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High optical density and low dielectric constant black matrix containing graphene oxide and carbon black on color filters

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ABSTRACT

To obtain a black matrix (BM) with high optical density (OD) and low dielectric constant, graphene oxide (GO) was prepared from synthetic graphite oxide and then incorporated into the conventional carbon black (CB) pigment to fabricate black matrix films. The introduction of insulating GO effectively lowered the dielectric constant of carbon black-based BM, but maintained the high optical density. The dielectric constant of the BM film significantly decreased from 26 (carbon black-based BM) to 4.5 (GO/CB-based BM). This work demonstrates the successful chemical modification and good dispersion of carbon-based materials (i.e. GO and CB) and their physical effects on the BM films.

1. Introduction

Graphene oxide (GO), with its carbon backbone and chemical tenability, has gained much attention for its potential in current electronic applications. Chemical modification of GO, which is generated from graphite oxide (GtO), has become a promising route to large-scale production of graphene materials [1–3]. GO contains a range of reactive oxygen functional groups, which render it insulating; but incremental removal of oxygen can transform it into a semiconductor and ultimately into a graphene semi-metal [4,5]. GO is being promoted as a useful compound for incorporation into polymers, ceramics, and metals to make novel forms of thin film electronic materials [6].

Black matrix (BM) film is a functional composite film, different from an engineering or high performance composite film that is commonly used to increase the contrast ratio of flat panel displays due to visible light shielding [7]. TFT-LCD is the most popular display among the various types of flat panel displays. A TFT-LCD is made of a TFT-array panel substrate and a color filter, which is critical for full color viewing (Fig. 1). A color filter consists of a clear substrate, black matrix, color filter layer (RGB colors), overcoat layer and ITO film. The clear substrate is generally made of thin glass or plastic and is deposited by the black matrix material. The black matrix is used to improve the contrast ratio of TFT-LCD due to the light-shading function to drive the electrodes in the thin-film transistors and to prevent inappropriate mixing of colorants in the color filters. The black matrix material can be organic or inorganic, with chromium the most popular inorganic choice. However, chromium has several disadvantages such as high cost, poor adhesion, high reflectance, as well as complex manufacturing process (sputtering) and potential environment problems. Under the current trend in the electronics industry, organic resin black matrices containing carbon black are being widely adopted in the color filters of flat panel displays as replacement for the conventional chromium-based film matrices. These resin black matrices are cheaper to produce than the conventional thin metal film matrices, especially for the larger glass substrates that are used in current generation fabrications. Generally, the black matrix needs to satisfy the requirements of a stable millbase and resist patternable coating, high optical density and controlled electrical properties [8].

Carbon black (CB) is an excellent black pigment which provides high optical density for black matrix development [9]. The turbostractic planes of its primary particles contain electrons that can absorb all wavelengths of light, ranging from ultraviolet to infrared. A BM film is usually required to have a very high optical density in the visible spectrum. The optical density of the film is proportional to the film thickness and to the loading of CB in the film. In order to achieve desired target level of opacity, the film must be prepared with a very high CB loading. However, increasing the carbon content negatively affects the electrical properties of the BM film. CB is also a semiconductor [10]. As the CB content increases in a polymer composite, the composite changes from being

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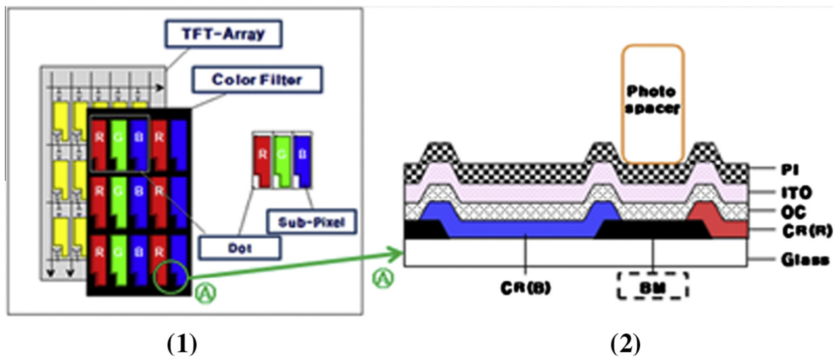

Fig. 1. Perspective of a thin film transistor liquid crystal display (1) and the cross section of the color filter (2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

an electrically resistive to an electrically conductive composite. This transition occurs at critical loading, also known as the percolation threshold. This threshold is influenced primarily by the structure of the CB particles and their loading amount. The electrical properties of the black matrix film show a similar transition, and the film becomes more conductive as its carbon content is increased. Consequently, the optical density and electrical performance of the BM film need to be balanced. The BM film must have good insulating and high optical density properties for TFT-LCD application. There are many efforts to improve the optical and physical properties of CB black matrix films such as mixed metal oxide, surface treated CB and doping of carbon nanotubes [9,11,12]. However, the incorporation of graphene oxide together with CB in the BM has been a novel approach for color filter in liquid crystal display.

