Thin Glass Film between Ultrafine Conductor Particles in 
Thick-Film Resistors

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Thick-film resistors are electrical composites containing ultrafine particles of ruthenate conductor (Pb,Ru,O₃ in the present materials) distributed in a highly modified silicate glass. We show that conductor particles remain flocced in the absence of any applied or capillary pressures, but are separated at equilibrium by a nanometer-thick film of glass. Microstructures show evidence for liquid-phase sintering, i.e., contact flattening of particles, under van der Waals attraction alone. Titania addition, which in dilute concentrations markedly increases the resistivity, decreases the temperature coefficient of resistance, and improves voltage stability and noise, is found to increase the equilibrium film thickness between particles by a few angstroms. STEM analyses show that the added titania preferentially concentrates in the silicate-rich grain boundary film, as well as at particle-glass interfaces. The roles of interparticle forces and adsorption on the glass film thickness with and without titania are discussed. The large increase in resistivity caused by titania additions is attributed to the increase in film thickness as well as to local chemical changes of two possible types. Titania enrichment within the glass film itself is expected to decrease the local ruthenium ion solubility, and this along with the possible formation of a more insulating titania-substituted surface layer on ruthenate grains will decrease the tunneling conductivity between conductor grains.

I. Introduction

Thick-film resistors are glass-conductor composites, widely used in discrete devices and hybrid circuits, in which the resistivity can be varied over 10 orders of magnitude (from $10^{-4}$ to $10^{5}\ \Omega\ \text{cm}$) by varying the conductor fraction, particle size, glass composition, and microstructure. They are prepared as inks which are screen-printed and fired on dielectric substrates, typically alumina. In a ruthenate thick-film resistor (using RuO₂, Pb,Ru,O₃, or Bi₂Ru₂O₇ as the metallically conducting phase) the volume fraction of conductor may vary from 5% to 60%. The microstructure can be quite complex, with the physical distribution of conductor particles often being determined by extrinsic processing parameters such as the relative particle sizes of the glass and ruthenate. A network structure in which conductor paths are separated by larger regions of glass has been observed, deduced to be the aftermath of a green microstructure wherein the coarser glass particles are initially coated with much finer ruthenate particles. Although the conductivity otherwise appears percolative, the chainlike distribution of conductor particles accounts for a surprisingly low threshold volume fraction for conduction, as low as 2% by volume. However, a critical electrical element is widely believed to be the thin glass film between conductor particles, through which it has been proposed that electron conduction occurs via a resonance tunneling mechanism involving impurity states in the glass film associated with dissolved conductor or impurity ions. Direct observations find evidence for the microstructure originally suggested by Pike and Seager of conductor particles separated by a thin film of glass.

In this work we examine the microstructure of model thick-film resistors, with emphasis on the thickness and composition of the glass film. One objective is to relate the characteristics of the glass film to resistor electrical properties. In addition, we find uniform glass film thicknesses indicative of an equilibrium between attractive van der Waals forces and disjoining forces, as proposed by Clarke. The present composites are an ideal configuration for studying this effect, since particles are fully immersed in a comparatively large volume of glass and come to an equilibrium thickness if a local minimum in the free energy exists, independent of the influence of externally applied or capillary pressures. Precise measurements of equilibrium glass film thickness have recently been reported in liquid-phase sintered silicon nitrides by Kleebe et al. and partially correlated with changes in chemistry that would also influence high-temperature creep properties. The present work assesses similar phenomena in an electrical composite, in which the electrical properties are no less profoundly influenced by the nature of the thin glass film.

II. Sample Preparation

A relatively simple thick-film resistor system consisting of Pb,Ru,O₃ (pyrochlore structure) conductor particles in a PbO–Al₂O₃–SiO₂ glass was studied. Glass compositions with and without TiO₂ were prepared in order to study the influence of this important additive on microstructure. In fairly dilute concentrations, TiO₂ is known to markedly increase the resistivity of ruthenate thick-film resistors. This effect is combined with a...
decrease in the temperature coefficient of resistance (TCR), which thereby improves the voltage stability of resistance and the characteristic noise.

