Low Temperature ac Dielectric Response of Glasses to High dc Electric Fields

D. J. Salvino, S. Rogge, B. Tigner, and D. D. Osheroff
Stanford University, Stanford, California 94305-4060
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We report the response of amorphous dielectrics to large dc electric fields **E**. Upon the rapid application of the field, the ac susceptibility ε' increases abruptly and then decays logarithmically for $t - t_0 \approx 1$ to 10^5 sec. Slow dc field sweeps show a minimum in ε' at the field present when the sample was cooled from 300 K. If **E** is held fixed at a different value, a second local minimum in ε' develops at that field, evident upon subsequent dc field sweeps. We present the temperature, frequency, and amplitude dependences of these related phenomena and discuss possible origins.

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Glassy and other amorphous materials exhibit unusual behavior at low temperatures which is believed to result from a distribution of tunneling two level systems (TLS) in these materials which is broad over both the asymmetry in the energy splittings and tunneling frequencies. At low temperatures properties such as heat capacity, thermal conductivity, sound attenuation and velocity, and in materials in which the TLS possess permanent electric dipole moments, even the ac dielectric constant ε', are known to exhibit anomolous behavior which can be attributed to the behavior of such structures. We have measured for the first time the long time relaxation of the ac susceptibility ε' in several dielectric glasses following the sudden application of a large dc field, $\mathbf{E} \approx 10^7$ V/m, such that $\mathbf{p} \cdot \mathbf{E} > k_B T$, where **p** is the electric dipole moment associated TLS in the glass, usually of order 1 D [1]. Measurements were obtained over the temperature range $20 < T < 1.5$ K, and at ac bridge frequencies from 100 Hz to 30 kHz. The details of the response of ε' during the ensuing relaxation of the TLS toward equilibrium are difficult to understand in terms of the noninteracting TLS model of glasses [2,3], but can be explained in terms of a spin-glass-like model of interacting TLS as we discuss below. Yu and Leggett [4] have suggested that such interactions might help explain the plateau seen in the heat capacity in insulating glasses near 10 K, although Coppersmith [5] has argued that such interactions will be renormalized away and that their effects will not be observable at low temperatures, such as those used in our measurements.

In the inset to Fig. 1 we show ε' for a 3 μm thick SiO$_x$ sample at 50 mK upon the application of a 10 MV/m electric field with an ac measurement frequency of 1 kHZ. We find ε' jumps upward abruptly once the dc field is applied, and then begins a slow logarithmic decay which continues for at least 10^5 sec, as can be seen from the open circles in the main part of the figure. The values of t_0 have been chosen to give the best logarithmic decay, but these values are within our 1.5 sec uncertainty in the starting time.

The changes in ε' are not simply due to heating upon application of the dc field. In most dielectric glasses [6], ε' increases roughly logarithmically as the temperature is raised or lowered from a value $T_{\min}$, which is about 150 mK at 1 kHz for the SiO$_x$ samples with an ac field amplitude of 100 kV/m. The sign of the jump is found to be independent of which side of $T_{\min}$ the experiment is performed, while if the effect were due to heating, the sign of the jump should be different above and below $T_{\min}$.

To further study this new behavior, we fabricated thin film capacitors of SiO$_2$, SiO$_x$ (where $x \approx 2.1$), and a polymer photoresist [7] on sapphire and oxidized silicon substrates, using both aluminum and niobium thin film electrodes. In addition, we etched a bulk fused silica plate to 17 μm thickness, and placed it between bulk copper electrodes. The characteristics of these capacitor types are shown in Table I. The values of $S_T = d(\delta C/C_0)/d\ln(T)$

