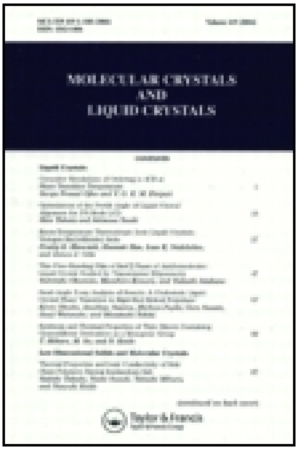

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Dielectric Properties and Electro-optic Characteristics of TN-LCDs Doped with Metal Nanoparticles Exhibiting Frequency Modulation Response Accompanying Fast Response

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TN-LCDs doped with metal nanoparticles such as Pd, Ag, and Au are shown to exhibit a frequency modulation response together with the ordinary root-mean-square response to operating voltages. These devices are called FM-LCDs. The frequency range in this phenomenon spreads from several tens Hz to several thousands Hz depending on the materials of nanoparticles, their diameters, and their concentrations. The central frequency of each FM-LCD almost coincides with the dielectric relaxation frequency. FM-LCDs shows a sensitivity to the high frequency component of the driving voltage, this in turn gives rise to a fast electro-optic response in ms and sub-ms order. The EO effect of the FM-TN-LCD effect is explained based on the Maxwell and Wagner effect and it is shown that the metal nanopatricles have the effective electrical conductivity of $\sigma_2 = 6.0 \times 10^5\ S/m$ *that is about 100 times smaller that of metal Ag.*

Keywords: FM-LCD; frequency modulation; liquid crystal; Maxwell–Wagner theory; metal nanoparticles; response time

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INTRODUCTION

In a previous paper, the author's research group reported that LCDs such as those in TN-mode LCDs and TB-mode LCDs fabricated by doping with metal nanoparticles such as Pd, Ag, and Au, which are protected with nematic liquid crystal, 5CB(Merck), exhibit a frequency modulation response together with the ordinary root-mean-square response to the driving voltage [1–5]. These LCDs are called FM-LCDs. The FM-LCDs exhibit remarkable sensitivity to the high frequency component of operating voltage; this in turn gives rise to fast electro-optic response. The present paper reports on the origin of the FM effect and its frequency range, response times, particularly on the over-driving, and the origin of these EO effects that are explained based on the Maxwell-Wagner theory on the heterogeneous dielectric material; and also discuss the effective value of the conductivity of metal nanoparticles resulting in our FM-LCD effect.

EXPERIMENTAL

The colloidal dispersion of metal nanoparticles were synthesized in terms of alcoholic reduction method by the UV irradiation of ethanol solution of the relevant salts in the presence of the nematic liquid crystal, 5CB(Merck), with the molar ratio to the metal of 5. The sizes of metal nanoparticle cores were measured with a transmission microscope to have the diameters of 3 nm to 5 nm depending on the materials and conditions. TN-LCD cells were constructed using NLC, 5CB, as a host material, which are doped with metal nanoparticles. The thickness of the NLC layers were 5 μm. The concentrations of Ag nanoparticles are 0.12 wt% and 0.24 wt%, which correspond to the spatial volume factor of the order of 10^{-4}. The electro-optic characteristics of FM-LCD cells were measured with a measuring instrument (Ohtsuka, Model LC-5200) and their dielectric properties were determined using an LCR meters (Hioki, Model l3522-50 or/and HP, Model-4284A). All the measurements were done at 25°C.

RESULTS

In this paper, the results on the FM-TN-LCD cells with Ag nanoparticles are mainly reported. Figure 1 shows the EO characteristics, called V-T curves, on a FM-TN-LCD cell with Ag nanoparticles of 0.12 wt% covered with 5CB that is denoted by Ag/5CB/0.12 wt%. Figure 2 demonstrates an example of frequency switching for square operating voltages by changing their frequency between 20 Hz and 500 Hz.

