Nature of Single-Localized-Electron States Derived from Tunneling Measurements

C. T. Rogers and R. A. Buhrman
School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853

(Received 14 June 1985)

We have used the resistance fluctuations of very small-area ($0.03\ \mu m^2 < A < 2\mu m^2$) tunnel junctions to study the population kinetics of *individual* localized electron traps in the tunnel-barrier material. We present evidence that the rate-limiting kinetic step for charge fluctuations above ~ 15 K is thermal activation between two low-energy ionic configurations. Below 15 K the transitions between these potential wells appear to be dominated by direct configurational tunneling of the ions forming the trap.

PACS numbers: 72.70.+m, 05.40.+j, 71.50.+t, 73.40.Rw

Over the last decade, major advances in the techniques of microlithography have made it possible to construct solid-state systems of exceedingly small physical dimensions. When a system's linear dimensions reach the submicron region, certain aspects of its behavior begin to reflect the detailed atomic structure of the device rather than the collective or average material properties. In this paper, we describe how the resistance fluctuations of very small-area tunnel junctions are used to obtain detailed information about the population kinetics of single electronic traps in the amorphous tunnel-barrier material. Our primary result is that the trapping kinetics is governed by transitions between two nearly energy-equivalent, but charge-inequivalent, local ionic configurations. We establish this result by resistance noise measurements of the high-temperature, thermally activated, single-state electron-capture and -escape processes, coupled with a clear observation of a transition from thermally activated behavior to a low-temperature trapping process governed by reversible ionic configurational tunneling. These data constitute the first direct observation of *individual* two-well tunneling systems in an amorphous material, as well as the first direct indication that configurational tunneling is an essential factor in electron trapping in amorphous materials at low temperatures.

Recently,[1] we reported the observation of single Lorentzian terms in the low-frequency voltage spectrum $S_v(f)$ of very small-area ($0.03\ \mu m^2 < A < 2\ \mu m^2$) current-biased Nb-Nb$_2O_5$-PbBi tunnel junctions. These voltage fluctuations arise directly from fluctuations in the tunnel-barrier resistance. For large devices S_v is roughly $\sim 1/f$, but for small devices for $T < \sim 100$ K the noise in our bandwidth from 1 Hz to 25.6 kHz is resolved into a sum of only a few[2,3] distinct Lorentzian noise spectra, each due to a discrete resistance fluctuation. At any given bias point and temperature, each device displays its own particular spectrum of essentially independent Lorentzians. Thus, the resistance power spectrum S_R is largely a sum of terms of the form

$$S_1\tau_{\rm eff}/(1+\omega^2\tau_{\rm eff}^2), \qquad (1)$$

where S_1 is the resistance variance due to that particular Lorentzian.

These discrete resistance changes are due to the slow charging and discharging of single localized electronic trap states in the barrier material.[1,2] When such a state changes its charge, the local electrostatic field changes the local barrier to electron tunneling and thus changes the tunnel-junction resistance, resulting in a single-Lorentzian spectrum for that fluctuation. Because our devices are so small, even single electronic charges can have an easily measured effect.[2] This phenomenon provides an excellent means for studying the population-fluctuation kinetics of single trap states by careful measurements of the Lorentzian noise properties.

The resistance fluctuations occur by a two-rate process[1,2]: Each fluctuation spends a certain mean time τ_1 in a high-resistance state and a mean time τ_2 in a low-resistance state, yielding a phase-random square wave. This aspect of the tunnel-junction noise behavior is easily verified by direct observation of the time record of the tunneling resistance. Machlup[3] described such "random telegraph noise" processes and showed that the power spectrum S_R is indeed a Lorentzian in which the total integrated power S_1 and effective rate $1/\tau_{\rm eff}$ are related to the two fundamental rates $1/\tau_1$ and $1/\tau_2$ by

$$1/\tau_{\rm eff} = 1/\tau_1 + 1/\tau_2 \qquad S_1 = S_0\tau_{\rm eff}/(\tau_1+\tau_2), \qquad (2)$$

where S_0 is the square of the total resistance change between the high- and low-resistance states. With these two relations we can convert a measured Lorentzian knee frequency and power into the trap emission and capture rates $1/\tau_1$ and $1/\tau_2$. By making such measurements over a wide range of temperature and voltage, we have been able to gain considerable insight into the microscopic nature of the trapping process.