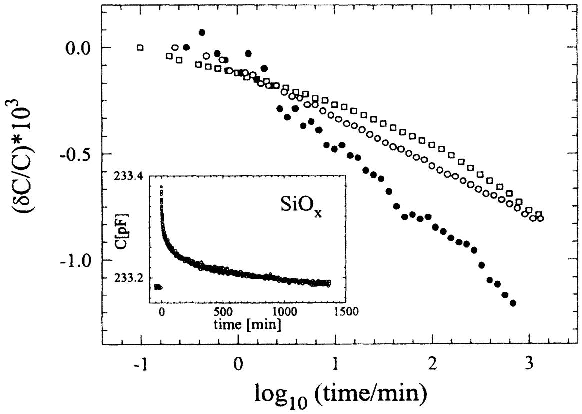

FIG. 1. The inset shows the capacitance jump and relaxation in the SiO$_x$ sample 2 upon application of a 10 MV/m dc electric field, measured at $\nu = 1$ kHz at $T = 50$ mK. The graph demonstrates the nearly logarithmic relaxations seen in three samples, SiO$_x$ sample 2 at 50 mK (open circles), SiO$_2$ sample 3 at 50 mK (solid circles), and polymer sample 5 at 80 mK (squares). The capacitances have been normalized and the SiO$_2$ fractional change has been multiplied by 100 for clarity. The changes are referred to the initial reading after the field has been applied. The frequency and dc field used for the SiO$_2$ sample are the same as those in Table I, while the values for the polymer were 1 kHz and 1.4 MV/m.

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TABLE. I. Comparison of the relaxation slope to the thermal dependence of the dielectric constant in five samples. Here t is the thickness, $S_t = d(\delta C/C_0)/d\ln t$, and $S_T = d(\delta C/C_0)/d\ln T$ on the low temperature side of the minimum in the dielectric constant. Relaxation slopes were taken at an ac field of 0.1 MV/m at 10 kHz, a dc jump of 10 MV/m, and a temperature of 50 mK. For the polymer, the dc field was 1.4 MV/m, but the response was adjusted to 10 MV/m according to Fig. 4(a). Systematic errors are typically 10%.

	Sample 1	2	3	4	5
Dielectric	SiO_x	SiO_x	SiO_2	SiO_2	Polymer
Electrode	Al	Nb	Al	Cu	Au
t (μm)	1	3	1	17	5
C_0 (pF)	230	400	320	35	480
$10^5 S_t$	5.9	5.3	0.12	0.17	1.7
$10^3 S_T$	2.8	2.3	0.17	0.23	0.38
$10^3 S_t/S_T$	21	23	7.3	7.4	45

shown in the table are for the low temperature side of the minimum, between 20 and 100 mK, although for the polymer sample, this value was inferred from the high temperature slope. Data were taken with a commercial Andeen-Hagerling capacitance bridge operating at a fixed frequency of 1 kHz, and a discrete component bridge at a number of frequencies.

The characteristic $\ln(\delta t)$ relaxation curves for the three sample types after the application of a 10 MV/m dc field (1.4 MV/m for the polymer) are shown in Fig. 1. The polymer relaxation does not appear to be entirely logarithmic; however, it cannot be fit as well by either an exponential or a stretched exponential function. The data were taken at ~ 50 mK, except for the photoresist data which was taken at ~ 80 mK, with an ac excitation field of 10^5 V/m. The results looked identical when the ac field was lowered to 10^4 V/m, within the scatter, showing that the effect is virtually amplitude independent. In one experiment, we turned off the ac field during a relaxation, and when it was turned back on, the capacitance returned to the same relaxation curve as would have been generated has the ac field remained on.