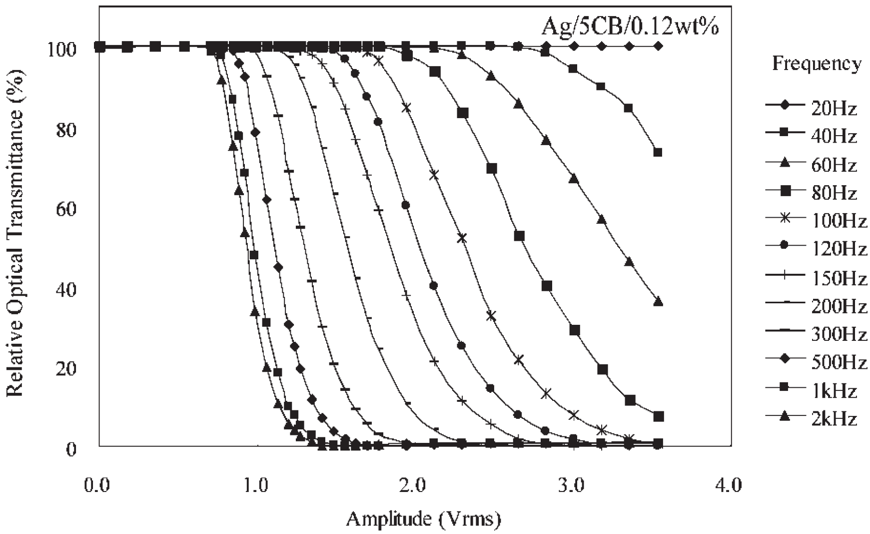

FIGURE 1 Relative optical transmittance versus sinusoidal applied voltage (V-T curves), where the frequencies are used as a parameter. Sample cell: TN-LCD/Ag/5CB/0.12 wt%.

Figures 3 and 4 show the magnified figures transferred from Figure 2. The values of response times for an AC square operating voltage are shown in Table 1 in comparison with the data of the FM-TN-LCD cell with pure 5CB. In the falling process, the delay times are always shorter by a tenth or half, and the decay times are also shorter by 30%. In the rising process, the delay times are always shorter by 30%, but the rise times are shorter only 10%.

In order to improve the rise time of the FM-TN LCDs, we investigated the over-driving effect in these devices. Figure 5 shows the operating voltages V_1 and V_2; further each voltage has the number of AC pulses at 4 kHz, that is n_1 and n_2. Figure 6 shows the results of the over-driving effect between two gray levels by changing the number of n_1, from 0 to 5; when $n_1 = 4$ and $n_2 = 480$; there occurs the reduction of the response times form 80 ms to 1.5 ms as shown in Figure 7; and further it is shown that when $n_1 = 4$, the response time is 1.5 ms without over-shooting; while the TN-cell with pure 5CB always shows an over-shooting.

In order to understand the FM-TN-LCD effect, we conducted the measurements of dielectric properties of the sample cells, since the OE effects of LCDs are governed by the dielectric torques. Figure 8 shows the dielectric dispersion curves, $\varepsilon'(\omega)$ of the samples

