Strain modulation of transport criticality in RuO$_2$-based thick-film resistors

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We show that in RuO$_2$–glass composites the nonuniversal resistivity exponent can be modulated by an applied mechanical strain, signaled by a logarithmic divergence of the piezoresistive response at the percolation threshold. We interpret this phenomenon as being due to a tunneling-distance dependence of the transport exponent, supporting therefore a theory of transport nonuniversality proposed some years ago. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1835996]

The study of transport properties of thick-film resistors (TFRs) is of crucial interest for the improvement of sensor devices based on thick-film technology.[1] In particular, the understanding of the interplay between microscopic properties, dc transport, and the piezoresistive response have important implications in the fabrication of robust force and pressure sensor devices.

The most common thick-film piezoresistors are composed by submicron conducting RuO$_2$ grains (or also Pb$_2$Ru$_2$O$_6$ and Bi$_2$Ru$_2$O$_7$) dispersed in an insulating host usually given by a lead-borosilicate glass.[2] The transport properties of TFRs are governed by two main ingredients. On the microscopic level, electron transport is via quantum tunneling through nanometer-thick films of glass separating two neighboring conducting particles,[3–5] while on macroscopic scale transport displays percolation-like behavior,[6,7] with resistivity ρ following a power-law of the form:

$$\rho \simeq \rho_0 (x - x_c)^{-t}, \tag{1}$$

where ρ_0 is a material-dependent prefactor, x_c is the percolation critical volume fraction below which ρ goes to infinity, and t is the dc transport critical exponent. According to the standard theory of transport percolation,[8,9] the microscopic properties, such as the intergrain tunneling in TFRs, do affect the values of ρ_0 and x_c, but should leave the critical exponent t unaltered and equal to the universal value $t_0 \simeq 2.0$ valid for three-dimensional disordered composites.[10]

In contrast to this view, the critical exponent of TFRs has been often found to be larger than t_0,[7,11] up to about $t \simeq 7.0$.[6] Despite the fact that such universality breakdown has been repeatedly reported for decades, and that it has been observed also for systems different from TFRs,[9] a common view regarding its origin is still lacking.[12] We show in this letter that breakdown of universality ($t > t_0$) in RuO$_2$-based TFRs is accompanied by a logarithmic divergence of the piezoresistive response at the percolation threshold x_c, providing evidence that the transport critical exponent t depends upon the mean intergrain tunneling distance, as proposed a few years ago in Ref. 13.

Our samples were prepared starting with a lead-borosilicate glass powder [PbO(75 wt %)-B$_2$O$_3$(10 wt %)–

SiO$_2$(15 wt % wt)]+2% of Al$_2$O$_3$ of 1–5 μm grain sizes. Differential scanning calorimetry measurements indicated a glass softening temperature of about 430 °C and absence of crystallization. TFRs were then fabricated by mixing two series of RuO$_2$ powders with 40 and 400 nm grain sizes with the glass particles together with a vehicle of terpineol and ethyl cellulose. The pastes were screen printed on Al$_2$O$_3$ substrates with gold electrical contacts and fired for 15 min at temperatures T_f (see Table I) higher than the glass softening temperature. The resulting films were about 10 μm thick and appeared dense and compact. The quality of the films were confirmed by scanning electron microscope analyses and x-ray measurements did not reveal other peaks in addition to those of RuO$_2$, confirming the absence of devitrification. Several resistivity measurements were taken over eight different samples for each RuO$_2$ volume fraction value.

In Fig. 1(a) we report the ln–ln plot of the room temperature resistivity ρ measured for four different series of TFRs (see Table I) as functions of the RuO$_2$ volume concentration x. The solid lines are fits to Eq. (1) and the best-fit parameters ρ_0, x_c, and t are reported in Table I. The resistivity data follow the power law behavior of Eq. (1) with exponent t close to the universal value $t_0 \simeq 2.0$ for the A1 series ($t = 2.15 \pm 0.06$) or markedly nonuniversal as for the A2, B1, and B2 series ($t > 3$).

