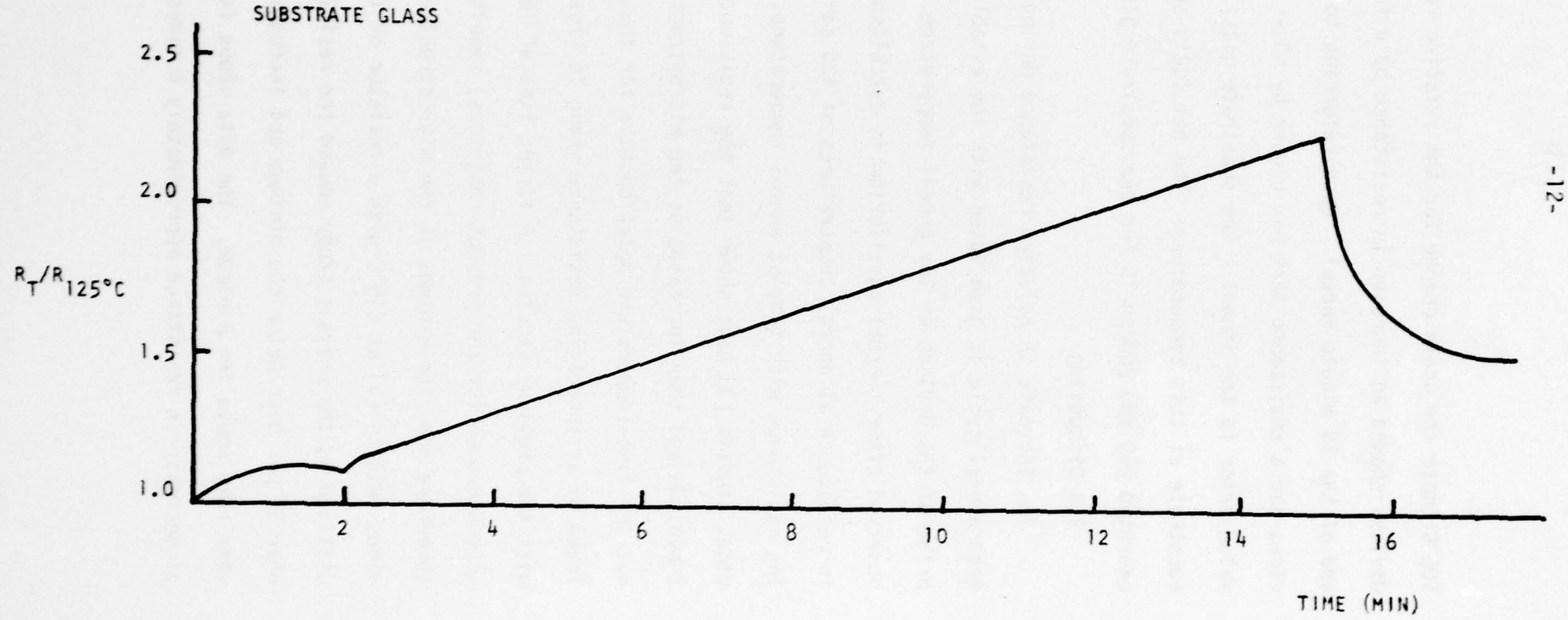

Figure 5. Relative Resistance During 525°C Anneal

500°C (note the scale change for the relative resistance axis). Some devices showed an increase in resistance by a factor of 2 or more by the end of the 15 minute anneal. Upon returning to 125°C the substrate devices had a resistance that was higher by 50 - 100% compared to the 125°C value prior to the anneal. The substrate glass devices sintered to the substrate at this temperature. The hot TCR's before and after this cycle averaged 250 and 200ppm/°C for the substrate glass resistors.

2.4 Discussion

The increase in relative resistance during the first few minutes of each anneal cycle is associated with the establishment of thermal equilibrium of the devices at the anneal temperature. Two major effects are observed after thermal equilibrium is established: (1) a slow decrease in resistance at anneal temperatures of 425 and 450°C, and (2) an increasing resistance with time at anneal temperatures of 475°C and above. Previous studies [3] have shown that the resistance decreases, passes through a minimum and then increases as the microstructure development proceeds, but the time-temperature relationships for the decreasing resistance followed by an increasing resistance shown in Figs. 1 - 5 are not compatible with the previous studies. A firing time of 10 minutes at 800°C (the schedule used for the present resistors) results in a sheet resistance somewhere near the minimum in the microstructure development curve. Previous results [3] at 610°C with a resistor of the same composition as utilized in the present study showed the resistance decreasing at a rate near 5% per hour below the minimum and increasing at approximately the same rate above the minimum. The data shown in Fig. 2 represent a rate of decrease in resistance approximately 6 times greater at 185° lower

temperature, and the data shown in Fig. 5 indicate a rate of increase 10 times greater at 85° lower temperature.

It is unlikely that either of the effects is associated with any of the primary microstructure development processes (glass sintering, glass spreading, microrearrangement, glass densification, conductive sintering, and conductive ripening). All processes except glass densification, conductive sintering and conductive ripening would have gone to completion during the initial firing of the resistors. The times and temperatures of the anneals were too low for significant sintering or ripening to occur, and the rearrangement of the macronetworks due to glass densification would be very slow because of the high glass viscosity at the anneal temperatures.

