Studies of charge transport in DNA films using the time-of-flight (TOF) technique

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ABSTRACT

Measurements were carried out on salmon DNA-based films, including as-received DNA (molecular weight, MW>2000 kDa) without and with hexacetyltrimethl-ammonium chloride (CTMA) surfactant, and sonicated DNA of MW~200 kDa with CTMA. The test specimens were spin-coated or drop-cast films on ITO-coated quartz slides with a gold charge-collecting electrode. To protect the films from atmospheric influences, the TOF devices were coated with a 200-400 nm polyurethane passivation layer. A quadrupled 20 ns, pulsed Nd:YAG laser with output at 266 nm was used for charge injection. The room temperature photoconductive transients were dispersive to varying degrees with hole mobilities in DNA materials films ranging between 2E-5 to 6E-3 cm^2/Vs for fields ranging from 8 to 58 kV/cm. Only hole response was observed in DNA. The dispersive data were analyzed using a simple, quasi-empirical equation for the photocurrent transient data.

Keywords: Time of flight, TOF, DNA, hole mobility, dispersive transport in polymers, passivation

1. INTRODUCTION

A great deal of study has been carried out on measuring and predicting the mobility of holes in single DNA molecules.[1,2,3,4,5,6,7] To date, however, there has been no reports of direct mobility measurements on thin, amorphous DNA films. There have been computed values from studies of DNA-based OFET devices that have indicated hole mobilities near 1E-3 cm^2/Vs.[8] This paper reports the first effort to directly measure the mobilities in amorphous thin films of as-received DNA and DNA treated with the hexacetyltrimethl-ammonium chloride (CTMA) surfactant to make it water insoluble.[9] Thin film devices using DNA has presented the challenge, to one degree or another, of removing the effect of atmospheric humidity (i.e., water) on the electrical properties of these devices.[10] The DNA devices used in this paper were coated with a 200-400 nm film of polyurethane in order to mitigate the effect of the atmosphere.

The time-of flight (TOF) technique consists of arranging a uniform polymer film between an optically transmitting electrode and a collecting electrode. A photocurrent response is generated by an incident laser pulse on the transmitting electrode when a voltage is applied to the electrodes. The laser pulse wavelength must fall in an absorption band of the film in order to generate charge carriers and the pulse width must be very short compared to the time of flight of the charges to the collecting electrode. The two classes of photocurrent responses are referred to as dispersive and non-dispersive.[11] By changing the polarity of the applied field, both electron and hole transport can be studied. The reported studies of conductive polymers[12] typically show transients that have a plateau followed by a shoulder that occurs at the onset of a continuously, exponential-like decay towards zero current. The "corner" formed by the shoulder is identified as the transit time, t_{TR}, of the charge cloud induced by the laser pulse. Dividing t_{TR} into the film thickness, d, gives a measure of the mean velocity of the charge cloud propagating from the injection electrode to the collecting electrode. For an applied voltage, V, the charge mobility, μ, obtained from this "mean" velocity is $\mu = (d/t_{TR})/(V/d) = d^2/Vt_{TR}$. This type of measurement is in the non-dispersive class of photocurrent transients. The photocurrent transients observed in this work were all dispersive to varying degrees. These transients are basically continuously decaying curves, which have some degree of exponential character. This type of curve is usually analyzed by plotting the photocurrent on a double log graph.[13] This type of plot often shows two regions of different slopes (often very slightly different) that allow the transit

time to be identified with the intersection of the two lines drawn parallel to the slopes of the two regions. This technique was not possible with our data, since none of our data showed regions with different slopes in dual exponential plots of transient curves. The most probable reasons for this is that the data were recorded at room temperature and the highest field used was ~60 kV/cm. Higher temperatures and higher fields provide larger amounts of charge injection and higher mean velocities, which can enhance the definition of the propagating charge cloud. The challenge was to determine a self-consistent method for analyzing our dispersive data. This was eventually solved by using a quasi-empirical equation for fitting to the data.

