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Saito et al.

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(54) **SOLID-STATE IMAGING ELEMENT, METHOD FOR MANUFACTURING SOLID-STATE IMAGING ELEMENT, PHOTOELECTRIC CONVERSION ELEMENT, IMAGING DEVICE, AND ELECTRONIC APPARATUS**

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H10K 85/20 (2023.01)

H10K 85/60 (2023.01)

(52) **U.S. Cl.**

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(58) **Field of Classification Search**

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See application file for complete search history.

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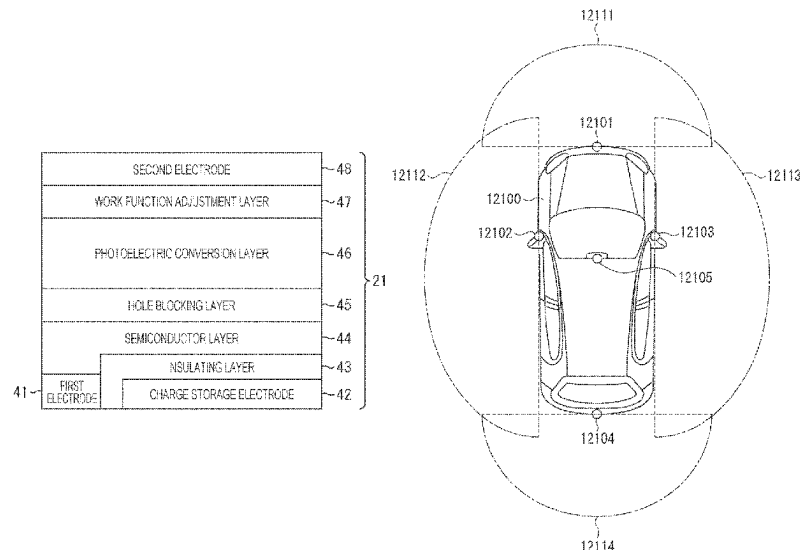
(57)

ABSTRACT

The present technology relates to a solid-state imaging element, a method for manufacturing a solid-state imaging element, a photoelectric conversion element, an imaging device, and an electronic apparatus that are capable of realizing highly efficient photoelectric conversion of blue light with organic photoelectric conversion element.

A first organic semiconductor having a characteristic of absorbing blue light, a second organic semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and a third organic semiconductor including a fullerene derivative are mixed to form an organic photoelectric conversion layer. The present technology can be applied to a solid-state imaging element.

16 Claims, 14 Drawing Sheets



(52) U.S. Cl.

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85/6574 (2023.02); *H10K 85/6576* (2023.02)

