PHYSICAL REVIEW B VOLUME 57, NUMBER 2 1 JANUARY 1998-II

Coulomb-glass-like behavior of ultrathin films of metals

G. Martinez-Arizala, C. Christiansen, D. E. Grupp, N. Marković, A. M. Mack, and A. M. Goldman
School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455

(Received 6 October 1997)

A field-effect conductance-modulation experiment has been performed on ultrathin films of metals deposited onto amorphous germanium substrates. For the thinnest films at the lowest temperatures, the conductance exhibits logarithmic decay, memory, aging, and hysteretic effects in its response to changes in gate voltage. These glasslike phenomena disappear above a characteristic temperature, and become immeasurable as film thickness is increased. [S0163-1829(98)50202-0]

The investigation of the evolution of conductive behavior, and superconductivity in ultrathin films has been pursued as a consequence of interest in the interplay of localization phenomena with superconductivity.[1–3] Our approach to this problem[1] has involved systematic investigation of these properties as a function of thickness in films deposited onto substrates held at liquid helium temperatures. Changing the carrier concentration by capacitive charging (the field effect) was perceived to be a possibly useful probe of the superconductor-insulator (S-I) transition. Although we found[4] no significant modification of the S-I transition, the field effect was observed to be anomalous in that the conductance *increased* with increasing gate voltages of *either* sign, for insulators, but *decreased* for superconductors. Qualitatively similar behavior was reported in earlier investigations of films of granular Au (Ref. 5) and amorphous In-In_2O_3 (Refs. 6 and 7) in their insulating states. The highest resistance films studied exhibited very slow relaxation, similar to that reported for amorphous In-In_2O_3.[6,7] This response, noted briefly in Ref. 4 together with observations of memory, aging, and hysteresis effects, is suggestive of a Coulomb or electron glass with a very long equilibrium time.[8,9] In a recent Letter Ovadyahu and Pollak described new work on the disorder and magnetic field dependence of the slow relaxation in In-In_2O_3.[10] Here we report temperature and disorder-dependent features of the glass behavior of metal films which differ in important ways from the behavior of In-In_2O_3 films.

Investigations were carried out on ultrathin films of Bi or Pb evaporated onto a predeposited layer of *a*-Ge, with all films being grown *in situ* at liquid helium temperatures under UHV conditions ($\sim 10^{-10}$ to 10^{-9} Torr). Single crystals of $SrTiO_3$ (100) which were 0.75 mm thick were used as substrates. The high dielectric constant of this material below 10 K ($\kappa\epsilon_0 \sim 8-20{,}000$) (Ref. 11) permits substantial charge to be induced at low gate voltages even though the substrate is of macroscopic thickness. The electrostrictive response of the substrate was determined to be on the order of parts per million over the range of temperatures and bias voltages used, and thus is not relevant to the effects found.[12] Substrates were kept cold and UHV conditions were sustained over extended periods so that sequential depositions to increase film thickness without contamination and without warming could be carried out. Details of the experimental procedures have been presented elsewhere.[4]

The zero-bias conductances could be fit using a hopping form $G = G_0 \exp[-(T_0/T)^a]$, with the power a on the order of 0.8 for the most resistive films, and 0.5 for less resistive films with sheet resistances greater than 24 kΩ.[13,14] For resistances below this value there was a logarithmic dependence on temperature. The range of temperatures available, one decade, was not sufficient to establish any temperature-dependent prefactor in the exponential regime.[15] However, Zabrodskii plots confirmed that the exponents were not artifacts of the fitting procedure.[16]

We now focus on the glasslike behavior observed in capacitative charging studies of highly resistive films. The temporal evolution of the conductance change in response to a gate voltage consisted of several segments: first there was a very fast initial rise in conductance. This was followed by an interval of relatively rapid relaxation over a period of minutes. Finally there was a long term relaxation which was logarithmic in time. Except for the time scales, this behavior is similar to that reported by Ovadyahu and Pollak.[10] As long as the applied gate voltage was sustained, the conductance never returned to its original value, in contrast with the observations on In-In_2O_3 films.[6,7] Figure 1 shows a representative plot of the time dependence of $\Delta G/G$ for a 3.1-Å-thick Pb film with a sheet resistance of 100 kΩ. The applied gate