2. FABRICATION AND MEASUREMENT OF TOF DEVICES

The as-received salmon DNA starting material used in these studies has a molecular weight greater than 2000 kDa. Since this material is soluble in water, films were usually formed by the drop casting method. To remove the water solubility, the DNA is treated with CTMA, which results in the DNA-CTMA material that is dissolved in butanol for spin casting the films. Low molecular weight DNA is obtained by sonication using a high power ultrasonic probe in a water solution of DNA.[9]

Figure 1. Absorption spectrum of a 127-μm thick film of low molecular weight DNA

Mobility measurements on conductive polymers using the TOF method typically use visible wavelength lasers, since the polymers have absorption bands in the visible. DNA, however, has negligible absorption below 1100 nm up to the band edge, which begins about 300 nm, which means an UV laser is required to inject charges into DNA films. See the absorption spectrum in Fig. 1 for a relatively thick DNA-CTMA film. A quadrupled Nd:YAG laser was used that provides ~20 ns pulse at 266 nm. In this region, quartz substrates are required since the laser light is incident on the substrate side of the specimen. The 0.5-mm thick fused quartz substrates were 1 in wide by ~2 in long. The "optically transmitting" electrode material was ITO, but ITO has high absorption at 266 nm. This actually turns out to be a convenience, because it provides a built-in optical attenuator that is required to prevent UV damage to the

Figure 2. Experimental TOF setup used in these

film. Two 6-mm wide ITO electrodes were deposited along the length of the quartz substrates and the DNA films were deposited by spinning or drop cast. These films are expected to be amorphous. The thickness was measured with Dektak 6M stylus profiler. Four or five gold 6-mm wide collecting electrode strips across the width were then deposited on the DNA films. Depending on the actual shape of the quartz substrates, which were cut from a 4-in quartz wafer, between seven and 10 devices were fabricated on a single substrate. After deposition of the gold electrodes, a 200-400 nm film of polyurethane was spin coated on the specimens. A schematic of the experimental setup is given in Fig. 2. All measurements were made at room temperature. A key element in this setup is the Pellin Broca prism, which is a constant deviation prism that refracts the desired wavelength at 90° to the incident beam. This wavelength is selected by rotating the prism. This prism, fabricated to withstand pulsed laser beams, safely sends the very intense beams at 1064 and 532 nm at >90° angles into a beam dump allowing only the 266 nm beam to be incident on the specimen.

There are two issues that required some attention: 1) the injected charge compared to the static charge induced by the applied voltage; and 2) the size of the load resistor, R_L, that converts the current transient into a voltage signal that can be captured by the LeCroy digital oscilloscope. The injected charge was kept well under 1% of the static charge in order that the internal electric field was not impacted significantly by the injected charge. The value of the load resistor depends primarily on the capacitance C of the test device. Ideally, the time constant $R_L C \ll t_{TR}$ is recommended to minimize instrumental influence on the recorded transients.[14] In practice, the lowest load
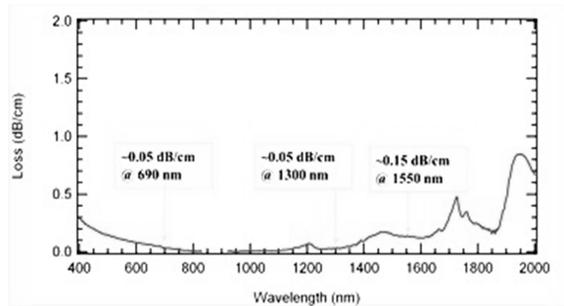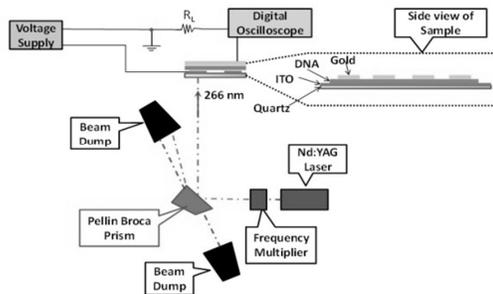
resistance for which a reasonable signal-to-noise ratio in the recorded transient is obtained for the films under study is also a governing factor. Load resistances between 1 and 100 kΩ were used in this work.