Above ~ 15 K, $1/\tau_{\rm eff}$ generally increases with T in a thermally activated manner.[1] The behavior of the Lorentzian noise power S_1 is typically somewhat more complicated. We have found that interactions between nearby trap sites can cause significant effects on S_1

whenever their respective $1/\tau_{\text{eff}}$ become comparable. We will describe these interaction effects in detail elsewhere. However, the qualitative result is that S_1 invariably changes much more slowly with T than does $1/\tau_{\text{eff}}$. Inspection of Eqs. (2) reveals that this behavior arises when both $1/\tau_1$ and $1/\tau_2$ increase rapidly with T but in a manner which keeps their ratio nearly fixed. In some instances we find that single Lorentzians can be followed over a wide temperature range without significant interaction effects occurring in our bandwidth. Figure 1 shows such a case. We can use these data to obtain more detailed information about the trap-charge fluctuation kinetics. Since $1/\tau_{\text{eff}}$ is thermally activated and the ratio of the two rates is nearly fixed, we conclude that both rates are activated:

$$1/\tau_i = (1/\tau_{0i})e^{-E_{Bi}/kT}. \tag{3}$$

With Eqs. (2) and (3), we obtain the fit shown as solid lines in Fig. 1.

This fit yields five quantities: (1) the two activation energies for $1/\tau_1$ and $1/\tau_2$, (2) the two attempt rates, (3) the total resistance change S_0. We usually find that the two attempt rates are the same within a factor of 3 although they can differ by a factor of 10; they lie in the range $10^9 < 1/\tau_0 < 10^{13}$ sec^{-1}. The two barrier heights usually differ by about 20% with no apparent correlation with the difference in $1/\tau_0$. E_B varies from roughly 10 meV at our lowest T to about 150 meV at 100 K, at which point we can no longer resolve single Lorentzians.[1]

From data such as those in Fig. 1, we conclude that the population kinetics of the individual traps is governed by the two-well potential-energy picture shown schematically in the inset in Fig. 1. $1/\tau_1$ and $1/\tau_2$ represents the transitions rates between the wells. This double-well picture is highly reminiscent of the ionic-reconfiguration model often used to describe the low-temperature properties of glasses.[4-6] In our system, the ionic reconfiguration represents the rate-limiting step in both the charge-capture and -emission processes; it proceeds via thermally activated transitions over the energy barrier separating the two nearly energy-equivalent ionic configurations. Although the range of $1/\tau_0$ extends to rather low frequencies, we note that the upper end of the range is indeed characteristic of ionic vibrational frequencies and that the relatively low energy scale of E_B is typical of that assumed to explain low-T properties of bulk amorphous materials. We also note that the reconfiguration is accompanied by a change in trap charge so that the two wells are also characterized in part by a difference in charge state.

The nature of this two-well system is further clarified by examining the low-temperature behavior of the Lorentzians: We find that for $T < \sim 15$ K there are striking deviations from the thermally activated kinetics described above. Figure 2 is a plot of all the τ_{eff} at 10 mV bias for a typical device as a function of $1/T$. Above ~ 15 K, all the τ_{eff} show the thermal-activation behavior described above. However, below this temperature, there is a rather abrupt change in behavior leading to a very weakly T-dependent region at the lowest temperatures. We have made several tests to ensure that this change in behavior is not due to local heating resulting in a temperature hangup at about 10–15 K. We have used the magnitudes of the Nb and PbBi superconducting energy gaps as local thermometers to establish that external heating and self-heating are minimal. We have tested junctions with resistances varying over several decades and have found the same type of low-temperature behavior for all samples independent of the power dissipated at the tunnel junction. Finally, we have found instances where thermally activated Lorentzians are commingled with near-

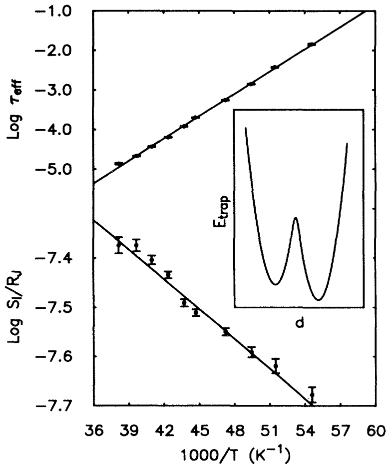

FIG. 1. Plot of logτ_{eff} and logS_1 vs $1/T$ showing thermally activated behavior. Solid lines are fits assuming Eqs. (2) and (3) in the text. Inset shows a two-well model which adequately describes the rate-limiting kinetics.