The effect of an applied strain ε on transport is obtained by recording the piezoresistive response, i.e., the relative resistivity change $\Delta\rho/\rho$ upon applied mechanical strain, by cantilever bar measurements. The RuO$_2$–glass pastes were screen printed on Al$_2$O$_3$ cantilever bars clamped at one end. Substrate tensile strains $\varepsilon > 0$ along the main cantilever axis were induced by applying different known weights on the free end of the cantilever. Compressive strains ($\varepsilon < 0$) were obtained by weights applied on the opposite face of the cantilever. In the whole range of applied strains (up to about $|\varepsilon| = 4.5 \times 10^{-4}$), $\Delta\rho/\rho$ changed linearly and symmetrically with ε [see inset of Fig. 1(b)], indicating the absence of false strain responses due to elastic faults of the resistive films.[14] The corresponding piezoresistive factors $\Gamma = d \ln(\rho)/d\varepsilon$ extracted from the slopes of the linear fits of $\Delta\rho/\rho$ *vs* ε are plotted in Fig. 1(b) for the four TFRs series of Fig. 1(a) as a function of x. With the exception of the A1 series, whose piezoresistive response is almost constant, Γ displays a

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TABLE I. Label legend of the various samples used in this work with fitting parameters of Eqs. (1) and (4).

Label	RuO_2 grain size (nm)	$T_f °C$	x_c	$\ln(\rho_0/\Omega\,m)$	t	Γ_0	$dt/d\varepsilon$
A1	400	525	0.0745	-11.1 ± 0.3	2.15 ± 0.06	5.5 ± 1.5	-0.2 ± 0.4
A2	400	600	0.0670	-14.2 ± 0.2	3.84 ± 0.06	-8.8 ± 1.6	5.4 ± 0.5
B1	40	550	0.0626	-14.3 ± 0.5	3.17 ± 0.16	-15.3 ± 3	8.7 ± 0.9
B2	40	600	0.0525	-13.7 ± 0.7	3.15 ± 0.17	-19.3 ± 2.4	11.0 ± 0.7

strong dependence upon x and tends to diverge as x approaches to the same critical concentrations x_c at which ρ goes to infinity (see Table I), confirming an earlier finding.[11]

In order to clarify the origin of the piezoresistive divergence, let us consider Eq. (1) and differentiate it with respect to ε:

$$\frac{d\ln(\rho)}{d\varepsilon} = \Gamma = \Gamma_0 - \frac{d}{d\varepsilon}[t\ln(x-x_c)]. \qquad (2)$$

Since $\Gamma_0 = d\ln(\rho_0)/d\varepsilon$ is a constant independent of x, all the x dependence of Γ must come from the last term of Eq. (2). Let us assume for the moment that t is independent of ε. According to Ref. 11, the divergence of Γ at x_c stems from $dx/d\varepsilon$ being nonzero. This has been argued to be trigged by the different values of the elastic moduli of RuO_2, B_{RuO_2}, and of the embedding glass, B_{glass}, which lead to $dx/d\varepsilon \simeq -Ax$ where $A \propto 1 - B_{glass}/B_{RuO_2}$. Since $B_{RuO_2} \simeq 270$ GPa and $B_{glass} \simeq 40-80$ GPa, A is expected to be different from zero and positive. If this reasoning held true, Eq. (2) would then reduce to[11]

$$\Gamma = \Gamma_0 + At\frac{x}{x-x_c} = K_1 + \frac{K_2}{x-x_c}, \qquad (3)$$

where we have defined $K_1 = \Gamma_0 + At$ and $K_2 = Atx_c$. In Fig. 2(a) we have replotted the Γ values of Fig. 1(b) as a function of $1/(x-x_c)$ with the same values of the critical concentrations x_c extracted from the resistivity data. According to Eq. (3), Γ should then follow a straight line as a function of $1/(x-x_c)$ which, although being rather correct for the A2 series, is manifestly not true for the B1 and B2 series. In addition, the A1 series remains almost constant, implying that $A=0$ for

this case, contrary to the premises of Ref. 11.