Somewhat similar relaxation behavior has been seen by other investigators [8–10] although all earlier experiments have measured the dc dielectric response to the application of a large dc field. The 1991 studies by Höhler *et al.* [10] were the most extensive, measuring the dc dielectric response over the time range 2–7000 sec. In their experiments, $\mathbf{p} \cdot \mathbf{E}/k_B T$ was typically 2 orders of magnitude smaller than in our experiments, always much less than unity, and most of their measurements were made at temperatures above 4 K. Thus their results cannot be directly compared to ours. In their work apparent capacitance increased during the relaxation, as one would expect for electric dipoles slowly aligning along an applied field, while our results showed a relaxation to a lower value of ε'. Höhler *et al.* did find behavior which departed from the standard model of independent TLS, however, and which could be interpreted in terms of interactions. In Ref. [8], which only extended over much shorter times, the relaxation was interpreted in terms of charge migration in granular electrodes. To test this hypothesis in our system, we measured the response of ε' to the dc field in a bulk SiO_2 sample between bulk copper plates, and found similar $\ln(\delta t)$ behavior. In addition, we found that aluminum and niobium electrodes gave almost identical results. We thus conclude that our observed effects are indeed properties of the glass.

The relaxation slopes S_t following the application of a dc field varied nearly logarithmically with the ac frequency, as shown in Fig. 2, decreasing as the frequency was raised. The data shown in the figure above 10 kHz are less reliable and should perhaps be discounted, as 10 kHz is the upper limit for which the bridge was designed to operate. Also shown as a dashed line is the behavior of sample 5, scaled to the SiO_x results at 83 mK and 300 Hz to show that the frequency dependence is similar in both kinds of samples. In addition, S_t also decreases with increasing temperature as can be seen for SiO_x in the figure, and decreases more strongly for the polymer sample than the SiO_x samples. These decreases are consistent with similar decreases seen in the height of the jump observed upon the application of the dc field. Thus it is not the relaxation *rate,* but the overall ac response to the dc field which is varying with temperature and frequency as shown in Fig. 2. These phenomena will be made clearer with the discussion of Fig. 3.

We find that the jumps and relaxation phenomena occur not only in ε', but also in ε''. After accounting for the

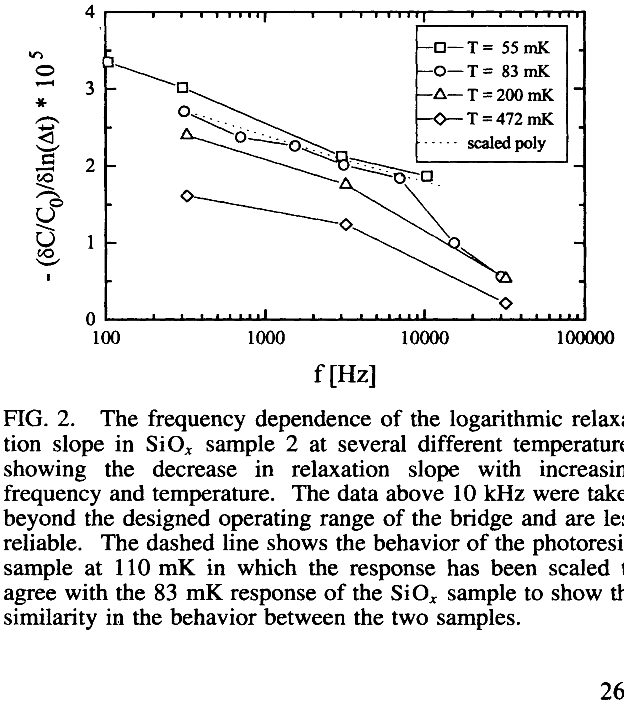

FIG. 2. The frequency dependence of the logarithmic relaxation slope in SiO_x sample 2 at several different temperatures showing the decrease in relaxation slope with increasing frequency and temperature. The data above 10 kHz were taken beyond the designed operating range of the bridge and are less reliable. The dashed line shows the behavior of the photoresist sample at 110 mK in which the response has been scaled to agree with the 83 mK response of the SiO_x sample to show the similarity in the behavior between the two samples.