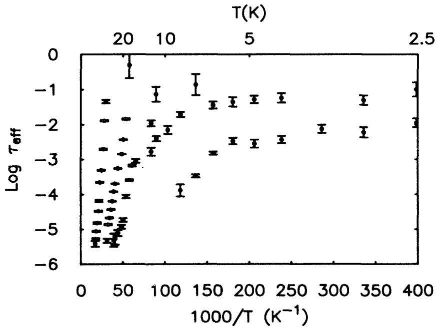

FIG. 2. Typical data set for τ_{eff} showing the abrupt change from thermally activated behavior above to nonactivated behavior below $T \sim 15$ K.

ly temperature-independent states at low T. All of these experiments consistently show that the saturation of $1/\tau_{\text{eff}}$ indicates an intrinsic change in the dominant process of well-to-well transitions.

A rather plausible explanation of this low-temperature effect is that the rate-limiting step in electron capture and emission at low T is a direct configurational tunneling of the ions forming the trap. This conclusion is supported by both the temperature and the voltage dependence of τ_{eff} at low T. Figure 3 shows $\log\tau_{\text{eff}}$ vs T at four different bias voltages for one particular defect state along with a thermally activated state at higher temperatures shown for comparison. Each low-T trace shows the transition from activated to nonactivated behavior. Below ~15 K, $1/\tau_{\text{eff}}$ has an exponential voltage dependence and is nearly independent of T, while at high T the voltage effect is quite weak. The temperature-independent exponential voltage dependence as well as the weak temperature dependence at fixed V is common in tunneling systems. Several authors (e.g., Pirc, Zeks, and Gosar[7] and Silsbee[8]) have shown that tunneling transitions between nonequivalent wells like those shown in Fig. 1 have rates which are roughly power-law T dependent at temperatures comparable to the difference in well depths. Both the weak T and strong V dependence of our data point to configurational tunneling as the rate-limiting step in the trap-population kinetics.

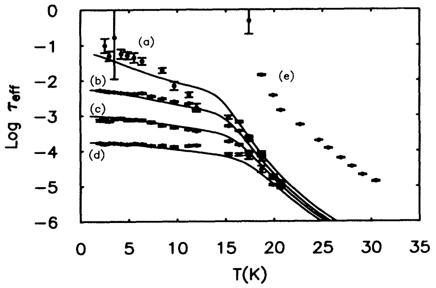

FIG. 3. Plot of τ_{eff} vs T for four different voltages: (a) 8 meV, (b) 15 meV, (c) 20 meV, and (d) 25 meV. Solid lines are fits by the functional form Eqs. (4) and (5) to explain the deviation from thermal activation due to a parallel tunneling process. (e) Thermally activated data for comparison.

We find further support for these ideas by making quantitative comparisons between the measured transition rates and those predicted by a very simple model where the high-temperature rate form, Eq. (3), is extended to include a parallel Wentzel-Kramers-Brillouin tunneling term. Then

$$1/\tau_i = 1/\tau_{\text{tun}} + 1/\tau_{\text{act}}, \tag{4}$$

where

$$1/\tau_{\text{tun}} = (1/\tau_0)\exp[-2(2mE_B/\hbar^2)^{1/2}d(1-\gamma_t eV)][1+C(kT/eV)^2], \tag{5a}$$

$$1/\tau_{\text{act}} = (1/\tau_0)\exp[-(E_B-\gamma_a eV)/kT]. \tag{5b}$$

In Eq. (5a), d is the ionic tunneling distance between the wells, and m is the mass of the tunneling particle. Because of the simple exponential voltage dependence of our data, we cannot immediately determine whether it is due to a barrier-lowering effect, barrier-thinning effect, or both, as each yields exponential voltage dependence in the low-V limit relevant for our data. Thus, we have assumed the usual generic voltage dependence leaving the details of its origin unresolved. The T-dependent term in Eq. (5a) is the leading functional temperature dependence for $eV > kT$ found for Poole-Frenkle type tunneling,[9] and is typical of the T dependence found for other systems.[10] In Eq. (5b) we have also included the possibility of a voltage-induced change in the activation energy as in the tunneling term.