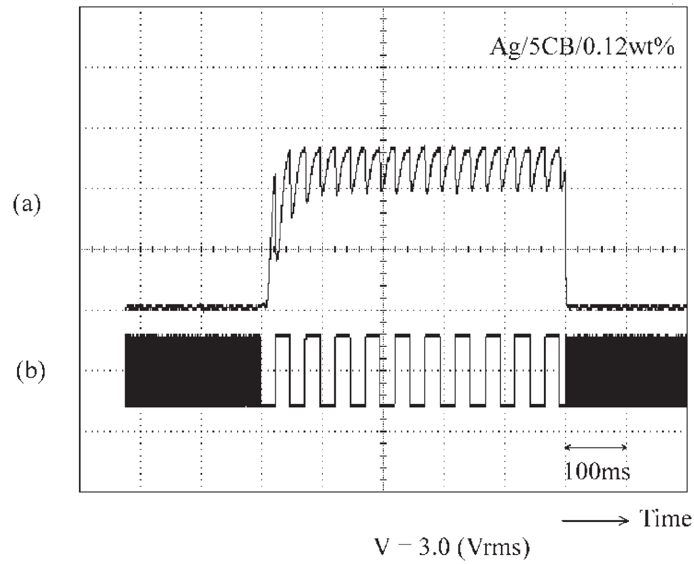

FIGURE 2 An example of the FM switching by changing frequencies: low frequency $f_1 = 20\,\text{Hz}$ and high frequency $f_2 = 500\,\text{Hz}$, the amplitude of the square wave voltage is 2.5 volt; (a) relative optical throughout and (b) operating voltage waveforms.

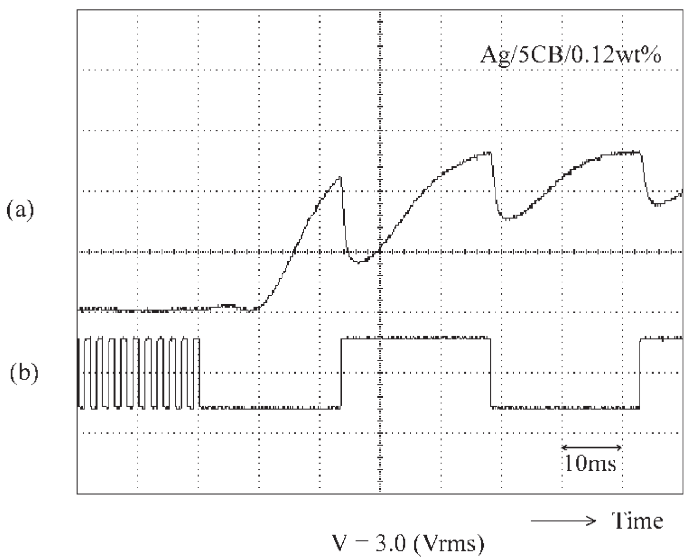

FIGURE 3 Magnified waveform of those of Figure 2 in the francium from $f_2 = 500\,\text{Hz}$ to $f_1 = 20\,\text{Hz}$.

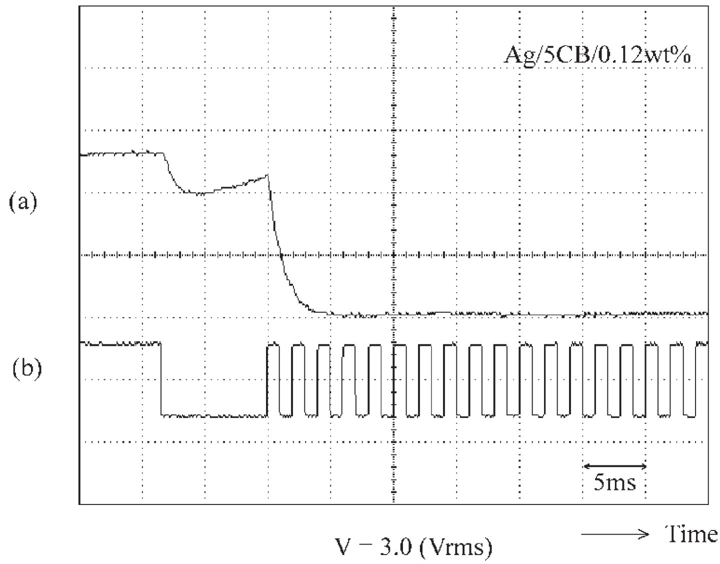

FIGURE 4 Magnified waveform of those of Figure 2 in the transition from $f_1 = 20\,\text{Hz}$ to $f1 = 500\,\text{Hz}$.