3. ANALYSIS OF TOF DATA

The essential effort of several published TOF studies has been to derive an equation for the photocurrent transient that can be fitted to the data from which the mean transit time t_{TR} is one of the parameters determined by the fit. This removes the necessity of doing a graphical analysis of the transient plots, which depends on the details of how this analysis is done. Of these papers, two were particularly interesting to our efforts to understand the observed photocurrent transients from our specimens. The objective was to identify an equation that could be fitted to our data from which the resulting parameters would give a self-consistent method of determining the transient time, t_{TR}. The paper of Scott, Pautmeier and Schein[15] was interesting due to its simplicity and that it provided a means for characterizing the degree of dispersion in the data. The equation that they derived is given as

$$s(t) = At^{-(1-\alpha)}\left[1 - \int_0^t \frac{1}{\sigma_I t'^2\sqrt{2\pi}} \exp\frac{-(1/t'-1/t_0)^2}{2\sigma_I^2} dt'\right] \tag{1}$$

where A is a scaling factor, α is the dispersion parameter, σ_I is the standard deviation of the inverse arrival times of charge carriers and $t_0 = d/<v>$ is the mean transit time of the injected charge carriers to the collecting electrode ($<v>$ is the mean velocity).[15] α tends to unity for a non-dispersive transient signal and the $t^{-(1-\alpha)}$ factor is the fractional power-law form of Scher and Montroll[16] who carried out extensive calculations on TOF transients. Equation (1) is based on the model where the charge arrival times result from a velocity distribution that very closely approximates a Gaussian. Extensive effort to fit Eq, (1) to our data was not successful, even though Scott et al. reported excellent results in measurements on doped polycarbonate.

Hirao et al.[17,18,19] developed a method for obtaining both the drift velocity v and the diffusion coefficient D from a theoretical photocurrent transient equation fitted to the data. They developed their theory using the work of Paulmeir, Richert and Bässler[20] and the disorder formalism developed by Bässler from Mont Carlo simulations.[11] This formalism identifies the energetic disorder σ as the width of the density of states and the spatial or positional disorder by the parameter Σ. These paramters are determined from measurements of the mobility versus temperature and applied electric field. Their equation for the photocurrent is given as

$$J = -\frac{en_0}{2L}\sqrt{\frac{D}{\pi t}}\left[\exp\left(-\frac{(L-vt)^2}{4Dt}\right) - \exp\left(-\frac{v^2t^2}{4Dt}\right)\right]$$
$$+ \frac{en_0 v}{2L}\left[\mathrm{erf}\left(\frac{vt}{2\sqrt{Dt}}\right) + \mathrm{erf}\left(\frac{L-vt}{2\sqrt{Dt}}\right)\right], \tag{2}$$

where e is the charge, n_0 is the number of charges, L is the thickness of the disordered organic film and erf(x) is the error function.[17] Extensive effort again was made to fit this equation to our data with little success. From these efforts using the above equations, it was clear that these equations are not able to characterize dispersive transients where there is no clear plateau and shoulder. Although some DNA data had short plateaus leading to soft shoulders with the intersection of the slope lines around 0.030 ms, it was not possible to obtain any self-consistent set values for t_{TR} using the graphical approach. The efforts, however, to make our data work with either Eqs. (1) or (2) suggested a simple quasi-empirical equation inspired by these equations. It became evident that our dispersive transients had power-law and exponential characteristics, which, after some trials, resulted in the working equation for the observed photocurrent transients $i(t)$ given by

$$i(t) = y_0 + A_1 t^{-(1-\alpha)} + A_2 e^{-t/\tau} \tag{3}$$

where y_0 is a baseline parameter, A_1 is the power-law scaling parameter, α is the dispersion parameter in Eq. (1), A_2 is the scaling
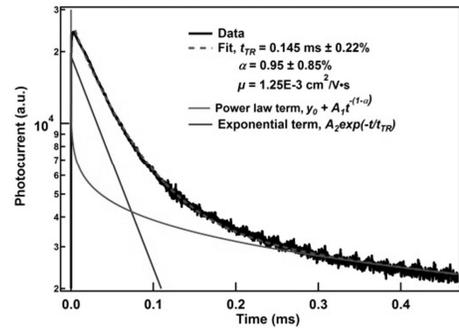

Figure 3. Example of Eq. (3) fit to dispersive transient data for a 23.35 μm film.