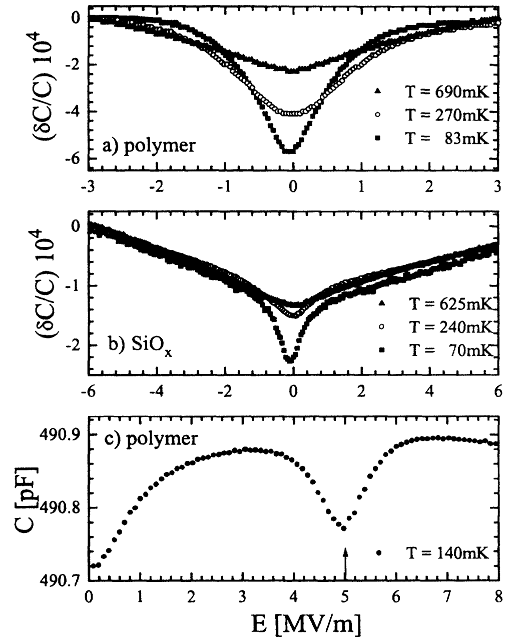

FIG. 3. (a), (b) Results of sweep experiments in the polymer sample 5 and SiO_x sample 2 at various temperatures. As explained in the text, both show hole formation at $\mathbf{E}_{\mathrm{dc}} = 0$, but the SiO_x sample also exhibits a temperature independent background. (c) Hole creation in the polymer. After applying a 5 MV/m dc electric field to the polymer for 2 h, the capacitance exhibits a local minimum at this field when the dc field is swept. This suppression in the capacitance was observed to persist for days after the removal of the bias field, consistent with logarithmic relaxation.

resistance in our leads, we find typical relaxation slopes for ε' in SiO_x are $d(\delta\varepsilon'/\varepsilon')/d\ln(\delta t) \approx 2 \times 10^{-5}$ while $d(\delta\varepsilon''/\varepsilon_0'')/d\ln(\delta t) \approx 2 \times 10^{-3}$ with $\varepsilon_0'' \approx 10^{-2}$. These are to be compared to values of $d(\delta\varepsilon'/\varepsilon_0')/d\ln(T)$ of 3×10^{-3}. Despite the relatively large change in the dissipative term, the two components are well separated, and indeed the change in ε'' affects the bridge balance less than the change in ε'.

For independent TLS, one would expect both the ε' relaxation slope and the log-temperature slope, $d(\delta\varepsilon'/\varepsilon_0')/d\ln(T)$, to be proportional to the density of TLS. It is thus useful to compare this ratio for similar materials. Notice that in Table I this ratio is nearly constant for a given material, independent of electrode type and fabrication technique, strongly suggesting that the observed effects are due to relaxation of the TLS.

We were also able to sweep the electric field across our samples while still measuring ε' with a capacitance bridge, provided the dc field was swept slowly. In Fig. 3(a) we show the results of a sweep for the polymer sample at three different temperatures, with $\nu = 1$ kHz. Because of the temperature dependence of the capacitance, the individual curves have been shifted so that δC is defined to be (roughly) zero at the largest applied fields. It is not clear that the sweeps extended to a high enough field to justify this procedure in all cases, and hysteresis at the ends of the sweep further complicated the adjustment. At the lowest temperature a deep hole is seen in the capacitance at zero field. As the sample was warmed, this hole became shallower and broader. The broadening of this zero bias hole may result from the fact that $\mathbf{p} \cdot \mathbf{E}$ must exceed $k_B T$ for the field to significantly change the distribution of the TLS. In Fig. 3(b) we show a similar set of curves for the SiO_x sample, but here the broadening is not as obvious. The SiO_x curves extend out to higher electric fields, and show a linear rise with applied dc field. The fact that the capacitance is not flat for fields well beyond the zero bias hole in SiO_x was contrary to our expectations. For the polymers we may not have swept far enough to see the limiting high field behavior, but at the highest temperature we may also be seeing a gradual rise with absolute field amplitude. We have also made dc field sweeps for a thin film SiO_2 sample, and again found field sweep curves which were V shaped. This linear rise in C vs applied field may result from a weak piezoelectric effect in our amorphous samples [11] introduced by anisotropic strain in our samples caused by differential contraction between the samples and their underlying substrates. This strain cannot explain the shape, temperature, or frequency dependence of the zero bias hole.