Thick-film pastes were prepared using Pb,Ru,O₃ powder of 10 m²/g specific surface area (34-nm equivalent spherical diameter) and glass powder of 3–5-µm average particle size, in proportions of 20 vol% ruthenate and 80 vol% glass. The nominal glass compositions are shown in Table I. For compositional homogeneity, the glass was roller-quenched from uniform melts prepared in platinum crucibles and then milled to the desired particle size. The dry powders were blended with an organic vehicle, and the resulting thick-film ink was screen-printed onto alumina substrates previously prepared with silver termination pads. The green films were fired in air in a standard belt furnace. Upon reaching a maximum firing temperature in the range of 700°–900°C they were held for a period of 10 min and then cooled at 50°C/min.

Electron microscopy was conducted on samples fired at 850°C unless otherwise noted. Specimens were core-drilled directly from the fired thick films on their alumina substrates, then thinned by dimple-grinding from the substrate side and ion-thinned to perforation from the substrate side, using a liquid-nitrogen chilled stage. Thus, the regions examined are close to the top surface of the fired resistors. No conductive coating was necessary for prevention of charging under the electron beam. High-resolution transmission electron microscopy (HREM) was performed using a Topcon (Pleasanton, CA) 002-B instrument operating at 200 kV. Scanning transmission electron microscopy (STEM) was conducted using a Vacuum Generators (East Grinstead, U.K.) HB5 instrument equipped with a Link Systems (now Oxford Instruments, Oak Ridge, TN) thin-window energy-dispersive X-ray detector.

III. Electrical Characteristics

The two-terminal resistance at room temperature of films of 13-µm fired thickness and 1-mm × 1-mm area are plotted in Fig. 1 against the firing temperature. Results are shown for the three glass compositions in Table I. At temperatures below 700°C, the resistance is low, because the conductor grains remain in direct contact, having not yet been wetted by the glass. The sudden increase in resistance at firing temperatures between 700° and 750°C is attributed to wetting and penetration of the glass between conductor particles. This stage of microstructure development has been observed by Nakano and Yamaguchi11 while conducting in situ resistance measurements in RuO₂-based resistors. Figure 1 shows that the TiO₂-containing compositions reach a resistivity after high-temperature firing that is two to three orders of magnitude greater than that of the composition prepared without TiO₂. A decrease in resistance with increasing firing temperature between 750° and 900°C is seen for some samples, the causes of which are considered later. Figure 2 illustrates the effect of adding 4.28 mol% TiO₂ to the glass of the resistivity and TCR, defined as

\[
TCR = \frac{R_{250°C} - R_{25°C}}{R_{25°C}} \times 10^6 \text{ (ppm/degree)}
\]

where \(R_{25°C}\) and \(R_{250°C}\) are the resistances at the indicated temperatures, in films fired at 850°C for 10 min and cooled at 50°C/min. Each pair of connected data points in Fig. 2 represents the change seen upon adding TiO₂ at a constant volume fraction of ruthenate conductor, with the volume fraction decreasing from left to right. Notice that in each case the resistivity increases by over two orders of magnitude, and the TCR decreases by over a factor of two, upon adding titania. Changes of nearly equal magnitude in these electrical characteristics are observed with as little as 1 mol% TiO₂.

IV. Microstructure and Grain Boundary Film Thickness

Transmission electron microscopy showed aggregates of ruthenate particles, each a few tens of nanometers in diameter, dispersed in the glass matrix (Fig. 3). No difference in microstructure at this scale was detectable between samples prepared with and without titania. At higher magnification, it becomes apparent that while particles are flocced, direct contact between grains does not occur. In all compositions, it was observed that most, if not all, grains are separated from their neighbors by a thin film of glass, as shown in Figs. 4–6. The thickness of the glass film was uniform along the length of many boundaries, including curved boundaries as seen in Figs. 4 and 5. We observed numerous instances of flattened contacts where grains approach one another, suggesting that liquid-phase sintering has occurred under van der Waals attraction alone. Two such contacts are denoted by the arrows in Figs. 5 and 6. Occasional

Table I. Glass Compositions Used in Pb,Ru,O₃ Thick-Film Resistors

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>65.27</td>
<td>62.48</td>
<td>59.76</td>
</tr>
<tr>
<td>PbO</td>
<td>33.60</td>
<td>32.16</td>
<td>30.76</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.13</td>
<td>1.08</td>
<td>1.03</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.00</td>
<td>4.28</td>
<td>8.44</td>
</tr>
</tbody>
</table>

Fig. 1. Resistance of thick-film resistors with and without titania additions, fired for 10 min at indicated temperature and cooled at 50°C/min: (0) no titania; (0) 4.28 mol% TiO₂ in glass phase; (0) 8.44 mol% TiO₂ in glass phase. Notice the 2–3 decades greater resistance of the titania-containing compositions after firing at temperatures above 750°C. The sharp increase in resistance at ~700°C is attributed to glass penetration of agglomerated ruthenate particles.