(A)-Ag/5CB/0.1wt% and (B)-Ag/5CB/0.24 wt%. The imaginary parts of the dielectric constants, $\varepsilon''(\omega)$ are shown in Figure 9; from these data we evaluated the values of the relaxation frequencies as: $f_R = 159\,\text{Hz}$ and 310 Hz, respectively. If we look at the data of Figure 1, it is possible to recognize that the threshold voltages increase as decreasing the frequency; from these behaviors we can derive the variation of the dielectric anisotropies, $\Delta\varepsilon(\omega)$, of the samples (A) and (B) as shown in Figure 10, where we used well known formula for threshold voltage in the TN device. According to this investigation, the dielectric anisotropy, $\Delta\varepsilon$, tends to saturate as the frequency approaching to 2 kHz; and as the frequency decreases, the $\Delta\varepsilon$ tends to decrease to zero or slightly negative. From these facts, it is claimed that the frequency

TABLE 1 Response Times of FM-TN-LCD

Rising process (at 4 V)	FM-TN-LCD	TN-LCD (pure 5CB)
Delay time	4 ms	5 ms
Rise time	3 ms	4 ms
Decaying process (at 4 V)	TN-TN-LCD	TN-LCD (pure 5CB)
Delay time	4 ms	9 ms
Decay time	7 ms	13 ms

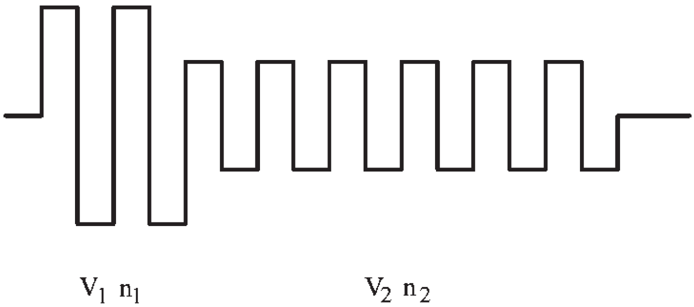

FIGURE 5 Operating voltages V_1 and V_2; further each voltage has the number of AC pulses at 4 kHz, that is n_1 and n_2.

region in the FM-TN LCD almost coincides with that of the dielectric dispersion. Although, it is not fully described in this paper, we compared the data on other several FM-TN LCD cells with Ag, Pd, and Au nanoparticles; as a result, we claim that the relaxation frequency of a sample cell depends on the kind of metal (whose electrical conductivity), the diameters of nanoparticles, and their concentration. For driving an LCD device the favorable frequency region is around several tens Hz to several hundreds Hz; these frequency ranges are

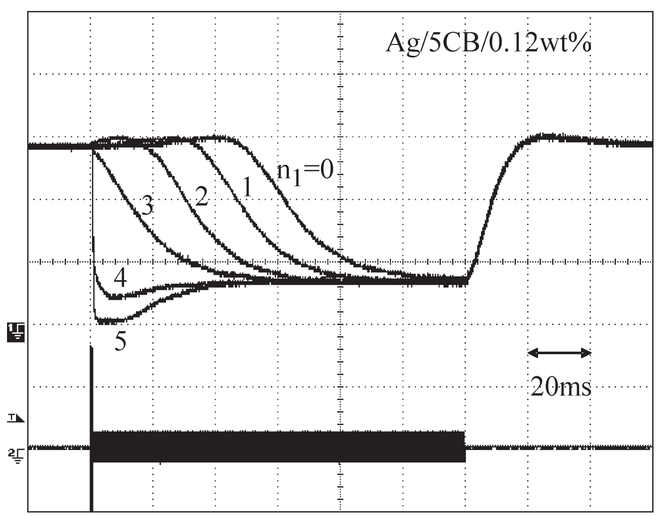

FIGURE 6 Results of the over-driving effect between two gray levels by changing the number of n_1, from 0 to 5, $V_1 = 8.0\,V$, $V_2 = 1.2\,V$.