It is also unlikely that either of the effects is associated with the relief of residual stresses. Previous studies [3] have shown no correlation between TCR and the magnitude of residual stress. In addition, it was observed in the present study that resistors would repeat their behavior at 425°C after they had gone through the 475°C anneal cycle.

It is more probable that both of the observed effects are associated with changes in transport properties of the various contacts involved in the chains of conductive phase throughout the body of the resistor. Both effects occur at a faster rate for the standard glass resistors as opposed to the substrate glass resistors, which suggests that the effects are associated with charge transport processes across the non-sintered contacts in the conductive chains. The non-sintered contacts will have charge transport properties which depend on the thickness and composition of the glass film separating the RuO_2 particles. A higher viscosity characteristic of

the substrate glass resistors would inhibit flow and make an increase in glass film thickness less probable. The influence of glass composition on charge transport across the non-sintered contacts is yet to be determined. These effects will be studied utilizing the MIM geometry with individual contacts.

3. RuO_2 SOLUBILITY STUDIES

In order to develop an adequate model for the influence of the substrate on microstructure development and electrical properties of thick film resistors, it is necessary to know the influence of dissolved substrate on conductive ripening and sintering. Sintering and ripening of the conductive phase are the two final processes in microstructure development of thick film resistors. In the initial stages of the sintering process, necks develop between adjacent RuO_2 conductive particles; as the sintering process proceeds, the necks grow until adjacent particles coalesce to form larger particles. In the ripening process, the smaller particles preferentially dissolve and the material is transported through the liquid phase to precipitate on larger particles. The primary driving force for both sintering and ripening processes is the reduction in interfacial area between the conductive phase and the glass phase.

Earlier studies [3] have shown that the rate limiting step for the ripening of RuO_2 in 63-25-12 glass is the phase boundary reaction, that is, the rate of dissolution at the surface of the smaller particles or the rate of precipitation at the surface of the larger particles. The kinetics of the sintering process could not be measured directly, but rates consistent with experimental observations were calculated from the ripening results based on a solution-dissolution mechanism. It was also observed in the earlier study [3] that the presence of AlSiMag 614 substrate dissolved in the resistor glass decreased the rate of RuO_2 ripening. The decreased ripening kinetics could be due to a decrease in C_o, the equilibrium solubility of RuO_2 in the glass, γ_{sl}, the interfacial energy between RuO_2 and the glass, or K_T, the transfer coefficient for the passage of material

across the interface. Research initiated during the present quarter will determine the influence of dissolved substrate on the equilibrium solubility of RuO_2 in the base glass.

The experimental procedure which has been developed to determine the equilibrium solubility of RuO_2 in glass is as follows:

1. Prepare a powder mixture containing 10w/oRuO_2 and 90w/o glass containing varying amounts of dissolved AlSiMag 614 substrate.
2. Hold the RuO_2 - glass mixture at the firing temperature (600, 700, 800, 900, and 1000°C) in a platinum crucible for approximately 12 hours.
3. Quench the crucible in deionized water to minimize the possibility of reprecipitation of RuO_2.
4. Decompose the mixture using concentrated HCl with ultrasonic agitation.
5. Filter to remove the residue consisting of SiO_2, $PbCl_2$ and undissolved RuO_2.
6. Reduce the volume of the solution to an appropriate amount and determine the concentration of ruthenium in the solution with a Perkin-Elmer 303 Atomic Absorption Spectrophotometer which has been calibrated using standard $RuCl_3$ solutions.

Previous studies [3] using a similar experimental technique have shown that all of the ruthenium which is in solution in the glass is determined and that RuO_2 has an insignificant solubility in HCl.

4. REFERENCES

1. R. W. Vest, "The Effects of Substrate Composition on Thick Film Circuit Reliability," Final Technical Report on Contract No. N00019-76-C-0354, 28 February 1977.

2. R. W. Vest, "The Effects of Substrate Composition on Thick Film Circuit Reliability," Final Technical Report on Contract No. N00019-77-C-0327, 28 February 1978

3. R. W. Vest, "Conduction Mechanisms in Thick Film Microcircuits," Final Technical Report, Purdue Research Foundation Grant Nos. DAHC-15-70-G7 and DAHC-15-73-G8, ARPA Order No. 1642, December 1975.

5. FUTURE PLANS

The studies of equilibrium solubility of RuO_2 as a function of glass composition and temperature will be completed. The kinetics of ripening of RuO_2 in the glass will be determined as a function of glass composition and the kinetics of the initial stage of liquid phase sintering of RuO_2 will be calculated from the ripening data and the solubility data. These results will then be correlated utilizing the previously developed models for microstructure development, and the influence of glass composition established. The effects of substrate dissolution on charge transport processes in non-sintered contacts will be determined by fabricating metal-insulator-metal (MIM) structures and measuring the dielectric properties, bulk resistivity and breakdown characteristics of the glass as well as the current-voltage characteristics of the MIM all as a function of glass composition. The dependence of both the glass properties and the electrical properties of the non-sintered contacts on glass composition will be incorporated into a revised charge transport model for thick film resistors.

6. STATEMENT OF ESTIMATED COSTS

Contract No. N00019-78-C-0236

February 1, 1978 - January 31, 1979

Beginning Fund Balance	$65,000
Funds Expended Through 4/30/78	9,201
Funds Remaining	$55,799

Planned Expenditures (Approximate)

May	$5300
June	5300
July	9400
August	9300
September	5300
October	5300
November	5300
December	5300
January	5300