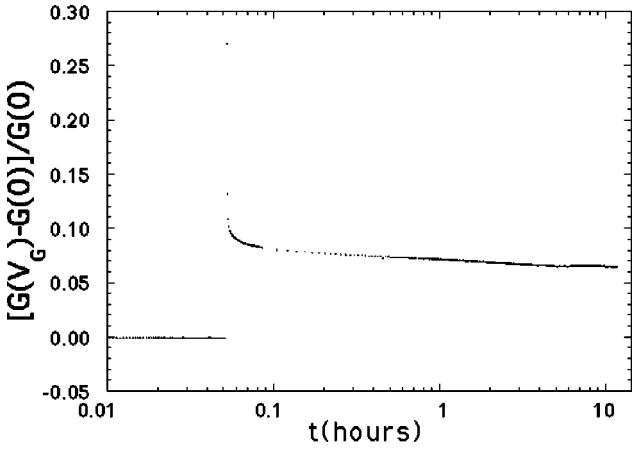

FIG. 1. Relaxation for a 13.1-Å-thick Pb film with a sheet resistance of 100 kΩ. The value of ΔV is -10 V and $T = 4.61$ K. The measuring current through the film was 50 nA. The short time response crossing over to a logarithmic decay is evident.

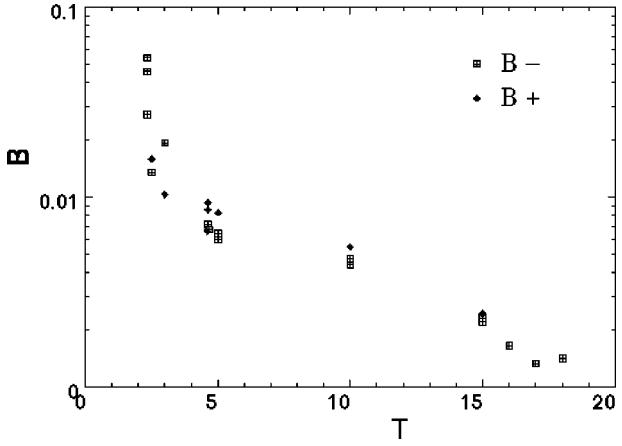

FIG. 2. Temperature dependence of the coefficient of the logarithm for data fit by $\Delta G/G = A - B\ \ln(t)$. Here $B+$ corresponds to conditions under which ΔV involved a change from zero volts to $V_G = +20$ V, and $B-$ involved zero volts to $V_G = -20$ V.

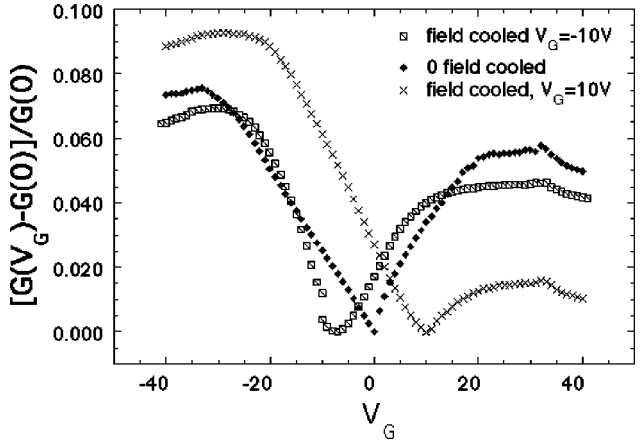

FIG. 3. Shift of minimum in $\Delta G/G$ caused by rapidly cooling in an applied field for 4.9 Å Pb film. The measurements were made at 4.7 K and the film was warmed to 24 K before V_G was turned on.

voltage step was $\Delta V = -10$ V and the measuring current in the film was 50 nA. After about 6 h, changes in conductance were no longer resolvable.

The temperature dependence of the decay of $\Delta G/G(V_G = 0)$ in the logarithmic regime was fit using the form $A - B\ \ln(t)$. The coefficients, B, plotted as a function of temperature for positive and negative gate voltage V_G are shown in Fig. 2. *B decreased* as the temperature increased, and *vanished* into the noise above 18 K. Remarkably, $G(V_G)$ retained a symmetric component of response to gate voltage. The fraction of the conductance in response to charging exhibiting logarithmic decay was larger, the lower the temperature. The hysteresis, aging, and memory effects also vanished near 18 K, which may be a glass temperature for this particular film. Glasslike behavior was not only temperature dependent, but as the films were made thicker and more conductive by sequential evaporations, it disappeared completely. Because of the tedious nature of the data acquisition, a detailed study of the thickness dependence of the glass temperature was not undertaken so that the precise conductance at which the glasslike effects disappeared was not identified. A significant difference between our observations and those of Ovadyahu and Pollak,[10] is that at high temperature they found the conductance vs gate voltage to be *antisymmetric*, whereas we found the *symmetric* response to persist above the temperature at which the glasslike behavior vanished. Furthermore, symmetric response with reversed sign was found in thicker films which were superconducting at low temperatures. Possible explanations of this behavior were discussed in Ref. 4, but the issue of the mechanism must be considered to be open at this time.

