Organic Photoconductive Films with Wavelength Selectivities

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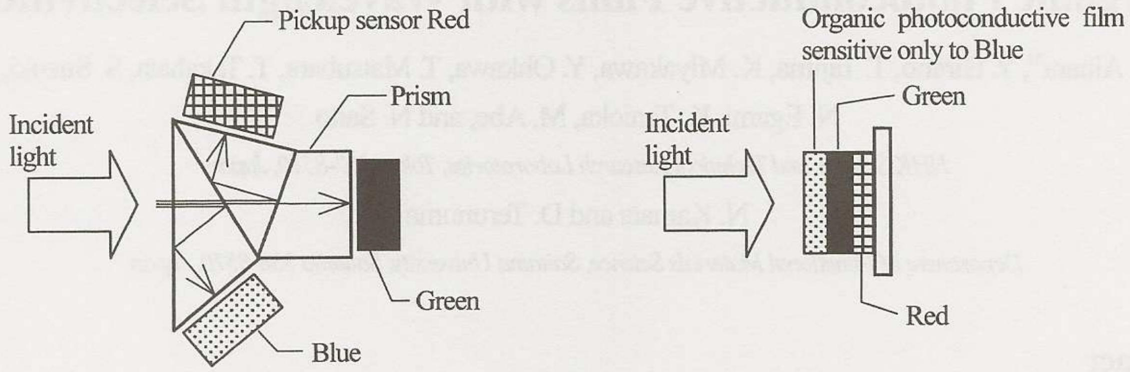
Abstract

Organic photoconductive films sensitive to blue-, green- and red-light were fabricated using coumarin 6-doped poly(*m*-hexoxyphenyl)phenylsilane (C6/PHPPS), rhodamine 6G-doped polymethylphenylsilane (R6G/PMPS) and zinc phthalocyanine/tris-8-hydroxyquinoline aluminum double layer (ZnPc/Alq_3), respectively. Selectivities of the spectral responses of these films were good enough to divide the incident light into three-color components, indicating the possibility of color separation without prism or color filter for video cameras. Quantum efficiency of ZnPc/Alq_3 film is over an order of magnitude better than those of C6/PHPPS and R6G/PMPS films due to the dissociation of electron-hole pair generated at the interface between ZnPc and Alq_3. Demonstration of image pickup operation from an organic photoconductive film incorporated into a pickup tube revealed that the limiting resolution is more than 800 TV lines, indicating that organic materials have large possibility as imaging device.

1. Introduction

For broadcast TV cameras, inorganic materials such as silicon or amorphous selenium are used as photoelectric conversion materials. Three-imagesensor pickup method is generally used for high- resolution color picture [1]: Incident light is separated into blue (B), green (G) and red (R) by a dichroic prism and then, they are detected individually by three photoelectric conversion devices such as charge-coupled device (CCD), CMOS sensor or image pickup tube configured after the prism as shown in Fig. 1(a).

On the other hand, single-photoconductor pick-up system consisting of color filter array (CFA)-coated CCD or CMOS sensor system is adopted for consumer-use video cameras. Each pixel of the CFA consists of B-, G- and R-subpixels at different locations. Though the system is beneficial to the small and lightweight camera, it is insufficient for broadcast camera due to its low spatial resolution and its low efficiency for incident photons. To realize compact, lightweight and high-resolution camera with high-efficiency for incident photons, prism-less single-photoconductor pick-up system other than the CFA is expected.



(a) Prism optical system of three-photosensor pickup camera.

(b) Novel single-photosensor pickup system.

Fig. 1. Optical arrangements for color cameras.

In a recent paper, photodetection with vertically stacked sensor structures, which detect the color information in the depth of the structure, have been demonstrated with amorphous silicon.[2] As color information is obtained at the same spatial position, stacked structures are useful for high-resolution camera. In addition, all the photons irradiated on the active area are used. The spectral sensitivity of the stacked sensors is controlled by both the carbon content in the amorphous silicon layers and the precise design of the devices. In the stacked system, one of the key points is simple fabrication of color-separation photoconductors.

