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Equivalent Circuit for Conductivity-Temperature Characteristics of the PdO/Ag-Pd Glaze Resistor

Abstract: It is shown that a reasonable fit of experimental to calculated data can be obtained with a simple model of the PdO/Ag-Pd glaze resistor. An equivalent circuit describing the temperature characteristics of the glaze resistor is proposed. The experimental measurements can be reproduced quite adequately over a considerable temperature range, using an equivalent circuit consisting of a semiconductor contact resistance in parallel with a metal. A quadratic term in $(1/T^2)$ in addition to the usual linear term with $(1/T)$ for $\ln \sigma$ is used to obtain a good fit at low temperatures. (T = absolute temperature; σ = conductivity.) This parabolic curve approaches the experimentally observed values for palladium oxide.

1. Introduction

The general success in manufacturing the glaze resistor has given very little incentive for an investigation of the more basic physics of this component. However, to predict its performance over extended periods of time in various atmospheres and in various liquids, and to predict the result of minor variations in the composition or processing, does require an accurate model of this component. It is generally known that it shows a negative temperature coefficient of resistance (TCR) at low temperatures, and a positive coefficient at high temperatures. On thermal aging its resistance generally increases; on load its resistance frequently decreases. Hypotheses to account for these effects have been given by A. H. Mones and E. H. Melan[1,2].

One can attempt to explain the behavior of the glaze resistor's conductivity vs temperature relationship in various ways. Attempts have been made for at least three of these approaches.

First, one can try to explain the glaze resistor characteristics in terms of those of the palladium oxide. One can follow the now well-established semiconductor theory. Madelung[3] summarized the conductivity of semiconductors in detail. Starting at low temperatures the conductivity increases with temperature because of an increase in the number of charge carriers with temperature. Eventually thermal scattering becomes a factor and the conductivity decreases. Finally, in the range of intrinsic conductivity, the conductivity again increases strongly. It is at this time impossible to follow Madelung's approach quantitatively, since such necessary characteristics as mean free path, impurity level energies, etc., are unknown for this polycrystalline material. One can see, however, even without this quantitative analysis, that the glaze resistor does not follow this pattern.

If one compares the curves obtained for PdO films by Okamoto and Aso[4] with those of Conwell[5] for germanium, one sees that PdO exhibits characteristics observed in a semiconductor. Although the PdO films show a certain instability, they exhibit a distinct transition at the point where the intrinsic conductivity becomes effective, i.e., at 500 K or $10^3/T = 2$. The TCR of the PdO becomes strongly negative. A comparative plot of $\ln \sigma/\sigma_0$ vs $10^3/T$ for the glaze resistor on the other hand exhibits no such striking change at the temperature at which the PdO becomes an intrinsic semiconductor (Fig. 1). (σ_0 = maximum conductivity.) Clearly this indicates that the behavior of the glaze resistor at high temperatures does not follow the pattern of the PdO film. It is necessary to assume that effects other than the behavior of the semiconductor alone control the temperature characteristics of the glaze resistor at high temperatures.

Second, one can accept with Mones and Melan the "hopping theory" of Heikes and Johnston[6] for conductivity in semiconductor oxides. This model assumes that the number of charge carriers is essentially independent of temperature, but that the mobility of the carriers introduces a temperature dependence. The motion of the

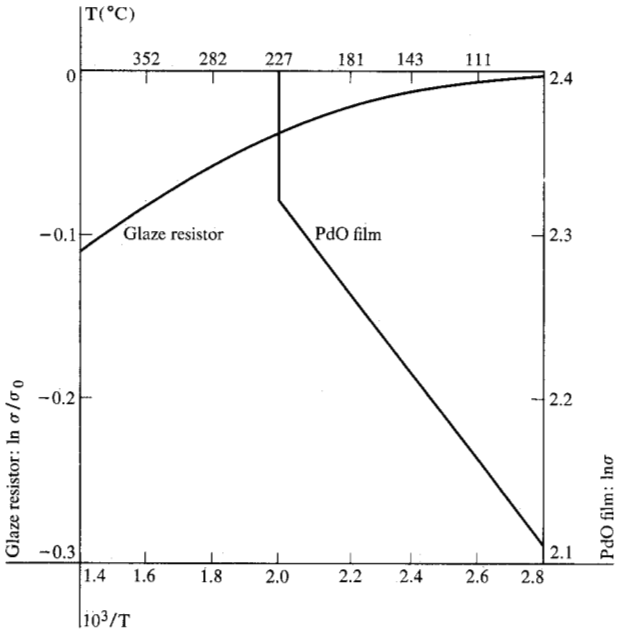

Figure 1 ln σ film vs $10^3/T$ from Okamoto and Aso[4], and ln σ/σ_0 vs $10^3/T$ for glaze resistor with $3 \times 10^3\Omega/\square$.

charge carriers requires an adjustment of the lattice; thus the diffusion coefficient of the charge carrier in the lattice and its temperature dependence become the determining factors. This leads to the equation $R = ATe^{H/kT}$, which is discussed later in the paper.

