ABSTRACT

Multi-Layered Electrochromic Display (mECD) we have demonstrated is superior in terms of brightness and color reproducibility to the conventional full-color reflective electronic papers. By utilizing a nematic liquid crystalline (LC) electrolyte, we have obtained high resolution images of mECD without any fine patterning in the front-plane.

1. INTRODUCTION

Full-color reflective displays have been eagerly developed for their applications to eBook readers, digital signage, which expected to replace ordinary paper. However, there is no reflective display that exceeds the paper media; it is more difficult for conventional reflective displays, based on the additive color mixing model with Red, Green and Blue, to achieve colorful images. One of the reasons is that reflectance of RGB subpixels of reflective display arranged in-plane is too low such as that used in LCD, which makes an output image dark or a contrast ratio low. Therefore, several technologies for full-color reflective display without subpixels arrayed in-plane are being developed [1,2,3].

We have developed a full-color reflective multi-layered electrochromic display (mECD) [4,5] . The mECD has a simple structure, consisting of a front-plane which has three kinds of electrochromic layers and an active-matrix (AM) TFT array as a back-plane (Fig.1). Each electrochromic layer has each electrochromic compound which can reversibly change their color from transparent to cyan, magenta and yellow respectively by external electrical stimulation. The electrochromic compounds have a feature of maintaining its coloration state in a certain period of time after the charge burst (memory performance). A projective image of selected pixel electrodes (anode) of the AM-TFT arranged backward of the mECD appears on each selected electrochromic layer (cathode). As a result, a sequential selection of electrochromic layers gives a full-color image on the mECD front-plane.

Although the transparent working electrodes and the electrochromic layers of the mECD needed no fine patterning, the fine images were achieved by partial reductive reaction on each electrochromic layer. The reduced electrochromic compounds become easily oxidized by ejection of charge to the common working electrodes, and the ions are easily diffused into the electrolyte media, which causes undesirable reduced reactions of other electrochromic compounds. That phenomenon is observed as a blur of output image and a low resolution of the mECD. The resolution of the mECD is basically depending on a stability of reduced conditions of the electrochromic compounds and a charge retention performance between the electrochromic layer and the counter electrode. So the resolution of the mECD is also depends on ionic diffusion of the electrolyte. However, the performances of resolution and response speed are intrinsically incompatible because both of them are trade-offs in relationship. The restriction of ionic concentration in electrolyte also keeps the output images fine at the expense of the high response speed. In other words, higher ionic conductivity gives high response speed but leads rapid blur and low resolution of images because of high ionic diffusion. On the other hand, lower ionic conductivity gives clear and sharp image but degrade the response speed.

To overcome this difficulty, we newly introduced nematic liquid crystalline (LC) electrolyte. The LC electrolyte shows higher ionic conductivity than solid electrolyte and lower volatility than liquid electrolyte used in conventional batteries and electrochemical devices. Additionally, the ionic conductivity is sufficient for driving the mECD. We optimized the component of the LC electrolyte, and achieved the best performance of lower blur, higher response and higher memory performance.
in the mECD. In this review, we referred to the improvement of the resolution of mECD with the LC electrolyte. The mECD showed high resolution in comparison with that of with a liquid electrolyte.

2. EXPERIMETAL

2.1 Single layer ECD test devices

To check the resolution of the single layer electrochromic device (ECD), we prepared test devices with an electrochromic layer by changing electrolyte. The electrochromic layer was formed by spincoating of titanium dioxide (TiO₂) dispersion and electrochromic dye solution on a sputtered ITO substrate. A viologen derivative shown in Fig.2 was used as electrochromic compound, which exhibit magenta color in reduced condition. Both ends of the compound were modified with phosphonate functional group, which gave chemical adsorption onto TiO₂ surface. The front-plane of the single layer ECD was obtained by further formation of the white reflective layer on the magenta electrochromic layer. The counter substrates with patterned ITO electrode (100um and 50um of line/space and matrix pattern) were prepared by photolithography. The LC electrolyte was prepared by 0.05M of tetrabutylammonium hexafluorophosphate salt (TBAPF₆) solved in nematic liquid crystal (5CB, 4-pentyl-4'-cyanobiphenyl). The liquid electrolyte was prepared by 0.05M of TBAPF₆ salt solved with the mixture of polyethylene glycol (200 in molecular weight) and dimethyl sulfoxide. The front-plane and counter substrate were assembled with each electrolyte. The resolution of each electrochromic test devices was evaluated.