Organic materials are one of the promising candidates because of their easiness of thin film fabrication as well as the variety of their spectral responses. Thin and lightweight photoconductors which have a large number of degrees of freedom in designing spectral sensitivity could be realized choosing organic molecules. Organic photoconductive films sensitive only to blue-, green-, or red-light lead us to realizing stacked color-imagesensor easily as shown in Fig. 1(b).

In this paper, we firstly focus on the fabrication of organic photoconductive films and their color-separation characteristics. Selectivities of the spectral responses of these films were good enough to divide the incident light into three-color components. Secondly, we demonstrate image pickup operation from an organic photoconductive film by incorporating it into a pickup tube for standard TV systems. The limiting resolution is more than 800 TV lines, indicating that organic materials have large possibility toward imaging device.

2. Experimental section

Polysilanes are chosen as the binder polymer of organic dyes in B- and G-sensitive films since polysilanes have a high hole drift mobility of as high as 10^{-4} cm^2/Vs.[3] We fabricated photoconductive films sensitive to B- and G-light composed of single layer structure with coumarin 6 (C6)-doped poly(*m*-hexoxyphenyl)phenylsilane (PHPPS) and rhodamine 6G (R6G)-doped polymethylphenylsilane (PMPS), respectively, and that sensitive to R-light composed of layer structure with zinc phthalocyanine

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(ZnPc) and tris-8-hydroxyquinoline aluminum (Alq_3).

PHPPS was synthesized by the conventional Wurtz-type reaction from (*m*-hexoxyphenyl) phenyldichlorosilane. The typical average molecular weight (Mw) of PHPPS was 80,000 revealed by gel permeation chromatography analysis based on polystyrene standard. The absorption peak wavelength of PHPPS is 395 nm with a full width at half maximum (FWHM) of 20 nm. The B-sensitive film was fabricated as follows. A chloroform solution of PHPPS (20 g/l) mixed with C6 of 5.0% (ratio of the number of C6 molecules to that of Si atoms in PHPPS) was spin-coated onto an indium-tin-oxide (ITO) coated quartz substrate to obtain a 1,000 nm-thick C6/PHPPS blend film. An aluminum electrode was then deposited onto the film with a thickness of 80 nm. As G-sensitive dye, R6G was chosen and dispersed in PMPS(Osaka gas chemicals Co., LTD.). Fabrication process, concentration of chloroform solution of PMPS mixed with R6G, and thickness of obtained film were the same as those of C6/PHPPS blend film.

For R-sensitive film, ZnPc was deposited onto an ITO-coated glass substrate with the deposition rate of 0.2 nm/s. Since ZnPc has hole transport nature, Alq_3 was deposited onto the ZnPc layer with the deposition rate of 0.15 nm/s as an electron transport layer. Thickness of both the layers is 100 nm. Then aluminum electrode was deposited onto the Alq_3 layer with the thickness of 80 nm.

3. Wavelength selectivities of fabricated organic photoconductive films

The solid line of Fig. 2 shows the absorption spectrum of R6G/PMPS blend film. There are two peaks at 510 nm and 545 nm, which correspond to the absorption of R6G. The open square of Fig. 2 represents the absorption spectrum of the pure PMPS film. PMPS has no absorption peak in visible wavelength region, which is suitable for the binder polymer of organic dye with the function of wavelength selectivities.

Current-voltage characteristics of the R6G/PMPS blend film (G-sensitive film) are shown in Fig. 3. Monochromatic light of 520 nm with the power of 0.05 $mWcm^{-2}$ was irradiated from the ITO side. The