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FIG. 1

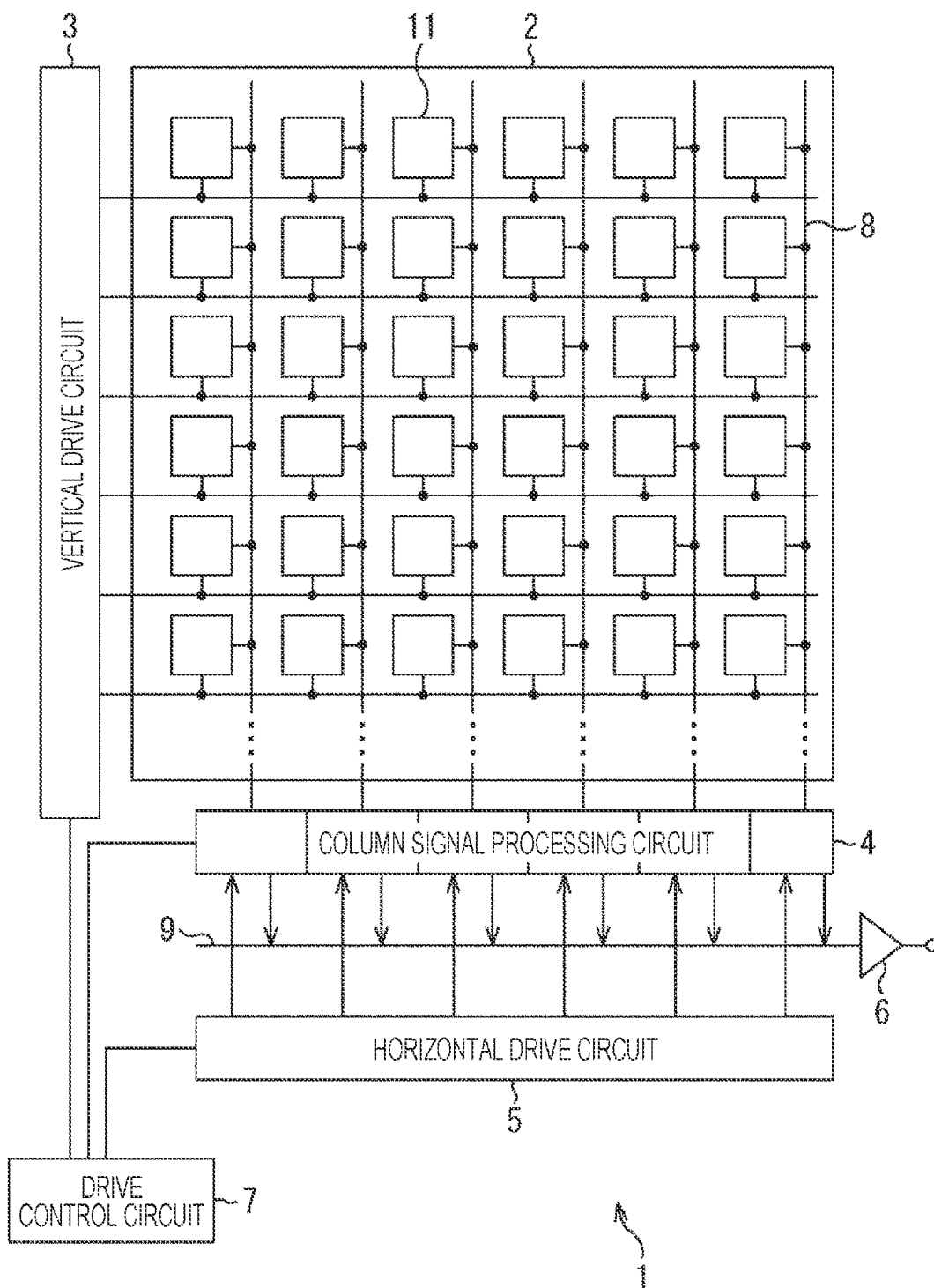


FIG. 2

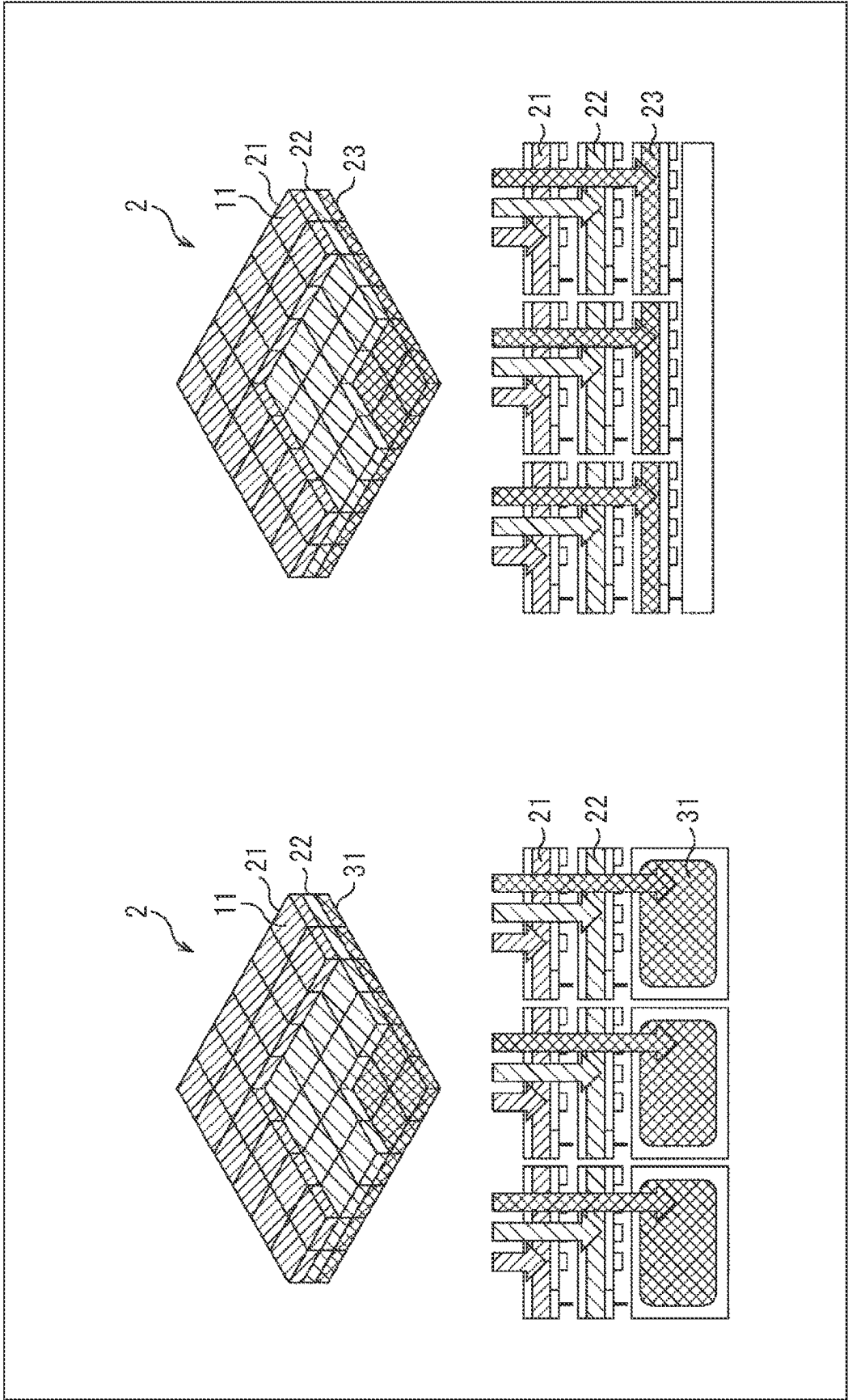


FIG. 3

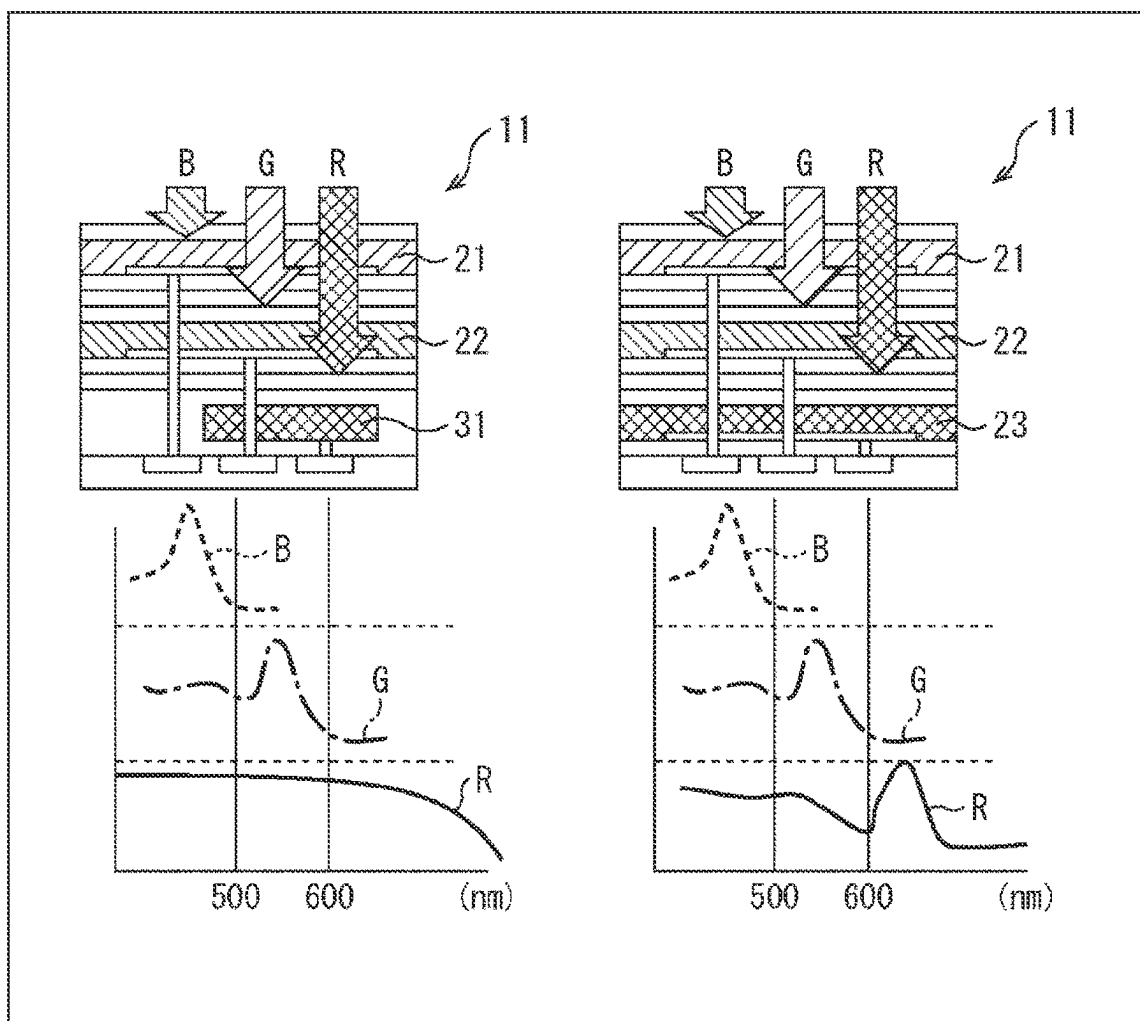


FIG. 4

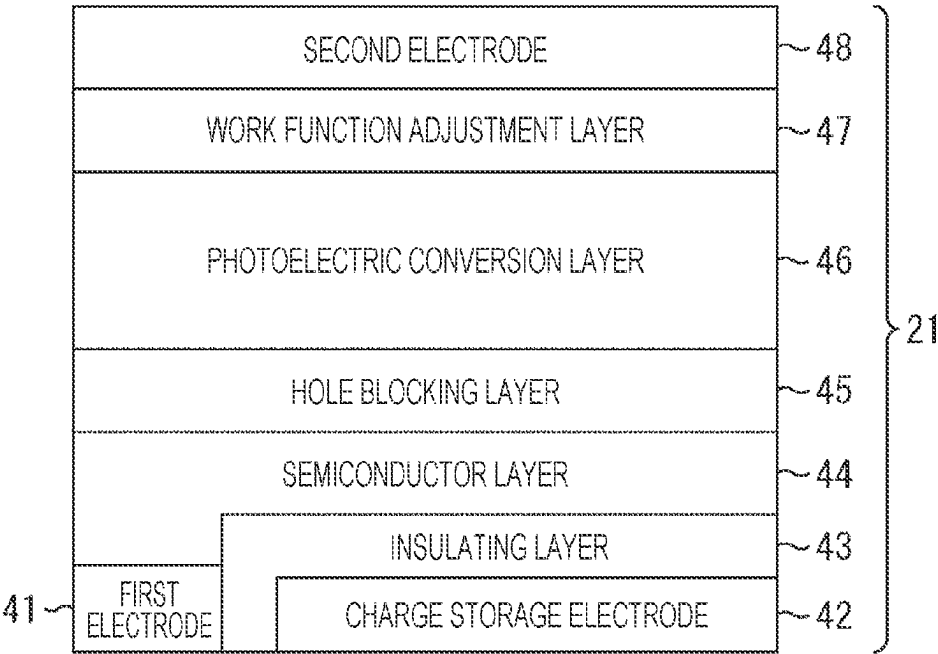


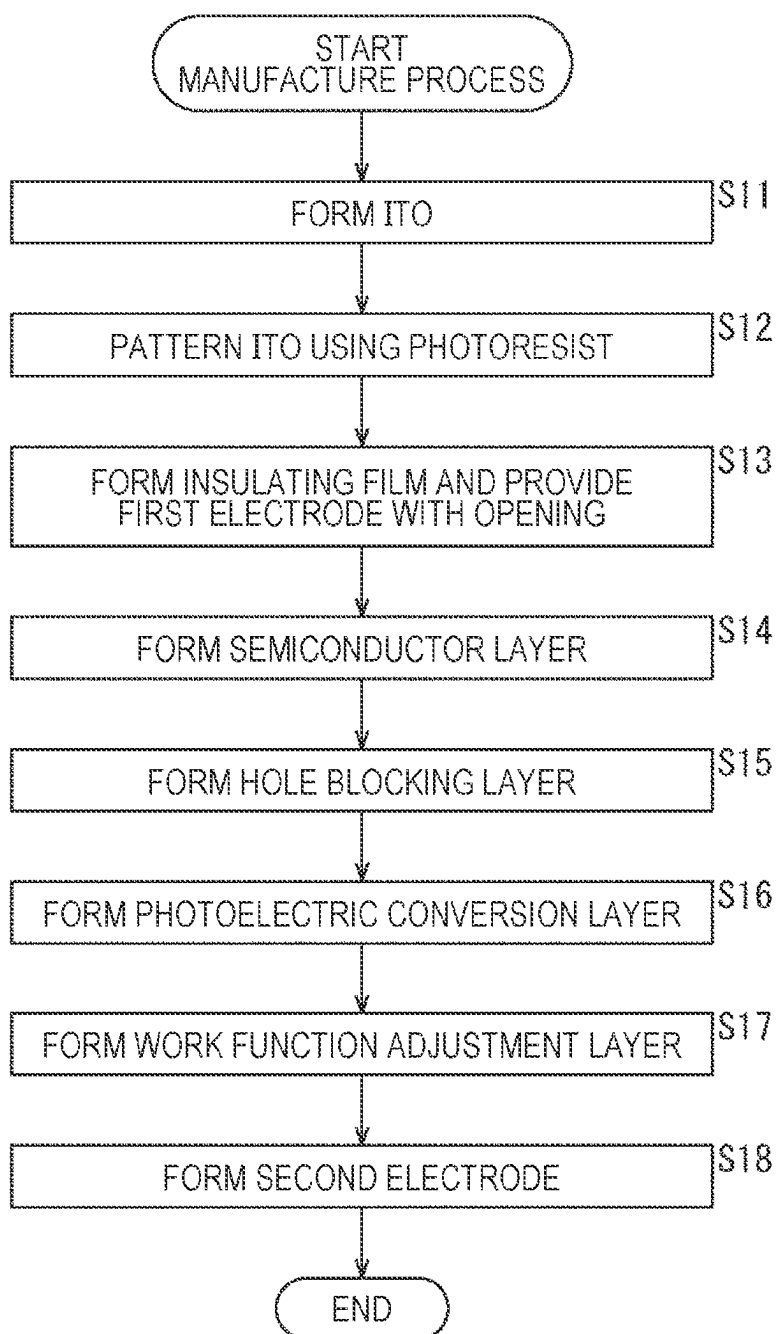
FIG. 5

FIG. 6

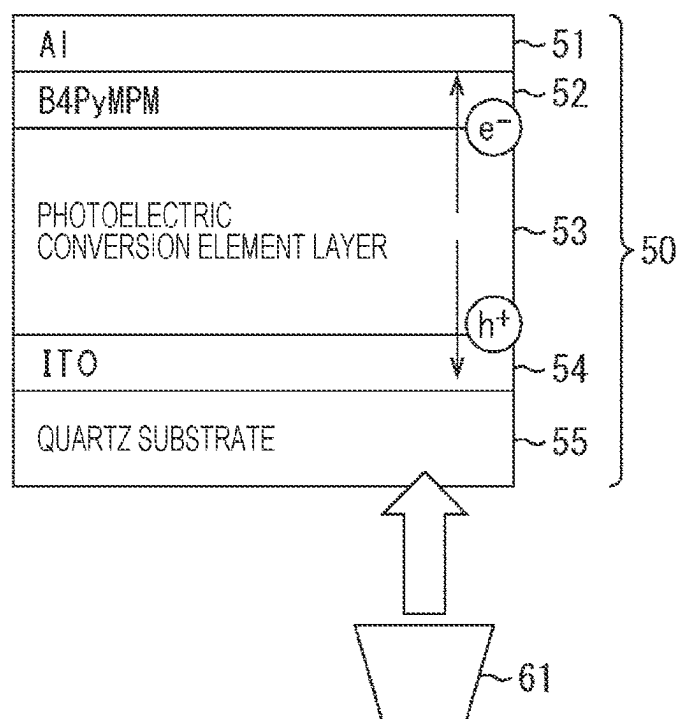


FIG. 7

EXAMPLE	FIRST ORGANIC SEMICONDUCTOR a	SECOND ORGANIC SEMICONDUCTOR b	THIRD ORGANIC SEMICONDUCTOR c	RATIO (a:b:c)	α 450nm (cm^{-1})	α 560nm (cm^{-1})	α 450nm/ α 560nm	Jdk (NORMALIZED)	EQE (NORMALIZED)	RESPONSE TIME (NORMALIZED)	CHARACTERISTICS SIGNIFICANTLY INFERIOR TO THOSE IN EXAMPLE 1
1	SG5	DNIT	C60	4:4:2	9.5E+4	4.2E+3	23	1.00	1.00	1.00	—
2	SG5	DNIT	C60	5:3:2	9.9E+4	4.2E+3	24	0.92	0.99	1.10	NONE
3	SG5	DNIT	C60	3:5:2	9.2E+4	4.1E+3	22	1.12	1.02	0.95	NONE
4	SG5	DNIT	C60	3.5:3.5:3	9.2E+4	6.1E+3	15	1.64	1.08	0.98	NONE
5	SG5	DNIT	C60	0:5:5	5.6E+4	1.9E+4	3	0.98	0.65	1.04	SPECTRAL/EQE
6	SG5	DNIT	C60	5:0:5	8.3E+4	1.4E+4	6	1.10	0.98	14.5	SPECTRAL/RESPONSE
7	SG5	DNIT	C60	5:5:0	1.3E+4	1.5E+3	87	23.0	0.45	n/a	DARK CURRENT/ EQE/RESPONSE
8	SG5	BTBT	C60	4:4:2	3.8E+4	4.2E+3	9	1.00	0.63	1.00	SPECTRAL/EQE

FIG. 8

EXAMPLE	FIRST ORGANIC SEMICONDUCTOR a	SECOND ORGANIC SEMICONDUCTOR b	THIRD ORGANIC SEMICONDUCTOR c	RATIO (a:b:c)	α 450nm (cm^{-1})	α 560nm (cm^{-1})	α 450nm/ α 560nm	Jdk (NORMALIZED)	EQE (NORMALIZED)	RESPONSE TIME (NORMALIZED)	CHARACTERISTICS SIGNIFICANTLY INFERIOR TO THOSE IN EXAMPLE 11
11	Coumarin 6	DBP— BTBDT	C60	4:4:2	1.9E+5	6.2E+3	31	1.00	1.00	1.00	—
12	Coumarin 6	DBP— BTBDT	C60	5:3:2	2.1E+5	5.4E+3	39	0.91	0.97	1.21	NONE
13	Coumarin 6	DBP— BTBDT	C60	3:5:2	1.8E+5	6.5E+3	28	1.24	1.08	0.93	NONE
14	Coumarin 6	DBP— BTBDT	C60	3:5:3.5:3	1.8E+5	8.1E+3	22	1.73	1.08	0.97	NONE
15	Coumarin 6	DBP— BTBDT	C60	0:5:5	5.9E+4	1.7E+4	3	1.02	0.70	1.01	SPECTRAL/EQE
16	Coumarin 6	DBP— BTBDT	C60	5:0:5	1.8E+5	2.2E+4	8	1.32	0.43	12.5	SPECTRAL/RESPONSE
17	Coumarin 6	DBP— BTBDT	C60	5:5:0	2.3E+5	1.9E+3	121	53.1	0.12	n/a	DARK CURRENT/ EQE/RESPONSE
18	Coumarin 6	BTBT	C60	4:4:2	1.2E+5	5.3E+3	23	0.98	0.56	1.02	SPECTRAL/EQE