Fig. 2. Simultaneous change in resistivity and temperature coefficient of resistance (TCR) of thick-film resistors (fired at 850°C for 10 min and cooled at 50°C/min) upon adding 4.28 mol% TiO₂ to the alumino-silicate glass phase. Three pairs of data points are shown, each of which represents a constant ruthenate volume fraction (decreasing from left to right). In each instance the addition of TiO₂ causes a hundredfold increase in resistivity and more than a factor of two decrease in TCR.
cooperative alignment of particles was also seen (Fig. 6), which may result from the rotation of initially faceted particles to a closer approach under van der Waals attraction. Both faceted and equiaxed particles are seen in the starting ruthenate powder by TEM.

In denser clusters of grains, grain shape accommodation was widely seen (Figs. 4 and 5), similar to that often observed at larger scales in liquid-phase sintered materials. However, a microstructure of this appearance can also result when glass penetrates into a previously sintered aggregate, as seen in glass-penetration experiments on polycrystalline sintered aluminas.\textsuperscript{12,13} In the absence of sequential observations of microstructure development, it cannot yet be conclusively determined whether van der Waals sintering, glass penetration, or both are responsible for the grain shape accommodation. The decrease in resistivity at higher firing temperatures (Fig. 1) does suggest an increase in the contact area between conductor particles as firing proceeds, consistent with further contact flattening.

The bright-field STEM images shown in Figs. 4-6 are slightly underfocused in order to enhance contrast. The appearance of sharp contrast between the glass film and the crystal is largely due to Fresnel diffraction from the interfaces, and the apparent thickness of the film increases with defocus. Thus, good contrast necessarily means that the film thickness will be overestimated, as recently discussed by Cinibulk et al.\textsuperscript{14} Since the STEM images were all taken at nearly the same defocus (from the point of minimum contrast), a comparative measurement of differences in film thickness between samples was nonetheless meaningful. We furthermore observed that the apparent thickness of the grain boundary glass films in STEM bright-field imaging was not especially sensitive to the parallel position, the imaged thickness remained the same. This is in marked contrast to the extreme sensitivity of the observed glass film thickness to tilting in lattice fringe imaging (discussed below) and also explains why one is often able to image several boundary films simultaneously in STEM (Figs. 4 and 5).

For a more accurate measurement of the absolute glass film thickness, we used HREM imaging in which the termination of the lattice planes of crystalline particles at the amorphous glass film could be directly imaged (Figs. 7 and 8). While this method is potentially the most accurate means of measuring film thicknesses,\textsuperscript{14} it is not free of difficulties when applied to the current samples. Both the ruthenate grains and the glass exhibit electron beam damage after prolonged exposure (in particular, the glass phase separates and then crystallizes nanometer-scale particles). Thus, it was necessary to operate quickly and with minimum dose in both STEM and HREM to preserve the initial state of the specimen. The very fine particle size and susceptibility to beam damage precluded using electron microdiffraction to attain optimal crystallographical alignment. Moreover, it was difficult to orient grain boundary films precisely parallel to the electron beam, for several reasons. Unlike, for example, sintered Si$_3$N$_4,\textsuperscript{9,10,14}$ which contains a coarser anisometric grain structure in which most grain boundaries are parallel to a low index plane of one grain, in the present samples neither grain morphology nor electron diffraction could be effectively used to orient the grain boundary plane. The ruthenate grains are equiaxed and do not terminate on a low-index plane at the grain boundaries, but instead are rougher owing to atomic level steps (Figs. 7 and 8) and are more likely curved through the thickness. Furthermore, due to the fine grain size, the planar section of the grain boundary film sometimes did not extend throughout the entire foil thickness (of 20–40 nm), and glass could occasionally be seen overlapping the crystalline particles. On the other hand, larger-scale faceting, which obscures the meaning of precise measurements of film thickness in Al$_2$O$_3,\textsuperscript{11}$ was not found.
Fig. 5. Higher magnification STEM bright-field image taken at slight underfocus, showing the 1–2-nm-thick grain boundary films. Arrow indicates region of evident contact flattening where two grains have approached while maintaining a uniform glass film.