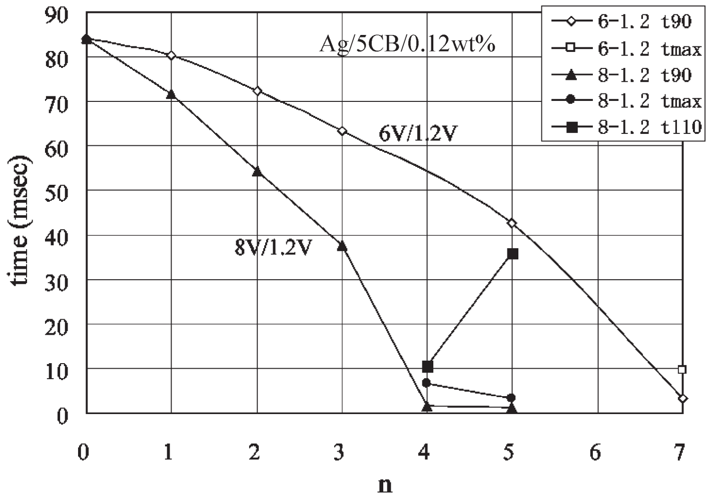

FIGURE 7 Dependence of response times to the number of n_1.

actually realized by adopting metal nanoparticles such as Ag, Pd, and Au or their composites (alloys) with the concentration of 0.1 to 0.4 wt% that corresponds to the spatial occupation factor of the order of 10^{-4} to 10^{-5} and the mean distance between nanoparticles are about 50 nm.

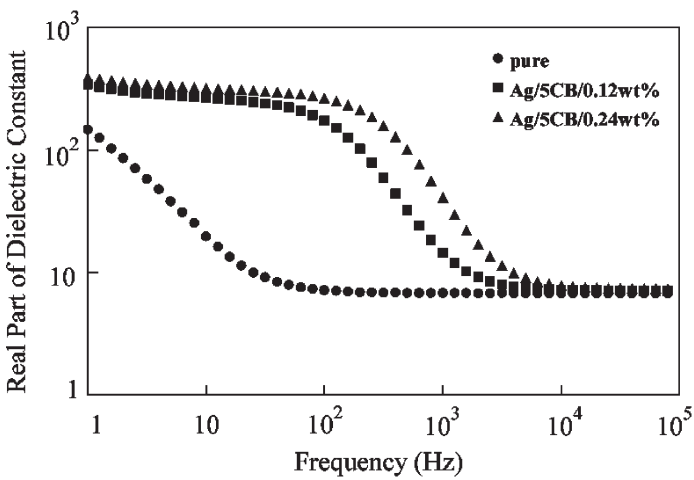

FIGURE 8 Dielectric dispersion, $\varepsilon'(f)$, of the sample cell, TN-LCD/5CB/0.12 wt% and 0.12 wt%.

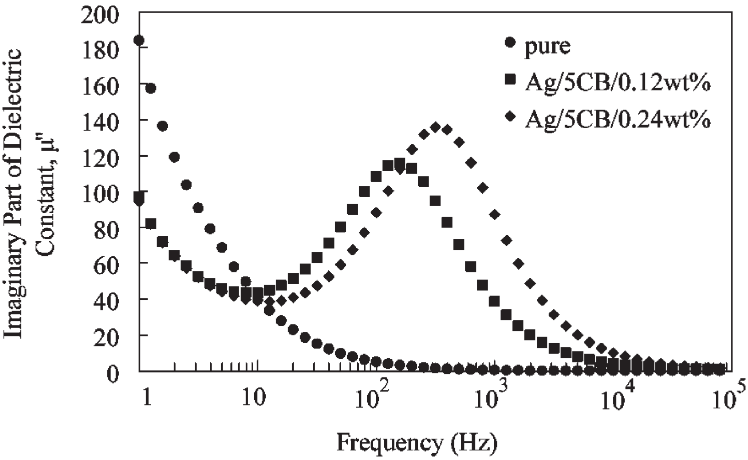

FIGURE 9 Imaginary part of dielectric constant $\varepsilon''(f)$ of three sample cells; TN-LCD with pure 5CB, Ag/5CB/0.12 wt%, Ag/5CB/0.24 wt% and 0.24 wt%.