![Fig.2 The molecular structure of the electrochromic compound for test devices](image)

2.2 AM-TFT mECD

An active-matrix mECD panel (3.5'' QVGA, 113.6ppi) was used for evaluation of the resolution of mECD. The front-plane of mECD was also formed by conventional thin-layer formation technology; spincoating the electrochromic layers, the insulating layers and the white reflective layer, and sputtering the transparent working electrodes. The viologen derivatives were also used as yellow and cyan electrochromic compounds. The insulating layer was composed of SiO₂ nano-particles and binder polymer. The front-plane and the AM-TFT were assembled with the LC electrolyte.

3 RESULTS AND DISCUSSIONS

3.1 The resolution of the single layer ECD

Fig.3 shows demonstrated images of test device for resolution evaluation using the liquid electrolyte and the LC electrolyte. Fine patterns of 50μm line and space or matrix were appeared in both test devices right after applying 5V between the transparent working electrode and the counter electrodes. However, the patterns of test device using the liquid electrolyte were immediately disappeared after about 10sec from the termination of applied potential. On the other hand, the patterns were remained after 10min in the case of the LC electrolyte. Fig.4 shows microscopic images of test device using the LC electrolyte right after the field application. The line patterns grew thicker by almost 5μm on one side.

The LC electrolyte seemed to have higher viscosity than the liquid electrolyte because of the liquid crystal phase; nematic liquid crystal shows the mesophase. This indicated that the ionic conductivity of the LC
electrolyte might be lower than that of the liquid electrolyte because of low ionic mobility. However, nematic liquid crystal has an intrinsic ability to align along the external electric field. When the alignment of liquid crystal molecules is achieved, the ionic conductivity along the electric field seems to be improved. That was the reason why the response speed in case of LC electrolyte was still fast enough to drive the mECD in spite of the higher viscosity of the LC electrolyte. On the other hand, the alignment of liquid crystal molecule was not achieved without electric field. The macroscopic disorder of liquid crystal molecules in that region seemed to work as a barrier of ionic conduction, resulting in lower blur of output images. This result was also expected to indicate the improvement of the ionic conductivity of LC electrolyte along the alignment of liquid crystal molecules under the applied electric field.

3.2 Ionic conductivity of the LC electrolyte

Next, impedance measurements of the LC electrolyte were carried out by changing the amplitude from 0.01V to 5V. The test cell was prepared by inserting the LC electrolyte between patterned ITO substrates. The cell gap was controlled by 100µm of bead spacers and the overlap area of electrodes was 100mm².

A dark image in the area of overlapped electrodes was observed under crossed Nicols with the applied field of 5V, which indicated a homeotropic alignment of the liquid crystal molecules. On the other hand, the alignment was lost after eliminating the field. This result was considered that the ionic conductivity degraded right after the termination of the electric field, which was consistent with the result that the patterns with the LC electrolyte were maintained longer than that with the liquid electrolyte.

Fig.5 shows results of impedance measurements plotted on a Cole-Cole diagram. The resistivity in the case of 5V in amplitude, which was estimated by the fitting to the charge transfer resistivity of equivalent circuit, was 25% decreased from that of 0.1V. This result is also expected to indicate the improvement of the ionic conduction of the LC electrolyte along the alignment of liquid crystal molecules.

3.3 The resolution of the AM-TFT mECD

Fig.6 shows the microscopic images of the AM-TFT mECD. Each electrochromic layer was driven to display a 223µm matrix pattern. Although the aperture ratio of the AM-TFT back-plane was about 80%, the pixels of output images on the mECD panel were rather broaden in comparison with that of on the single ECD. In addition, the resolution of the magenta electrochromic layer was poorer than that of yellow and cyan electrochromic layer, which seemed to be caused by the distance between each electrochromic layer and the pixel electrodes of the AM-TFT. Additionally, the ionic conduction between magenta electrochromic layer and the pixel electrodes of the AM-TFT was assumed to be disturbed by other two transparent working electrodes, electrochromic layers and insulating layers. This speculation was also consistent with the result of low resolution of magenta electrochromic layer in the mECD.

4. CONCLUSION

We studied an improvement of the resolution of mECD with the LC electrolyte. The mECD with the LC electrolyte showed higher resolution image in comparison with that of with the liquid electrolyte. Moreover, the ionic conductivity improvement of the LC electrolyte under the electric field permits not only the high resolution but also low voltage driving of the mECD. Further improvement of the resolution of mECD can be expected by the reduction in driving voltage due to the increasing of ionic conductivity, decreasing the distance.
between each electrochromic layer and the pixel electrodes of the AM-TFT by optimizing the each layer thickness and the improvement of ionic permeability of each layer.

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REFERENCES