Fig. 6. Cooperative alignment of ruthenate particles in the glass matrix. Arrow indicates contact flattening where two particles approach.
These difficulties notwithstanding, numerous observations using both HREM and STEM established a characteristic range of glass film thickness for each composition and clearly showed differences in the film thickness between undoped and titania-doped compositions. Figure 7 shows HREM images of glassy grain boundary films in the sample with no titania (glass A in Table I), taken under conditions where the film was very nearly parallel to the electron beam. In the 20–40-nm range of foil thickness used, tenths of a degree of additional tilt results in perceptible narrowing of the gap between grains, consistent with a geometrical model wherein the error in projected width of an inclined film varies as \( t \tan \theta \), with \( t \) the foil thickness and \( \theta \) the angular deviation from parallelity. Careful observations of about 10 glass films showed thicknesses ranging from 0.8 to 1.1 nm, as illustrated by Fig. 7. In the sample containing 8.44 mol% TiO₂ (glass C in Table I) the grain boundary films were clearly thicker, as shown in the four HREM images in Fig. 8. These film thicknesses ranged from 1.2 to 1.6 nm. In STEM bright-field imaging, a larger number of films were measured, due to the imaging issues mentioned above, from which distributions in film thickness for samples A and C were obtained (Fig. 9). The apparent film thickness for each sample has an average value approximately 30% greater than that measured from HREM images, but the difference in thickness between the two samples is clear and is about equal in magnitude to that seen by HREM. These results taken together show that the thin glass film in the titania-doped composition (glass C) is ~0.5 nm thicker than that in the undoped composition.

V. Composition of Grain Boundary Films

Quantitative STEM microanalysis was conducted using a method which emphasizes the measurement of interfacial coverage, as opposed to local spatial distribution. As illustrated in Fig. 10, the composition of a well-defined volume containing the grain boundary plane is analyzed, scanning the STEM probe over an area \((l \times w)\) chosen to be sufficiently large relative to the electron beam width plus associated beam broadening that the incident electron intensity is essentially uniform across the volume. The volume is also kept small enough for a high sensitivity to interfacial segregation. The concentration of solute \( i \) per unit area of glass film is given by

\[
\Gamma_i \text{ (cm}^{-2}\text{)} = \frac{C_{\text{excess}}^i NV}{A} = C_{\text{excess}}^i Nw
\]

where \( C_{\text{excess}}^i \) is the excess of solute \( i \) observed in the grain boundary analysis, expressed as a molar concentration relative...
Fig. 9. Distribution in the apparent film thickness of glass films in samples with and without titania, measured from STEM bright-field images under slight underfocus conditions. As discussed in text, these results overestimate the absolute film thickness, but clearly show the greater average film thickness of the titania-containing samples.

to a reference lattice cation (e.g., Si/Ru and Ti/Ru), \( N \) is the site density of the lattice cation in the parent ruthenate crystal, \( V \) is the analyzed volume \((l \times w \times t)\), and \( A \) is the interfacial area \((l \times t)\). The scanned area used \((l \times w)\) was typically 17.0 nm \( \times \) 13.3 nm or 34.0 nm \( \times \) 26.6 nm, corresponding to a reduced-area raster in the HB5 STEM at magnifications of 2 million and 1 million, respectively. The foil thickness in the regions containing boundary films was in the range 20–40 nm, determined from the Ru X-ray count rate of the adjacent grains. In this thickness range, the radius of the STEM probe plus the half-width of beam broadening, estimated (conservatively) from the single scattering model, is 1.5–2 nm. Thus one can imagine the actual analyzed volume as the ideal volume in Fig. 10 plus an additional “skirt” of \(-2\)-nm width.

Measurements of interfacial segregation are often conducted in STEM, using spot analyses with a fixed probe or by integrating under a concentration profile obtained by stepping the electron probe across an interface. The observed results in both cases are a convolution of the beam-analyzed volume and the solute profile, often neither of which are precisely known (see Refs. 15–18 and references therein for more detailed discussion). In particular, the extent of beam broadening in nanoprobe STEM remains under dispute. The principal advantage of the present microanalysis is the attainment of a uniform electron intensity across a well-defined volume, which allows the coverage to be determined without assumptions regarding either the beam intensity distribution or the solute distribution. While spatial information is sacrificed, that is usually available by other methods. A further advantage is that beam damage is lessened by distributing the electron dose over a greater area. Coverage-based segregation measurements of this kind have recently been used by Ikeda et al. to quantify space-charge segregation parameters at TiO, grain boundaries and by Terwilliger and Chiang to characterize grain-size-dependent solute segregation at very fine grain sizes.

