

## Trend in research on organic imaging devices

At NHK Science and Technology Research Laboratories, we are researching and developing organic imaging devices. An organic imaging device is a new kind of single-chip imaging device that consists of a stack of organic photoelectric conversion layers for each primary color, each having a charge readout circuit that is transparent to visible light. We are using such devices as the basis for a new generation of super-compact high-quality color cameras. With the single-chip color imaging device, it is possible to separate light into different colors along the direction in which the light travels. This means it is possible in principle for it to have color imaging with the same picture quality as a system that uses a color separation prism. In this article, we discuss the concept of organic imaging devices and the characteristics of organic photoelectric conversion layers. We also describe the current status of device development.

### 1. Introduction

Today, almost all cameras used in broadcasting are based on a three-chip color imaging method that uses three imaging devices and a color separation prism to obtain high-quality color images. The increasing diversity of program production has led to a strong demand for broadcast cameras that are more compact and lightweight and have greater mobility, but this is difficult to achieve with three-chip cameras. A possible solution to this problem is to use a single-chip color imaging device, which eliminates the need for a color separation prism. However, single-chip technology has not been used much in broadcast cameras because its picture quality is still inferior to that of three-chip technology.

To comprehensively resolve this issue, STRL is researching and developing organic imaging devices. An organic imaging device is a new kind of single-chip

color imaging device that can independently extract the photo-generated charges corresponding to each primary color by separating light into its constituent primary colors as it passes through the device in the depth direction. Since an organic imaging device can generate a color video signal by using all of the incident light, it can in principle be used to implement a single-chip color imaging device that has the same picture quality as a three-chip system.

In this paper, after a discussion of the issues of modern camera imaging systems and the operating principles of organic imaging devices, we describe the characteristics of a prototype organic photoelectric conversion layer we made to verify these principles. Then, we discuss the current development status of organic imaging devices made by stacking such layers together.

### 2. Modern camera imaging systems

Figure 1 illustrates the color imaging systems used in modern cameras. A three-chip system obtains color information with three imaging devices, while a single-chip system obtains color information with a single imaging device. The three-chip system is mainly used in professional cameras. In this system, light that has passed through an optical lens is separated into the three primary colors - red (R), green (G) and blue (B) - by a color separation prism, and it is then converted into electrical signals by three separate imaging devices (Figure 1(a)). Although the three-chip system offers better sensitivity, resolution and color fidelity, it requires a color separation prism and three imaging devices. This limits the extent to which cameras based on this system can be made more compact and lightweight. On the other hand, most consumer-oriented video cameras and digital cameras use a single-chip color imaging system (Figure 1(b)), where the surface of a single imaging device is covered with a mosaic of color filters corresponding to the three