FIG. 9

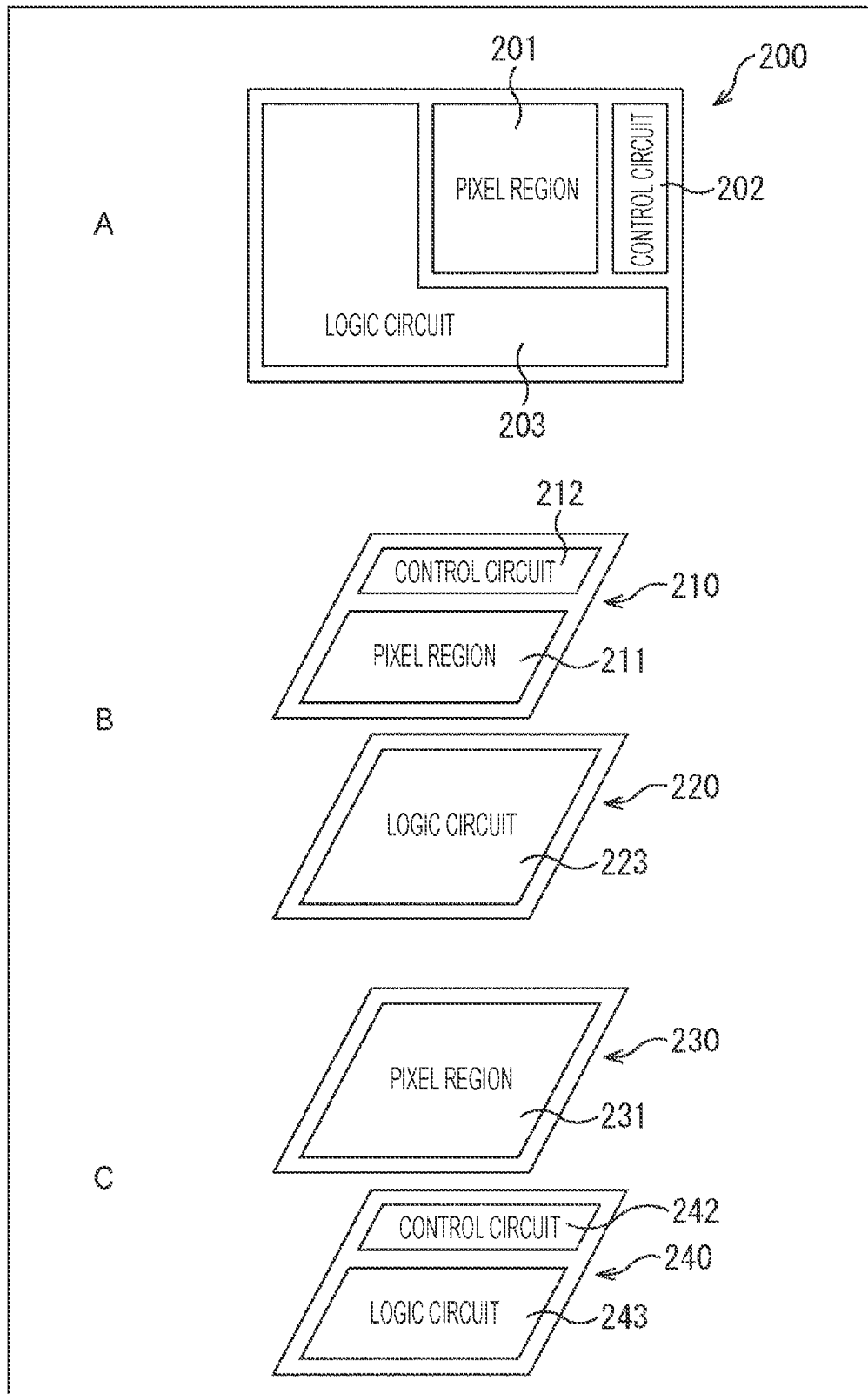


FIG. 10

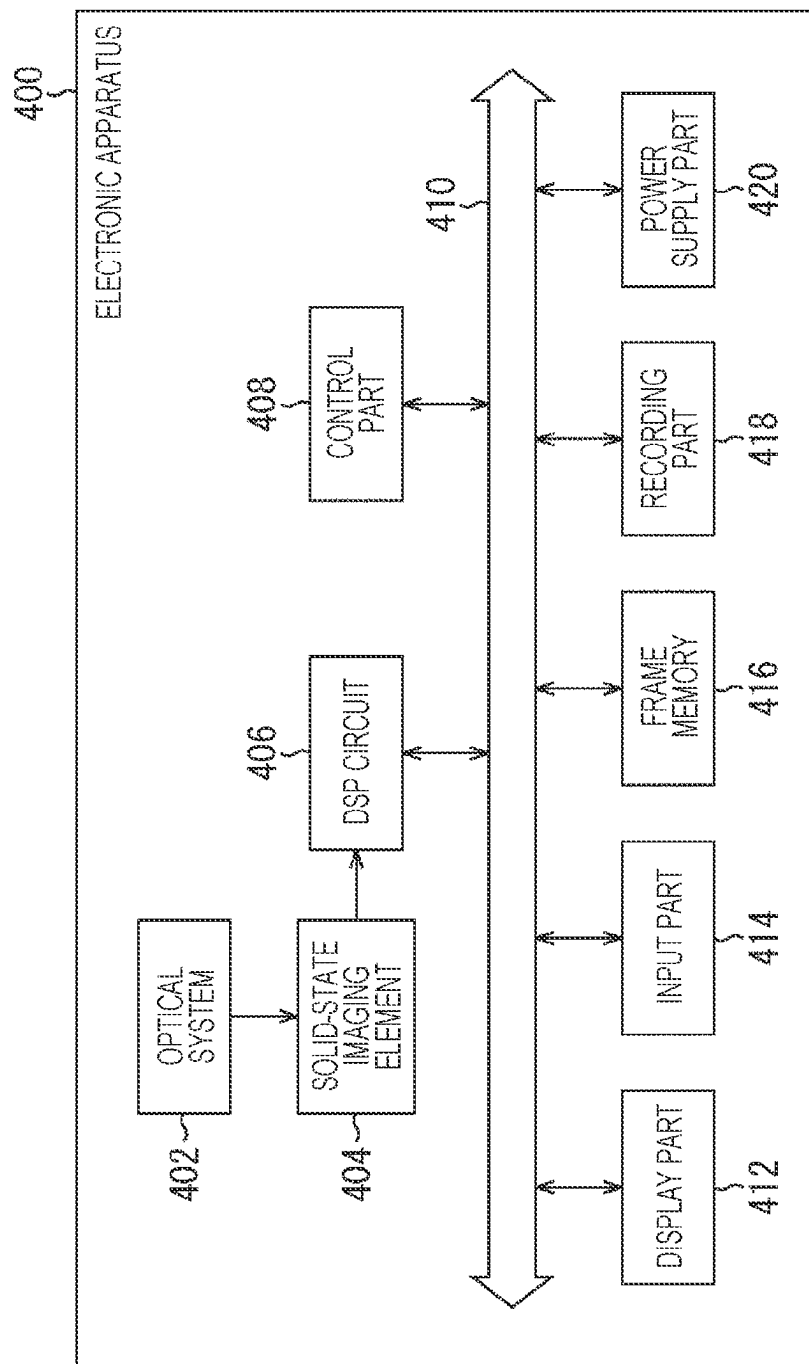


FIG. 11

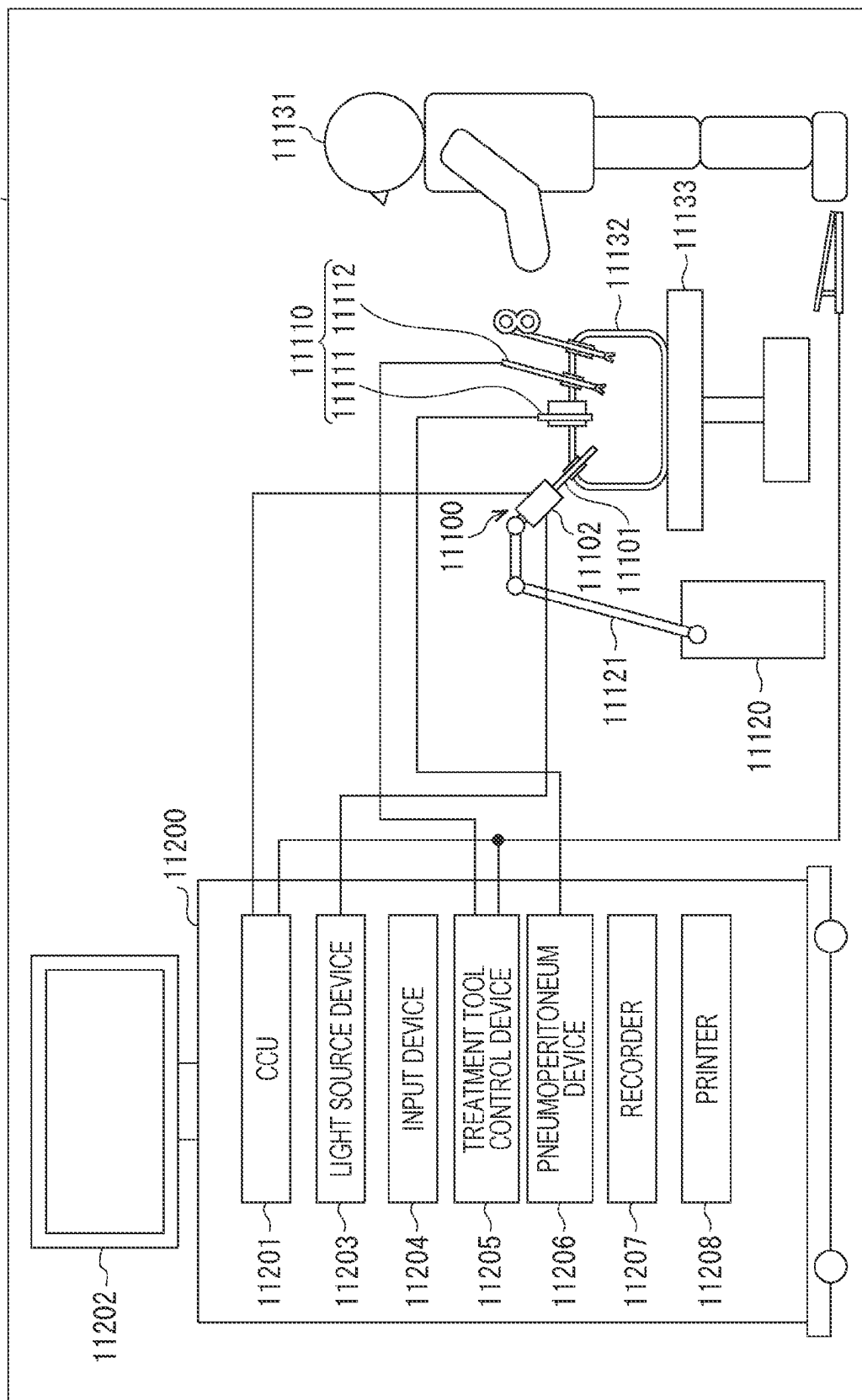


FIG. 12

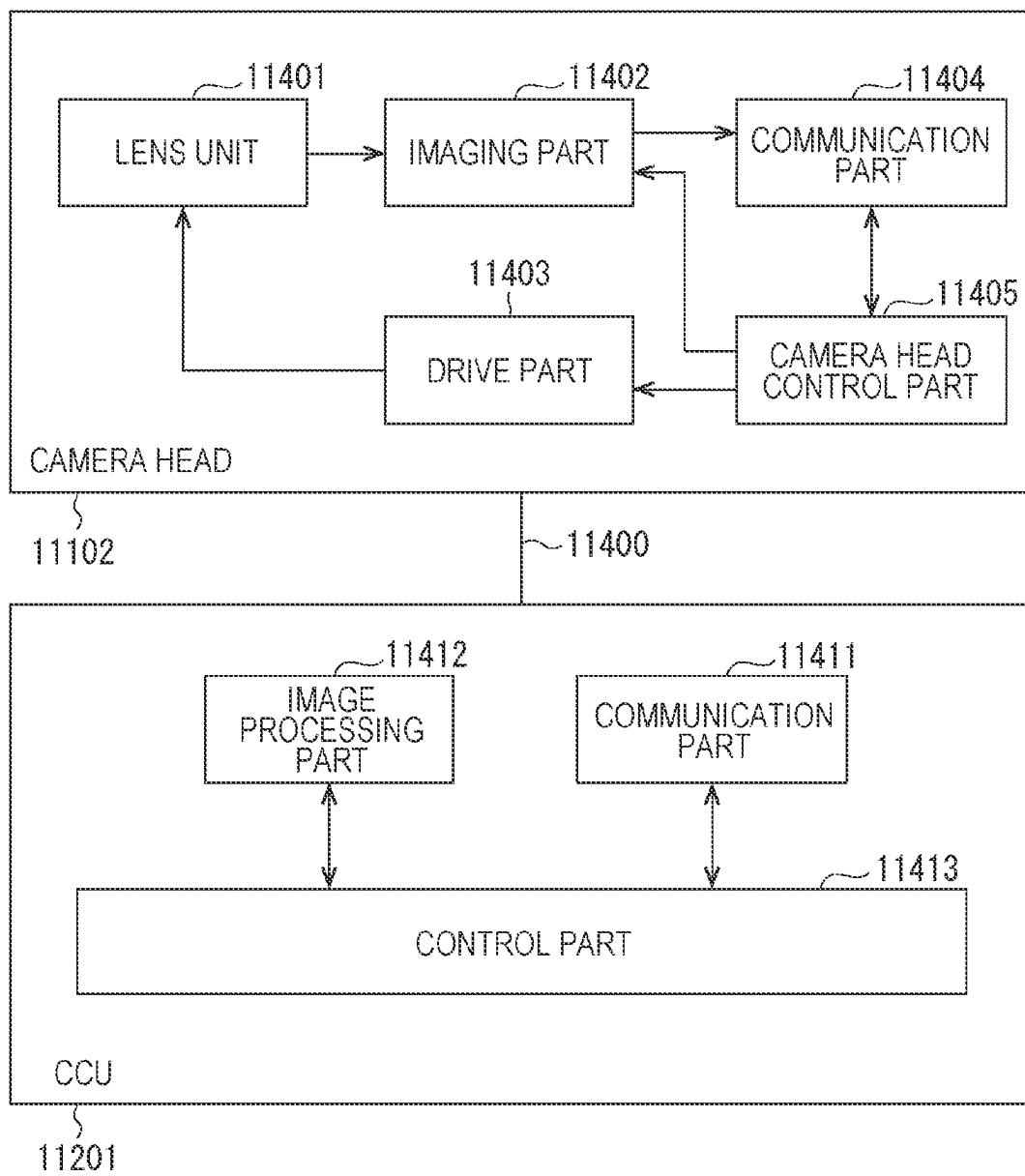


FIG. 13

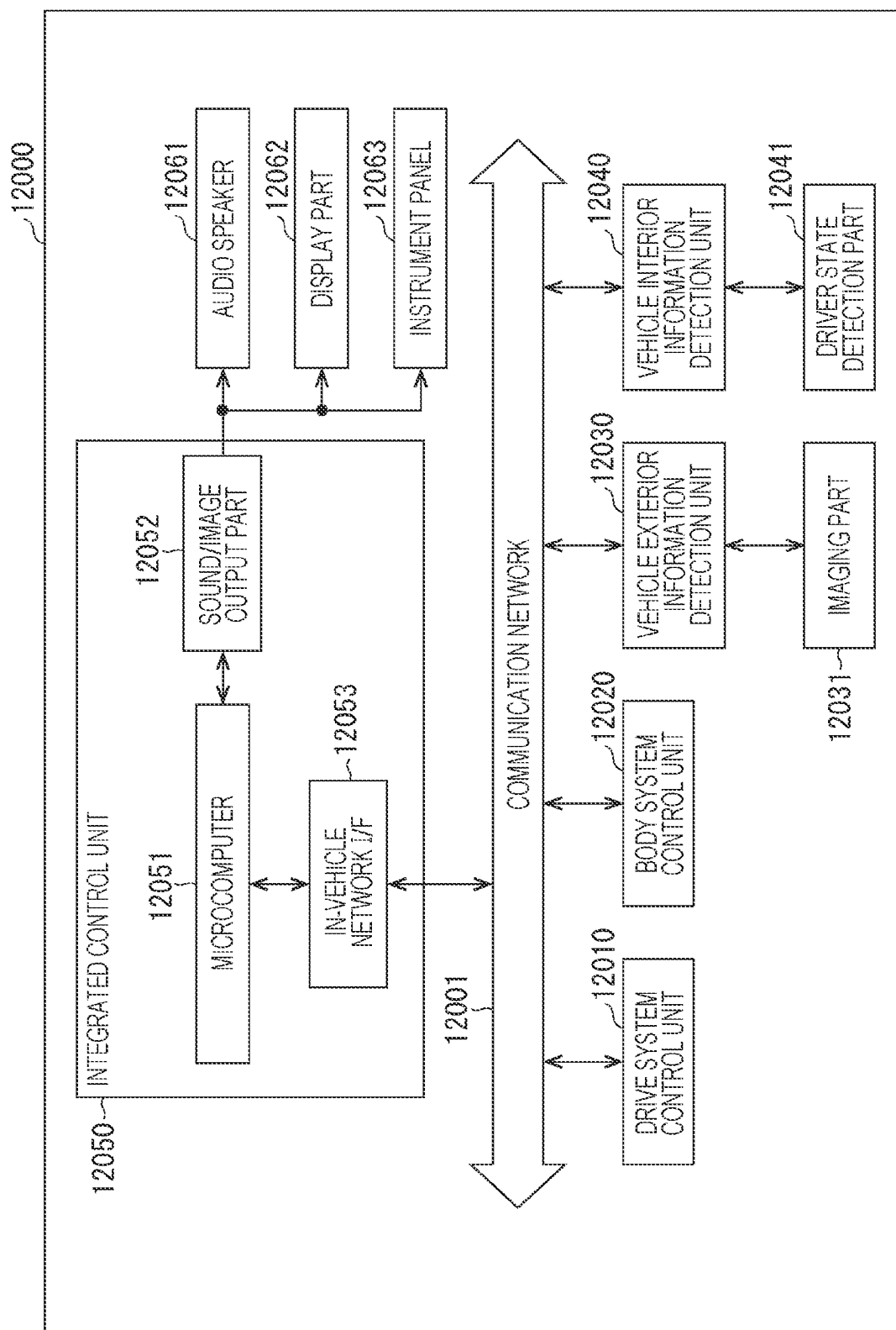
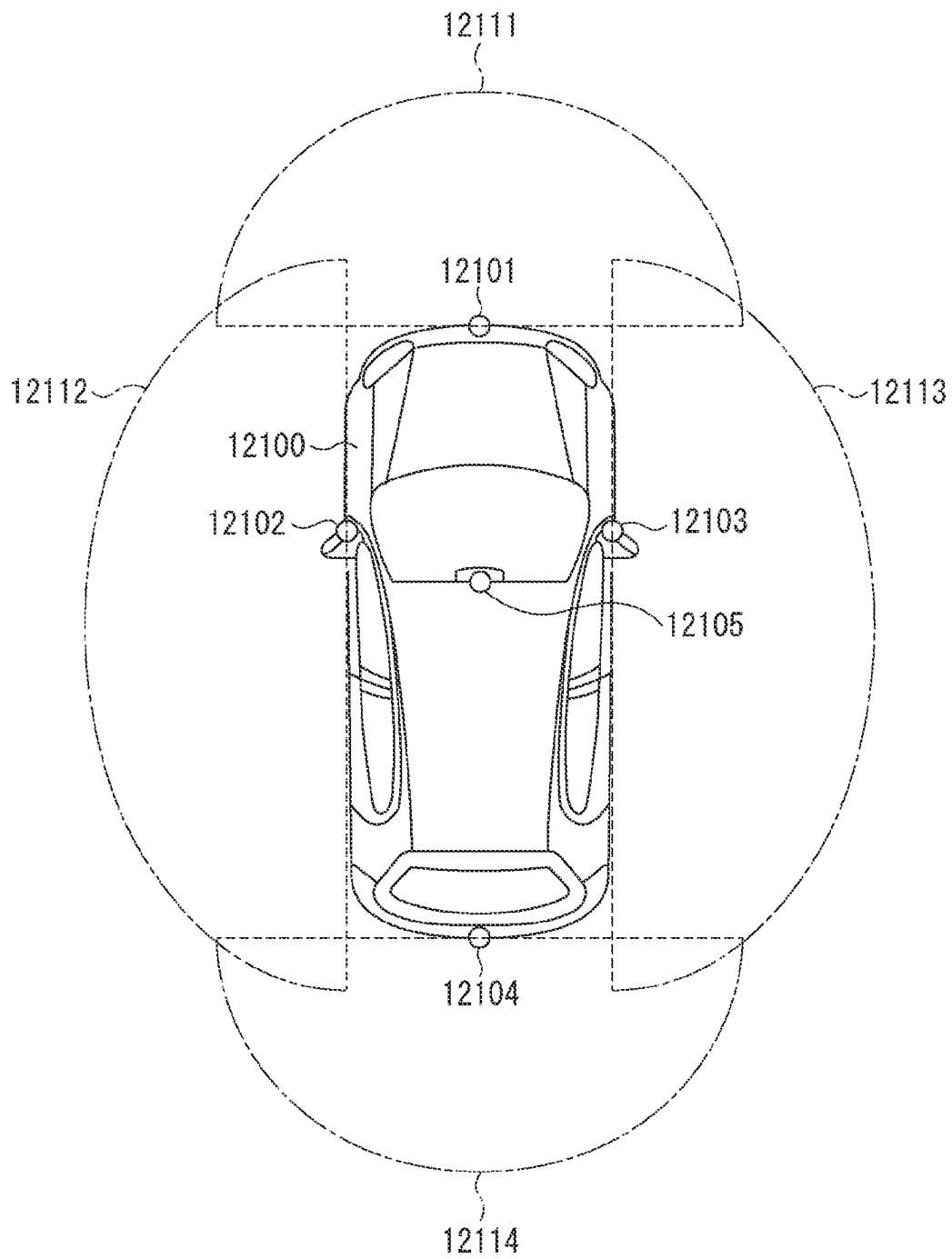


FIG. 14

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**SOLID-STATE IMAGING ELEMENT,
METHOD FOR MANUFACTURING
SOLID-STATE IMAGING ELEMENT,
PHOTOELECTRIC CONVERSION
ELEMENT, IMAGING DEVICE, AND
ELECTRONIC APPARATUS**

TECHNICAL FIELD

The present technology relates to a solid-state imaging element, a method for manufacturing a solid-state imaging element, a photoelectric conversion element, an imaging device, and an electronic apparatus, and particularly relates to a solid-state imaging element, a method for manufacturing a solid-state imaging element, a photoelectric conversion element, an imaging device, and an electronic apparatus that are capable of realizing photoelectric conversion of blue light with high efficiency.

BACKGROUND ART

A vertical spectral solid-state imaging element has been awaited that is called a vertical spectral solid-state imaging element and to have high color reproducibility.

As this vertical spectral solid-state imaging element, a vertical spectral solid-state imaging element has been recently proposed that has a multilayer structure in which photoelectric conversion films are stacked. The photoelectric conversion film includes an organic material and formed into a film.

For example, a solid-state imaging element is disclosed in which organic photoelectric conversion films that respectively absorb blue light, green light, and red light are stacked in this order (see Patent Document 1).

Furthermore, a solid-state imaging element is disclosed in which organic photoelectric conversion films that absorb blue light are stacked (see Patent Document 2).

CITATION LIST

Patent Documents

Patent Document 1: Japanese Patent Application Laid-Open No. 2006-010076

Patent Document 2: Japanese Patent Application Laid-Open No. 2018-026559

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

However, neither of the above-described organic photoelectric conversion films in Patent Documents 1 and 2 can secure sufficient blue photoelectric conversion efficiency.

The present technology has been made in view of such a situation to particularly realize an organic photoelectric conversion film capable of photoelectrically converting blue light selectively with high efficiency.

Solutions to Problems

A solid-state imaging element, a photoelectric conversion element, an imaging device, and an electronic apparatus of a first aspect of the present technology include an organic photoelectric conversion element including at least two electrodes in which an organic photoelectric conversion layer is arranged between the two electrodes, the organic

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photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor, the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light, the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and the third organic semiconductor includes a fullerene derivative.

In the first aspect of the present technology, an organic photoelectric conversion element including at least two electrodes is provided, an organic photoelectric conversion layer is arranged between the two electrodes, the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor, the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light, the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and the third organic semiconductor includes a fullerene derivative.

A method for manufacturing a solid-state imaging element of a second aspect of the present technology includes a first step of forming a first electrode, a second step of forming an organic photoelectric conversion layer over the first electrode, and a third step of forming a second electrode over the organic photoelectric conversion layer, in which the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor, the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light, the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and the third organic semiconductor includes a fullerene derivative.

In the second aspect of the present technology, a first electrode is formed by a first step, an organic photoelectric conversion layer is formed over the first electrode by a second step, and a second electrode is formed over the organic photoelectric conversion layer by a third step, the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor, the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light, the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and the third organic semiconductor includes a fullerene derivative.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagram illustrating a configuration example of an embodiment of a solid-state imaging device to which the present technology is applied.

FIG. 2 is a view illustrating configuration examples of an embodiment of a solid-state imaging element in FIG. 1.

FIG. 3 is a view illustrating the configuration examples of a solid-state imaging element in FIG. 2.

FIG. 4 is a view illustrating a configuration example of an organic photoelectric conversion element that photoelectrically converts blue light.

FIG. 5 is a flowchart illustrating a method for manufacturing an organic photoelectric conversion element.

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FIG. 6 is a view illustrating a configuration example of an evaluation element.

FIG. 7 is a table showing a first example of the characteristics of an organic material layer that depend on the combination and the mixing ratios of materials of a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor.

FIG. 8 is a table showing a second example of the characteristics of an organic material layer that depend on the combination and the mixing ratios of materials of a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor.

FIG. 9 is a schematic view illustrating the structure of a solid-state imaging element to which a photoelectric conversion element according to the present technology is applied.

FIG. 10 is a block diagram illustrating the configuration of an electronic apparatus to which a photoelectric conversion element according to the present technology is applied.

FIG. 11 is a view illustrating an example of the schematic configuration of an endoscopic surgical system.

FIG. 12 is a block diagram illustrating an example of the functional configuration of a camera head and a camera control unit (CCU).

FIG. 13 is a block diagram illustrating an example of the schematic configuration of a vehicle control system.

FIG. 14 is an explanatory view illustrating an example of the installation positions of a vehicle exterior information detection part and imaging parts.

MODE FOR CARRYING OUT THE INVENTION

Configuration Example of Embodiment of Solid-State Imaging Device to which the Present Technology is Applied

FIG. 1 illustrates a configuration example of an embodiment of a solid-state imaging device to which the present technology is applied. A solid-state imaging device 1 in FIG. 1 includes an imaging region 2 in which laminated solid-state imaging elements 11 are arranged in a two-dimensional array form and drive circuits (peripheral circuits) of the imaging region 2 such as a vertical drive circuit 3, a column signal processing circuit 4, a horizontal drive circuit 5, an output circuit 6, and a drive control circuit 7.

Note that these circuits can include well-known circuits, or another circuit configuration (including, for example, various circuits used in conventional charge coupled device (CCD) imaging devices and complementary metal oxide semiconductor (CMOS) imaging devices) can be used.

The drive control circuit 7 generates a clock signal and a control signal on the basis of the vertical synchronizing signal, the horizontal synchronizing signal, and the master clock. The clock signal and the control signal serve as references of the operation of the vertical drive circuit 3, the column signal processing circuit 4, and the horizontal drive circuit 5. Then, the generated clock signal and control signal are input to the vertical drive circuit 3, the column signal processing circuit 4, and the horizontal drive circuit 5.

The vertical drive circuit 3 includes, for example, a shift register, and selectively scans the solid-state imaging elements 11 in the imaging region 2 in units of rows sequentially in the vertical direction. Then, a pixel signal (image signal) based on the current (signal) generated according to the amount of light received in each solid-state imaging

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element 11 is sent to the column signal processing circuit 4 via a signal line (data output line) 8 and a vertical signal transfer line (VSL).

The column signal processing circuit 4 is arranged, for example, for each column of the solid-state imaging elements 11, and performs signal processing such as noise removal and signal amplification on the image signal output from each imaging element in the solid-state imaging elements 11 in units of rows on the basis of a signal from a black reference pixel (not illustrated in FIG. 1 and formed around the effective pixel region). In the output stage of the column signal processing circuit 4, a horizontal selection switch (not illustrated) is provided between the column signal processing circuit 4 and a horizontal signal line 9 so that the horizontal selection switch is connected to the column signal processing circuit 4 and the horizontal signal line 9.

The horizontal drive circuit 5 includes, for example, a shift register and outputs horizontal scanning pulses sequentially to select circuits in the column signal processing circuit 4 sequentially so that each circuit in the column signal processing circuit 4 outputs a signal to the horizontal signal line 9.

The output circuit 6 performs signal processing on the signals supplied from the circuits in the column signal processing circuit 4 sequentially via the horizontal signal line 9, and outputs the processed signals.

Configuration Example of Embodiment of Solid-State Imaging Element in FIG. 1

FIGS. 2 and 3 are views illustrating configuration examples of an embodiment of a vertical spectral solid-state imaging element 11 in which the organic photoelectric conversion film applied to the solid-state imaging device in FIG. 1 is used.

The configuration examples of a vertical spectral solid-state imaging element in which the organic photoelectric conversion film is used are, for example, two configurations including a first solid-state imaging element 11 and a second solid-state imaging element 11 that are illustrated in the left part and the right part of FIG. 2 respectively. Both the two configurations have a structure in which photoelectric conversion elements each including a photoelectric conversion element or a photodiode are stacked in the direction from a light source in the upper part of FIG. 2 or 3 to the lower part of the drawing.