Third, one can consider a suggestion put forward recently by Brady[7] that contact resistance in addition to bulk resistance determines the conduction mechanism in the glaze resistor and thus the temperature-resistance characteristics. In the manufacture of the resistor, the starting materials are metal, glass and semiconductor powders. Since metal powders can show 100 times the resistance of bulk metal, the effect of contact resistance may be large indeed. It is not altogether surprising to find the suggestion made that contact resistance may be of importance.

2. Experimental

Resistors were fabricated from a $3000\Omega/\square$ paste, with a silver/palladium electrode and an aluminum oxide (96.5%) substrate. Contact was made to the electrode with platinum wires and rivets. The electrodes were not tinned.

Measurements on resistors were made by passing a current of about 1 mA from a storage battery through both the glaze resistor and a standard resistor, then measuring the voltages across the resistors with digital voltmeters of several-megohm input resistance. Temperatures were maintained automatically in a Delta temperature chamber and measured with a copper/constantan thermocouple and a bridge.

The palladium oxide, prepared by oxidizing a fine palladium powder at 400°C, was compressed in a steel mold to about 1000 psi so the green slug would hold its shape. This green slug was then compressed isostatically to 30,000 psi and fired in a tube furnace in 1 atmosphere of oxygen at 810 to 820°C or, in another case, in 6 atmospheres of oxygen at 950°C.

Measurements on the palladium oxide cylinders were made by using a fixture which applied the pressure from a steel spring to the two platinum electrodes. Separate current and voltage leads went to the platinum foil.

Resistance measurements in PdO pellets were made by passing the current from a storage battery through the palladium oxide cylinder and a standard resistor. The voltage drop across the palladium oxide was measured with a 412A Hewlett Packard voltmeter set to the millivolt scale. The current was derived from the reading of a digital voltmeter across the standard resistor.

3. Results

The measurements from a representative module, with a $3000\Omega/\square$ paste and silver palladium electrodes, are represented as the experimental points in Fig 2. To obtain basic material constants, measurements were made on palladium oxide in the form of compressed cylinders. The data thus obtained were plotted as the logarithm of the conductivity vs $10^3/T$. It was established that a significant fraction of the cylinder resistance was contact resistance. The density of the cylinder was 4.4 gm/cm³ as compared to a theoretical density for palladium oxide of 8.7. Thus, we were dealing with a very porous slug; this explains at least in part the role played by contact resistance.

The measured ln σ vs $10^3/T$ curve for the fired PdO cylinder can reasonably well be represented by a parabola

$$\ln \sigma/\sigma_0 = 5.84 \times 10^{-3}(10^3/T)^2 - 0.160\,(10^3/T) + 0.434 \qquad (1)$$

The general form

$$\ln \sigma/\sigma_0 = A/T^2 - B/T + C$$

approximates the shape of the experimental curve. In the 200 to 300 K range, the data followed a straight line closely enough to give

$$\ln \sigma/\sigma_0 = -B/T + C,$$

with B measured between 90 and 120 K.

Above room temperature the measurements on PdO become extremely erratic. Slow drifts of the resistance make the measurement of temperature-resistance curves

impossible. Okamoto and Aso[4] show a rather sharp transition in the slope of the ln σ vs $10^3/T$ curve at low temperatures, which is approximated in the following calculations by the parabola. This change in the slope has been observed for other semiconductor materials. Rogers, Shannon and Gillson[8] measured single crystals of PdO and confirmed the fact that PdO behaves like a semiconductor. Their measurements covered the 4.2 to 300 K range. The form

$$\sigma = Ae^{-E_1/kT} + Be^{-E_2/kT}$$

suggested by Fritzsche and Lark-Horowitz[9] does not lend itself to the reproduction of our data. A parabolic shape of the ln σ vs $10^3/T$ curve is used only for the sake of mathematical convenience.