The solid lines in Fig. 3 show the results of a nonlinear least-squares fit to the dominant rate in τ_{eff} by the model form above. While this very approximate model clearly does not fit the data exactly, it does describe the general trend and does so with very reasonable parameter values: In the case of Fig. 3, from the high-temperature data we find $1/\tau_0 = 5\times10^{10}$ sec^{-1} and $E_B = 24$ meV. The value $\gamma_a = 0.1$ indicates that the applied voltage is not very effective at direct lowering of E_B, which implies that most of the V dependence in the tunneling term is due to some type of barrier-thinning process. One possibility is that the barrier is distinctly nonrectangular as is the case for the barrier shown in the inset in Fig. 1, while another possibility is that the applied field couples through the dielectric constant of the barrier material to cause lattice strains, thereby altering the distance d. From the tunneling term, we find that $\gamma_t = 12.8$ eV^{-1}, which implies that $\gamma_t eV \ll 1$ for all our voltage data, consistent with the assumption that the linear V dependence is a first-order expansion of some more complicated term. The value $C = 540$ is of the appropriate order of magnitude for the case of Poole-Frenkle tunneling of ions.[9] The final parameter is the product $m^{1/2}d = 3\times10^{-23}$ kG$^{1/2}$ m. The mass m and distance d cannot be separated by the fit alone, but this value is consistent with ionic tunneling. The barrier material for our tunnel junctions is amorphous Nb_2O_5; the dominant defect in bulk samples of this material is an oxygen vacancy.[11,12] If this type of defect also dominates in our tunnel barriers, then a likely ionic reconfiguration would be an oxygen vacancy moving between nearly equivalent sites. Assuming that m is an oxygen atomic mass yields an experimental value of d of ~ 3 Å in good agreement with the O-O distance in bulk Nb_2O_5. Note that the use of an electron mass requires a tunneling distance d that is completely inappropriate for our experimental system.

Clearly, this model is very preliminary; there is a definite need for detailed transition-rate calculations for such systems. However, the basic idea that ionic configurational tunneling is the dominant term in the electron population kinetics is very well supported by this simple picture. We note here that, while the proposal of a detailed mechanism by which the ionic reconfiguration makes a change in trapped charge favorable is beyond the scope of this paper, the electrochemical potential gradients in the tunnel barrier are clearly strong enough that by the simple motion of an ion by a lattice spacing or less, the electron occupation probability can change dramatically.

In summary, we have used direct measurements of individual resistance fluctuations in small-area tunnel junctions to obtain detailed information about the fluctuation kinetics of *single* electron trap states in the barrier material. The results indicate that the rate-limiting factor in the trapping process is a reversible displacement or reconfiguration of the ions forming the trap. This reconfiguration proceeds by thermal activation at high T and by ionic tunneling at low T. While our model is at best very preliminary, we have demonstrated the apparent wealth of information about defect states which can be extracted by this type of measurement. Supported by a realistic calculation of tunneling rates for such defect configurations, this technique can be expected to provide a sensitive probe of single defects in solids.

This work was supported by the Office of Naval Research and by the National Science Foundation through the use of the National Research and Resource Facility for Submicron Structures and the facilities of the Cornell Materials Science Center. We gladly acknowledge helpful discussions with J. Wilkins, M. Nelkin, and especially J. P. Sethna, M. Randeria, and D. Rokhsar.

---

[1] C. T. Rogers and R. A. Buhrman, Phys. Rev. Lett. **53**, 1272 (1984).

[2] C. T. Rogers and R. A. Buhrman, IEEE Trans. Magn. **21**, 126 (1985).

[3] S. Machlup, J. Appl. Phys. **25**, 341 (1954).

[4] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

[5] W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972), and Philos. Mag. **34**, 983 (1976).

[6] R. O. Pohl, in *Phonon Scattering in Solids,* edited by L. J. Callis *et al.* (Plenum, New York, 1976), p. 107.

[7] R. Pirc, B. Zeks, and P. Gosar, J. Phys. Chem. Solids **27**, 1219 (1966).

[8] R. H. Silsbee, J. Phys. Chem. Solids **28**, 2525 (1967).

[9] Robert M. Hill, Philos. Mag. **23**, 59 (1971).

[10] John G. Simmons, J. Appl. Phys. **37**, 2823 (1966).

[11] W. K. Chen and R. A. Swalin, J. Phys. Chem. Solids **27**, 57 (1966).

[12] P. Kofstad, J. Less-Common Met. **14**, 153 (1968).