Another important difference between the metal films and the In-In_2O_3 films of Ref. 10 is that the magnetoresistance is negative rather than positive, at levels of disorder in which there are glassy effects. Whether this is a consequence of the strong spin-orbit interaction in Pb and Bi not present in In-In_2O_3 is also an open question.

We now describe the memory and aging effects in the extreme insulating regime. It was possible to ''pin'' the system in a particular configuration by ''field cooling,'' i.e., rapidly cooling from a high temperature with an applied gate voltage, $V_G = V_a$. Usually, the minimum of the conductance was at the value $V_G = 0$, if the system was cooled in zero field. When the film was warmed above T_g, and cooled with a gate voltage V_a applied, the minimum would shift to V_a. Repeated scanning at this point would result in the minimum being returned to $V_G = 0$. This behavior is illustrated in Fig. 3. A 4.9 Å Pb film, with a sheet resistance equal to 65 kΩ, was warmed to 24 K. After the field was applied, the film was rapidly cooled to 4.7 K and the voltage was scanned. This was done for $V_a = \pm 10$ V. As the data show in each case the minimum was pinned at the value V_a in which the film was cooled. Similarly fixing V_G at a particular value at low temperature would result in the minimum being shifted to that value.

The symmetric response to gate voltage and memory and aging effects are similar to those found in studies of amorphous In-In_2O_3 (Refs. 6, 7, and 10) films. In these investigations films were about 200 Å thick, with sheet resistances on the order of GΩ, whereas in our work films had sheet resistances ranging from hundreds of kΩ down to the order of 10 kΩ, but were on the order of 10 Å in thickness.

The similarity of the behaviors discussed above to memory and aging effects observed in structural[17] and spin glasses[18] is notable. The functional form of $G(V_G)$, as shown in Fig. 3, also resembles that of the dependence of the electric and magnetic susceptibilities of structural and spin glasses on electric and magnetic fields, respectively. These have been described as evidence for ''holes'' in the density of states. The functional form of $G(V_G)$ (see Fig. 3) is also quite similar to the results of various simulations and calculations of the density of states (DOS) for two-dimensional (2D) disordered electronic systems.[19,20] These observations lead to the speculation that $G(V_G)$ might measure the 2D electronic density of states (DOS). A single-particle nonequilibrium picture is presented in Ref. 10 to explain the symmetric response to gate voltage of In-In_2O_3 films. However, the differences between the observations in metals and in In-In_2O_3, together with the almost certainly higher electron concentration in the former make the applicability of such an explanation problematical.

Conductance studies are generally thought not to probe the DOS of electronic systems, since disturbances to the

electron energy distribution relax, and carriers added during the measurement are screened.[21] In contrast, the physical processes in tunneling are fast relative to relaxation times, and for this reason tunneling is a standard tool for measuring the DOS.[22–27] However, in very glassy systems with long relaxation times, there is no easy path from an excited state resulting from injected carriers back to the state of minimum free energy as there are many energy barriers against this relaxation. If the conductance were proportional to the density of states, as is the case in the hopping regime,[28] a simple field effect conductance modulation experiment might provide a measure of the electronic DOS in the extreme glassy limit.

In a capacitive charging experiment one would ordinarily expect the electron distribution to relax after the gate voltage and the carrier concentration are changed. The new carrier concentration would determine the new value of the chemical potential E_F, and any features in the DOS such as its zero, or minimum at E_F (Ref. 14) would track that new value. In the extreme glassy limit, changing V_G would change the carrier concentration and the chemical potential, but as long as the system remained out of equilibrium, the minimum might not track E_F, and the value of the DOS would be determined by the chemical potential at $E_F+\delta E_F$, where δE_F, determined by the charge transfer, is proportional to $|V_G|$. For a film cooled to low temperatures from 25 K with a nonzero value of V_G, that voltage would determine the equilibrium chemical potential, and as a consequence, the minimum of $G(V_G)$. Biasing at a particular value of V_G at fixed low temperature and waiting a long time could result in a similar shift in the minimum to the value of the chemical potential corresponding to the bias voltage. The above considerations would describe the behavior of only the thinnest or most insulating films in which the fraction of the conductivity controlled by charging dominates the total conductivity. As the thickness of the metal layer is increased, additional conductive channels, which are not glassy, are added. When these are dominant, the system loses its glassy character and behaves reversibly.