parameter for the exponential function and τ is a time constant that we connect to the characteristic transient time t_{TR}. Figure 3 illustrates how this equation provided fits to out dispersive transients. The vertical axis is the log $i(t)$ to show how the two terms contribute to the fit of Eq. (3). The dispersion parameter α adjusts the shape of the power law term to the shape of the data curve that the exponential term does not complete, and y_o and A_1 sets the effective amplitude of this term. These three parameters characterize the dispersive part of the curve. Another example is given in Fig. 4 showing the fitting residuals. As suggested by the quality of the fit in Fig. 4, the fitting uncertainties obtained from fits of Eq. (3) to our data for t_{TR} and α were typically <1%, which was essential to obtaining self-consistent measurements of the transport times of the charge clouds and the resulting mobility values. The precision uncertainties in t_{TR} propagated with the voltage and thickness uncertainties give estimated precisions of the mobility values of 1 to 2%; however, the

Figure 4. Fitting example of data from a 15.4 μm film of DNA(as-rcvd)-CTMA showing the fitting residuals.

accuracy of the thickness measurements depends on the uniformity of the films between the electrodes. The variations in the residuals near zero time are due, in part, to instrumental effects. A central issue was the criterion for connecting t_{TR} to τ. It became evident that setting these two parameters equal would give unusually high mobilities. Moreover, the decay of the exponential term would not be completed, which is really the key issue. We chose to set $t_{TR} = 3\tau$ at which the exponential term has decayed to 5% of its initial value. If the transport was non-dispersive, this choice should be close to the time where the shoulder occurs. Independent of this choice is the fact that τ is a characteristic parameter of the dispersive data the interpretation of which is open for future consideration.

4. RESULTS

Extensive studies of the electrical resistivities of DNA films[10] made it clear that these films must be protected from the atmospheric humidity. In our early TOF studies, we again confirmed this dictum. Figure 5 shows an example of the doubling of the time to ½ peak due to exposure to atmospheric humidity.

Measurements of both hole and electron transport were carried out on all TOF devices, but only hole transport was observed in DNA films. The transient curves for drop-cast as-received DNA are given in Fig. 6, which include the fitted values of t_{TR} and α and their fitting uncertainties. The mean value of α is 0.65 ± 26%. It is not evident why the spread in these values is rather wide; however, this relatively low mean value suggests that the charge transport was strongly dispersive. The fits to the data shown by the dashed curves are perfect to the eye, which is supported by the small fitting uncertainties in the parameters. These measurements were done at low fields

Figure 5. TOF transients showing effect of exposure to atmospheric humidity on 6.80 μm thick DNA films with 44 kV/cm applied.

to preserve the integrity of the devices in case further measurements were needed, which occurred in some cases. Figure 7 gives the plot of the mobilities, which shows excellent agreement with the Poole-Frenkel form of $\ln \mu \propto \sqrt{E}$, which describes conduction in amorphous insulating solids, such as polymer films.[21]

The TOF responses of spin-cast DNA(as-rcvd)-CTMA and sonicated DNA(~200 kDa)-CTMA films were studied. Although these materials are less susceptible to humidity than water-soluble DNA without CTMA, these devices were also coated with polyurethane. The "conformable" urethane used is soluble in xylene, which is a non-polar solvent; thus it does not attack the alcohol-soluble DNA-CTMA or the water-soluble DNA films. We have compared the resistivities of coated to uncoated films and found only minor differences.
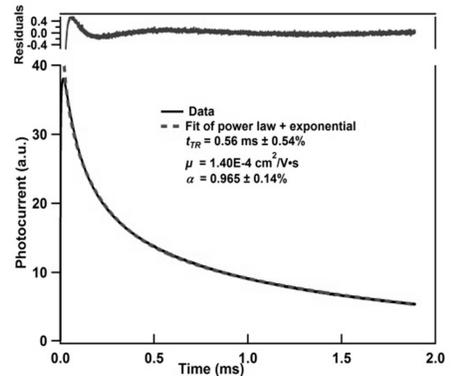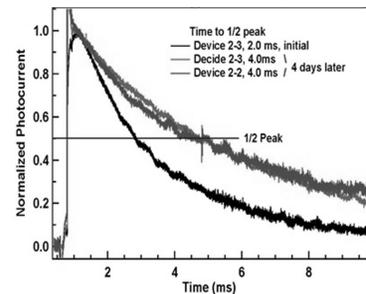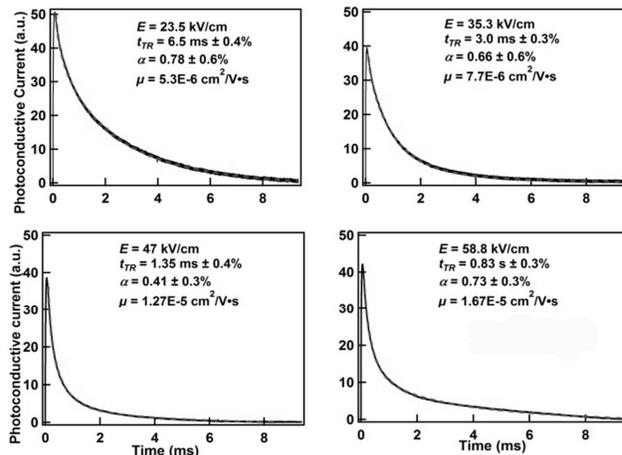
Figure 6. TOF transients for a polyurethane-coated device with a 8.33 μm DNA(as-rcvd) film, where the data are the solid (black) curves and the fits are the dashed (red) curves.
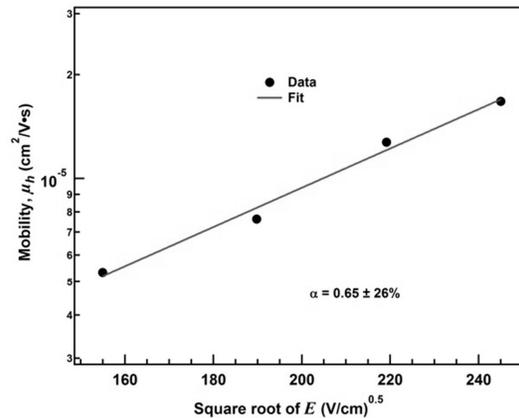