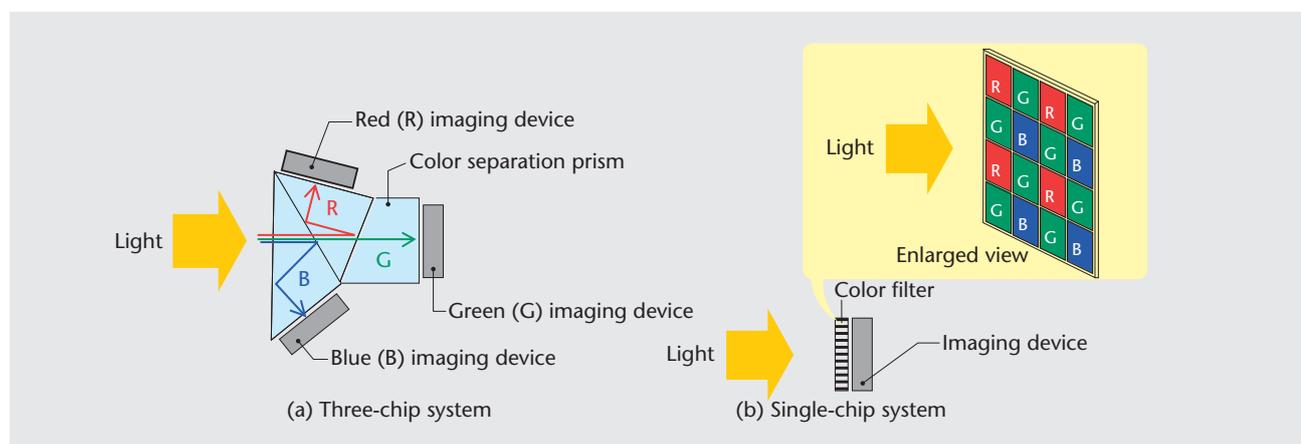
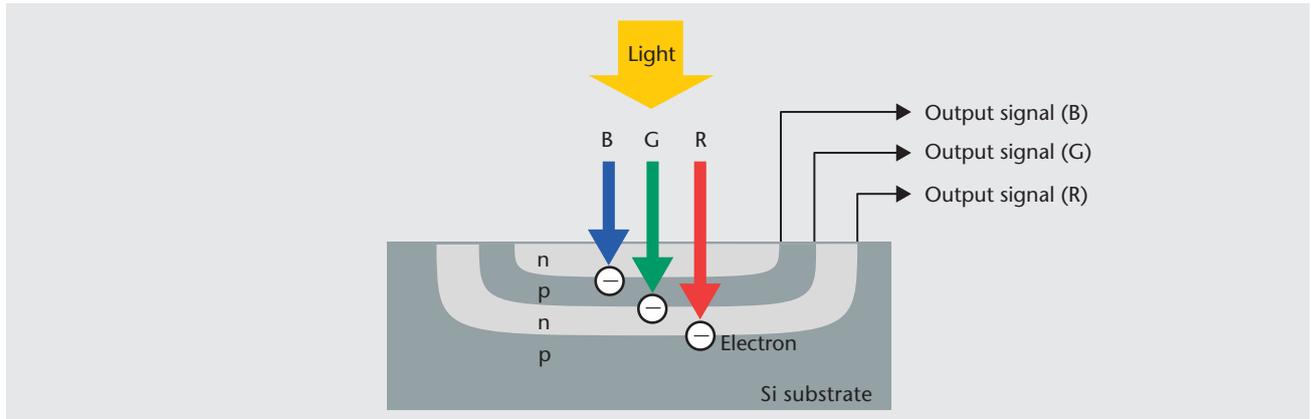


Figure 1: Modern color imaging systems



**Figure 2: Schematic diagram of a pixel in a single-chip color imaging device comprising a stack of Si photodiodes**

primary colors. Because a single-chip system needs only one imaging device and does not require a color separation prism, it allows cameras to be made more compact and lightweight. However, since the surface of the imaging device is covered with a color filter mosaic, this system is in principle inferior to a three-chip system in terms of its resolution and sensitivity.

It can thus be seen that current three-chip and single-chip systems have their advantages and disadvantages. However, if a way can be found to independently extract electrical charges corresponding to each primary color from each layer of a three-layer structure that separates light into primary colors as it passes through the structure (i.e., in the depth direction), then it should in principle be possible to capture images with a single-chip color imaging system whose picture quality matches that of a three-chip system.

An imaging device based on this idea has already been proposed. This device consists of a stack of photodiodes<sup>1</sup> formed on a silicon (Si) substrate.<sup>1)</sup> It relies on a phenomenon whereby when light enters a Si substrate, longer wavelengths penetrate deeper into the substrate. Figure 2 shows the cross-sectional structure of a single pixel in this device. It is formed from three layers of photodiodes comprising pn junction layers<sup>2</sup> in the depth direction of the Si substrate. When illuminated with white light, blue light (which has the shortest wavelengths) is absorbed by the photodiode in the first layer at the substrate surface, green light (which has longer wavelengths than blue light) is absorbed by the photodiode in the second layer, and red light (which

has longer wavelengths than both blue and green) is absorbed by the photodiode in the third layer. Electrical charges are generated corresponding to the amount of light absorbed in each photodiode, and they are independently extracted to obtain the color information. However, in this device, the Si used as a photoelectric conversion material absorbs light across the entire visible region, so, for example, some of the green and red light is also absorbed in the blue photodiode, and the spectral characteristics of each photodiode are wider than those of a color separation prism or color filter. Consequently, in this system, it is difficult to obtain color fidelity and sensitivity of the same standard as a three-chip system.