In more detail, as illustrated in the lower left part of FIG. 2 and the upper left part of FIG. 3, the first solid-state imaging element 11 is provided with photoelectric conversion elements 21 and 22 in this order from the uppermost layer. The photoelectric conversion element 21 includes an organic photoelectric conversion film that photoelectrically converts light of blue (B) color, and the photoelectric conversion element 22 includes an organic photoelectric conversion film that photoelectrically converts light of green (G) color. The photoelectric conversion elements 21 and 22 and a photoelectric conversion element 31 under the photoelectric conversion elements 21 and 22 are stacked. The photoelectric conversion element 31 includes a silicon photodiode for red (R) color.

With such a configuration, as illustrated in the lower left part of FIG. 3, light in the blue (B) color and green (G) color wavelength bands is photoelectrically converted in the ascending order of the wavelength bands by the photoelectric conversion elements 21 and 22, and then light of red (R) color is photoelectrically converted by the photoelectric

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conversion element **31** to disperse and photoelectrically convert light of red color, green color, and blue color (RGB) in the vertical direction.

Furthermore, as illustrated in the lower right part of FIG. 2 and the upper right part of FIG. 3, the second solid-state imaging element **11** includes photoelectric conversion elements **21**, **22**, and **23** that are stacked in this order from the uppermost layer. The photoelectric conversion element **21** includes an organic photoelectric conversion film that photoelectrically converts light of blue (B) color, the photoelectric conversion element **22** includes an organic photoelectric conversion film that photoelectrically converts light of green (G) color, and the photoelectric conversion element **23** includes an organic photoelectric conversion film that photoelectrically converts light of red (R) color.

With such a configuration, as illustrated in the lower right part of FIG. 3, light in the blue (B) color, green (G) color, and red (R) color wavelength bands is photoelectrically converted in the ascending order of the wavelength bands by the photoelectric conversion elements **21**, **22**, and **23** to disperse light of red color, green color, and blue color (RGB) in the vertical direction and generate a pixel signal.

In more detail, as indicated by the waveforms of a dotted line in the lower left part and the lower right part of FIG. 3, the photoelectric conversion element **21** selectively absorbs light having a wavelength of approximately 400 to 500 nm and being generally classified as blue light, and generates a charge by photoelectric conversion.

Furthermore, as indicated by the waveforms of an alternate long and short dash line in the lower left part and the lower right part of FIG. 3, the photoelectric conversion element **22** selectively absorbs light having a wavelength of approximately 500 to 600 nm and being generally classified as green light, and generates a charge by photoelectric conversion.

Moreover, as indicated by the waveforms of a solid line in the lower left part and the lower right part of FIG. 3, the photoelectric conversion element **23** or the photoelectric conversion element **31** selectively absorbs light having a wavelength of approximately 600 nm or more and being generally classified as red light, and generates a charge by photoelectric conversion.

Note that, in the lower part of FIG. 3, the horizontal axis in the graphs shows the wavelength of incident light, and the vertical axis shows the amount of charge generated by photoelectric conversion.

Configuration Example of Photoelectric Conversion Element that Photoelectrically Converts Blue Light

Next, a configuration example of the photoelectric conversion element **21** including an organic photoelectric conversion film will be described with reference to FIG. 4.

The photoelectric conversion element **21** has a configuration in which a first electrode **41**, a charge storage electrode **42**, an insulating layer **43**, a semiconductor layer **44**, a hole blocking layer **45**, a photoelectric conversion layer **46**, a work function adjustment layer **47**, and a second electrode **48** are stacked as illustrated in FIG. 4. Note that, although not illustrated, the photoelectric conversion element **21** is stacked on a semiconductor substrate provided with a floating diffusion amplifier for signal reading, a transfer transistor, an amplifier transistor, and multilayer wiring, and the photoelectric conversion element **21** is provided with optical members such as a protective layer, a planarization layer, and an on-chip lens on the light incident side.

The first electrode **41** and the charge storage electrode **42** include a conductive film having light transmissivity such as indium tin oxide (ITO). However, as a material included in

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the first electrode **41** and the charge storage electrode **42**, a tin oxide (SnO₂)-based material to which a dopant is added or a zinc oxide-based material including an aluminum zinc oxide (ZnO) to which a dopant is added may be used in addition to the ITO. Examples of the zinc oxide-based material include aluminum zinc oxide (AZO) doped with aluminum (Al) as a dopant, gallium zinc oxide (GZO) doped with gallium (Ga), and indium zinc oxide (IZO) doped with indium (In). Furthermore, CuI, InSbO₄, ZnMgO, CuInO₂, MgIn₂O₄, CdO, ZnSnO₃, or the like may be used. The insulating layer **43** is formed so as to cover the charge storage electrode **42**.

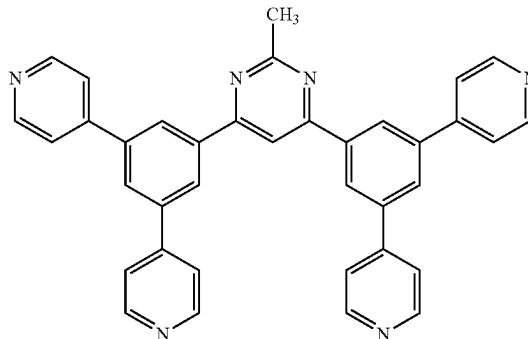
The semiconductor layer **44** is provided between the insulating layer **43** and the hole blocking layer **45**, and configured to store a signal charge (here, an electron) generated in the photoelectric conversion layer **46**. In the present embodiment, an electron is used as a signal charge, and therefore, the semiconductor layer **44** is preferably formed using an n-type semiconductor material. It is preferable to use, for example, a material in which the lowermost end of the conduction band has an energy level shallower than the work function of the semiconductor layer **44**. Examples of such an n-type semiconductor material include In—Ga—Zn—O-based oxide semiconductors (IGZOs), Zn—Sn—O-based oxide semiconductors (ZTOs), In—Ga—Zn—Sn—O-based oxide semiconductors (IGZTOs), Ga—Sn—O-based oxide semiconductors (GTOs), and In—Ga—O-based oxide semiconductors (IGO). In the semiconductor layer **44**, it is preferable to use at least one oxide semiconductor material described above, and among the above-described oxide semiconductor materials, IGZO is suitably used. The semiconductor layer **44** has a thickness of, for example, 30 nm or more and 200 nm or less, and preferably 60 nm or more and 150 nm or less. As a result of providing the semiconductor layer **44** including the above-described material under the hole blocking layer **45**, charge recombination can be prevented at the time of charge storage to improve the transfer efficiency.

The hole blocking layer **45** is provided between the semiconductor layer **44** and the photoelectric conversion layer **46**, and configured to transfer a signal charge (here, an electron) generated in the photoelectric conversion layer **46** to the semiconductor layer **44** and prevent hole injection from the semiconductor layer **44** to the photoelectric conversion layer **46**.

The hole blocking layer **45** includes, for example, a substance (1) (4,6-bis(3,5-di(pyridin-4-yl)phenyl)-2-methylpyrimidine (B4PyMPM)) represented by the following chemical formula (1).

[Chem. 1]

Chemical Formula (1)



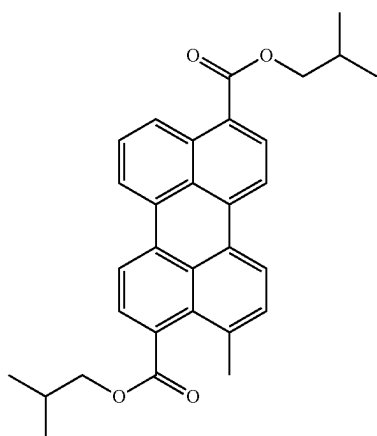
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In the present embodiment, an electron is used as a signal charge in the hole blocking layer **45**, and therefore, the hole blocking layer **45** is preferably formed using an n-type semiconductor material. It is preferable to use, for example, a material in which the electron affinity has an energy level equivalent to or shallower than that at the lower end of the conductor in the semiconductor layer **44**. Examples of such an n-type semiconductor material included in the hole blocking layer **45** include naphthalene diimide derivatives, triazine derivatives, and fullerene derivatives in addition to the substance (1) (B4PyMPM).

The photoelectric conversion layer **46** includes a mixed layer including a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor, and generates an electron and a hole (charges) by photoelectric conversion according to the amount of blue light.

The first organic semiconductor is a semiconductor that absorbs blue light and generates an electron and a hole (charges) by photoelectric conversion, and is, for example, a substance (2) (Solvent Green 5 (SG5)) represented by the following chemical formula (2).

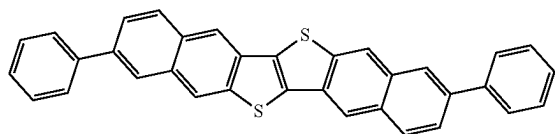
Chemical Formula (2)



[Chem. 2]

The second organic semiconductor is a hole-transporting material that absorbs blue light and transports a hole, and has crystallinity. The second organic semiconductor is, for example, a substance (3) (2,9-diphenyl-dinaphtho[2,3-b]naphtho[2',3':4,5]thieno[2,3-d]thiophene: DNTT) represented by the following chemical formula (3).

Chemical Formula (3)



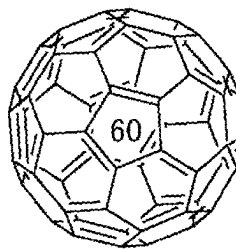
[Chem. 3]

The third organic semiconductor is a fullerene derivative, and is, for example, a substance (4) (C60) represented by the following chemical formula (4).

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Chemical Formula (4)

[Chem.4]



The work function adjustment layer **47** is provided between the photoelectric conversion layer **46** and the second electrode **48**, and configured to change the internal electric field in the photoelectric conversion layer **46** to transfer the signal charge generated in the photoelectric conversion layer **46** to the semiconductor layer **44** promptly so that the semiconductor layer **44** stores the signal change. The work function adjustment layer **47** has light transmissivity, and preferably has, for example, a light absorption rate of 10% or less with respect to visible light. Furthermore, the work function adjustment layer **47** is preferably formed using a carbon-containing compound having an electron affinity larger than the work function of the semiconductor layer **44**. Examples of such a material include tetracyanoquinodimethane derivatives, hexaazatriphenylene derivatives, hexaazatrinaphthylene derivatives, phthalocyanine derivatives, and fluorinated fullerenes such as C60F36 and C60F48. Alternatively, the work function adjustment layer **47** is preferably formed using an inorganic compound having a larger work function than the charge storage electrode **42**. Examples of such a material include transition metal oxides such as molybdenum oxide (MoO₃), tungsten oxide (WO₃), vanadium oxide (V₂O₅), and rhenium oxide (ReO₃), and salts such as copper iodide (CuI), antimony chloride (SbCl₃), iron oxide (FeCl₃), and sodium chloride (NaCl).

Another layer may be provided between the photoelectric conversion layer **46** and the second electrode **48** (for example, between the photoelectric conversion layer **46** and the work function adjustment layer **47**) or between the photoelectric conversion layer **46** and the charge storage electrode **42**. Specifically, for example, the photoelectric conversion layer **46** and the work function adjustment layer **47** may be stacked with an electron blocking layer interposed therebetween. The ionization potential of the electron blocking layer preferably has an energy level shallower than the work function of the work function adjustment layer **47**. Furthermore, the electron blocking layer is preferably formed using, for example, an organic material having a glass transition point higher than 100° C.

The second electrode **48** is configured to collect the hole (h⁺) generated by photoelectric conversion of blue light in the photoelectric conversion layer **46**. Similarly to the first electrode **41** and the charge storage electrode **42**, the second electrode includes a conductive film having light transmissivity. In an imaging device in which the photoelectric conversion element **21** is used as one pixel, the second electrode **48** may be separated for each pixel, or may be formed as a common electrode for the pixels. The second electrode **48** has a thickness of, for example, 10 nm to 200 nm.

In a configuration example of the photoelectric conversion element that photoelectrically converts blue light of the present embodiment, the incident direction of the light may be upward or downward. More specifically, in FIG. 4, light may be incident from the second electrode 48 side or the charge storage electrode 42 side.

Furthermore, the second electrode 48 located on the light incident side may be shared by a plurality of solid-state imaging elements 11. That is, the second electrode 48 can be a so-called solid electrode. The photoelectric conversion layer 46 may be shared by the plurality of solid-state imaging elements 11, that is, one photoelectric conversion layer 46 may be formed for the plurality of solid-state imaging elements 11, or one photoelectric conversion layer 46 may be provided for each solid-state imaging element 11.

Moreover, the photoelectric conversion layer 46 may have a stacked structure including a lower semiconductor layer and an upper photoelectric conversion layer. With the stacked structure, recombination at the time of charge storage can be prevented by the lower semiconductor layer to increase the transfer efficiency of the charge stored in the photoelectric conversion layer 46 to the first electrode 41 and suppress generation of dark current.

Method for Manufacturing Photoelectric Conversion Element that Photoelectrically Converts Blue Light

Next, a method for manufacturing a photoelectric conversion element that photoelectrically converts blue light will be described with reference to the flowchart of FIG. 5. In a case where a vertical spectral solid-state imaging element as illustrated in FIGS. 2 and 3 is manufactured, a silicon substrate (not illustrated) is usually used. In brief, on the silicon substrate (not illustrated), a circuit layer is formed in which a floating diffusion amplifier, a transfer transistor, an amplifier transistor, and multilayer wiring are formed, and on the circuit layer, photoelectric conversion films that photoelectrically convert R, G, and B light respectively are formed together with a readout wiring. The photoelectric conversion films are insulated from each other by an interlayer insulating film.

In a step S11, in an element in which a circuit layer provided on a silicon substrate (not illustrated), an R layer, and a G layer are stacked in this order, an ITO layer having a predetermined thickness (for example, of 100 nm) is formed on an interlayer insulating film on the G layer by sputtering.

In a step S12, a photoresist is formed at a predetermined position on the ITO layer. Thereafter, etching is performed to remove the photoresist, and thus, the first electrode 41 and the charge storage electrode 42 illustrated in FIG. 4 are patterned.

In a step S13, after the insulating layer 43 is formed on the interlayer insulating layer, the first electrode 41, and the charge storage electrode 42, the insulating layer 43 on the first electrode 41 is removed, and the first electrode 41 is provided with an opening.

In a step S14, the semiconductor layer 44 having a predetermined thickness (for example, of 100 nm) is formed on the insulating layer 43 by sputtering.

In a step S15, the hole blocking layer 45 is formed on the semiconductor layer 44 with a vacuum deposition method. For example, a substrate 55 is placed on a substrate holder in a vacuum deposition device in a state where the pressure is reduced to 1×10^{-5} Pa or less, and while the substrate 55 set to a temperature of 0° C. is rotated, the substance (1)

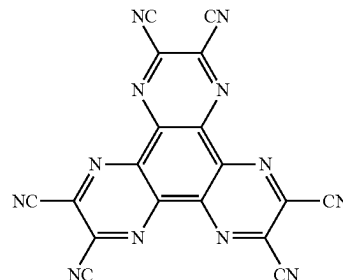
(B4PyMPM) having a temperature of 0° C. is formed into a film having a predetermined thickness on the semiconductor layer 44. More specifically, the hole blocking layer 45 including the substance (1) (B4PyMPM) is formed to have a predetermined thickness of, for example, 5 nm in a state where the substrate 55 has a temperature of 0° C.

In a step S16, the photoelectric conversion layer 46 is formed on the hole blocking layer 45 with a vacuum deposition method. For example, a substrate 55 is placed on a substrate holder in a vacuum deposition device in a state where the pressure is reduced to 1×10^{-3} Pa or less, and while the substrate 55 set to a temperature of 0° C. is rotated, the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are each mixed at a predetermined film formation rate to form the photoelectric conversion layer 46 having a predetermined thickness (for example, of 200 nm) on the hole blocking layer 45.

In a step S17, the work function adjustment layer 47 is formed on the photoelectric conversion layer 46 with a vacuum deposition method. For example, a substrate 55 is placed on a substrate holder in a vacuum deposition device in a state where the pressure is reduced to 1×10^{-3} Pa or less, and while the substrate 55 set to a temperature of 0° C. is rotated, a substance (5) (1,4,5,8,9,12-hexaazatriphenylene-2,3,6,7,10,11-hexacarbonitrile) represented by the following chemical formula (5) having a temperature of 0° C. is formed into a film having a predetermined thickness on the photoelectric conversion layer 46. More specifically, the work function adjustment layer 47 is formed to have a predetermined thickness of, for example, 10 nm in a state where the substrate 55 has a temperature of 0° C.

[Chem. 5]

Chemical Formula (5)



In a step S18, ITO is formed into a film having a predetermined thickness (for example, of 50 nm) as the second electrode 48.

In the above description of the method for manufacturing a photoelectric conversion element that photoelectrically converts blue light, the case of the configuration in which light is incident from the second electrode 48 side has been described, but this configuration may be vertically inverted. Specifically, the configuration may be a configuration in which the second electrode 48 is on the substrate 55 side, and light is incident from the charge storage electrode 42 side.

By the above-described processing, the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed to form the photoelectric conversion layer 46 in which the absorption of light of colors other than blue is reduced to reduce the amount of charge generated by photoelectric conversion of light other than blue light, and the absorption of blue light is enhanced to

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increase the amount of charge generated by photoelectric conversion through absorption of blue light.

The characteristic of the photoelectric conversion layer **46** depends on the combination and the mixing ratios of the materials of the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor that are included. Therefore, it is desirable to form a film at a combination and mixing ratios of the materials of the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor so that the absorption of light other than blue light is suppressed while blue light is further easily absorbed to enhance the photoelectric conversion efficiency of blue light in the photoelectric conversion layer **46**.

Acquisition of Blue Signal by Photoelectric Conversion Element **21**

Among the light incident on the first solid-state imaging element **11** or the second solid-state imaging element **11**, first, blue light is selectively detected (absorbed) and photoelectrically converted by the photoelectric conversion element **21**.

The charge storage electrode **42** side is positively biased and the second electrode **48** side is negatively biased to storage the electron generated in the photoelectric conversion layer **46** in the semiconductor layer **44** and transfer the hole generated in the photoelectric conversion layer **46** to the second electrode **48**. In the storage of the electron in the semiconductor layer **44**, the potential of the first electrode **41** is set negative with respect to the potential of the charge storage electrode **42** to form a potential barrier so that electrons do not flow.