Figure 7. Hole mobilities of the data shown in Fig. 6. The fit of the data to the Poole-Frenkel form is shown.

Examples of the TOF transients observed from DNA-CTMA films are given in Fig. 8. These curves are remarkable due to the large difference in transit times. To the best of our knowledge, the only difference in these films was the thickness. The mobility data from these films are given in Figure 9. The mobilities of the DNA(as-rcvd)-CTMA films are somewhat higher than expected. From the Monte Carlo simulations of Bässler[11] and studies of Borsenberger et al.,[21] the extraordinary values of mobilities shown by the ~24 μm-thick films could be, in part, an example of an increase in spatial disorder with thickness. Borsenberger et al. showed that higher mobilities can occur with high spatial disorder, which characterizes the fluctuations of intersite hopping distances. They state that "the reason is that fluctuations of intersite distances establish fast diffusion routes that permit a carrier to arrive at an acceptor or donor site earlier than would occur in the absence of disorder."[21] They found that negative slopes in Fig. 9 are typical of dispersive transport at low applied fields and high spatial disorder. As the field is increased above ~200 kV/cm, the curves can show a positive slope depending on the sizes of the energetic and spatial disorder parameters.
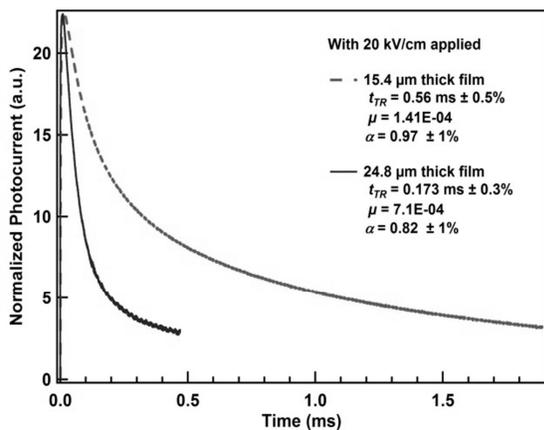