Let us stress that, actually, x is just as an operative estimate of the concentration p of intergrain tunneling junctions with finite resistances present in the sample.[8,9] Hence, instead of following the arguments of Ref. 11, one could argue more correctly that $dx/d\varepsilon \simeq (dx/dp)(dp/d\varepsilon)$. Also in this case however one would expect a $1/(x-x_c)$ divergence which we have seen to lead to poor fits for our data. Furthermore, the values of the applied strains in our measurements are so small ($|\varepsilon| < 4.5 \times 10^{-4}$) that their effect is that of changing the value of the tunneling resistances without affecting their concentration p, so that one realistically expects that $dp/d\varepsilon = 0$.

Let us reconsider now Eq. (2). If $dp/d\varepsilon = 0$, then the only way to have an x dependence of Γ is to allow the transport exponent t to have nonvanishing derivative. In this way Eq. (2) reduces to

$$\Gamma = \Gamma_0 + \frac{dt}{d\varepsilon}\ln(x-x_c), \qquad (4)$$

which predicts a *logarithmic* divergence of Γ at x_c. In Fig. 2(b) we plot the piezoresistive data of Fig. 1(b) as a function of $\ln(x-x_c)$. Now, contrary to the previous fit with the $1/(x-x_c)$ divergence [Fig. 2(a)], all the series A1, …,B2 follow the logarithmic fit with rather good agreement in the entire range of x values. The fitting values with Eq. (4), solid lines, are reported in Table I. Furthermore, the x-independence of the A1 series can now be explained by noticing that A1 is the only series whose transport exponent displays universal-like value ($t \simeq 2.15 \pm 0.06$), leading us to infer that $dt/d\varepsilon = 0$ because in this case $t = t_0$.

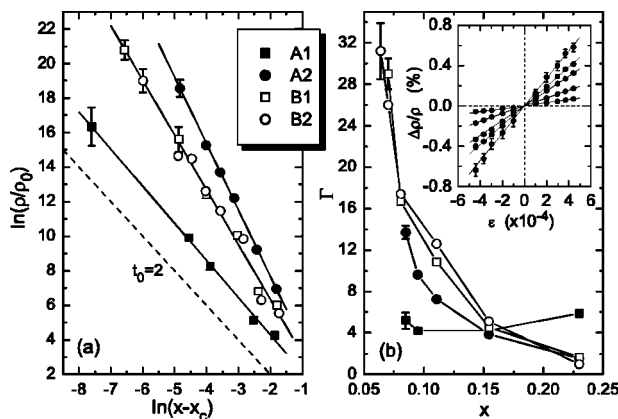Let us discuss now what this finding implies in terms of the microscopic origin of nonuniversality. The main effect of

FIG. 1. (a) ln–ln plot of resistivity ρ as a function of RuO_2 volume concentration x for four different series of TFRs with fits to Eq. (1) shown by solid lines. The corresponding values of ρ_0, x_c, and t are reported in Table I. The dashed line has slope $t_0 = 2$ corresponding to universal behavior of transport. (b) Isotropic piezoresistivity response $\Gamma = d\ln(\rho)/d\varepsilon$ as a function of x for the TFRs series of (a). Inset: resistivity variation $\Delta\rho/\rho$ of the A2 series as a function of strain ε and for different RuO_2 volume concentrations.
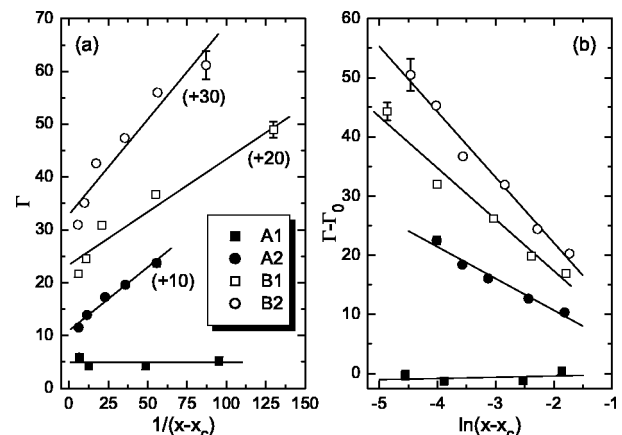