ANALYTICAL CONSIDERATIONS OF THE EFFECT OF FM-TN LCD AND DISCUSSIONS

Analytical formulae for a heterogeneous dielectric medium were derived based on the potential theory and this leads to the Debye type

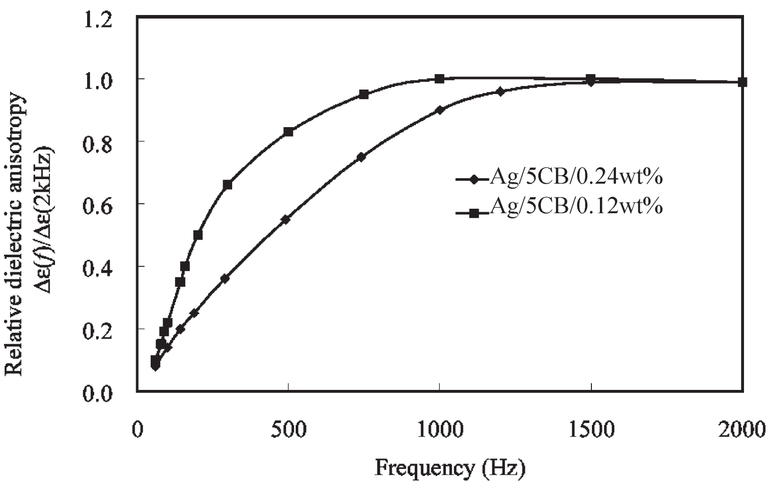

FIGURE 10 Frequency dependence of the relative dielectric anisotropy, $\Delta\varepsilon(f)/\Delta\varepsilon(2\,\text{kHz})$ of the sample TN-LCD/5CB/0.12 wt% and 0.24 wt%.

dispersion formula [6,7],

$$\varepsilon'(\omega) = \varepsilon(\infty) + \frac{\varepsilon(0) - \varepsilon(\infty)}{1 + (\omega\tau)^2}, \tag{1}$$

where

$$\varepsilon(\infty) = \varepsilon_1 \left[1 + 3\phi_2 \frac{\varepsilon_2 - \varepsilon_1}{2\varepsilon_1 + \varepsilon_2} \right], \tag{2}$$

and

$$\varepsilon(0) - \varepsilon(\infty) = \frac{9(\varepsilon_1\sigma_2 - \varepsilon_2\sigma_1)\phi_2(1 - \phi_2)}{(2\varepsilon_1 + \varepsilon_2)(2\sigma_1 + \sigma_2)^2}, \tag{3}$$

where ε_1 and σ_1 being the dielectric constant and the conductivity of the host medium, NLC, and ε_2 and σ_2 are those of the metal nanoparticles; and ϕ_2 being the volume occupation factor of nanoparticles. The relaxation time f_R is given as,

$$\tau_R = \frac{2\varepsilon_1 + \varepsilon_2 + \phi_2(\varepsilon_1 - \varepsilon_2)}{2\sigma_1 + \sigma_2 + \phi_2(\sigma_1 - \sigma_2)}. \tag{4}$$

The factor, $\varepsilon_1\sigma_2 - \varepsilon_2\sigma_1$ appearing in Eq. (3) is originated from the discontinuity in the relaxation: $\tau_1 - \tau_2 = (\varepsilon_1/\sigma_1 - \varepsilon_2/\sigma_2) \neq 0$; this effect is called the Maxwell–Wagner effect.