After storage of the electron in the semiconductor layer **44** for a certain period, the potential of the first electrode **41** is set positive with respect to the potential of the charge storage electrode **42** to transfer the electron to the first electrode **41** side. The electron collected to the first electrode is subjected to voltage conversion and processed as a pixel signal by, for example, a capacitor part of a floating diffusion amplifier connected to the end of the first electrode **41**.

First Example of Characteristics of Organic Material Layer that Depend on Combination and Mixing Ratios of Materials of First Organic Semiconductor, Second Organic Semiconductor, and Third Organic Semiconductor

Next, a first example will be described of the characteristics of the photoelectric conversion layer **46** that depend on the combination and the mixing ratios of the materials of the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor with reference to FIG. 7.

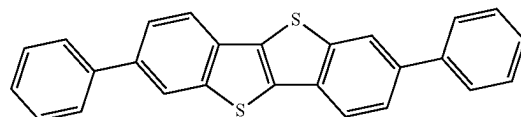
The test cell evaluated here is an evaluation element for simple evaluation. Specifically, the evaluation element has an element structure as shown by an evaluation element **50** in FIG. 6, and has a configuration in which a quartz substrate is used as a substrate **55**, and on the quartz substrate, ITO **54** as a second electrode, a photoelectric conversion layer **53**, a hole blocking layer **52** including the substance (1) B4PyMPM, and a first electrode **51** including Al are stacked in this order. Here, the second electrode (ITO) **54**, the photoelectric conversion layer **53**, the hole blocking layer **52**, and the first electrode **51** correspond to the second electrode **48**, the photoelectric conversion layer **46**, the hole blocking layer **45**, and the first electrode **41** in FIG. 4,

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respectively. That is, the evaluation element **50** has an element structure vertically inverted from the photoelectric conversion element **21** illustrated in FIG. 4 excluding the charge storage electrode **42**, the insulating layer **43**, the semiconductor layer **44**, and the work function adjustment layer **47**.

Furthermore, here, a comparison will be described of the characteristics of the photoelectric conversion layer **46** in cases where the first organic semiconductor is the substance (2) (Solvent Green 5 (SG5)) represented by the chemical formula (2), the second organic semiconductor is the substance (3) (DNTT) represented by the chemical formula (3) or a substance (6) (BTBT) represented by the following chemical formula (6), the third organic semiconductor is the substance (4) (C60) represented by the chemical formula (4), and the film formation rate of each organic semiconductor is adjusted to change the mixing ratio.

Chemical Formula (6)



[Chem. 6]

Furthermore, FIG. 7 shows the characteristics of the photoelectric conversion layer **46** in Examples 1 to 7 for comparison in order from the top.

Note that the characteristics of the photoelectric conversion layer **46** are shown for cases where, as illustrated in FIG. 6, blue light (light having a wavelength of 450 nm) is emitted from a light emitting part **61** provided in the lower part of the drawing and no electrode **51** is provided.

Moreover, when the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor shown from the left of FIG. 7 are represented by a, b, and c, respectively, the mixing ratio of each organic semiconductor, a:b:c is shown for each Example. Furthermore, on the right side of the mixing ratio, the absorption coefficient of light having a wavelength of 450 nm (blue light) (α 450 nm (cm⁻¹)) and the absorption coefficient of light having a wavelength of 560 nm (green light) (α 560 nm (cm⁻¹)) are shown from the left, and on the right side of the absorption coefficients, the coefficient ratio of the absorption coefficient (α 450 nm (cm⁻¹)) to the absorption coefficient (α 560 nm (cm⁻²)) (α 450 nm/ α 560 nm) is shown. Furthermore, on the right side of the coefficient ratio (α 450 nm/ α 560 nm), the relative values of the dark current (j_{dk}), the external quantum efficiency (EQE), and the response time in each Example with respect to those in Example 1 are shown from the left, and moreover, the characteristics significantly inferior to those in Example 1 are shown.

Here, in the light emitting part **61**, the wavelength of light emitted from a blue LED light source to the photoelectric conversion element **21** via a band pass filter is set to 450 nm, and the light amount is set to 1.62 μ W/cm². The current-voltage curve is measured by controlling the bias voltage applied between the electrodes of the photoelectric conversion element using a semiconductor parameter analyzer and sweeping the voltage applied to the lower electrode (second electrode **54**) with respect to the voltage of the upper electrode (first electrode **51**) in FIG. 6. Furthermore, the dark current value (J_{dk}) and the light current value are measured

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in a state where a voltage of -2.6 V is applied to the lower electrode (second electrode **54**) with respect to the voltage of the upper electrode (first electrode **51**), the dark current value is subtracted from the light current value, and from the resulting value, the external quantum efficiency EQE is calculated.

Moreover, the bias voltage applied between the electrodes of the photoelectric conversion element **21** is controlled, the photoelectric conversion element **21** is irradiated with a light pulse on a rectangle having a wavelength of 450 nm and a light amount of $1.62 \mu\text{W}/\text{cm}^2$ in a state where a voltage of -2.6 V is applied to the lower electrode (second electrode **54**) with respect to the upper electrode (first electrode **51**), the attenuation waveform of the current is observed using an oscilloscope, and the time during which the current at the time of light pulse irradiation attenuates to 3% immediately after the light pulse irradiation is regarded as the response time as an index of the response speed.

Example 1

As shown in the uppermost row below the header row of FIG. 7, Example 1 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (2) (Solvent Green 5 (SG5)), the substance (3) (DNITT), and the substance (4) (C60), respectively, and the uppermost row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 1, and the characteristics significantly inferior to those in Example 1 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of $0.50 \text{ \AA}/\text{sec}$, $0.50 \text{ \AA}/\text{sec}$, and $0.25 \text{ \AA}/\text{sec}$, respectively to form the photoelectric conversion layer **46** so as to have a predetermined thickness (for example, of 200 nm).

In the case of Example 1 in the uppermost row below the header row of FIG. 7, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 4:4:2 ($=0.50 \text{ \AA}/\text{sec}:0.50 \text{ \AA}/\text{sec}:0.25 \text{ \AA}/\text{sec}$).

At this time, the absorption coefficient (α 450 nm (cm^{-1})) is $9.5\text{E}+4$, the absorption coefficient (α 560 nm (cm^{-1})) is $4.2\text{E}+3$, and the coefficient ratio (α 450 nm/ α 560 nm) is 23.

Note that Example 1 serves as a reference and therefore, all of the dark current, the EQE, and the response time are 1.00.

The experimental result for the photoelectric conversion element **21** in which the photoelectric conversion layer **46** is used in Example 1 is obtained using a ternary photoelectric conversion layer including the substance (2) (SG5), the substance (3) (DNITT), and the substance (4) (C60) at a ratio of 4:4:2, and the result shows a relatively high absorption coefficient at 450 nm in the blue light region, a relatively low absorption coefficient at 560 nm in the green light region, a good dark current characteristic, a good EQE characteristic, and a good response characteristic.

Example 2

As shown in the second row below the header row of FIG. 7, Example 2 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic

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semiconductor are the substance (2) (Solvent Green 5 (SG5)), the substance (3) (DNITT), and the substance (4) (C60), respectively, and the second row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 1, and the characteristics significantly inferior to those in Example 1 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of $0.50 \text{ \AA}/\text{sec}$, $0.30 \text{ \AA}/\text{sec}$, and $0.20 \text{ \AA}/\text{sec}$, respectively to form the photoelectric conversion layer **46** so as to have a predetermined thickness (for example, of 200 nm).

In the case of Example 2 in the second row below the header row of FIG. 7, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate a:b:c, and therefore, is 5:3:2 ($=0.50 \text{ \AA}/\text{sec}:0.30 \text{ \AA}/\text{sec}:0.20 \text{ \AA}/\text{sec}$).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is $9.9\text{E}+4$, the absorption coefficient (α 560 nm (cm^{-1})) is $4.2\text{E}+3$, and the coefficient ratio (α 450 nm/ α 560 nm) is 24.

Moreover, the dark current is 0.92 with respect to that in Example 1, the EQE is 0.99 with respect to that in Example 1, and the response time is 1.10 with respect to that in Example 1.

The experimental result for the photoelectric conversion element **21** in which the photoelectric conversion layer **46** is used in Example 2 is obtained using a ternary photoelectric conversion layer including the substance (2) (SG5), the substance (3) (DNITT), and the substance (4) (C60) at a ratio of 5:3:2, and the result shows values close to those in Example 1, such as a relatively high absorption coefficient at 450 nm in the blue light region, a relatively low absorption coefficient at 560 nm in the green light region, a good dark current characteristic, a good EQE characteristic, and a good response characteristic. Therefore, in Example 2, it can be considered that there is no characteristic significantly inferior to that in Example 1.

Example 3

As shown in the third row below the header row of FIG. 7, Example 3 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (2) (Solvent Green 5 (SG5)), the substance (3) (DNITT), and the substance (4) (C60), respectively, and the third row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 1, and the characteristics significantly inferior to those in Example 1 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of $0.30 \text{ \AA}/\text{sec}$, $0.50 \text{ \AA}/\text{sec}$, and $0.20 \text{ \AA}/\text{sec}$, respectively to form the photoelectric conversion layer **46** so as to have a predetermined thickness (for example, of 200 nm).

In the case of Example 3 in the third row below the header row of FIG. 7, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 3:5:2 ($=0.30 \text{ \AA}/\text{sec}:0.50 \text{ \AA}/\text{sec}:0.20 \text{ \AA}/\text{sec}$).

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Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is $9.2\text{E}+4$, the absorption coefficient (α 560 nm (cm^{-1})) is $4.1\text{E}+3$, and the coefficient ratio (α 450 nm/ α 560 nm) is 22.

Moreover, the dark current is 1.12 with respect to that in Example 1, the EQE is 1.02 with respect to that in Example 1, and the response time is 0.95 with respect to that in Example 1.

The experimental result for the photoelectric conversion element **21** in which the photoelectric conversion layer **46** is used in Example 3 is obtained using a ternary photoelectric conversion layer including the substance (2) (SG5), the substance (3) (DNNT), and the substance (4) (C60) at a ratio of 3:5:2, and the result shows values close to those in Example 1, such as a relatively high absorption coefficient at 450 nm in the blue light region, a relatively low absorption coefficient at 560 nm in the green light region, a good dark current characteristic, a good EQE characteristic, and a good response characteristic. Therefore, in Example 3, it can be considered that there is no characteristic significantly inferior to that in Example 1.

Example 4

As shown in the fourth row below the header row of FIG. 7, Example 4 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (2) (Solvent Green 5 (SG5)), the substance (3) (DNNT), and the substance (4) (C60), respectively, and the fourth row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 1, and the characteristics significantly inferior to those in Example 1 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.35 Å/sec, 0.35 Å/sec, and 0.3 Å/sec, respectively to form the photoelectric conversion layer **46** so as to have a predetermined thickness (for example, of 200 nm).

In the case of Example 4 in the fourth row below the header row of FIG. 7, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 3.5:3.5:3 (=0.35 Å/sec:0.35 Å/sec:0.30 Å/sec).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is $9.2\text{E}+4$, the absorption coefficient (α 560 nm (cm^{-1})) is $6.1\text{E}+3$, and the coefficient ratio (α 450 nm/ α 560 nm) is 15.

Moreover, the dark current is 1.64 with respect to that in Example 1, the EQE is 1.08 with respect to that in Example 1, and the response time is 0.98 with respect to that in Example 1.

The experimental result for the photoelectric conversion element **21** in which the photoelectric conversion layer **46** is used in Example 4 is obtained using a ternary photoelectric conversion layer including the substance (2) (SG5), the substance (3) (DNNT), and the substance (4) (C60) at a ratio of 3.5:3.5:3, and the result shows values close to those in Example 1, such as a relatively high absorption coefficient at 450 nm in the blue light region, a relatively low absorption coefficient at 560 nm in the green light region, a good dark current characteristic, a good EQE characteristic, and a good

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response characteristic. Therefore, in Example 4, it can be considered that there is no characteristic significantly inferior to that in Example 1.

Example 5

As shown in the fifth row below the header row of FIG. 7, Example 5 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (2) (Solvent Green 5 (SG5)), the substance (3) (DNNT), and the substance (4) (C60), respectively, and the fifth row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 1, and the characteristics significantly inferior to those in Example 1 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.00 Å/sec, 0.50 Å/sec, and 0.50 Å/sec, respectively to form the photoelectric conversion layer **46** so as to have a predetermined thickness (for example, of 200 nm).

Note that the case where the film formation rate is 0.00 Å/sec does not refer to a state where no film is formed, but refers to a state where a film is formed at a small film formation rate that is extremely close to 0.00 Å/sec. Therefore, the photoelectric conversion layer **46** will be described as a mixture of the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor in principle. However, the case where the film formation rate is close to 0.00 Å/sec is substantially similar to a state where no film is formed.

That is, in Example 5, the photoelectric conversion layer **46** includes substantially no substance (2) (Solvent Green 5 (SG5)) as the first organic semiconductor.

In the case of Example 5 in the fifth row below the header row of FIG. 7, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 0:5:5 (=0.00 Å/sec:0.50 Å/sec:0.50 Å/sec).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is $5.6\text{E}+4$, the absorption coefficient (α 560 nm (cm^{-1})) is $1.9\text{E}+4$, and the coefficient ratio (α 450 nm/ α 560 nm) is 3.

Moreover, the dark current is 0.98 with respect to that in Example 1, the EQE is 0.65 with respect to that in Example 1, the response time is 1.04 with respect to that in Example 1, and the characteristics significantly inferior to those in Example 1 are the coefficient ratio as a spectral characteristic and the EQE.

The experimental result for the photoelectric conversion element **21** in which the photoelectric conversion layer **46** is used in Example 5 is obtained using a ternary photoelectric conversion layer including the substance (2) (SG5), the substance (3) (DNNT), and the substance (4) (C60) at a ratio of 0:5:5, and the result shows a low absorption coefficient of blue light (α 450 nm (cm^{-1})) and a small coefficient ratio because the blue selectivity as the characteristic of the substance (2) is low due to the fact that substantially no substance (2) is included. Furthermore, the dark current characteristic and the response characteristic are substantially the same as those in Example 1, but the EQE characteristic is inferior because the absorption of blue light is inferior.

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Example 6

As shown in the sixth row below the header row of FIG. 7, Example 6 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (2) (Solvent Green 5 (SG5)), the substance (3) (DNTT), and the substance (4) (C60), respectively, and the sixth row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 1, and the characteristics significantly inferior to those in Example 1 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.50 Å/sec, 0.00 Å/sec, and 0.50 Å/sec, respectively to form the photoelectric conversion layer 46 so as to have a predetermined thickness (for example, of 200 nm).

That is, in Example 6, the photoelectric conversion layer 46 includes substantially no substance (3) (DNTT) as the second organic semiconductor.

In the case of Example 6 in the sixth row below the header row of FIG. 7, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 5:0:5 (=0.50 Å/sec:0.00 Å/sec:0.50 Å/sec).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is $8.3\text{E}+4$, the absorption coefficient (α 560 nm (cm^{-1})) is $1.4\text{E}+4$, and the coefficient ratio (α 450 nm/ α 560 nm) is 6.

Moreover, the dark current is 1.10 with respect to that in Example 1, the EQE is 0.98 with respect to that in Example 1, the response time is 14.5 with respect to that in Example 1, and the characteristics significantly inferior to those in Example 1 are the coefficient ratio as a spectral characteristic and the response time.

The experimental result for the photoelectric conversion element 21 in which the photoelectric conversion layer 46 is used in Example 6 is obtained using a ternary photoelectric conversion layer including the substance (2) (SG5), the substance (3) (DNTT), and the substance (4) (C60) at a ratio of 5:0:5, and the result shows a high absorption coefficient of green light (α 560 nm (cm^{-1})) and a small coefficient ratio. Furthermore, the dark current characteristic and the EQE characteristic are substantially the same as those in Example 1, but the response characteristic is inferior because substantially no substance (3) (DNTT) as a hole-transporting material is included.

Example 7

As shown in the seventh row below the header row of FIG. 7, Example 7 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (2) (Solvent Green 5 (SG5)), the substance (3) (DNTT), and the substance (4) (C60), respectively, and the seventh row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 1, and the characteristics significantly inferior to those in Example 1 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation

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rates of 0.50 Å/sec, 0.50 Å/sec, and 0.00 Å/sec, respectively to form the photoelectric conversion layer 46 so as to have a predetermined thickness (for example, of 200 nm).

That is, in Example 7, the photoelectric conversion layer 46 includes substantially no substance (4) (C60) as the third organic semiconductor.

In the case of Example 7 in the seventh row below the header row of FIG. 7, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 5:5:0 (=0.50 Å/sec:0.50 Å/sec:0.00 Å/sec).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is $1.3\text{E}+5$, the absorption coefficient (α 560 nm (cm^{-1})) is $1.5\text{E}+3$, and the coefficient ratio (α 450 nm/ α 560 nm) is 87.

Moreover, the dark current is 23.0 with respect to that in Example 1, the EQE is 0.45 with respect to that in Example 1, the response time is unmeasurable (n/a) because the dark current is too large, and the characteristics significantly inferior to those in Example 1 are the spectral dark current, EQE, and response time.

The experimental result for the photoelectric conversion element 21 in which the photoelectric conversion layer 46 is used in Example 7 is obtained using a ternary photoelectric conversion layer including the substance (2) (SG5), the substance (3) (DNTT), and the substance (4) (C60) at a ratio of 0:5:5, and the result shows a high absorption coefficient of blue light (α 450 nm (cm^{-1})) and a large coefficient ratio. However, all of the dark current characteristic, the EQE characteristic, and the response characteristic are poor. The reason is considered to be that due to the fact that substantially no substance (4), C60, to be an electron-transporting material was included, no donor/acceptor interface was formed in the organic material layer (photoelectric conversion layer) 53 and as a result, exciton dissociation rarely occurred.

Example 8

As shown in the eighth row below the header row of FIG. 7, Example 8 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (2) (Solvent Green 5 (SG5)), the substance (6) (BTBT), and the substance (4) (C60), respectively, and the eighth row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 1, and the characteristics significantly inferior to those in Example 1 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.50 Å/sec, 0.50 Å/sec, and 0.25 Å/sec, respectively to form the photoelectric conversion layer 46 so as to have a predetermined thickness (for example, of 200 nm).

That is, in Example 8, the second organic semiconductor is the substance (6) (BTBT).