We again reiterate that we have no strong physical basis for our speculation other than the similarity of these results to work on the low-temperature ac dielectric response of structural glasses to dc electric fields[17] and on the response of the magnetic susceptibility in CuMn spin glasses to magnetic fields.[18] Particularly bothersome is the fact that the symmetric response persists in films which are of higher conductivity, and are not glassy. However, it is clear that glassy behavior is due to general mechanisms, involving multistate relaxations, which can be common to rather different physical systems. As a consequence a picture like that involved in our speculation may be important in the ultimate theoretical understanding of these systems.

The authors would like to acknowledge very useful conversations with Boris Shklovskii, Boris Spivak, and Steve Kivelson. This work was supported in part by the National Science Foundation under Grant No. NSF/DMR 9623477.

[1] D. B. Haviland, Y. Liu, and A. M. Goldman, Phys. Rev. Lett. **62**, 2180 (1989).
[2] A. F. Hebard and M. A. Paalanen, Phys. Rev. Lett. **65**, 927 (1990).
[3] J. M. Valles, Jr., R. C. Dynes, and J. P. Garno, Phys. Rev. Lett. , **69**, 3567 (1992).
[4] G. Martinez-Arizala, D. E. Grupp, C. Christiansen, A. Mack, N. Markovic, Y. Seguchi, and A. M. Goldman, Phys. Rev. Lett. **78**, 1130 (1997).
[5] C. J. Adkins, J. D. Benjamin, J. M. D. Thomas, J. W. Gardner, and A. J. McGeown, J. Phys. C **17**, 4633 (1984).
[6] M. Ben-Chorin, D. Kowal, and Z. Ovadyahu, Phys. Rev. B **44**, 3420 (1991).
[7] M. Ben-Chorin, Z. Ovadyahu, and M. Pollak, Phys. Rev. B **48**, 15 025 (1993).
[8] J. H. Davies, P. A. Lee, and T. M. Rice, Phys. Rev. B **29**, 4260 (1984).
[9] R. N. Bhatt and T. V. Ramakrishnan, J. Phys. C **17**, L639 (1984).
[10] Zvi Ovadyahu and Michael Pollak, Phys. Rev. Lett. **79**, 459 (1997).
[11] H. M. Christen, J. Mannhart, E. J. Williams, and Ch. Gerber, Phys. Rev. B **49**, 12 095 (1994).
[12] Daniel E. Grupp and Allen M. Goldman, Phys. Rev. Lett. **78**, 3511 (1997).
[13] A. L. Efros and B. I. Shklovskii, J. Phys. C **8**, L49 (1975).
[14] B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer, Berlin, 1984).
[15] F. W. Van Keuls, X. L. Hu, H. W. Jiang, and A. J. Dahm, Phys. Rev. B **56**, 1161 (1997).
[16] A. G. Zabrodskii and K. N. Zinov'eva, Zh. Éksp. Teor. Fiz. **86**, 727 (1984) [Sov. Phys. JETP **59**, 425 (1984)].
[17] Sven Rogge, Douglas Natelson, and D. D. Osheroff, Phys. Rev. Lett. **76**, 3136 (1996).
[18] P. W. Fenimore and M. B. Weissman, J. Appl. Phys. **76**, 6192 (1994).
[19] E. I. Levin, V. L. Nguen, B. I. Shklovskii, and A. L. Efros, Zh. Éksp. Teor. Fiz. **92**, 1499 (1987) [Sov. Phys. JETP **65**, 842 (1987)].
[20] Masoud Sarvestani, Michael Schreiver, and Thomas Bojta, Phys. Rev. B **52**, R3850 (1995).
[21] Don Monroe, A. C. Gossard, J. H. English, B. Golding, W. H. Haemmerle, and M. A. Kastner, Phys. Rev. Lett. **59**, 1148 (1987).
[22] J. G. Massey and Mark Lee, Phys. Rev. Lett. **75**, 4266 (1995).
[23] W. L. McMillan and J. Mochel, Phys. Rev. Lett. **46**, 556 (1981).
[24] G. Hertel *et al.*, Phys. Rev. Lett. **50**, 743 (1983).
[25] A. E. White, R. C. Dynes, and J. P. Garno, Phys. Rev. Lett. **56**, 532 (1985).
[26] A. E. White, R. C. Dynes, and J. P. Garno, Phys. Rev. B **31**, 1174 (1986).
[27] H. Fritzshe, in *Electronic and Structural Properties of Amorphous, Semiconductors* (Academic Press, New York, 1973), p. 55.
[28] Hiroshi Kamimura and Hideo Aoki, *The Physics of Interacting Electrons in Disordered Systems* (Oxford Science Publications, Clarendon Press, Oxford, 1989), p. 123.