Figure 8. Photocurrent transients observed from two DNA(as-rcvd)-CTMA devices with a large difference in film thickness. The data from these devices are included in Fig. 9.
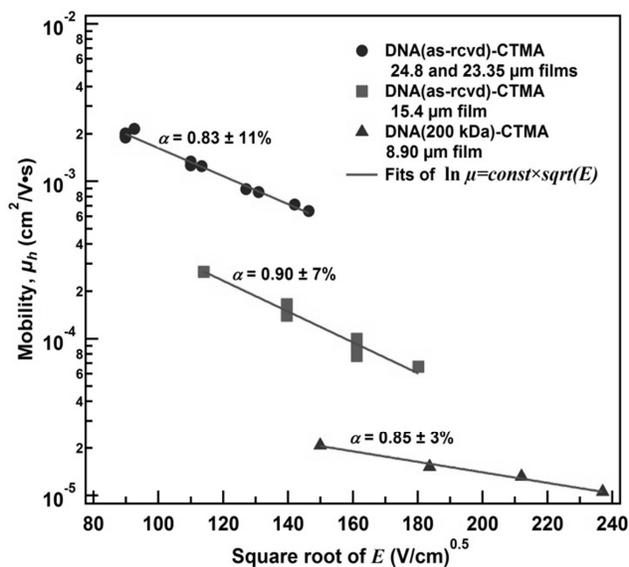

Figure 9. Hole mobilities in DNA-CTMA films. Test devices were polyurethane coated.

Figure 9 includes mobility data from a sonicated DNA(200 kDa)-CTMA film the values of which are closer to expectations. One cannot avoid noting that the three sets of data plotted in Fig. 9 suggest some dependence on

thickness, which is discussed in Section 5. It should be noted that data presented in Fig. 9 are well-behaved showing very little scatter. This is a vindication of the use of Eq. (3) to do the fits to the transient plots. Many approaches were tried, none of which provided this degree of correlation.

5. SUMMARY AND CONCLUSIONS

The results presented here are the first reported studies of TOF measurements on DNA films. To accomplish the analysis of the data, a four-parameter semi-empirical equation for dispersive charge transport was developed which was fitted to all DNA TOF data with a precision of $\leq 1\%$. The key parameter from the fitting of this equation is the time constant τ in the exponential term. The transit time t_{TR} was set equal to 3τ, which corresponds to the nearly completed decay (to 5%) of the charge cloud formed initially at the injection electrode. The resulting fits to the data showed how the fitting parameters provide a self–consistent characterization of the charge transport in DNA films. To protect the test devices from atmospheric humidity, passivating polyurethane films were deposited on the devices. The mobility values and the dependence on the electric field of the drop-cast as-received DNA film was quite different than that obtained with the spin-cast DNA-CTMA film of similar thickness, which appears to be due to higher dispersion indicated by the lower value of the dispersion parameter α for the former (0.65) compare to the latter (0.85). These differences are most likely related to the two methods of forming the films and the degree and type of disorder (spatial and energetic) introduced by the two methods.

The mobility values for the DNA-CTMA films showed a remarkable change with film thickness, ranging from 7E-4 cm^2/Vs for ~24 μm down to 2E-5 cm^2/Vs for ~9 μm at ~20 kV/cm. Added to this surprising result is the high value of 2E-3 cm^2/Vs mobility for the ~24 μm film. These observations can, to some extent, be connected to a high spatial disorder as explained by Borsenberger et al. as quoted in Section 4.[21] This dependency on disorder is usually observed in much thinner films than studied here, but the length of the DNA molecules adds another dimension to the statistical "disorder" issue, which includes statistical angular alignment. Although choosing, for example, $t_{TR} = 5\tau$, would lower the mobility values given in Section 4, it would not significantly change the wide range of these results with film thickness. We can, however, speculate as follows: The statistical distribution of the alignment of the DNA molecules in a spun DNA film can be expected to be very dependent on the thickness of the film. The long DNA molecules will tend to lay more in the plane of the film as the film thickness decreases. Our studies of DNA-CTMA resistivities showed a behavior that can be tied to this type of statistical alignment.[10] If DNA molecules provide fast hole transport along the helical axis as has been reported,[1,2,3] then as the film thickness increases and the fraction of DNA molecules increases that have one end aligned near one electrode with the other end near the opposite electrode, it can be expected that there will be enhanced transport of the holes. This would be a "first" order alignment, where "higher" orders would be for two or more molecules "connecting" the electrodes. In effect, the statistical distribution of the alignment of the DNA molecules could provide fast transport "tunnels" between the electrodes in thick films. More experimental and simulation studies are needed to either validate this speculation or provide another explanation for the results obtained here. In addition, to obtain quantitative comparisons to the fitting equation used in this work, studies are needed to achieve non-dispersive behavior with DNA films by increasing the applied field or the temperature both of which will move dispersive transients into the non-dispersive regime.[21]

6. ACKNOWLEDGMENTS

7. REFERENCES

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