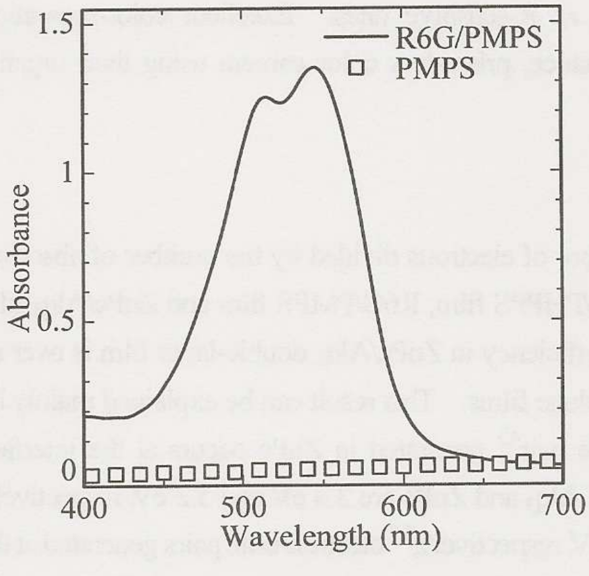


Fig. 2. Optical absorption spectrum of the R6G/PMPS film.

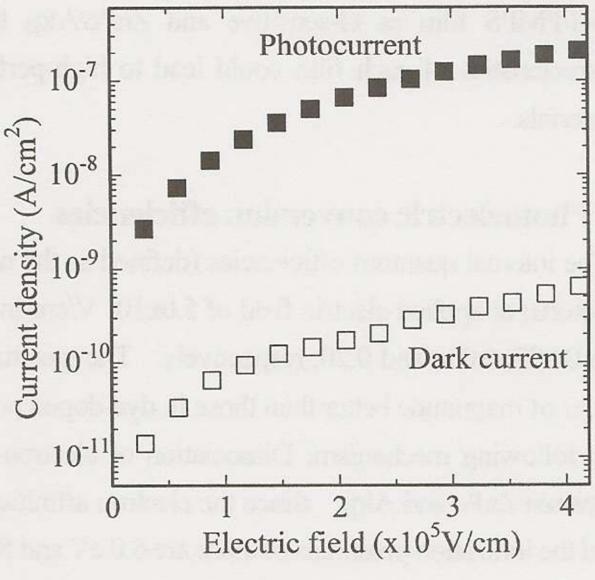


Fig. 3. Current-voltage characteristics of the R6G/PMPS film.

photocurrent rapidly increases to the applied electric field of 1.0×10^5 V/cm (ITO electrode is positively biased). When the target voltage is increased further, increase of the photocurrent tends to saturation. Since no photocurrent was observed in the PMPS film without R6G doping at the same wavelength, it is confirmed that the electric charges generated inside the R6G molecules contribute to the photocurrent observed in the film.

Figure 4(a) shows the absorption spectra of the three color-separation films. The dashed line represents the C6/PHPPS blend film as B-sensitive layer. The absorption peak of C6 is 450 nm. The dashed-dotted line in Fig. 4 (a) represents the absorption spectrum of ZnPc/Alq_3 double-layer film. The absorption peaks at 625 nm and 690 nm were observed. The film has also a weak absorption in the wavelength region shorter than 430 nm. This edge corresponds to the absorption of Alq_3.

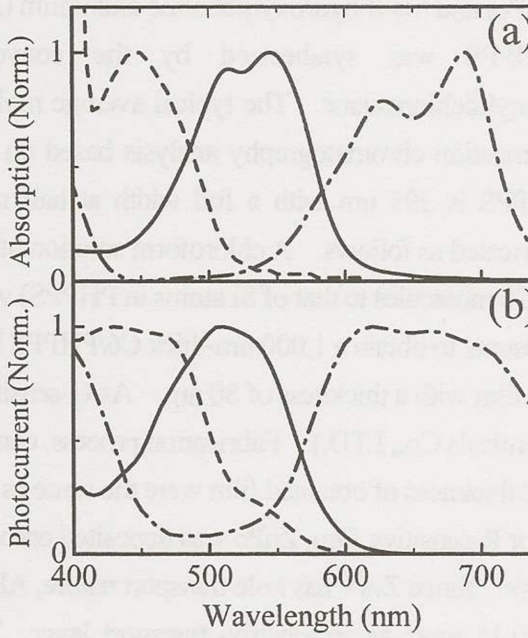


Fig. 4. Absorption spectra (a) and spectral photoresponse characteristics (b) of fabricated films. The dashed line, solid line and dashed-dotted line represent the C6/PHPPS blend film, R6G/PMPS blend film and ZnPc/Alq_3 double-layer film, respectively.