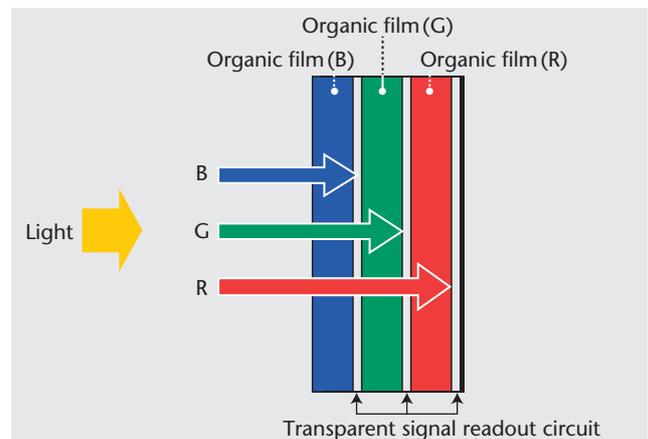
### 3. Structure and operating principle of an organic imaging device

Most organic materials<sup>3</sup> have the property of selectively absorbing only light of specific wavelengths, so by forming a stack of organic photoelectric conversion layers (referred to as “organic layers” below) that accurately select the three primary colors of light, it should be possible to implement a single-chip color

<sup>3</sup> Compounds with a basic structure made of carbon atoms.

<sup>1</sup> Photosensors that absorb light and output electrical current.

<sup>2</sup> A pn junction layer is a layer where a p-type semiconductor (where holes contribute to electrical conduction) and an n-type semiconductor (where electrons contribute to electrical conduction) are bonded together. This is a fundamental structure of semiconductor devices that exhibits phenomena such as rectification (only allowing currents to flow in one direction), photoelectric currents, photovoltaic effects and light emission.



**Figure 3: Conceptual structure of an organic imaging device**

imaging device that has the same image quality as a three-chip system. Figure 3 shows the structure and operating principle of an organic imaging device. An organic imaging device consists of a stack of three organic layers which are alternated with transparent circuits that read out the electric charges generated in each layer. When light strikes the device, blue light is absorbed by the layer that is sensitive to this color (the B organic layer), causing the creation of electron-hole pairs corresponding to the amount of absorbed light. These electron-hole pairs are separated into charges (electrons and holes) by an electric field, and these charges travel through the transparent circuits so they can be read out externally. The green and red light components pass through the B organic layer to the layer that is sensitive to green light (the G organic layer), where the green light is absorbed and a corresponding quantity of electron-hole pairs is generated. Similarly, the red light passes through the G organic layer and is absorbed by the layer that is sensitive to red light (the R organic layer), thereby generating a corresponding quantity of electron-hole pairs. In this way, the incident light is separated into the three primary colors in each organic layer, where it is converted into corresponding electric charges and output externally. Since an organic imaging device can accurately split light into the three primary colors as it propagates deeper into the device, it can use light much more efficiently than a single-chip system that uses color filters. Also, compared with a stacked photodiode single-chip imaging device made with Si, this device has superior sensitivity and color fidelity.

#### 4. Characteristics of organic layers

Since most organic materials have the property of only absorbing light in specific wavelength regions, we decided to use organic materials in the photoelectric converter. However, with regard to device implementation, it was considered that (i) each organic layer should selectively absorb and generate charges from light of just one primary color, and should be transparent to light of other colors, (ii) the organic layers should have high sensitivity (quantum efficiency<sup>\*4</sup>), and (iii) it should be possible to achieve high resolution without having to subdivide the layers into individual pixels.