The zero bias hole is found to be associated with the field in which the sample was cooled, as was demonstrated by cooling a sample in a 5 MV/m field, and observing that the "zero" bias hole was shifted to the same field value. The jump in ε' upon the sudden application of a dc electric field presumably is due to the change in ε' associated with moving out of the zero bias hole. As the temperature rises and the hole depth decreases, the jump in ε' also decreases and so does the relaxation slope.

If the dc field sweep was stopped at a nonzero value E_1 for several minutes to several hours, a secondary hole would be seen at E_1 once we again swept the dc field. Such a hole is shown in Fig. 3(c) for the polymer sample. After we changed the field from E_1, this secondary hole would begin to decay away logarithmically in time, and at a rate comparable to the rate measured in the original experiment described above. During the decay, the width of the hole would not change. Slow dc field sweeps disturb the system under study, and the actual curves show significant hysteresis at the extremes of each sweep. Unfortunately, it is not possible to sweep more rapidly, as the capacitance bridge then cannot be balanced.

Comparing the results of the experiments detailed above, we conclude that the jump in capacitance upon the sudden application of a dc field is associated with the jump out of the zero bias hole, and that the logarithmic relaxation of ε' results from the creation of the secondary hole. Thus all of the observed phenomena are closely related.

We now address the question of what causes the logarithmic relaxation and hole formation we have observed.

It seems clear that the answer must involve the TLS, and not simply a piezoelectric response or electrostriction which thins the samples upon the application of the dc field. Such mechanisms will not give rise to the observed frequency and temperature dependences. Resonances in the electrode structures seem unlikely, since similar structures for the deposited $\mathrm{SiO_2}$ and SiO_x samples give very different results, while very different structures for the deposited $\mathrm{SiO_2}$ and bulk $\mathrm{SiO_2}$ structures give similar results.

The heat capacity of glasses depends logarithmically upon the time scale over which the measurement is made [12], owing to the broad distribution of tunneling and relaxation rates. The dielectric response reported in Ref. [10] is also a direct result of this broad distribution. We are not measuring the polarization of the dipole moments, however, but their response to a small ac field. Within the context of independent TLS, either the polarizability of the TLS must be higher in their high energy states than in their low energy states, or the relaxation of the distribution must occur in phase with the ac electric field in order to increase ε'. The polarizability argument is complex, but unlikely. Recently, however, Carruzzo, Grannan, and Yu [13] have developed a model based on dynamical effects through the Bloch equations in which relaxing TLS do oscillate in phase with the ac field, and contribute to ε'. This effect will mimic our data, but the mechanism is frequency independent at low frequencies, in contrast to what is seen in Fig. 2. Thus we conclude that additional physics must be involved.

Another mechanism suggested to explain most of the behavior we have observed involves a model of TLS coupled through lattice strain fields [13, 14]. In the model by Caruzzo, Grannan, and Yu the TLS resemble an Ising spin glass, where it is generally expected that there will be a hole in the distribution of sites vs internal field at zero field [15] based on stability arguments. The application of a dc field drives the system away from this equilibrium, producing regions of very low internal field, which respond easily to an external field. As the system relaxes, the hole in the internal field distribution reappears, causing the ac susceptibility to drop. This spin-glass-like model predicts a decrease in ε' with increasing frequency as observed, and temperature dependence arises because $\mathbf{p} \cdot \mathbf{E}$ must be comparable to $k_B T$ to significantly change the equilibrium distribution of TLS. Both of these models make predictions which may be tested by later experiments. Independent of any model, however, the observed relaxation phenomena probably have important implications regarding the use of dielectric glass capacitors or thermometry. The dominant changes in ε' with temperature arise from changes in the phonon spectrum, but our results show that the relaxation of the TLS distribution toward equilibrium will also be an important, although not a dominant effect, as can be seen from the small size of S_t/S_T.

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