The spectral photoresponse characteristics of the three films are summarized in Fig. 4(b). Applied electric field was 5.0×10^5 V/cm for all the films. Positive bias was applied to the ITO electrode for C6/PHPPS and R6G/PMPS films, and to the Al electrode for ZnPc/Alq_3 film. As shown in the figure, each film works as a photoconductive film with a color-separation function: C6/PHPPS film as B-sensitive photoconductor, R6G/PMPS film as G-sensitive and ZnPc/Alq_3 film as R-sensitive ones. Excellent color-separation characteristics of each film could lead to high-performance, prism-less color camera using their organic materials.

4. Photoelectric conversion efficiencies

The internal quantum efficiencies (defined as the number of electrons divided by the number of absorbed photons) at applied electric field of 5.0×10^5 V/cm in C6/PHPPS film, R6G/PMPS film and ZnPc/Alq_3 film are 0.007, 0.008 and 0.20, respectively. The quantum efficiency in ZnPc/Alq_3 double-layer film is over an order of magnitude better than those in dye-doped polysilane films. This result can be explained mainly by the following mechanism: Dissociation of electron-hole pair[4,5] generated in ZnPc occurs at the interface between ZnPc and Alq_3. Since the electron affinities of Alq_3 and ZnPc are 3.3 eV and 3.2 eV, respectively, and the ionization potentials of those are 6.0 eV and 5.1 eV, respectively,[6,7] electron-hole pairs generated at the interface between Alq_3 and ZnPc are efficiently dissociated and the electrons are transferred to the higher-electron-affinity side immediately. These spatially separated photocarriers are driven to electrodes by applied electric field with low recombination probability.

In case of dyes/polysilanes blend films, it is reported that the electron affinities of C6 and polysilanes are 2.7 eV and 1.0 eV-1.5 eV, respectively, and the ionization potentials of those are 5.4 eV and 5.5 eV-5.6 eV, respectively.[8,9] Therefore, polysilanes work as potential barrier of the electron-hole pair generated in C6 rather than hole transport materials. Photocarriers move among dyes dominantly by hopping with the aid of applied electric fields. Optimization of energy levels in both polysilanes and doped dyes to efficiently transfer generated holes from a dye to a polysilane enables us to obtain a more efficient and high-speed photosensor.

5. Picture-image characteristics of an organic film at TV-frame rate incorporated into a pickup tube

We demonstrate image pickup operation from an organic film by incorporating it into a pickup tube to confirm that organic materials could work as photoconductor for TV camera.