##### 4.1 Photoresponse characteristics and optical transmittance

The color of an organic layer that generates electric charge by absorbing one of the three primary colors of light is the complement of the color that the layer absorbs. We therefore investigated organic materials that form layers with the complementary colors to red, green and blue - i.e., cyan, magenta and yellow respectively. As examples of materials that satisfy this condition, we

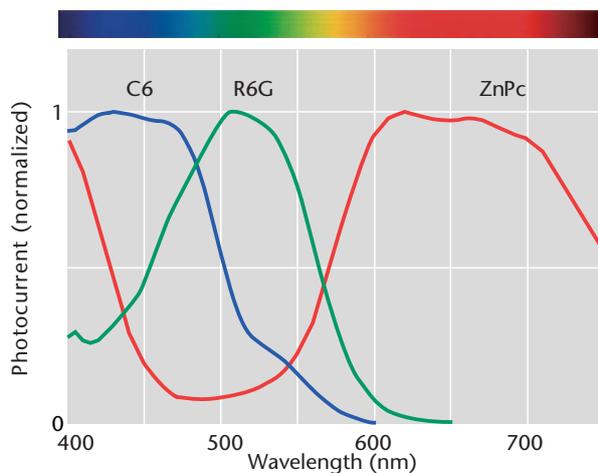


Figure 4: Example of the spectral photoresponse characteristics of organic layers

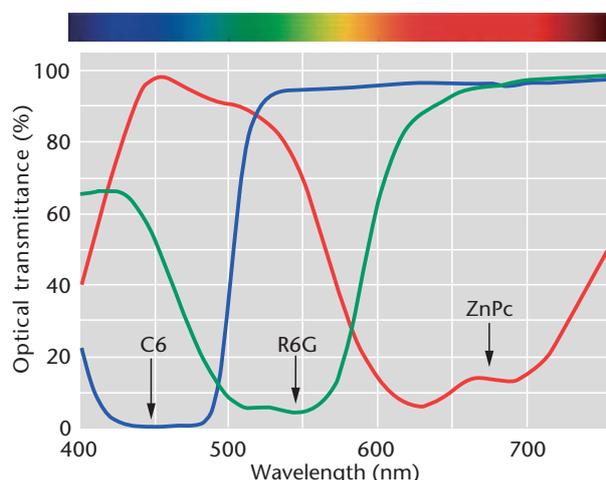


Figure 5: Example of the optical transmittance of organic layers

selected coumarin 6 (C6) for blue light, rhodamine 6G (R6G) for green light, and zinc phthalocyanine (ZnPc) for red light. We made experimental prototype cells by sandwiching these materials between a transparent electrode and an aluminum electrode, and we investigated their spectral photoresponse characteristics<sup>2)</sup> and optical transmittance. The spectral photoresponse characteristics and optical transmittance of each cell are shown in Figures 4 and 5 respectively. As Figure 4 shows, it is possible to obtain photo-generated charges that correspond closely to the three primary colors in each cell. Also, Figure 5 shows that the C6 layer absorbs light in the blue region but allows over 90% of the light in the green and red regions to pass through, the R6G layer absorbs light in the green region but allows over 90% of the light in the red region to pass through, and the ZnPc layer absorbs light in the red region.

The R6G and ZnPc layers have low transmittance in the blue region, but although this does not necessarily satisfy condition (i) above, we confirmed that it is still possible to separate the three primary colors and convert them into electric charges in the depth direction of the

\*4 The number of electrons output when the device is irradiated with a single photon.

device by stacking the chosen organic materials in a suitable order.