In this study, we introduce novel organic black matrices containing insulating GO and CB, providing unique optical and tunable dielectric properties.

2. Experimental

2.1. Materials

Graphite powder (<150 μm) and carbon black (Markos 5333) were obtained from Aldrich. For millbase preparation, a typical industrial solvent was used, which was PGMEA (propylene glycol methyl ether acetate). The dispersant we employed, BYK2150 was claimed by the producer (BYK chemie) to be a block copolymer with basic pigment affinic groups with an amine value 57 mg KOH g^{-1}. The organic black matrix for the color filter included carbon black, acryl binder, multifunctional monomer and photo-initiator. Commercial acryl binder for negative photoresist, which consists of dicyclopentanyl methacrylate, benzyl methacrylate, methacrylic acid and other monomers, was obtained from Jooeun Co., Ltd (Korea, JEBM 427, Mn 1500, acid value 120).

2.2. Synthesis of graphite oxide and exfoliated graphene oxide

Graphite oxide (GtO) was synthesized from commercial graphite according to Ref. [13]. The published process does not involve a large exotherm and produces no toxic gas. Moreover, the improved method yields a higher fraction of well-oxidized hydrophilic carbons. Graphite powder (10 g) was added to a mixture of concentrated H_2SO_4/H_3PO_4 (1080/120 mL) and $KMnO_4$ (54 g), which led to produce a slight exotherm. The reaction mixture was then heated to 50 °C and stirred for 12 h. The mixture was cooled to RT and poured onto ice (∼1200 mL) with 30% H_2O_2 (9 mL). For work-up, the whole mixture was added to excess water, filter, washed with 400 mL of 30% HCl, and then repeatedly washed with water until the pH of the filtrate became neutral. The solid obtained on the filter was dried by freeze drying for 24 h. The dried graphite oxide was vacuum-dried at 60 °C prior to use.

2.3. Preparation of carbon black millbase

CB millbase was prepared by the ultrasonication process. A mixture consisting of 16 wt.% CB, BYK2150 dispersant, and PGMEA solvent was added into a vial. The vial was sonicated for 30 min. The optimum amount of BYK2150 was determined by viscosity measurement and size distribution of CB.

2.4. Preparation of graphene oxide millbase

Synthetic graphite oxide was first ultrasonicated in polar solvent such as ethanol in the presence of BYK2150 dispersant. In this step, graphite oxide is mostly exfoliated into individual, single-layer graphene oxide, which can be effectively re-dispersed in the PGMEA solvent to form the GO millbase. The optimum amount of BYK2150 was also determined by viscosity measurement and size distribution of GO.

2.5. Preparation of black matrix film and pattern formation

The optimum millbases of CB and GO were mixed together in a specific ratio to form a GO/CB hybrid-type millbase, which was used for BM formulation. For typical BM formulation, in a 200 mL round bottomed flask, we added 2-hydroxy-2-methyl–1-phenyl–1-propanone (0.9 g), and PGMEA (83.8 g), and the mixture was stirred with a Teflon magnetic stirring bar at room temperature. After complete dissolution, we added pentaerythritol tetraacrylate (2 g) and acryl binder (4 g), and stirred for 2 h. Then, we added GO/CB millbase and stirred for 4 h. The specified size of glass substrates (Corning Co.) for organic BM films on the color filter is 50.8 × 50.8 mm^2 with a thickness of 0.6 mm. The BM coating process conditions are as follows: spin coating at 600 rpm for 10 s and baking on a hot plate at 90 °C for 90 s. And UV exposure experiments using a patterned photo-mask were performed under the irradiation energy of 80 mJ at 20 °C. These experiments were followed by post-baking at 220 °C for 30 min. The optical density of the patterned samples was measured using an X-Rite 361T transmission densitometer, and the dielectric constants of the films were obtained from measured capacitances. UV (i-line) exposure equipment (Thermo-oriel Model 66902) was used for irradiation. Nikon Optiphot optical microscopy was used to measure the pattern properties.