In the case of Example 8 in the eighth row below the header row of FIG. 7, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 4:4:2 (=0.50 Å/sec:0.50 Å/sec:0.25 Å/sec).

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Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is $3.8\text{E}+4$, the absorption coefficient (α 560 nm (cm^{-1})) is $4.2\text{E}+3$, and the coefficient ratio (α 450 nm/ α 560 nm) is 9.

Moreover, the dark current is 1.00 with respect to that in Example 1, the EQE is 0.63 with respect to that in Example 1, the response time is 1.00 with respect to that in Example 1, and the characteristics significantly inferior to those in Example 1 are the coefficient ratio as a spectral characteristic and the EQE.

The experimental result for the photoelectric conversion element **21** in which the photoelectric conversion layer **46** is used in Example 8 is obtained using a ternary photoelectric conversion layer including the substance (2) (SG5), the substance (6) (BTBT), and the substance (4) (C60) at a ratio of 4:4:2, and the result shows a low absorption coefficient of blue light (α 450 nm (cm^{-1})), poor blue light selectivity, and a small coefficient ratio. Furthermore, the dark current characteristic and the EQE characteristic are poor. The reason is considered to be that the absorption rate of blue light is low.

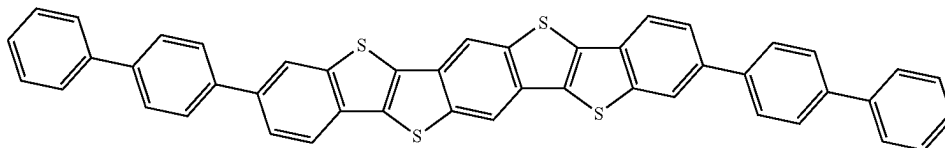
From a comparison among Examples 1 to 8 illustrated in FIG. 7 above, it is considered that the photoelectric conversion element **21** including the photoelectric conversion layer **46** formed in Examples 1 to 4 can photoelectrically convert blue light selectively with high efficiency.

That is, it can be considered that desirable characteristics can be obtained in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (2) (Solvent Green 5 (SG5)), the substance (3) (DNNT), and the substance (4) (C60), respectively, and the photoelectric conversion layer **46** is formed to have a ratio of each organic semiconductor, a:b:c so that the proportion of the substance (4) (C60) to the whole is about 20% to 30%, the remaining 70% to 80% is occupied by the substance (2) (Solvent Green 5 (SG5)) and the substance (3) (DNNT), and the substance (2) (Solvent Green 5 (SG5)) and the substance (3) (DNNT) are mixed at a ratio of approximately 3:5 to approximately 5:3.

Second Example of Characteristics of Organic Material Layer that Depend on Combination and Mixing Ratios of Materials of First Organic Semiconductor, Second Organic Semiconductor, and Third Organic Semiconductor

Next, a second example will be described of the characteristics of the photoelectric conversion layer **46** that depend

[Chem. 8]



on the combination and the mixing ratios of the materials of the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor with reference to FIG. 8.

A comparison has been described above of the characteristics of the photoelectric conversion layer **46** in cases where the first organic semiconductor is the substance (2) (Solvent

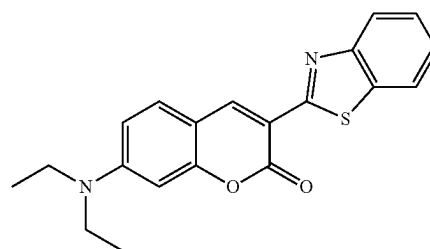
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Green 5 (SG5)) represented by the chemical formula (2), the second organic semiconductor is the substance (3) (DNNT) represented by the chemical formula (3) or the substance (6) (BTBT) represented by the chemical formula (6), the third organic semiconductor is the substance (4) (C60) represented by the chemical formula (4), and the film formation rate of each organic semiconductor is adjusted to change the mixing ratio.

However, the first organic semiconductor may be a substance other than the substance (2) (Solvent Green 5 (SG5)) as long as the substance is a semiconductor that absorbs blue light and generates an electron (charge) by photoelectric conversion. Furthermore, the second organic semiconductor may be a substance other than the substance (3) (DNNT) and the substance (6) (BTBT) as long as the substance is a hole-transporting material that absorbs blue light and has crystallinity.

Therefore, the first organic semiconductor may be, for example, a substance (7) (3-(2-benzothiazolyl)-7-(diethyl-amino) coumarin (Coumarin 6)) represented by the following chemical formula (7) as a semiconductor that absorbs blue light and generates an electron (charge) by photoelectric conversion.

Chemical Formula (7)



[Chem. 7]

Furthermore, the second organic semiconductor may be, for example, a substance (8) (2,9-bis([1,1'-biphenyl]-benzo[1'',2'':4,5;4'':5'':4',5']dithieno[3,2-b:3',2'-b']bis[1]benzothio-ophene (DBP-BTBDT))) represented by the following chemical formula (8) as a hole-transporting material that absorbs blue light and has crystallinity.

Chemical Formula (8)

Therefore, here, a comparison will be described of the characteristics of the photoelectric conversion layer **46** in cases where the first organic semiconductor is the substance (7) (Coumarin 6) represented by the chemical formula (7), the second organic semiconductor is the substance (8) (DBP-BTBDT) represented by the chemical formula (8) or the substance (6) (BTBT) represented by the chemical

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formula (6), the third organic semiconductor is the substance (4) (C60) represented by the chemical formula (4), and the film formation rate of each organic semiconductor is adjusted to change the mixing ratio.

Example 11

As shown in the uppermost row below the header row of FIG. 8, Example 11 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60), respectively, and the uppermost row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 1, and the characteristics significantly inferior to those in Example 11 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.50 Å/sec, 0.50 Å/sec, and 0.25 Å/sec, respectively to form the photoelectric conversion layer 46 so as to have a predetermined thickness (for example, of 200 nm).

In the case of Example 11 in the uppermost row below the header row of FIG. 8, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 4:4:2 (=0.50 Å/sec:0.50 Å/sec:0.25 Å/sec).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is 1.9E+5, the absorption coefficient (α 560 nm (cm^{-1})) is 6.2E+3, and the coefficient ratio (α 450 nm/ α 560 nm) is 31.

Note that Example 11 serves as a reference and therefore, all of the dark current, the EQE, and the response time are 1.00.

The experimental result for the photoelectric conversion element 21 in which the photoelectric conversion layer 46 is used in Example 11 is obtained using a ternary photoelectric conversion layer including the substance (7) (Coumarin 6), the substance (3) (DNTT), and the substance (4) (C60) at a ratio of 4:4:2, and the result shows a relatively high absorption coefficient at 450 nm in the blue light region, a relatively low absorption coefficient at 560 nm in the green light region, a good dark current characteristic, a good EQE characteristic, and a good response characteristic.

Example 12

As shown in the second row below the header row of FIG. 8, Example 12 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60), respectively, and the second row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 11, and the characteristics significantly inferior to those in Example 11 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.50 Å/sec, 0.30 Å/sec, and 0.20 Å/sec, respectively

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to form the photoelectric conversion layer 46 so as to have a predetermined thickness (for example, of 200 nm).

In the case of the second row below the header row of FIG. 8, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 5:3:2 (=0.50 Å/sec:0.30 Å/sec:0.20 Å/sec).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is 2.1E+5, the absorption coefficient (α 560 nm (cm^{-1})) is 5.4E+3, and the coefficient ratio (α 450 nm/ α 560 nm) is 39.

Moreover, the dark current is 0.91 with respect to that in Example 11, the EQE is 0.97 with respect to that in Example 11, and the response time is 1.21 with respect to that in Example 11.

The experimental result for the photoelectric conversion element 21 in which the photoelectric conversion layer 46 is used in Example 12 is obtained using a ternary photoelectric conversion layer including the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60) at a ratio of 5:3:2, and the result shows values close to those in Example 11, such as a relatively high absorption coefficient at 450 nm in the blue light region, a relatively low absorption coefficient at 560 nm in the green light region, a good dark current characteristic, a good EQE characteristic, and a good response characteristic. Therefore, in Example 12, it can be considered that there is no characteristic significantly inferior to that in Example 11.

Example 13

As shown in the third row below the header row of FIG. 8, Example 13 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60), respectively, and the third row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 11, and the characteristics significantly inferior to those in Example 11 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.30 Å/sec, 0.50 Å/sec, and 0.20 Å/sec, respectively to form the photoelectric conversion layer 46 so as to have a predetermined thickness (for example, of 200 nm).

In the case of the third row below the header row of FIG. 8, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 3:5:2 (=0.30 Å/sec:0.50 Å/sec:0.20 Å/sec).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is 1.8E+5, the absorption coefficient (α 560 nm (cm^{-1})) is 6.5E+3, and the coefficient ratio (α 450 nm/ α 560 nm) is 28.

Moreover, the dark current is 1.24 with respect to that in Example 11, the EQE is 1.08 with respect to that in Example 11, and the response time is 0.93 with respect to that in Example 11.

The experimental result for the photoelectric conversion element 21 in which the photoelectric conversion layer 46 is used in Example 13 is obtained using a ternary photoelectric conversion layer including the substance (7) (Coumarin 6),

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the substance (8) (DBP-BTBDT), and the substance (4) (C60) at a ratio of 3:5:2, and the result shows values close to those in Example 11, such as a relatively high absorption coefficient at 450 nm in the blue light region, a relatively low absorption coefficient at 560 nm in the green light region, a good dark current characteristic, a good EQE characteristic, and a good response characteristic. Therefore, in Example 13, it can be considered that there is no characteristic significantly inferior to that in Example 11.

Example 14

As shown in the fourth row below the header row of FIG. 8, Example 14 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60), respectively, and the fourth row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 11, and the characteristics significantly inferior to those in Example 11 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.35 Å/sec, 0.35 Å/sec, and 0.30 Å/sec, respectively to form the photoelectric conversion layer 46 so as to have a predetermined thickness (for example, of 200 nm).

In the case of the fourth row below the header row of FIG. 8, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 3.5:3.5:3 (=0.35 Å/sec:0.35 Å/sec:0.30 Å/sec).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is 1.8E+5, the absorption coefficient (α 560 nm (cm^{-1})) is 8.1E+3, and the coefficient ratio (α 450 nm/ α 560 nm) is 22.

Moreover, the dark current is 1.73 with respect to that in Example 11, the EQE is 1.08 with respect to that in Example 11, and the response time is 0.97 with respect to that in Example 11.

The experimental result for the photoelectric conversion element 21 in which the photoelectric conversion layer 46 is used in Example 14 is obtained using a ternary photoelectric conversion layer including the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60) at a ratio of 3.5:3.5:3, and the result shows values close to those in Example 11, such as a relatively high absorption coefficient at 450 nm in the blue light region, a relatively low absorption coefficient at 560 nm in the green light region, a good dark current characteristic, a good EQE characteristic, and a good response characteristic. Therefore, in Example 14, it can be considered that there is no characteristic significantly inferior to that in Example 11.

Example 15

As shown in the fifth row below the header row of FIG. 8, Example 15 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60), respectively, and the fifth row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α

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450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 1 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.00 Å/sec, 0.50 Å/sec, and 0.50 Å/sec, respectively to form the photoelectric conversion layer 46 so as to have a predetermined thickness (for example, of 200 nm).

That is, in Example 15, the photoelectric conversion layer 46 includes substantially no substance (7) (Coumarin 6) as the first organic semiconductor.

In the case of the fifth row below the header row of FIG. 8, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 0:5:5 (=0.00 Å/sec:0.50 Å/sec:0.50 Å/sec).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is 5.9E+4, the absorption coefficient (α 560 nm (cm^{-1})) is 1.7E+4, and the coefficient ratio (α 450 nm/ α 560 nm) is 3.

Moreover, the dark current is 1.02 with respect to that in Example 11, the EQE is 0.70 with respect to that in Example 11, the response time is 1.01 with respect to that in Example 11, and the characteristics significantly inferior to those in Example 11 are the coefficient ratio as a spectral characteristic and the EQE.

The experimental result for the photoelectric conversion element 21 in which the photoelectric conversion layer 46 is used in Example 15 is obtained using a ternary photoelectric conversion layer including the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60) at a ratio of 0:5:5, and the result shows a low absorption coefficient of blue light (α 450 nm (cm^{-1})) and a small coefficient ratio because the blue selectivity as the characteristic of the substance (7) is low due to the fact that substantially no substance (7) is included. Furthermore, the dark current characteristic and the response characteristic are substantially the same as those in Example 11, but the EQE characteristic is inferior because the absorption of blue light is inferior.

Example 16

As shown in the sixth row below the header row of FIG. 8, Example 16 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60), respectively, and the sixth row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 1, and the characteristics significantly inferior to those in Example 11 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.50 Å/sec, 0.00 Å/sec, and 0.50 Å/sec, respectively to form the photoelectric conversion layer 46 so as to have a predetermined thickness (for example, of 200 nm).

That is, in Example 16, the photoelectric conversion layer 46 includes no substance (8) (DBP-BTBDT) as the second organic semiconductor.

In the case of the sixth row below the header row of FIG. 8, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third

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organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 5:0:5 ($=0.50 \text{ Å/sec}:0.00 \text{ Å/sec}:0.50 \text{ Å/sec}$).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is $1.8\text{E}+5$, the absorption coefficient (α 560 nm (cm^{-1})) is $2.2\text{E}+4$, and the coefficient ratio (α 450 nm/ α 560 nm) is 8.

Moreover, the dark current is 1.32 with respect to that in Example 11, the EQE is 0.43 with respect to that in Example 11, the response time is 12.5 with respect to that in Example 11, and the characteristics significantly inferior to those in Example 11 are the coefficient ratio as a spectral characteristic and the response time.

The experimental result for the photoelectric conversion element **21** in which the photoelectric conversion layer **46** is used in Example 16 is obtained using a ternary photoelectric conversion layer including the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60) at a ratio of 5:0:5, and the result shows a high absorption coefficient of green light (α 560 nm (cm^{-1})) and a small coefficient ratio. Furthermore, the dark current characteristic and the EQE characteristic are substantially the same as those in Example 11, but the response characteristic is inferior because substantially no substance (8) (DBP-BTBDT) as a hole-transporting material is included.

Example 17

As shown in the seventh row below the header row of FIG. 8, Example 17 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60), respectively, and the seventh row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 11, and the characteristics significantly inferior to those in Example 11 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.50 Å/sec , 0.50 Å/sec , and 0.00 Å/sec , respectively to form the photoelectric conversion layer **46** so as to have a predetermined thickness (for example, of 200 nm).

That is, in Example 17, the photoelectric conversion layer **46** includes substantially no substance (4) (C60) as the third organic semiconductor.

In the case of the seventh row below the header row of FIG. 8, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 5:5:0 ($=0.50 \text{ Å/sec}:0.50 \text{ Å/sec}:0.00 \text{ Å/sec}$).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is $2.3\text{E}+5$, the absorption coefficient (α 560 nm (cm^{-1})) is $1.9\text{E}+3$, and the coefficient ratio (α 450 nm/ α 560 nm) is 121.

Moreover, the dark current is 53.1 with respect to that in Example 11, the EQE is 0.12 with respect to that in Example 11, the response time is unmeasurable (n/a) because the dark current is too large, and the characteristics significantly inferior to those in Example 11 are the spectral dark current, EQE, and response time.

The experimental result for the photoelectric conversion element **21** in which the photoelectric conversion layer **46** is used in Example 17 is obtained using a ternary photoelectric

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conversion layer including the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60) at a ratio of 5:5:0, and the result shows a high absorption coefficient of blue light (α 450 nm (cm^{-1})) and a large coefficient ratio. However, all of the dark current characteristic, the EQE characteristic, and the response characteristic are poor. The reason is considered to be that due to the fact that substantially no substance (4), C60, to be an electron-transporting material was included, no donor/acceptor interface was formed in the organic material layer (photoelectric conversion layer) **53** and as a result, exciton dissociation rarely occurred.

Example 18

As shown in the eighth row below the header row of FIG. 8, Example 18 is a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are the substance (7) (Coumarin 6), the substance (6) (BTBT), and the substance (4) (C60), respectively, and the eighth row shows the absorption coefficient (α 450 nm (cm^{-1})), the absorption coefficient (α 560 nm (cm^{-1})), the ratio of the absorption coefficient (α 450 nm/ α 560 nm), the relative values of the dark current, the EQE, and the response time with respect to those in Example 11, and the characteristics significantly inferior to those in Example 11 in a case where the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at film formation rates of 0.50 Å/sec , 0.50 Å/sec , and 0.25 Å/sec , respectively to form the photoelectric conversion layer **46** so as to have a predetermined thickness (for example, of 200 nm).

That is, in Example 18, the second organic semiconductor is the substance (6) (BTBT).

In the case of the eighth row below the header row of FIG. 8, the ratio a:b:c, that is, the mixing ratio of the first organic semiconductor:the second organic semiconductor:the third organic semiconductor corresponds to the ratio of the film formation rate, and therefore, is 4:4:2 ($=0.50 \text{ Å/sec}:0.50 \text{ Å/sec}:0.25 \text{ Å/sec}$).

Furthermore, the absorption coefficient (α 450 nm (cm^{-1})) is $1.2\text{E}+5$, the absorption coefficient (α 560 nm (cm^{-1})) is $5.3\text{E}+3$, and the coefficient ratio (α 450 nm/ α 560 nm) is 23.

Moreover, the dark current is 53.1 with respect to that in Example 11, the EQE is 0.12 with respect to that in Example 11, the response time is 1.02 with respect to that in Example 11, and the characteristics significantly inferior to those in Example 11 are the coefficient ratio as a spectral characteristic and the EQE.

The experimental result for the photoelectric conversion element **21** in which the photoelectric conversion layer **46** is used in Example 18 is obtained using a ternary photoelectric conversion layer including the substance (7) (Coumarin 6), the substance (6) (BTBT), and the substance (4) (C60) at a ratio of 4:4:2, and the result shows a low absorption coefficient of blue light (α 450 nm (cm^{-1})). Furthermore, the EQE characteristic is poor. The reason is considered to be that the absorption rate of blue light is low.

From a comparison among Examples 11 to 18 illustrated in FIG. 8 above, it is considered that the photoelectric conversion element **21** including the photoelectric conversion layer **46** formed in Examples 11 to 14 can photoelectrically convert blue light selectively with high efficiency.