#### 4.2 Quantum efficiency

In the organic layers, the absorption of light causes electron-hole pairs to be generated with very high efficiency. Therefore, high quantum efficiency can be achieved if these electron-hole pairs can be efficiently separated and retrieved outside the device. However, in most organic materials, electron-hole pairs have a large binding energy<sup>5</sup> and cannot easily be separated. This problem has become a major obstacle to achieving high efficiency in organic solar cells, which have been actively developed in recent years. However, in the field of organic solar cells it is known that if a material with a strong ability to draw in electrons (an electron-accepting material) is brought into contact with a photoelectric conversion material at the molecular level, then electron-hole pairs can easily be separated at the contact interface.<sup>3</sup> Since this phenomenon may also be effective for improving the quantum efficiency of photoelectric conversion layers used in organic imaging devices, we investigated how the addition of fullerenes<sup>6</sup> (typical electron-accepting materials) improves the quantum efficiency of a prototype layer of the organic material coumarin 30 (C30), which is sensitive to blue light. As a result, we found that the addition of 10% fullerene boosts the quantum efficiency of a C30 layer by a factor of at least six.<sup>4</sup> We have thus found that with the appropriate combination of organic materials having different functions, it is possible to obtain an organic layer with high quantum efficiency that satisfies requirement (ii).

#### 4.3 Resolution

To verify requirement (iii), we examined the resolution of a prototype HDTV camera tube made using dimethyl quinacridone (an organic material that is sensitive to green light) as the photoelectric conversion layer. In the

camera tube, photo-generated charges are accumulated in the organic layer for up to 1/60th of a second. The organic layer is not separated into pixels, so if the layer itself has insufficient resolution, this is due to the lateral diffusion of accumulated charges across the organic layer. From the results of image capture tests, we were able to obtain images with good resolution, as shown in Figure 6. This shows that it is possible to achieve high resolution comparable to HDTV even if the organic layers are not subdivided into individual pixels,<sup>5</sup> thus satisfying condition (iii).

#### 5. Development status of organic imaging devices

We are currently working on a prototype single-chip color imaging device based on stacked organic layers.<sup>6,7</sup> To read out the accumulated charges from the organic layers, it is appropriate to use thin film transistor (TFT) circuits that are capable of being formed on a transparent substrate. Currently, amorphous silicon (a-Si)<sup>7</sup> and polysilicon (poly-Si)<sup>8</sup> are widely used in the TFTs of liquid crystal displays, but a-Si and poly-Si are both sensitive to visible light. This means that the transistor parts must be protected from light when used in a single-chip color imaging device, causing a reduction in light utilization efficiency. We therefore turned our attention to oxide semiconductors that are not sensitive to the visible light region. Typical oxide semiconductor materials include zinc oxide (ZnO) and indium gallium zinc oxide (IGZO). Both of these materials have a band gap<sup>9</sup> that is larger than the maximum energy of visible light (3.0 eV), which means they are not sensitive to visible light so there is no need to protect them from it. In other words, with oxide semiconductors it is possible to make TFT circuits that have no light-shielding parts.

So far, to verify the principle of a single-chip color imaging device, we have produced three separate elements by forming R, G and B organic layers and a ZnO charge readout TFT circuit layer on three glass substrates, and we stacked these elements together to produce an imaging device with the B layer closest to the incident light, followed by the G and R layers (128×96 pixels, pixel pitch 100 μm).<sup>7</sup> From the results of imaging tests, we were able to confirm that this device is able to obtain color video images, and that the organic imaging device can function as a single-chip color imaging device.

Here, as shown in Figure. 7, organic layers

<sup>5</sup> The energy generated by the mutual attraction between electrons and holes.

<sup>6</sup> Substances consisting of several dozen carbon atoms in a spherical arrangement

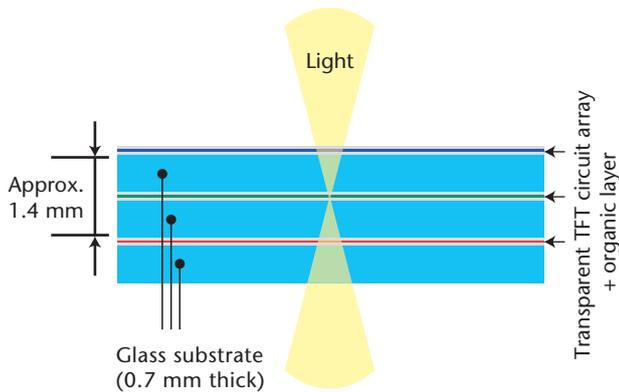


**Figure 6: Example of an image obtained by an imaging tube incorporating an organic layer**

<sup>7</sup> Silicon with a non-crystalline structure that can easily be applied to devices with a large area.