4. Discussion

• *The Mones-Melan model*

The glaze resistor shows a negative TCR at low temperatures and a positive TCR at high temperatures. This led Mones and Melan to apply the Heikes-Johnston model[6] of conduction in semiconductor oxides to the glaze resistor. This model leads to a dependence of the resistance on temperature of the form

$$\sigma = BT^{-1}e^{-H/kT} \tag{2}$$

This resistance-temperature relationship leads to a minimum resistance[1,2] at $T_0 = T_{TCR=0} = H/k$. If T_0 is fixed, σ/σ_0 is entirely determined:

$$\sigma/\sigma_0 = (T_0/T)e^{1-T_0/T}. \tag{3}$$

It must also be pointed out that Heikes and Johnston applied their theory to materials in a temperature range where the exponential term determines the temperature dependence and the effect of the linear term is negligible. Their graphs demonstrate that for all practical purposes the resistance follows a curve given by $R = Ae^{H/kT}$. Mones and Melan, on the other hand, apply this theory to a range of temperatures where the linear term in T becomes dominant.

Heikes and Johnston's model involves the assumption that the number of carriers is essentially temperature independent, but that the mobility of the carriers is temperature dependent. The motion of the carriers requires an adjustment of the lattice; thus the temperature dependence of the diffusion coefficient of the charge carrier in the lattice becomes the determining factor. The point at which the sign reversal of the TCR is observed is then that temperature at which the energy required for the adjustment of the lattice to the motion of the carriers is equal to the thermal energy of the atom $T_0k = H$ where H is the activation enthalpy and k the Boltzmann constant. Since H is rather large in the semiconductors

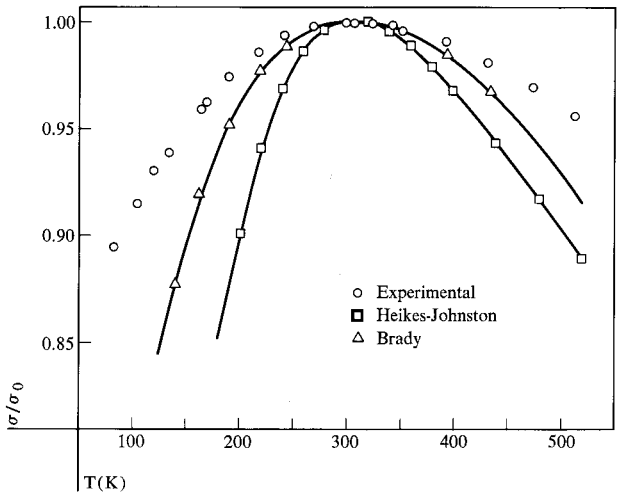

Figure 2 σ/σ_0 vs T, Heikes-Johnston theoretical curve, and Brady theoretical curve applied to semiconductor powder.

measured by Heikes and Johnston, T_0 is also a very high temperature.

Our glaze resistors show a minimum of resistance at about 306 K. A plot of σ/σ_0 vs T using a value of $T_0 =$ 306 K is shown in Fig. 2. This clearly shows the need for a more accurate model of the glaze resistor.

• *The Brady model applied to a semiconductor powder*

Brady[7] evaluated a model of elemental resistors, arranged jack-straw fashion and bonded to each other. The positive temperature coefficient part of the contact resistance is generated, according to Brady, through the interaction of the glass-substrate combination with the conducting material. As the glass contracts on cooling from its softening point at a rate greater than the conducting oxide-metal mixture, a pressure is generated on the contact areas. On reheating, this pressure is reduced, causing an increase in resistance, i.e., a positive temperature coefficient of resistance[7].

Brady uses the well known equation for the contact resistance by Holm[10]:

$$R_c = \rho/2r,$$

where R_c is the contact resistance, ρ the resistivity and r the radius of actual microscopic contact area. He introduces the pressure P, through

$$r = S_1P^{1/3},$$

where S_1 is a proportionality constant, and the temperature through

$$P = S_2(T_s - T),$$

where S_2 is a proportionality constant and T_s is the softening point of the glass. This, put all together, gives

$$R_c = S_3\rho(T_s - T)^{-1/3}, \tag{4}$$

where S_3 is a constant.