The excess of Si and Ti in the grain boundary film was obtained by analyzing volumes as shown in Fig. 10 and subtracting the background Si and Ti counts from similar analyses conducted in the adjacent grains (assumed to be of equal thickness to the grain boundary region). Coincidentally, the mass absorption coefficients of the ruthenate grains and the glass for the X-ray lines of interest are very similar. Since the experimental range of thickness is well below the “thin film limit” for the elemental ratios which were quantified, no absorption corrections were necessary. Two standards of known composition, the starting glass frit and the ruthenate grains in the samples themselves, were used to determine calibration factors for quantification of the X-ray data (the so-called \( k \)-factors in the Cliff-Lorimer method).

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**Fig. 10.** STEM-analyzed volume containing the grain boundary plane, defined by the beam-rastered area, used for measurement of solute coverage.
The energy-dispersive X-ray spectrum from a giant boundary analysis (with glass C), as illustrated in Fig. 11, showing a strongly increased Ti signal and moderately increased Si compared to (B), a similar analysis performed within the grain. Enrichment of Ti is also detected in (C), an analysis of the interface between free ruthenate particles and the glass.

The excesses of Si and Ti in the grain boundary film, $\Gamma_\text{Si}$ and $\Gamma_\text{Ti}$, are shown in Table II for samples A and C. The results are expressed both in terms of atom density (no./cm$^2$) and as equivalent monolayers of SiO$_2$ and TiO$_2$. The table also lists the sum $(\Gamma_\text{Si}/N_\text{Si}) + (\Gamma_\text{Ti}/N_\text{Ti})$, which may be considered to be the "chemical thickness" of the films. These would be the nominal widths if the films contained only SiO$_2$ and TiO$_2$, at their bulk molar volumes and no Si or Ti was in the adjoining crystals. In each case, several monolayers of coverage are associated with the glass film. In sample A, containing no Ti addition, the average coverage is 2.90 SiO$_2$ monolayers. In sample C, the Si coverage is slightly reduced, but well over a monolayer of Ti segregation is also present. The total coverage including Si and Ti is greater than in sample A. In both samples the total coverage, neglecting any possible Pb content, corresponds surprisingly well with the observed boundary film thicknesses of 0.8–1.1 and 1.2–1.6 nm, respectively, for samples A and C.

Isolated observations of RuO$_2$-containing resistors suggest that the distribution in film thickness and composition is not always as uniform as those shown here. In samples of similar glass composition, loading fraction, and processing treatment, measurements of boundary film composition showed a broad distribution ranging from virtually no Si segregation to thick boundary layers of ~8 monolayers. It is not yet clear whether the behavior of this system intrinsically differs from that of Pb,Ru$_3$O$_6$ resistors or whether the approach to equilibrium in the Ru$_3$O$_6$ resistors is simply slower, as suggested by other properties measurements.

From the results represented in Table II, the Ti/Si molar ratios of boundary films in sample C are plotted in Fig. 12. In all boundary films, the Ti/Si ratio exceeds that of the starting glass (shown as the horizontal line) by at least a factor of two, in a number of cases the Ti/Si ratio approaches or exceeds unity. The glass matrix of the resistors was also analyzed for compositional changes relative to the starting glass frit. The high level of Ti enrichment at grain boundaries, and also at particle surfaces, apparently depletes the matrix glass of Ti, as seen in Fig. 13. Although the results have not been quantified, strong adsorption of Ti to the free particle–glass interfaces is evident by comparing Figs. 11(C) and (B) and appreciating that the Ti signal from the glass itself would be much smaller (Fig. 13) than it is in the spectrum in Fig. 11(C). Thus, a strong adsorption of Ti to ruthenate interfaces from the surrounding glass accompanies the increase in grain boundary film thickness shown in Figs. 7–9 and the change in electrical properties shown in Fig. 1.