<sup>8</sup> Silicon consisting of a large number of crystal grains. Its electron mobility is substantially greater than that of a-Si.

<sup>9</sup> The energy difference between the top of a semiconductor's valence band (the band of energy levels occupied by electrons) and the bottom of the conduction band (the band of unoccupied energy levels). A semiconductor can only absorb light of energies that exceed the band gap.



**Figure 7: Stacked layer structure used so far**

corresponding to the three primary colors of light are formed on separate glass substrates to form three elements which are stacked together to form a single imaging device. With this configuration, when the optical image is focused on the G organic layer in the middle of the three layers, the images formed on the B and R optical layers are blurred, and this can cause a loss of resolution in the output image. The range of depths within which departure from the focal point does not cause any noticeable blurring – i.e., the depth of focus  $\Delta X$  – can be expressed by the following formula:

$$\Delta X = \pm F\delta \dots \dots \dots (1)$$

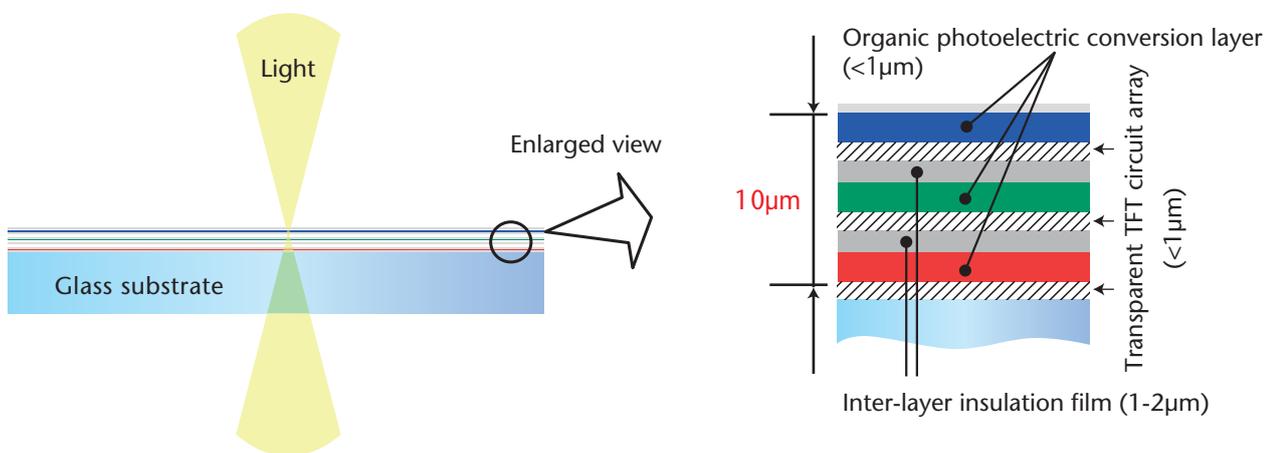
where  $F$  is the lens aperture value, and  $\delta$  is the amount of spreading in the optical image that can be tolerated by the device (the diameter of the permissible circle of confusion).

In the prototype imaging device, assuming the diameter of the permissible circle of confusion is equal to the pixel pitch (100  $\mu\text{m}$ ), the depth of focus  $\Delta X$  is  $\pm 200 \mu\text{m}$  for an aperture value of  $F=2.0$ . This means that when the optical image is focused on the G organic layer, the gap between the G layer and the R or B layer must not exceed 200  $\mu\text{m}$  if there is to be no blurring of the output