That is, it can be considered that desirable characteristics can be obtained in a case where the first organic semiconductor, the second organic semiconductor, and the third

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organic semiconductor are the substance (7) (Coumarin 6), the substance (8) (DBP-BTBDT), and the substance (4) (C60), respectively, and the photoelectric conversion layer 46 is formed to have a ratio of each organic semiconductor, a:b:c so that the proportion of the substance (4) (C60) to the whole is about 20% to 30%, the remaining 70% to 80% is occupied by the substance (7) (Coumarin 6) and the substance (6) (BTBT), and the substance (7) (Coumarin 6) and the substance (6) (BTBT) are mixed at a ratio of approximately 3:5 to approximately 5:3.

Note that although Examples have been described above in which the substance (2) (SG5) and the substance (7) (Coumarin 6) are used as the first organic semiconductor, the first organic semiconductor may be another semiconductor as long as, for example, the another semiconductor absorbs blue light and generates an electron (charge) by photoelectric conversion.

More specifically, the first organic semiconductor is a film that absorbs blue light (including blue light in the range of, for example, 400 to 500 nm in which the wavelength used in the experiment, 450 nm, is included) but does not absorb green light (including green light in the range of, for example, 500 to 600 nm in which the wavelength used in the experiment, 560 nm, is included as a center) and red light (including red light in the range of, for example, 600 to 700 nm). Specifically, it is sufficient if the first organic semiconductor has an absorption coefficient of blue light (including blue light in the range of, for example, 400 to 500 nm in which the wavelength used in the experiment, 450 nm, is included) of $40,000\text{ cm}^{-1}$ or more and absorption coefficients of green light (including green light in the range of, for example, 500 to 600 nm in which the wavelength used in the experiment, 560 nm, is included) and red light (including red light in the range of, for example, 500 to 700 nm) of $10,000\text{ cm}^{-1}$ or less. For example, the first organic semiconductor may be dipyrromethane, azadipyrromethane, dipyrrolyl, azadipyrrolyl, coumarin, perylene, pyrene, naphthalenediimide, xanthene, xanthenoxanthene, phenoxazine, indigo, azo oxazine, benzodithiophene, naphthodithiophene, anthradithiophene, anthracene, tetracene, anthraquinone, tetraquinone, dinaphthothienothiophene, oligothiophene, cyanine, squalium, porphyrin, phthalocyanine, or a derivative thereof.

Furthermore, although Examples have been described above in which the substance (3) (DNTT), the substance (6) (BTBT), and the substance (8) (DBP-BTBDT) are used as the second organic semiconductor, the second organic semiconductor may be another semiconductor as long as the another semiconductor is a hole-transporting material that absorbs blue light and has crystallinity.

More specifically, the first condition is that the film in which the second organic semiconductor is deposited absorbs blue light (including blue light in the range of, for example, 400 to 500 nm in which the wavelength used in the experiment, 450 nm, is included) but does not absorb green light (including green light in the range of, for example, 500 to 600 nm in which the wavelength used in the experiment, 560 nm, is included) and red light (including red light in the range of, for example, 500 to 700 nm), and has an absorption coefficient of blue light of $40,000\text{ cm}^{-1}$ or more and an absorption rate of blue light of 80% or more, and an absorption coefficient of green and red light of $10,000\text{ cm}^{-1}$ or less and an absorption rate of green and red light of less than 20%.

Furthermore, the second condition is that the film in which the second organic semiconductor is deposited is a hole-transporting material having a highest occupied

28

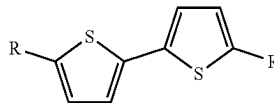
molecular orbital (HOMO) energy level of 5.0 to 6.2 eV and has a hole mobility of $1\text{E-}6\text{ cm}^2/\text{Vs}$ or more.

Moreover, the third condition is that the film in which the second organic semiconductor material is deposited shows a peak of the crystallinity by out-of-plane X-ray measurement, and the organic photoelectric conversion layer in the photoelectric conversion element 21 including the second organic semiconductor material has a peak of the crystallinity by out-of-plane X-ray measurement at the position equivalent to that of the peak of the crystallinity by out-of-plane X-ray measurement of the second organic semiconductor single film.

That is, it is sufficient that the second organic semiconductor satisfies the above-described first to third conditions, and the second organic semiconductor may be, for example, any of substances (9) to (25) respectively represented by the following chemical formulae (9) to (25).

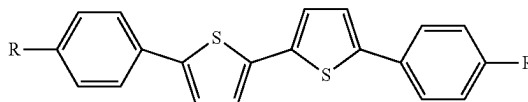
[Chem. 9]

Chemical Formula (9)



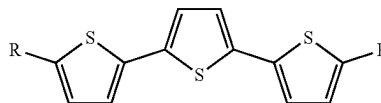
[Chem. 10]

Chemical Formula (10)



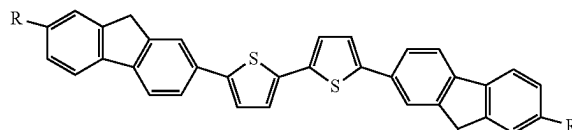
[Chem. 11]

Chemical Formula (11)



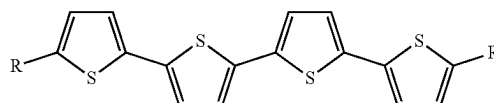
[Chem. 12]

Chemical Formula (12)



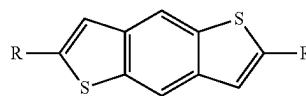
[Chem. 13]

Chemical Formula (13)



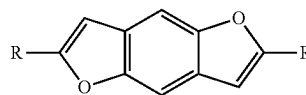
[Chem. 14]

Chemical Formula (14)



[Chem. 15]

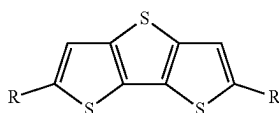
Chemical Formula (15)



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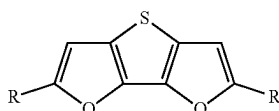
-continued

[Chem. 16]



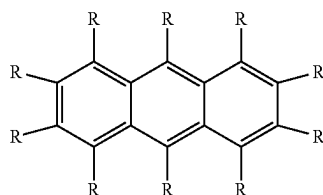
Chemical Formula (16)

[Chem. 17]



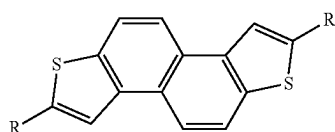
Chemical Formula (17)

[Chem. 18]



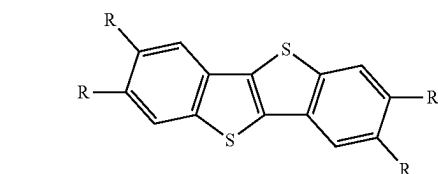
Chemical Formula (18)

[Chem. 19]



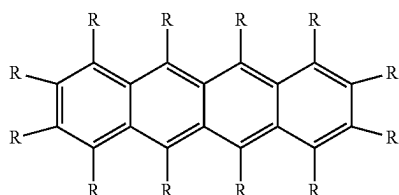
Chemical Formula (19)

[Chem. 20]



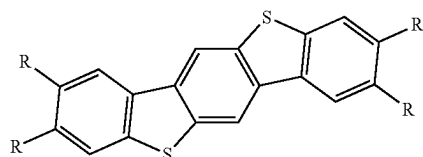
Chemical Formula (20)

[Chem. 21]



Chemical Formula (21)

[Chem. 22]

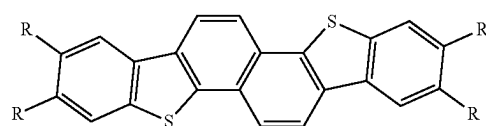


Chemical Formula (22)

30

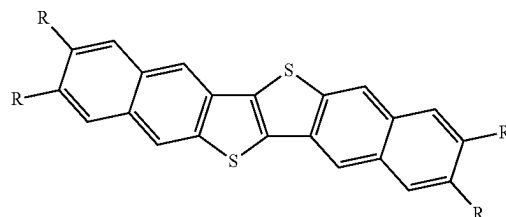
-continued

[Chem. 23]



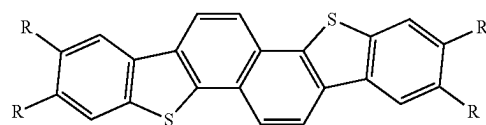
Chemical Formula (23)

[Chem. 24]



Chemical Formula (24)

[Chem. 25]

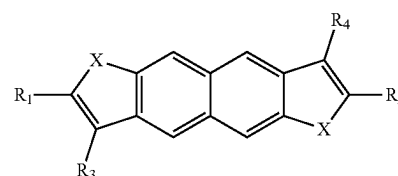


Chemical Formula (25)

Moreover, the second organic semiconductor that satisfies the above-described first to third conditions may be a substance (26) including a naphthodichalcogenophene-based compound represented by the following chemical formula (26).

Chemical Formula (26)

[Chem. 26]



Here, X represents oxygen, sulfur, or selenium. Furthermore, at least one of R1, R2, R3, or R4 is a substituent other than hydrogen.

Examples of the substituent other than hydrogen include unsubstituted or substituted phenyl, biphenyl, terphenyl, naphthalene, phenylnaphthalene, biphenylnaphthalene, binaphthalene, thiophene, bithiophene, terthiophene, benzothiophene, phenylbenzothiophene, biphenylbenzothiophene, benzofuran, phenylbenzofuran, biphenylbenzothiophene, alkanes, cycloalkanes, fluorene, and phenylfluorene.

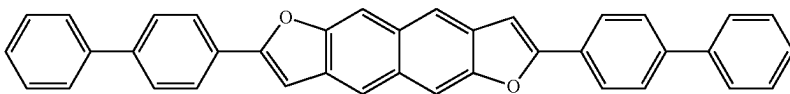
In more detail, the substance (26) including a naphthodichalcogenophene-based compound is, for example, any of substances (27) to (44) that include a naphthodifuran derivative, a naphthonaphthodithiophene derivative, or a naphthodiselenophene derivative and are respectively represented by the following chemical formulae (27) to (44).

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32

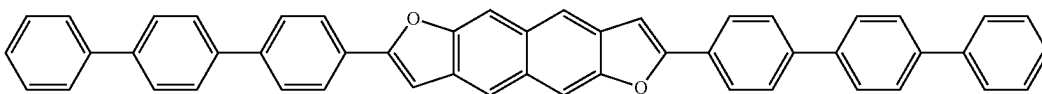
[Chem. 27]

Chemical Formula (27)



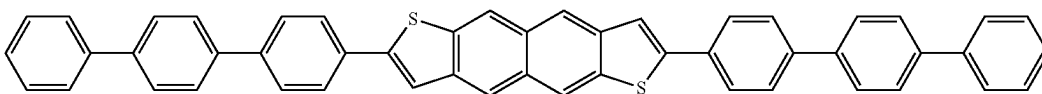
[Chem. 28]

Chemical Formula (28)



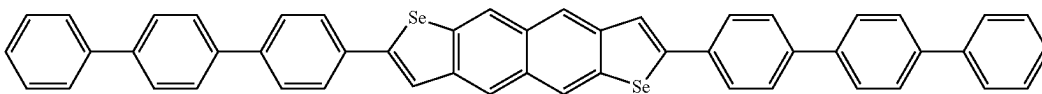
[Chem. 29]

Chemical Formula (29)



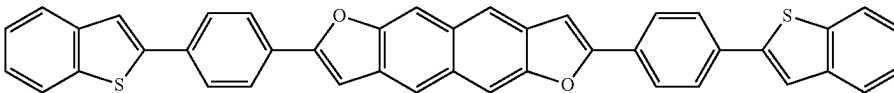
[Chem. 30]

Chemical Formula (30)



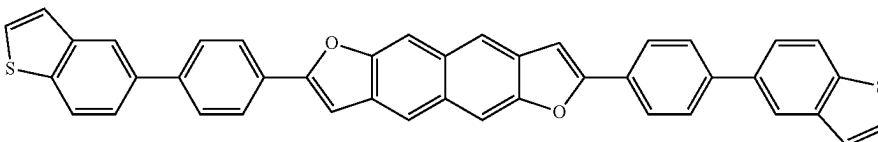
[Chem. 31]

Chemical Formula (31)



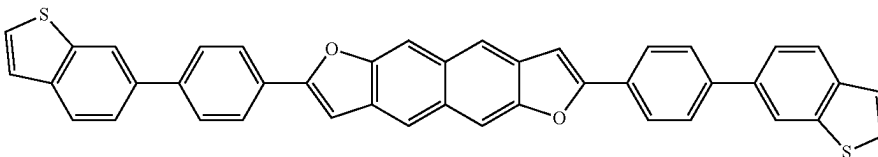
[Chem. 32]

Chemical Formula (32)



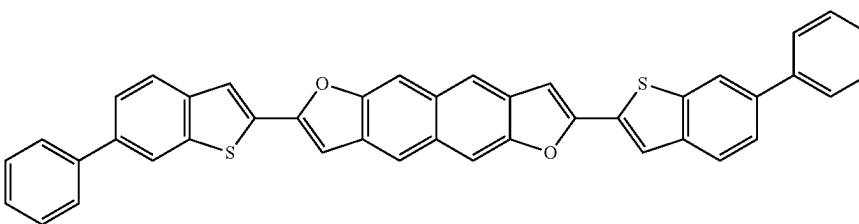
[Chem. 33]

Chemical Formula (33)



[Chem. 34]

Chemical Formula (34)



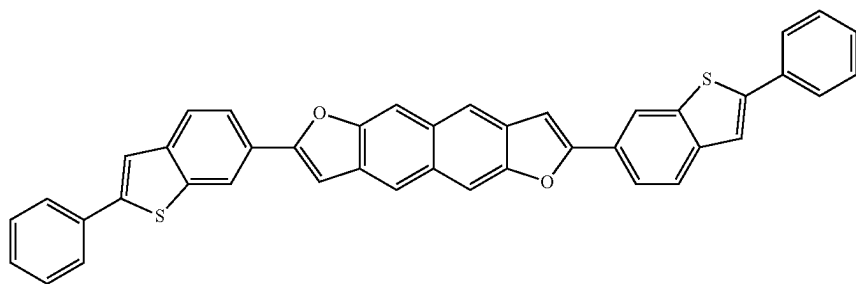
33

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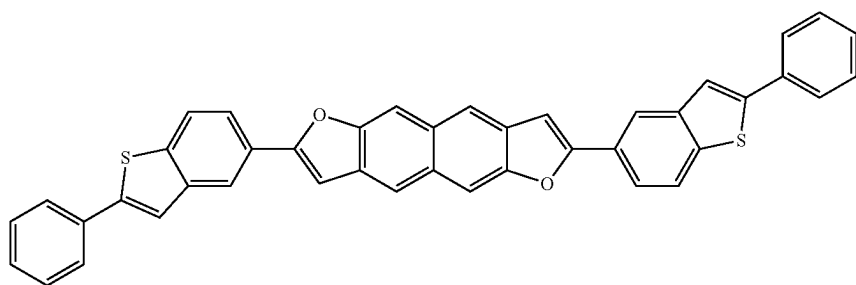
[Chem. 35]

Chemical Formula (35)



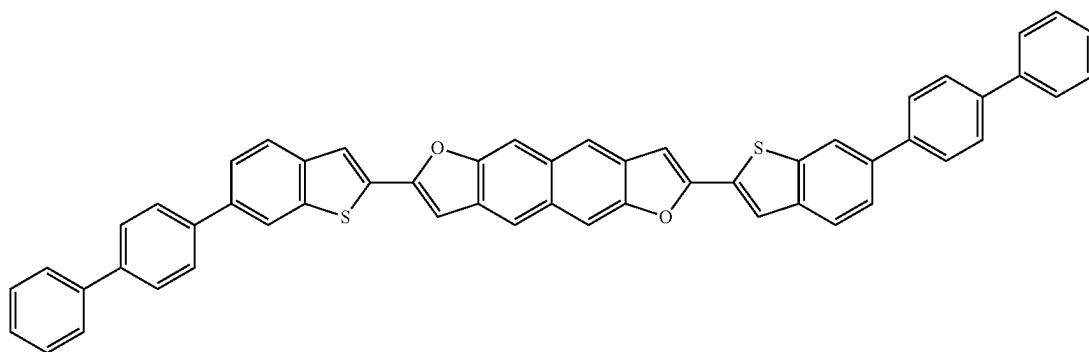
[Chem. 36]

Chemical Formula (36)



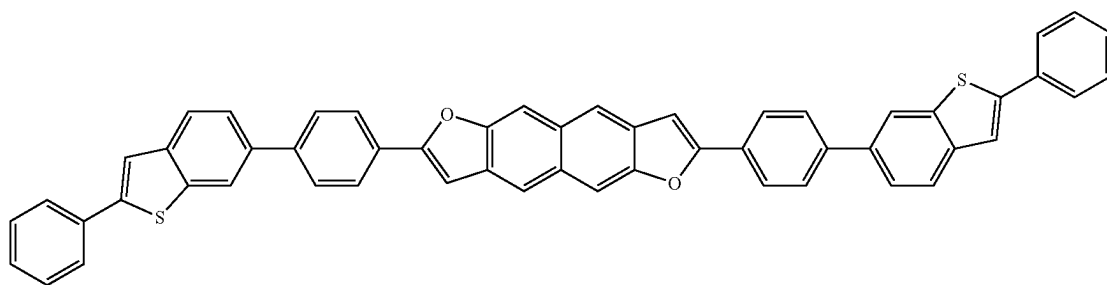
[Chem. 37]

Chemical Formula (37)



[Chem. 38]

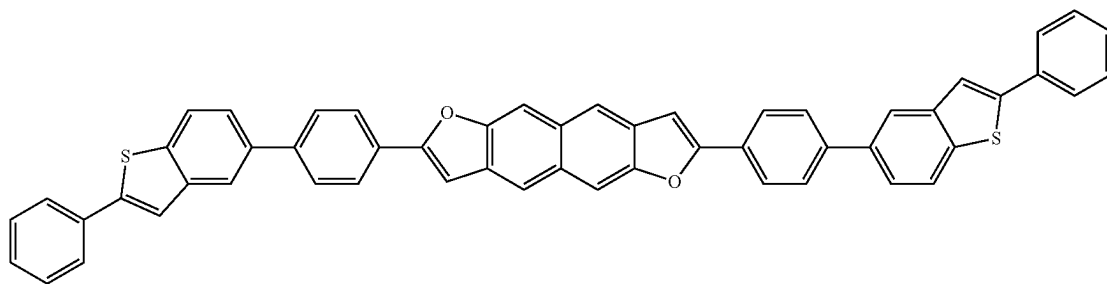
Chemical Formula (38)