FIG. 2. (a) Piezoresistive factor Γ plotted as a function of $1/(x-x_c)$ (symbols) with fits to Eq. (3) (lines). For clarity, the data of different series have been shifted vertically by the amounts reported in brackets. (b) $\Gamma-\Gamma_0$ as a function of $\ln(x-x_c)$ and fits (solid lines) to Eq. (4). The fit parameters $dt/d\varepsilon$ and Γ_0 are reported in Table I.

the applied strain on the microscopic properties of RuO_2–glass composites is that of changing the mean intergrain tunneling distance a, $a \to a(1+\varepsilon)$, leading to a variation of the microscopic tunneling resistances. Hence, in order to have $dt/d\varepsilon \neq 0$, the transport exponent itself must depend on a. A scenario of this kind was proposed by Balberg a few years ago in his tunneling-percolation theory of nonuniversality in carbon-black–polymer composites,[13] recently adapted to TFRs.[15] According to this theory, when the distribution function of the tunneling distance d between two neighboring grains decays with d much slower than the tunneling decay $\exp(-2d/\xi)$, where ξ is the localization length, then the distribution function $h(r)$ of the intergrain tunneling resistances r develops a power-law tail such that $h(r) \propto r^{-1-\xi/2a}$ for $r \to \infty$. It is well known[16] that such power-law diverging distribution functions lead to a breakdown of transport universality with critical exponent given by[17]

$$
t = \begin{cases} t_0 & \text{if } \nu + 2/\xi < t_0 \\ \nu + 2a/\xi & \text{if } \nu + 2a/\xi > t_0, \end{cases} \tag{5}
$$

where $t_0 \simeq 2.0$ is the universal transport exponent and $\nu \simeq 0.88$ is the three-dimensional correlation-length exponent. In view of Eq. (5), the term which multiplies the logarithm in Eq. (4) is $dt/d\varepsilon = 2a/\xi > 0$ when t is given by the second line of Eq. (5) or $dt/d\varepsilon = 0$ when $t = t_0$. Note however that in RuO_2-based TFRs the large difference between the bulk moduli of RuO_2 and of the glass leads to local strain variations so that the $dt/d\varepsilon$ values of A2, B1, and B2 reported in Table I are not simply equal to $2a/\xi$ but incorporate also the effect of the strain heterogeneity.

The tunneling-percolation picture is able to explain also the change of sign of Γ_0 which from positive for the universal series A1 becomes negative for the nonuniversal ones (A2,B1 and B2, see Table I). In fact an effective medium calculation with the tunneling-percolation distribution function $h(r) \propto r^{-1-\xi/2a}$ leads to $\Gamma_0 > 0$ when $t = t_0$ and $\Gamma_0 < 0$ when $t > t_0$,[18] in agreement with the experimental results (see Table I).

In summary, we have shown that the piezoresistive response of disordered RuO_2–glass composites has a logarithmic divergence at the percolation threshold when dc transport is nonuniversal. A coherent interpretation of this result calls into play a mean tunneling distance dependence of the resistivity exponent, in agreement with a tunneling-percolation origin of nonuniversality proposed some time ago.[13] Such mechanism of universality breakdown could apply also to other materials for which transport is governed by tunneling such as carbon-black–polymer composites, and experiments on their piezoresistive response could confirm such conjecture.

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