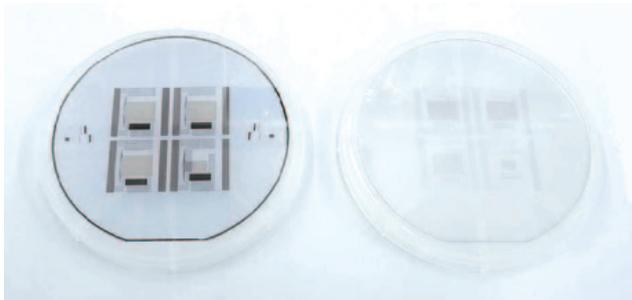
images from the B and R layers. However, blurring currently occurs in the device because the organic layers are formed on glass substrates that are 700  $\mu\text{m}$  (0.7 mm) thick. This blurring becomes more pronounced as the aperture of the optical lens is increased. When the pixels are made smaller and integrated more densely to approach the 5  $\mu\text{m}$  pixel pitch of the 2/3-inch imaging devices<sup>10</sup> currently used in broadcast-quality HDTV handheld cameras, the gap between the G organic layer and the B/R layers must be within 10  $\mu\text{m}$ , so it will be impossible to suppress blurring of the output image in techniques where individual organic layers are formed on three separate glass substrates.

We have therefore started work on developing a directly stacked organic imaging device where the R, G and B organic layers are formed close to each other on a single glass substrate and separated by inter-layer insulation films<sup>8)</sup> (Figure 8). If the organic layers and the transparent TFT circuits are each less than 1  $\mu\text{m}$  thick and the inter-layer insulation film thickness is 1-2  $\mu\text{m}$  thick, then the distance between the outermost and innermost organic layers can be reduced to approximately 10  $\mu\text{m}$ . This means that a directly stacked configuration enables the construction of devices that be applied to HDTV cameras. To develop a directly stacked organic imaging device, it will be necessary to fabricate inter-layer insulation films and TFT circuit arrays on the lower organic layers as shown in Fig. 8. However, organic materials generally have poor heat resistance, while the fabrication of inter-layer insulation films and TFT circuits requires high temperatures of 300°C or more, so it is not possible to produce these devices with current process technology. At STRL, we are therefore developing core technologies for the fabrication of devices at temperatures below 150°C in consideration of the poor heat resistance of organic materials.

<sup>10</sup> Imaging devices with an effective imaging region that has a diagonal length of approximately 11 mm.



**Figure 8: Directly stacked structure**



(a)TFT circuit with metal wirings (b)Transparent TFT circuit

**Figure 9: Side-by-side comparison of glass wafers with TFT circuits formed on their surfaces**

In the experiments to verify the principle of this device, we used a TFT circuit with metal wirings, which resulted in a device with low transparency (approximately 52%). We recently made a new prototype single-layer imaging device that combines a red-sensitive organic layer with a TFT circuit in which the metal circuit wirings have been replaced with indium tin oxide (ITO).<sup>9)</sup> Figure 9(a) shows a glass wafer that has a TFT circuit made with metal wirings formed on its surface, and Figure 9(b) shows a glass wafer on which a transparent TFT circuit has been formed. By making the wirings transparent, we were able to improve the optical transmittance of the TFT circuit to 80%, resulting in a device with substantially higher light utilization efficiency. Also, for a fully transparent TFT circuit, we used the oxide semiconductor material IGZO, which should be able to operate stably even when formed into tiny pixels, and we were able to reduce the pixel pitch to 50  $\mu\text{m}$ , which is half the size achieved hitherto.

## 6. Conclusion

We presented an overview of our research and development of organic imaging devices — a new kind of single-chip imaging device that can be expected to achieve the same level of picture quality as three-chip systems that use a color separation prism.

An organic imaging device consists of a stack of organic layers that are sensitive to blue, green and red light respectively, alternated with TFT circuits that independently read out the charges accumulated in each of these organic layers. So far, we have completed our verification of the principles of this technology, and we are currently working on the development of core technologies that will allow us to produce smaller, more densely integrated pixels in order to achieve devices with higher resolution.

If it is possible to implement a single-chip color imaging device with the same picture quality as a three-chip system, this will lead not only to more compact broadcast-quality cameras, but also to higher performance video and digital cameras for domestic use. To hasten the development of practical organic single-chip color imaging devices, we plan to further accelerate our research and development in this field.