It is shown that the relaxation frequency increases with increasing the occupation factor ϕ_2 (concentration); that is, $f_R = 159\,\text{Hz}$ and 310 Hz for the sample cells (A) and (B) as shown in Figures 7 and 8; this corresponds to $\tau_R = 1.0 \times 10^{-3}$ (s) and 5.1×10^{-4} (s), respectively. The phenomena that the relaxation frequency depends on the occupation factor of nanoparticles are not fully explained by Eq. (4). In order to solve this problem, we introduced the system relaxation time τ_S as follows:

$$\tau_S = \frac{1}{\tan\delta \cdot \omega} \qquad \text{at } \omega = 2\omega_D, \tag{5}$$

where ω_D is the angular frequency that gives rise to the maximum in the $\tan\delta(= \varepsilon''/\varepsilon')$ [4,5]. Through the τ_S, one obtains τ_R as

$$\tau_R = \frac{\varepsilon(0) - \varepsilon(\infty)}{\varepsilon(\infty)} \tau_S, \tag{6}$$

The τ_R calculated in this manner well in a agreement with their measured values [4,5]. This means that the concentration dependence of the relaxation frequency is explained. It is impossible to estimate the value of the electrical conductivity of nanoparticles using Eq. (4), however it may be possible to estimate the electrical conductivity of the system at low frequency, say at 100 Hz, in such a way that we are able to estimate the value of $2\sigma_1 + \sigma_2$ using Eq. (5) by taking $2\varepsilon_1 + \varepsilon_2 \approx 10^{-1}$ (as seen later) such that $2\sigma_1 + \sigma_2 \approx 9 \times 10^{-10}$(S/m). This means that that an FM-TN-LCD behaves as an insulator when it is under operation, even though it contains metal nanoparticles. On the other hand, from the dielectric strength (Eq. (3)), one may be able to estimate the electrical conductivity of the nanoparticles. The measured values of the dielectric strengths $\varepsilon(0) - \varepsilon(\infty)$, called the jump, are 250 and 310 for the sample cells (A) and (B), respectively. This means that the amplification factor is $(\varepsilon(0) - \varepsilon(\infty))/\varepsilon_1$ and it has the value of 35.7 and 44.2, respectively. Further $(\varepsilon(0) - \varepsilon(\infty))/\varepsilon_1 \approx \varepsilon_1 q\phi_2/(2\varepsilon_1 + \varepsilon_2)$, if we assume that $\sigma_2 > \sigma_1$. From these values, we obtain the value of $2\varepsilon_1 + \varepsilon_2 \approx 10^{-1}$; therefore $2\varepsilon_1 \approx -\varepsilon_2$ and further $\varepsilon_2 = 1 - \sigma_2\tau_e/\varepsilon_0$ (Drude model); from these relations one obtains $\sigma_2 = (2\varepsilon_1 + 1)\varepsilon_0/\tau_e$, where ε_0 is the dielectric constant of vacuum and τ_e is the relaxation time of electrons. For the value of $\varepsilon_1 = 7.1$, $\sigma_2 = 15.2(\varepsilon_0/\tau_e)$ that is commonly for both two samples. Regarding τ_e, there are two independent opinions: one is that τ_e is determined by the diameter of a metal nanoparticle, d, as $\tau_e(\mathbf{d}) = \mathbf{d}/v_{\mathrm{F}}$, where v_{F} being the Fermi velocity ($=1.1 \times 10^6$ m/s in Ag), and τ_e (d) $= 4.0 \times 10^{-15}$(s) [9]; and the other is that τ_e is determined by the width of the plasmas resonance, $\Delta\omega_{\mathrm{R}}$, as $\tau_e(\Delta\omega_{\mathrm{R}})$ and it has the value of $\tau_e(\Delta\omega_{\mathrm{R}}) = 2.4 \times 10^{-16}$ (s) [10]. Then we have $\sigma_2(\mathbf{d}) = 3.0 \times 10^4$ (S/m) and $\sigma_2(\Delta\omega_{\mathrm{R}}) = 6.4 \times 10^5$ (S/m); whereas the correspondence values of Ag metal are: $\sigma = 6.21 \times 10^7$ (S/m) and $\tau_e = 4.5 \times 10^{-14}$ (s), respectively [11]. The electrical conductivity of metal nanoparticles is about 1,000 or 100 times smaller that of the corresponding crystal metal. The value of σ_2 may be effective one and depends on the nature of the ligand molecules. The existing theory of the Maxwell–Wagner effect using potential theory has no compatibility between the dielectric strength (Eq. (3)) and the relaxation time (Eq. (4)); for this reason, we have formulated an alternative theory.