Assuming with Brady that the semiconductor obeys a $\sigma = \sigma_0 e^{-E/kT}$ law, we obtain

$$R_{sc} = Le^{W/T}(T_s - T)^{-1/3}, \tag{5}$$

where $W = E/k$. E is the activation energy for conduction and k is the Boltzmann constant. L is a constant into which all previous constants have coalesced. R_{sc} is the contact resistance between the semiconductor particles.

To this must be added the bulk resistance R_{sb} of the semiconductor:

$$R = R_{sb} + R_{sc}$$
$$= R_0 e^{W/T} + Le^{W/T}(T_s - T)^{-1/3}; \tag{6}$$

$$dR/dT = -(W/T^2)R_{sb} + [(1/3)/(T_s - T) - W/T^2]R_{sc}. \tag{7}$$

At $T = T_0$,

$$0 = -(W/T_0^2)(R_{sb} + R_{sc}) + R_{sc}/3(T_s - T_0); \tag{8}$$

$$R_{sc}/(R_{sc} + R_{sb}) = 3W(T_s - T_0)/T_0^2. \tag{9}$$

If R_{sb} is negligible compared to R_{sc}, then T_0 defines the activation energy uniquely, once the softening point of the glass is fixed.

The equation for the resistance is similar in this respect to the Heikes-Johnston formula. With T_s, T_0 and therefore W fixed and $R_{sb} = 0$, the entire curve σ vs T is defined (Fig. 2). Then with $T_0 = 306$ K and $T_s = 861$ K, one obtains $W = 56$. The fit of the curve in Fig. 2 is poor. On adding bulk semiconductor resistance R_{sb} one finds that as R_{sb} increases with fixed T_0, W decreases. With W reduced to 28.1, a rather good fit is actually obtained, except in the low temperature range. This, however, contradicts the measurements of the activation energy made on pure PdO cylinders, where values of 90 to 125 were observed in the 200–300 K range. Thus, we find that neither the Heikes-Johnston model nor the Brady model applied to a semiconductor powder as such gives a satisfactory fit to our data.

These simplified models do not take into consideration the actual structure of our resistor, which contains a two-phase mixture of metal and semiconductor, besides glass and substrate. Because the accurate treatment of the two-phase mixture of semiconductor and metal combined with the contact resistance problem is quite difficult, a simplified equivalent circuit is used.

• *Application of the parallel model to an actual glaze resistor*

A calculation was carried out on an equivalent circuit containing a semiconductor contact resistance in parallel with a metal. The semiconductor contact resistance is due to the contact resistance between the particles of PdO powder; the parallel metallic resistance is the resistance of the Ag/Pd alloy formed by firing the resistor glaze. It was thought that the alloy with a resistivity of about 15×10^{-6} ohm-cm would act as a shunt to the semiconducting oxide, which has a resistivity of about 15×10^{-2} ohm-cm.

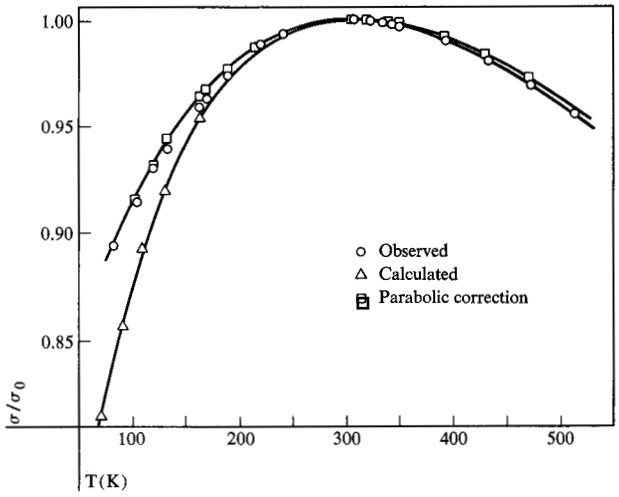

Figure 3 σ/σ_0 vs T, calculated curve for parallel model resistor, and curve calculated with parabolic correction of semiconductor characteristics.