The research of organic photoelectric conversion layers discussed in this article was carried out with the cooperation of Saitama University, and the research of TFT charge readout circuits was carried out with the cooperation of Kochi University of Technology.

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## References

- 1) R.B. Merrill: U.S. Patent, No. 5,965,875 (1999)
- 2) S. Aihara, Y. Hirano, T. Tajima, K. Tanioka, M. Abe, N. Saito, N. Kamata and D. Terunuma: "Wavelength Selectivities of Organic Photoconductive Films: Dye-doped Polysilanes and Zinc Phthalocyanine/Tris-8-hydroxyquinoline Aluminum Double Layer," *Appl. Phys. Lett.* Vol. 82, No. 4, pp. 511-513 (2003)
- 3) M. Hiramoto, H. Fujiwara and M. Yokoyama: "Three-layered Organic Solar Cell with a Photoactive Interlayer of Codeposited Pigments," *Appl. Phys. Lett.*, Vol. 58, No. 10, pp. 1062-1064 (1991)
- 4) H. Seo, S. Aihara, M. Kubota and N. Egami: "Improvement in Photoconductive Properties of Coumarin 30 - Evaporated Film by Fullerene Doping for Blue - Sensitive Photoconductors," *Jpn. J. Appl. Phys.*, Vol. 49, No. 11, pp. 111601.1-111601.4 (2010)
- 5) S. Aihara, K. Miyakawa, Y. Ohkawa, T. Matsubara, T. Takahata, S. Suzuki, N. Egami, N. Saito, K. Tanioka, N. Kamata and D. Terunuma: "Image Pickup from Zinc Phthalocyanine/Bathocuproine Double-Layer Film Using Pickup Tube," *Jpn. J. Appl. Phys.*, Vol. 42, No. 7 B, pp. L801-L803 (2003)
- 6) S. Aihara, H. Seo, M. Namba, T. Watabe, H. Ohtake, M. Kubota, N. Egami, T. Hiramatsu, T. Matsuda, M. Furuta, H. Nitta and T. Hirao: "Stacked Image Sensor with Green- and Red-Sensitive Organic Photoconductive Films Applying Zinc-Oxide Thin Film Transistors to a Signal Readout Circuit," *IEEE Trans. Electron Devices*, Vol. 56, No. 11, pp. 2570-2576 (2009)
- 7) H. Seo, S. Aihara, T. Watabe, H. Ohtake, T. Sakai, M. Kubota, N. Egami, T. Hiramatsu, T. Matsuda, M. Furuta, H. Nitta and T. Hirao: "A 128 x 96 Pixel Stack-Type Color Image Sensor: Stack of Individual Blue-, Green-, and Red-Sensitive Organic Photoconductive Films Integrated with a ZnO Thin Film Transistor Readout Circuit," *Jpn. J. Appl. Phys.*, Vol. 50, No. 2, pp. 024103.1-024103.6 (2011)
- 8) H. Seo, S. Aihara, T. Watabe, H. Ohtake, T. Sakai, M. Kubota, N. Egami, T. Hiramatsu, T. Matsuda, M. Furuta and T. Hirao: "A 128 x 96 Pixel Stack-Type Color Image Sensor with B-, G-, R-sensitive Organic Photoconductive Films," *Proc. 2011 International Image Sensor Workshop (IISW2011) R33*, pp. 236-239 (2011)
- 9) T. Sakai, H. Seo, S. Aihara, M. Kubota, N. Egami, D. Wang and M. Furuta: "A 128 x 96 Pixel, 50  $\mu\text{m}$  Pixel Pitch Transparent Readout Circuit Using Amorphous In-Ga-Zn-O Thin Film Transistor Array with Indium-Tin Oxide Electrodes for an Organic Image Sensor," *Jpn. J. Appl. Phys.*, Vol. 51, No. 1, pp. 010202.1-010202.3 (2012)