### Table II. Excess Concentration of Si and Ti in Grain Boundary Films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration ($\times 10^{10}$ cm$^{-2}$)</th>
<th>Concentration (equivalent monolayers)</th>
<th>Chemical thickness, $\Delta L$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Gamma_{\text{Si}}$</td>
<td>$\Gamma_{\text{Ti}}$</td>
<td>$\Gamma_{\text{Si}}$</td>
</tr>
<tr>
<td>A</td>
<td>2.10 ± 0.74</td>
<td>1.77 ± 0.25</td>
<td>2.45 ± 0.86</td>
</tr>
<tr>
<td>C</td>
<td>2.27 ± 0.89</td>
<td>1.54 ± 0.33</td>
<td>2.65 ± 1.04</td>
</tr>
</tbody>
</table>

*Notation and units: $\Gamma$ = no./area, $\Gamma/N^0$ = no./surface sites, $\Gamma/N = (\Gamma/N^0) \times N^{-1/3}$ = nominal width. Relative to the average cation site density per unit area, given by $N^0$ where $N$ is the cation site density in the bulk. One monolayer is equivalent to 8.56 $\times 10^{10}$ cm$^{-2}$ for SiO$_2$ and 1.01 $\times 10^{11}$ cm$^{-2}$ for TiO$_2$. The summation in the last column neglects any Al, Pb, or Ru in the film.
Strong adsorption of Ti to the grain boundary film in sample C (fired at 850°C for 10 min) is shown by this plot of the Ti/Si molar ratio of the glass film composition. Each bar represents a measurement on one grain boundary film. The Ti/Si ratio of the starting glass is shown by the horizontal line.

Corresponding to the Ti enrichment at grain boundary films and particle surfaces is a depletion of the Ti/Si ratio in the glass, shown here for several analyzed regions in the matrix glass.

VI. General Discussion

We first address the electrical conductivity of the resistors, which depends upon the density of grain-to-grain contacts within the particle network and the resistance of these contacts. For samples without Ti, the analytical and structural information suggests that the ubiquitous, 1-nm intergranular film is largely SiO₂ with minor Al₂O₃. The concentration of multivalent ions, likely percent levels of Ru, necessary to yield sufficient conductance (tunneling) across the film has not been established. There are several likely causes of the large increase in electrical resistivity which occurs upon adding titania (Fig. 1). Clearly, by simple tunneling, the increase in the glass film thickness alone (all else being constant) will increase electrical resistivity, since the tunneling conductance across a thin insulating film decreases exponentially with increasing separation. However, local chemical changes may have an equal or greater influence on the grain-to-grain conductivity in thick-film resistors, in light of the generally accepted resonance tunneling conduction model of Pike and Seager. With the level of microanalytical resolution used in the present work, it cannot be conclusively determined whether the titanium enrichment occurs in (1) the glass film itself, (2) the very surface layer of the crystalline ruthenate particles, or (3) both regions. The rather good correspondence between the excesses of Si and Ti (Table II) and the glass film thicknesses suggests that the Ti enrichment occurs in the film itself, although some diffusive incorporation of Ti in the surface layers of the grains also seems likely. A decrease in the grain-to-grain conductivity is expected in both instances, for the following reasons.

An increase in the titanium concentration within the glass film will likely lower the local ruthenium solubility. Separate experiments by Silverman²² have shown that the solubility of ruthenium in bulk lead aluminosilicate glass is suppressed by the addition of titania. Representative results are shown in Fig. 14 for the three glass compositions. The ruthenium concentration was determined by sputtered neutrals mass spectrometry (SNMS) after annealing the glass in contact with sintered Pb,RuO₃ compacts at 850°C for 4 h. In each instance, a significant decrease in the ruthenium solubility is observed with just 1.5 wt% titania. We therefore expect the ruthenium solubility in the film between particles to be decreased upon segregation of titania, which in turn should lower the resonance tunneling conductance.

Titanium substitution at the surfaces of the ruthenate grains would also result in a more resistive surface layer. Bulk substitution of titania in lead ruthenate is known to raise the resistivity. In glasses of related composition to those used in this study, PbTiO₃ precipitation has been seen when titania and lead oxide activities are increased. While discrete precipitation does not occur in the present resistors, epitaxial growth of a titania-enriched solid solution at the glass–particle interface and interdiffusion of titanium and ruthenium cannot be ruled out. Fixed-probe STEM analyses show that any enrichment of this type is confined to the first nanometer or so of the surface. The effective width of the tunneling barrier between conductor grains may nonetheless increase, causing a decrease in grain-to-grain conductivity. Further work is necessary to clarify the relative roles of these effects on the electrical properties.

With respect to the study of equilibrium glass films, the present experimental configuration of mobile particles within a comparatively large volume of glass provides two particular advantages. One is the absence of the applied or capillary pressures normally present in hot-pressed or liquid-phase sintered materials, where the liquid fraction is typically small. A second, pertaining to the influence of secondary additives, is the presence of a large liquid reservoir, which buffers the activities of components which can be equilibrated with the thin glass films.