As shown in Eq (5), we represent as a first approximation the contact resistance of the semiconducting oxide by

$$R_{sc} = Le^{W/T}(T_s - T)^{-1/3},$$

and the alloy resistance by

$$R_m = R_m{}^0(1 + \alpha[T - 273]).$$

Writing these equations as conductivities, we have

$$\sigma_{sc} = \sigma_s{}^0 e^{-W/T}(T_s - T)^{1/3}; \sigma_m = \sigma_m{}^0/(1 + \alpha[T - 273]).$$

Then

$$\sigma = \sigma_{sc} + \sigma_m$$
$$= \sigma_s{}^0 e^{-W/T}(T_s - T)^{1/3} + \sigma_m{}^0/(1 + \alpha[T - 273]); \tag{10}$$

$$d\sigma/dT = [\sigma - \sigma_m][W/T^2 - 1/3(T_s - T)]$$
$$- \alpha\sigma_m{}^0/(1 + \alpha[T - 273])^2$$
$$= [(\sigma - \sigma_m{}^0/(1 + \alpha[T - 273])]$$
$$\times [W/T^2 - 1/3(T_s - T)]$$
$$- \alpha\sigma_m{}^0/(1 + \alpha[T - 273])^2. \tag{11}$$

At $T = T_0$ the derivative $d\sigma/dT = 0$; as a normalization we set $\sigma(T_0) = 1$. The determination that the resis-

tor should have a resistance minimum at 306 K puts a considerable constraint on the adjustable components in the equivalent circuit. Assuming TCR $= 3.6 \times 10^{-4}$[11], $W = 120$, and $T_s = 861$ K, we observe that the ratio of semiconductor contact resistance to metallic resistance is fixed, and we obtain $\sigma_m{}^0 = 0.661$. With $\sigma(T_0) = 1$, $\sigma_m{}^0 = 0.661$ and the constants for α, W and T_s fixed, the entire σ/σ_0 vs T curve is determined and is shown in Fig. 3. It shows a good fit over a considerable temperature range. We can improve this fit still more if we consider that the ln σ/σ_0 vs $1/T$ curve measured on PdO cylinders showed considerable deviation from the straight line at low temperatures.

To allow for this effect, we introduce a quadratic term U/T^2 into the activation energy for conduction:

$$\sigma = \sigma_{sc} + \sigma_m, \tag{12}$$

with

$$\sigma_{sc} = \sigma_{sc}{}^0 e^{-W/T+U/T^2}(T_s - T)^{1/3};$$

$$\sigma_m = \sigma_m{}^0/[1 + \alpha(-273 + T)].$$

Differentiating with regard to temperature gives

$$d\sigma/dT = \sigma_{sc}[W/T^2 - 2U/T^3 - (1/3)/(T_s - T)] - (\alpha\sigma_m{}^0)/[1 + \alpha(T - 273)]^2.$$

Substituting from Eq. (10), we have

$$d\sigma/dT = [\sigma - \sigma_m{}^0/(1 + \alpha[T - 273])] \times [W/T^2 - 2U/T^3 - (1/3)/(T_s - T)] - \alpha\sigma_m{}^0/[1 + \alpha(T - 273)]^2 \tag{13}$$

We now normalize the resistance by assuming $\sigma_{T_0} = \sigma_{306K} = 1\Omega^{-1}\text{cm}^{-1}$ and use the value of $\sigma_m{}^0 = 0.661$ established in the previous calculation. If we measure $d\sigma/dT$ and σ at a low temperature T_1 we obtain one equation for W and U in very simple form. The equation for $d\sigma/dT$ at T_0 gives a second equation for W and U. We can calculate the values for W and U from these two equations; $W = 145.1$ and $U = 3982$.

The resulting equation for σ, Eq. (12), with $T_s = 861$ K, $\alpha = 3.6 \times 10^{-4}$, $T_0 = 306$ K, and W and U derived from the slope of the experimental σ/σ_0 vs T curve at one low temperature and at T_0, is shown in Fig. 3. Quite a good fit is shown over the entire range.

5. Conclusions

It is shown in this paper that the Mones-Melan conduction model when applied to the glaze resistor leaves a significant discrepancy between experiment and theory. The data of Okamoto and Aso on palladium oxide films show that the behavior of the palladium oxide alone does not account for the behavior of the glaze resistor, for the glaze resistor shows a high positive TCR where the onset of intrinsic conduction gives the palladium oxide a high negative TCR. This then suggests that a different phenomenon is involved and Brady's suggestion on the effect of contact resistance becomes more plausible.

To obtain quantitative agreement between calculated and measured data, one has to go one step further and examine the role of the total composition of the resistor, i.e., take account of the presence of the significant amounts of metal in the resistor paste. In this manner improved agreement between calculations and experiments can be obtained.

It is shown that an equivalent parallel circuit of metal and semiconductor contact resistance can be used to give an adequate representation. It has been the purpose of this paper to show in principle that the resistor can be represented with reasonable assumptions about basic material characteristics.

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