Now, we will discuss the response times of out FM-TM-LCDs.

Basically, our FM-LCDs has a unique characteristics such that the optical transmission changes with the change of the frequency that will be derived from the data of Figure 1. This means that both the voltage and the frequency plays a common role each other; therefore, it is possible to define the voltage sharpness $\mathrm{S}(V) = (V_1 - V_2)/V_1$ and the frequency sharpness $\mathrm{S}(f) = (f_1 - f_2)/f_1$; the latter may be attributed to the frequency dependence of $\Delta\varepsilon$ through the change of the torque given by $\Delta\varepsilon\mathbf{E}^2$. For this reason the response time may be inversely proportional to the temporal rate of the frequency $\partial f/\partial t$. This makes it possible to reduce the respects time to be ms or sub-ms order in the rising process and over-driving. Retarding the falling process, one possible mechanism is supposed to be attributed to a peculiar stability of the planar configuration of NLC medium that is induced by the introduction of metal nanoparticles that are protected by NLC, 5CB, molecules. The detailed research on this topics is now underway and the results will be published elsewhere.

CONCLUSIONS

A TN-LCD containing metal nanoparticles of Ag, Pd, or Au, which are protected form their aggregation by covering with NLC molecules, 5CB, exhibits a frequency modulation response together with the ordinary RMS response; and further the device shows a fast response to the high frequency component of the operating voltage. The frequency range spreads from several tens Hz to 2 kHz the depends on the material of metal nanoparticles, specified by their electrical conductivity; their diameters, 3 nm to 5 nm; and further concentrations, 0.1 wt% to 0.4 wt%, which corresponds to the occupation factors from 10^{-5} to 10^{-4} and the mean distance is about 50 nm.

For an AC square operating, the delay time and decay time in the falling process are always remarkably shorter about one order of magnitude compared to those of a TN-LCD with pure 5CB. The rise time constant is remarkably reduced about 10 times effectively by adopting the over-driving method. These dynamics may be understood by the rapid change of the dielectric anisotropy which is sensitive to the high frequency component of an operating voltage.

The dielectric properties of our FM-TN-cells are featured by the dielectric relaxation frequency of severed tens Hz or reveal hundreds Hz and the dielectric strengths defined below several kHz are almost 10 to 40 times larger than the dielectric constant of the host NLC.

These phenomena are explained as the Maxwell–Wagner effect of a heterogeneous dielectrics. It is possible to obtain the effective value of the electrical conductivity of metal nanopatricles form the experimentally determined values of the dielectric strength such that: $\sigma_2(\mathbf{d}) = 3.0 \times 10^4 (\mathrm{S/m})$, where electron collision time τ_e is determined by the diameter of the nanopaticles; and $\sigma_2(\Delta\omega_{\mathrm{R}}) = 6.4 \times 10^5 (\mathrm{S/m})$, where the τ_e is determined form the width of plasmon recurrence. The values of σ_2 are smaller by 1,000 and 100 times compared to that of metal Ag.

The origin of the fast response of our FM-TN-LCDs may be attributed to two mechanisms: one is that the their optical transmission sharply depends on the temporal variation of the frequency, $\partial f/\partial t$; and the other is that the NLC system is stabilized by the introduction of ligand protected nanoparticles, this effect works well in the decaying process.

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