The microstructural observations are a clear, if not the first by TEM, observation of contact flattening by solution/precipitation solely in response to long-range interparticle forces, which may be termed van der Waals sintering. It may be that, in some instances, there are preexistent flats on the particles and the particles rotate upon initial approach in response to the attractive forces. This would immediately provide flats between particles, as suggested in Fig. 6. In other instances, there may be necks with grain boundaries within prior agglomerates, which are subsequently penetrated by liquid. Indeed, both processes may have been active. This would reinforce the notion that the equilibrium condition is the formation of flats between particles with an intervening film and that these two mechanisms (squeezing out liquid and penetrating dry boundaries) simply reflect approach from opposite directions. In either event, and

However, some ambiguity remains regarding the degree to which the behavior in Ti-containing samples reflects nonequilibrium effects such as segregation during cooling.
especially for the approach of eqauxed particles, there has almost certainly been some solution/perturbation to further adjust the particle phases. This is strongly suggested by the existence of denser regions, e.g., Figs. 4 or 7, wherein several neighbors fit together quite well, but with nanometer film between virtually all grains. This is likely the equilibrium toward which most flocs are tending. (The increase in contact area accompanying flattening is also suggested by the reduction of resistivity, especially with Ti present, once initial wetting by the glass has occurred, Fig. 1.)

The formation of a stable glass boundary film may be conceived in two ways. First, it may be considered in terms of a force balance between attractive forces, presumably dominantly van der Waals forces, and disjoining forces, which include the primary adsorption force causing the first layers (analogous to solvation forces) and secondary forces, such as the steric or electrostatic forces proposed by Clarke. Due to the excess of liquid, the force balance in the present case is unambiguously free of capillary forces, which normally drive densification by liquid-phase sintering. Note, however, that the formation of an equilibrium film wherein the thickness is dictated by local chemical forces is essentially equivalent to the condition that the liquid is not fully wetting between grains. That is, the dihedral angle at the grain boundary—liquid junction is finite. Instead, the intergranular film is an adsorbate layer in equilibrium with the second-phase glass which exists in the large interparticle regions and possibly at three or four grain junctions. If the liquid were fully wetting, no limit to the number of adsorbed liquid layers would exist, and the particles should separate widely rather than expelling some liquid.

Although siliceous films have been observed between a variety of ceramic materials, the nanometer-scale thicknesses observed here are most like those found in Si,N with various additives. For Si,N, it has often been supposed, but not proved, that capillary forces are unimportant. For the present case, a more detailed comparison between theory and experiment requires additional information. Since the ruthenate is a metallic conductor, the Hamaker constant cannot be estimated using dielectric and optical constants; it is necessary to perform an integration over frequency of the high-frequency dielectric properties of the ruthenate and the glass, in accordance with Lifshitz theory. The specific form and length scale of the steric repulsion, as well as any electrostatic repulsion, can only be speculated upon at present; the glass films may contain significant amounts of aluminum and lead in addition to silicon. For Si,N, it has been shown that incorporation of various cations can change the boundary film thicknesses within the range of 0.5–1.5 nm. Recently, to explain monomolecular changes in thickness, it has been argued that incorporation of submonolayer levels of Ca can both reduce the steric forces by breaking up the silicate network and enhance the double-layer repulsion.

For the Ti-containing materials, this work shows an unequivocal, again possibly first, demonstration of differing composition between a grain boundary film and the bulk glass from which it is supposed to originate. A simple explanation is that the titanium is preferentially adsorbed within the film and perhaps onto the ruthenate particle surface with more or less local order. Thus, the entire film represents equilibrium, multilayer adsorption, which is not necessarily uniform in composition across the thickness. Although this origin is conceived in terms of isothermal adsorption, no doubt some adjustment occurs upon cooling. A more complex argument is that Ti has begun to interdiffuse into the ruthenate particles, giving the appearance of nonequilibrium segregation, or that the Ti was virtually precipitating on cooling. However, were the initial film of the same composition as the bulk glass, there would not be enough Ti in the film region to plate out laterally, and so diffusion from the edge would have been required. That would not only require more time, but would have a diminished driving force relative to simply plating out the Ti on the regions of particle directly exposed to the multigrain junctions and larger pools of glass-forming liquid. The simpler argument seems more appealing, but must be afirmed by further experimentation. (Preliminary observations show that the Ti/Si ratio within boundary films is similar or higher after firing at lower temperatures, Table II; this is more consistent with an adsorption mechanism.)