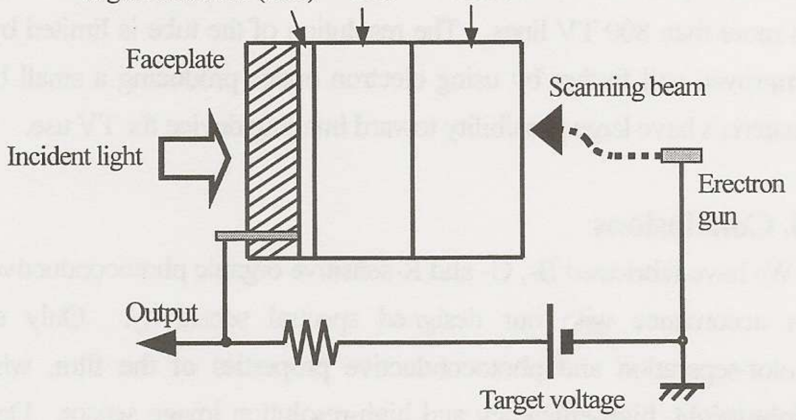
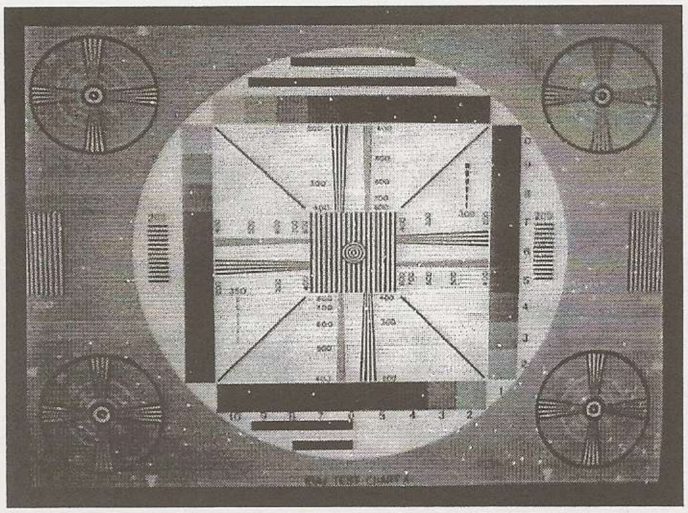
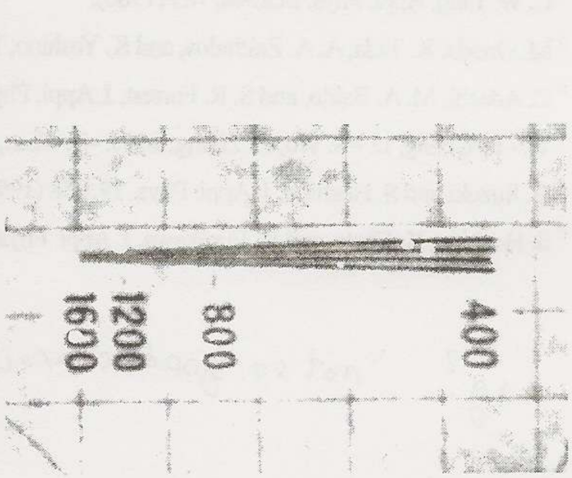


Fig. 5. The schematic arrangement of fabricated pickup tube.

Figure 5 shows the schematic arrangement of fabricated organic pickup tube. A 2/3 inch electromagnetic-focusing electro- magnetic-deflection (MM) tube has been employed. The organic film was fabricated as follows. First, bathocuproine (BCP) was evaporated with a deposition rate of 0.05 nm/s onto ITO electrode for hole blocking layer. Then ZnPc was evaporated with the rate of 0.05 nm/s as a



(a) NTSC operation.



(b) HDTV operation.

Fig. 6. Monitor photograph of fabricated organic pickup tube.

photoconductive layer. ZnPc has photosensitivity at R-band as shown in the dashed-dotted line of Fig. 4(b). Thickness of both the BCP and the ZnPc layer is 100nm (whole thickness of organic film is 200 nm).

Figure 6(a) shows a monitor picture of the Electronic Industries Association of Japan (EIAJ) test chart-A obtained from the fabricated-tube at NTSC operation. Applied voltage to the target is 50 V. As shown in the figure, very high-resolution image is obtained. This means that the surface resistivity of ZnPc is high enough to store the generated charges for TV use. White blemishes are shown in the picture since high electric fields are applied (2.5×10^6 V/cm). Optimization of film fabrication technique could reduce the number of white blemishes.

Monitor picture from the fabricated tube at HDTV operation is shown in Fig. 6(b). The limiting resolution is more than 800 TV lines. The resolution of the tube is limited by the size of the beam, so that it can be improved still further by using electron optics producing a small beam spot, which indicates that organic materials have large possibility toward imaging device for TV use.

6. Conclusions

We have fabricated B-, G- and R-sensitive organic photoconductive films and observed their photocurrents in accordance with our designed spectral sensitivity. Only choosing organic molecules can tune color-separation and photoconductive properties of the film, which enables us to approach toward a lightweight, high-efficiency and high-resolution image sensor. Demonstration of image pickup operation from an organic photoconductive film incorporated into a pickup tube revealed that the limiting resolution of the organic pickup tube is more than 800 TV lines.

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