An increase in the equilibrium number of adsorbed layers (Table II) upon the addition of titania is consonant with the observed increase in the glass film thickness, assuming that the titania is not present as a discrete crystalline layer (for which no evidence appears in the HRTEM images, Fig. 8). Mechanistically, the adsorption of titania may modify the van der Waals interaction, the steric term, and any electrostatic repulsion. The large change in composition of the glass film must be accompanied by a change in its structural character. Precursory studies indicate that titania enters silica glass in fourfold coordination at lower concentrations and in sixfold coordination at higher concentrations, if it is distributed through the thickness, incorporation as octahedrally coordinated Ti is likely at the high Ti/Si ratios of these glass films (Table II and Fig. 12), which could alter the range of the steric repulsion relative to the titania-free glass. It is also possible that adsorption of Ti at the ruthenate—glass interface causes an electrical double-layer repulsion which is in part responsible for the increase in film thickness.

A strong segregation of titania may also alter the van der Waals interaction. A simple view is that the titania-substituted glass film, which undoubtedly has a higher static dielectric constant and refractive index than the glass film in the titania-free case, will have a lower value of the Hamaker constant when separating the ruthenate particles. However, if the local structure of the contact flats is better represented by a Ti-doped glass layer, adjacent to which are Ti-substituted pyrochlore layers on the surface of the ruthenate particles, the Hamaker constant of this multilayer assembly in which all layers are of similar thickness will be strongly influenced by the dielectric properties of the individual layers. In the absence of detailed information regarding local composition and dielectric properties, the sign—much less the magnitude—of any such changes in Hamaker constant seems difficult to determine at present. Additional studies are clearly necessary to distinguish between these various possible influences on the equilibrium thickness.

As a final comment, it is pointed out that were it not for the flocculation of particles and the resultant uniformity of grain contact conductance afforded by an equilibrium separation, the properties of thick-film resistors would in all likelihood be even more process and volume fraction dependent than they are. For the case of complete wetting, i.e., a net repulsive interaction leading to grain deflocculation, the film thickness and therefore the resistance per contact would be time and volume fraction dependent (presuming an initial state of agglomerated conductor particles). Among other effects, one would expect the resistance to increase even more sharply upon initial glass penetration and to reach much higher values than it currently does (Fig. 1). The net resistance of the composite after some equilibration would then be a very sharp function of conductor volume fraction, since grains will separate as much as capillary forces allow, and a higher conductor fraction would be necessary to achieve conductivities comparable to the flocced case. In addition, relatively slow changes in the number of contacts per particle may be imparted by the microstructural stability which results from attractive interparticle forces leading to flocculation. Thus, the relative stability and reproducibility of thick-film resistor properties may be a fortuitous consequence of the formation of an equilibrium glass film.

VII. Summary

We find microstructural and microchemical evidence that the properties of these thick-film resistors are intimately tied to the thickness, composition, and area of the nanometer-thick glass film separating conductor particles. High-resolution TEM and STEM show that nanometer-scale ruthenate particles remain
flocced in a glass matrix, but do not come into direct contact, being separated by a uniform glass film. The glass film thickness is 0.8–1.1 nm in resistors prepared without titania and increases to 1.2–1.6 nm upon adding 8.44% titania to the silicate glass. Although there are no capillary forces, the local interparticle attraction drives a flattening of the particles in the regions of near contact. The observations are consistent with an equilibrium separation being reached between particles when van der Waals and other attractive forces are balanced by repulsive forces likely involving steric and electrostatic elements.

Using a novel STEM microanalysis method, the excesses of silica and titania in the glass films were shown to be equivalent to several monolayers and are essentially consistent with the glass film thicknesses. In addition, a strong segregation of titania to the glass film and to particle–glass interfaces has been observed. The simplest interpretation of these observations is that the glass films are multilayer adsorbates in equilibrium with, but not identical to, the bulk liquid.

The hundredfold increase in resistivity observed upon adding titania is attributed to the increase in film thickness, combined with a decrease in ruthenium ion solubility in the thin glass film, and possibly the formation of a thin ion-exchanged or epitaxially grown titanita-enriched insulating layer of subnanometer thickness on ruthenate particle surfaces.

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