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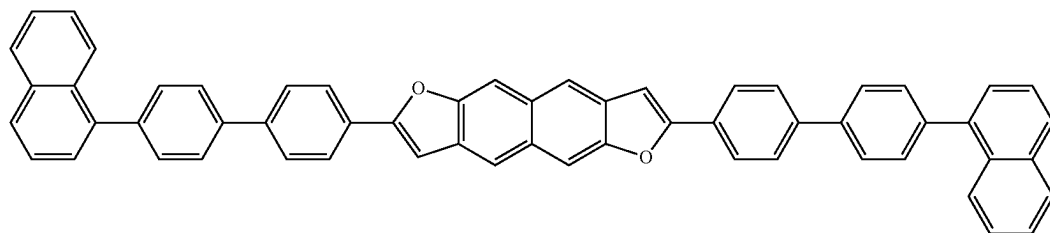
[Chem. 39]

Chemical Formula (39)



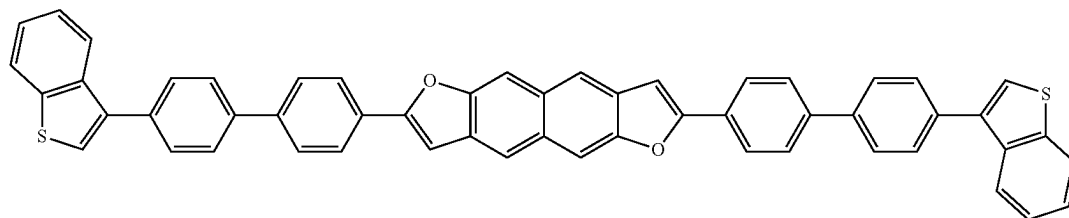
[Chem. 40]

Chemical Formula (40)



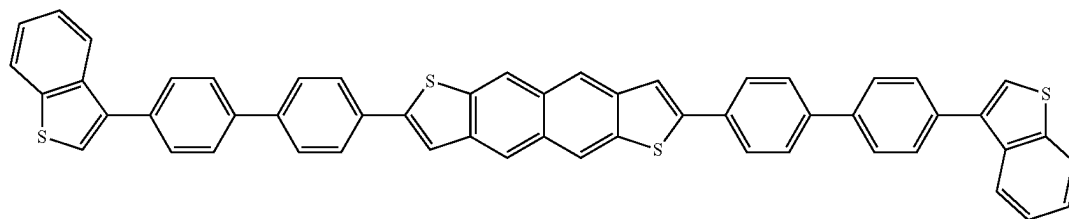
[Chem. 41]

Chemical Formula (41)



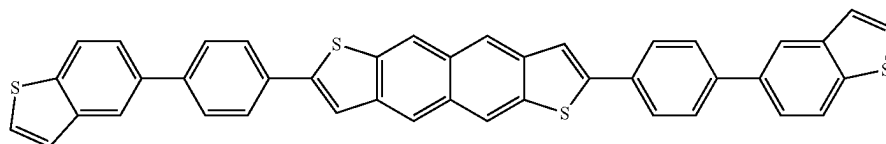
[Chem. 42]

Chemical Formula (42)



[Chem. 43]

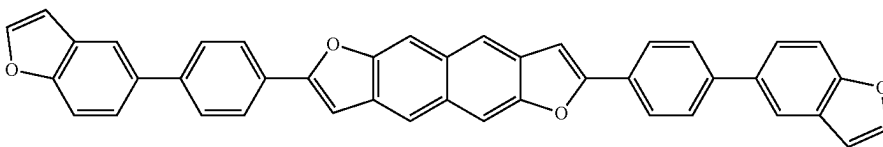
Chemical Formula (43)



-continued

[Chem. 44]

Chemical Formula (44)



The second organic semiconductor including the substance (26) represented by the chemical formula (26), such as any of the substances (27) to (44) that include a naphthodifuran derivative, a naphthonaphthodithiophene derivative, or a naphthodiselenophene derivative and are respectively represented by the chemical formulae (27) to (44), has a face-on orientation in which the major axis of a molecule is parallel to the substrate surface.

Furthermore, the second organic semiconductor including the substance (26) can be a herringbone type crystal advantageous for carrier transport, by strong intermolecular interaction due to the naphthodichalcogenophene skeleton.

Therefore, the second organic semiconductor including the substance (26) exhibits high carrier mobility in the direction perpendicular to the upper and lower electrodes, and has an excellent on/off response characteristic of photocurrent in response to the presence or absence of light irradiation.

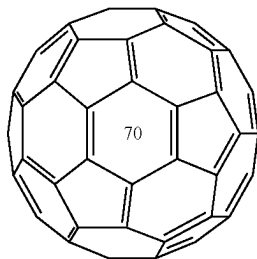
For example, the substance (26) has a lower dark current value (j_{dk}), higher external quantum efficiency (EQE), a shorter response time, and higher responsiveness than the substance (3) (DNTT) described above.

Furthermore, the second organic semiconductor including the substance (26) has a transition dipole moment parallel to the light incident direction (substrate surface), and therefore, can strongly absorb light having a wavelength in the range of approximately 400 nm to 550 nm.

Therefore, in a case where a solid-state imaging device includes the photoelectric conversion element, an on-chip color filter is unnecessary, and the photoelectric conversion element can be multilayered.

Furthermore, the third organic semiconductor may be other than the substance (4) (C60) as long as the third organic semiconductor is a fullerene derivative, and may be, for example, a substance (45) (C70) represented by the following chemical formula (45).

Chemical Formula (45)



[Chem. 45]

<Configuration of Solid-State Imaging Element>

Next, a configuration of a solid-state imaging element to which the photoelectric conversion element according to the present technology is applied will be described with reference to FIG. 9. FIG. 9 is a schematic view illustrating the structure of a solid-state imaging element to which the photoelectric conversion element according to the present technology is applied.

Here, in FIG. 9, pixel regions **201**, **211**, and **231** are a region in which a photoelectric conversion element including the photoelectric conversion film according to the present technology is arranged. Furthermore, control circuits **202**, **212**, and **242** are an arithmetic processing circuit that controls each configuration of the solid-state imaging element, and logic circuits **203**, **223**, and **243** are a signal processing circuit configured to process a signal photoelectrically converted by the photoelectric conversion element in the pixel region.

For example, as illustrated in the configuration A in FIG. 9, the solid-state imaging element to which the photoelectric conversion element according to the present technology is applied may include the pixel region **201**, the control circuit **202**, and the logic circuit **203** that are formed in one semiconductor chip **200**.

Furthermore, as illustrated in the configuration B in FIG. 9, the solid-state imaging element to which the photoelectric conversion element according to the present technology is applied may be a laminated solid-state imaging element in which the pixel region **211** and the control circuit **212** are formed in a first semiconductor chip **210**, and the logic circuit **223** is formed in a second semiconductor chip **220**.

Moreover, as illustrated in the configuration C in FIG. 9, the solid-state imaging element to which the photoelectric conversion element according to the present technology is applied may be a laminated solid-state imaging element in which the pixel region **231** is formed in a first semiconductor chip **230**, and the control circuit **242** and the logic circuit **243** are formed in a second semiconductor chip **240**.

In the solid-state imaging element illustrated in the configurations B and C in FIG. 9, at least one of the control circuit or the logic circuit is formed in a semiconductor chip other than the semiconductor chip in which the pixel region is formed. Therefore, the pixel region can be larger in the solid-state imaging element illustrated in the configurations B and C in FIG. 9 than in the solid-state imaging element illustrated in the configuration A to increase the number of pixels installed in the pixel region and improve the lateral resolution. Therefore, the solid-state imaging element to which the photoelectric conversion element according to the present technology is applied is more preferably the laminated solid-state imaging element illustrated in the configurations B and C in FIG. 9.

<Configuration of Electronic Apparatus>

Next, a configuration of an electronic apparatus to which the photoelectric conversion element according to the present technology is applied will be described with reference to FIG. 10. FIG. 10 is a block diagram illustrating the configuration of an electronic apparatus to which the photoelectric conversion element according to the present technology is applied.

As illustrated in FIG. 10, an electronic apparatus 400 includes an optical system 402, a solid-state imaging element 404, a digital signal processor (DSP) circuit 406, a control part 408, an output part 412, an input part 414, a frame memory 416, a recording part 418, and a power supply part 420.

Here, the DSP circuit 406, the control part 408, the output part 412, the input part 414, the frame memory 416, the recording part 418, and the power supply part 420 are connected to each other via a bus line 410.

Incident light from a subject enters the optical system 402, and the optical system 402 forms an image of the incident light on the imaging surface of the solid-state imaging element 404. Furthermore, the solid-state imaging element 404 includes the photoelectric conversion element according to the present technology. The solid-state imaging element 404 converts the amount of incident light formed as the image on the imaging surface by the optical system 402 into an electric signal in units of pixels and outputs the electric signal as a pixel signal.

The DSP circuit 406 processes the pixel signal transferred from the solid-state imaging element 404 and outputs the processed signal to the output part 412, the frame memory 416, the recording part 418, and the like. Furthermore, the control part 408 includes, for example, an arithmetic processing circuit and the like, and controls the operation of each configuration of the electronic apparatus 400.

The output part 412 is, for example, a panel display device such as a liquid crystal display or an organic electroluminescence display, and displays a moving image or a still image captured by the solid-state imaging element 404. Note that the output part 412 may include an audio output device such as a speaker or a headphone. Furthermore, the input part 414 is a device for a user to input an operation, such as a touch panel or a button, and issues an operation command for various functions of the electronic apparatus 400 according to the user's operation.

The frame memory 416 temporarily stores the moving image, the still image, or the like captured by the solid-state imaging element 404. Furthermore, the recording part 418 records the moving image, the still image, or the like captured by the solid-state imaging element 404 on a removable storage medium such as a magnetic disk, an optical disk, a magneto-optical disk, or a semiconductor memory.

The power supply part 420 appropriately supplies various power sources serving as operation power sources of the DSP circuit 406, the control part 408, the output part 412, the input part 414, the frame memory 416, and the recording part 418 to these supply targets.

The electronic apparatus 400 to which the photoelectric conversion element according to the present technology is applied has been described above. The electronic apparatus 400 to which the photoelectric conversion element according to the present technology is applied may be, for example, an imaging device.

Furthermore, although the solid-state imaging element and the electronic apparatus to which the photoelectric conversion element according to the present technology is applied have been described above, the photoelectric con-

version element can also be applied to another technology, and for example, can also be applied as a sensor in which a solar cell or light is used.

An embodiment of the present technology has been described above in detail with reference to the accompanying drawings, but the technical scope of the present technology is not limited to the above-described examples. It is obvious that a person having ordinary knowledge in the technical field of the present technology can conceive various changes or modifications within the scope of the technical concept described in the claims, and it is naturally understood that these changes or modifications also belong to the technical scope of the present technology.

Furthermore, the effects described in the present description are merely illustrative or exemplary, and are not restrictive. That is, the present technology can exhibit another effect obvious to those skilled in the art from the description in the present description together with or instead of the above-described effects.

Application Example to Endoscopic Surgical System

The technology according to the present disclosure (present technology) can be applied to various products. For example, the technology according to the present disclosure may be applied to an endoscopic surgical system.

FIG. 11 is a view illustrating an example of the schematic configuration of an endoscopic surgical system to which the technology according to the present disclosure (the present technology) can be applied.

FIG. 11 illustrates a state in which an operator (doctor) 11131 is performing surgery on a patient 11132 on a patient bed 11133 using an endoscopic surgical system 11000. As illustrated, the endoscopic surgical system 11000 includes an endoscope 11100, other surgical tools 11110 such as a pneumoperitoneum tube 11111 and an energy treatment tool 11112, a support arm device 11120 that supports the endoscope 11100, and a cart 11200 on which various devices for endoscopic surgery are installed.

The endoscope 11100 includes a lens barrel 11101 in which a region of a predetermined length from the distal end is inserted into the body cavity of the patient 11132, and includes a camera head 11102 connected to the proximal end of the lens barrel 11101. In the illustrated example, the endoscope 11100 is illustrated that is configured as a so-called rigid scope having the rigid lens barrel 11101, but the endoscope 11100 may be configured as a so-called flexible scope having a flexible lens barrel.

The distal end of the lens barrel 11101 is provided with an opening into which an objective lens is fitted. To the endoscope 11100, a light source device 11203 is connected, and light generated by the light source device 11203 is guided to the distal end of the lens barrel 11101 by a light guide extending inside the lens barrel 11101, and is emitted toward an observation target in the body cavity of the patient 11132 via the objective lens. Note that the endoscope 11100 may be a forward-viewing endoscope, an oblique-viewing endoscope, or a side-viewing endoscope.

The camera head 11102 is provided with an optical system and an imaging element inside, and reflected light (observation light) from the observation target is condensed on the imaging element by the optical system. The imaging element photoelectrically converts the observation light, and thus, an electric signal corresponding to the observation light, that is, an image signal corresponding to the observation image is

generated. The image signal is transmitted to a camera control unit (CCU) **11201** in the form of RAW data.

The CCU **11201** includes a central processing unit (CPU), a graphics processing unit (GPU), and the like, and integrally controls the operation of the endoscope **11100** and a display device **11202**. Moreover, the CCU **11201** receives the image signal from the camera head **11102**, and performs various image processing to display of an image based on the image signal, such as development processing (demosaic processing), on the image signal.

In response to the control of the CCU **11201**, the display device **11202** displays an image based on the image signal subjected to the image processing by the CCU **11201**.

The light source device **11203** includes a light source such as a light emitting diode (LED), and supplies the endoscope **11100** with irradiation light at the time of imaging a surgical site or the like.

An input device **11204** is an input interface for the endoscopic surgical system **11000**. The user can input various information and instructions to the endoscopic surgical system **11000** via the input device **11204**. For example, the user inputs an instruction or the like to change an imaging condition (such as the type of irradiation light, the magnification, or the focal length) of the endoscope **11100**.

A treatment tool control device **11205** controls driving of the energy treatment tool **11112** for cauterization and incision of tissue, sealing of a blood vessel, and the like. A pneumoperitoneum device **11206** feeds gas into the body cavity of the patient **11132** via the pneumoperitoneum tube **11111** in order to inflate the body cavity of the patient **11132** for the purpose of securing the visual field of the endoscope **11100** and securing the working space of the operator. A recorder **11207** is a device capable of recording various information regarding surgery. A printer **11208** is a device capable of printing various information regarding surgery in various formats such as text, image, and graph formats.

Note that the light source device **11203** that supplies the endoscope **11100** with irradiation light at the time of imaging the surgical site can include, for example, an LED, a laser light source, or a white light source including an LED and a laser light source in combination. In a case where the white light source includes RGB laser light sources in combination, the output intensity and the output timing of each color (at each wavelength) can be controlled with high accuracy, and therefore, the white balance of the captured image can be adjusted in the light source device **11203**. Furthermore, in this case, it is also possible to capture an image corresponding to each of RGB in a time division manner by irradiating the observation target with laser light from each of the RGB laser light sources in a time division manner and controlling the driving of the imaging element of the camera head **11102** in synchronization with the irradiation timing. According to this method, a color image can be obtained without providing a color filter for the imaging element.

Furthermore, the driving of the light source device **11203** may be controlled so as to change the output light intensity every predetermined time. It is possible to generate an image of a high dynamic range, without so-called underexposure and overexposure, by controlling the driving of the imaging element of the camera head **11102** in synchronization with the timing of the change of the light intensity to acquire images in a time division manner and synthesizing the images.

Furthermore, the light source device **11203** may be configured to be capable of supplying light in a predetermined wavelength band for special light observation. In the special

light observation, so-called narrow band imaging is performed in which, using, for example, the wavelength dependency of light absorption in a body tissue, a predetermined tissue such as a blood vessel in a mucosal surface layer is irradiated with light in a narrower band than irradiation light at the time of normal observation (that is, white light) to be imaged with high contrast. Alternatively, in the special light observation, fluorescence observation may be performed in which an image is obtained using fluorescence generated by irradiation with excitation light. In the fluorescence observation, it is possible, for example, to irradiate a body tissue with excitation light and observe the fluorescence from the body tissue (autofluorescence observation), or to locally inject a reagent such as indocyanine green (ICG) into a body tissue and irradiate the body tissue with excitation light corresponding to the fluorescence wavelength of the reagent to obtain a fluorescence image. The light source device **11203** can be configured to be capable of supplying narrow band light and/or excitation light for such special light observation.

FIG. **12** is a block diagram illustrating an example of the functional configuration of the camera head **11102** and the CCU **11201** illustrated in FIG. **11**.

The camera head **11102** includes a lens unit **11401**, an imaging part **11402**, a drive part **11403**, a communication part **11404**, and a camera head control part **11405**. The CCU **11201** includes a communication part **11411**, an image processing part **11412**, and a control part **11413**. The camera head **11102** and the CCU **11201** are communicably connected to each other via a transmission cable **11400**.

The lens unit **11401** is an optical system provided at a connection portion with the lens barrel **11101**. Observation light taken in from the distal end of the lens barrel **11101** is guided to the camera head **11102** and enters the lens unit **11401**. The lens unit **11401** includes a plurality of lenses including a zoom lens and a focus lens in combination.

The imaging part **11402** includes an imaging element. The imaging part **11402** may include one imaging element (may be a so-called single-plate imaging part) or may include a plurality of imaging elements (may be a so-called multi-plate imaging part). In a case where the imaging part **11402** is a multi-plate imaging part, for example, the imaging elements may generate image signals corresponding to RGB respectively, and the image signals may be synthesized to obtain a color image. Alternatively, the imaging part **11402** may include a pair of imaging elements that are respectively configured to acquire right-eye and left-eye image signals for three-dimensional (3D) display. By performing 3D display, the operator **11131** can further accurately grasp the depth of the living tissue in the surgical site. Note that, in a case where the imaging part **11402** is a multi-plate imaging part, a plurality of lens units **11401** can be provided corresponding to the imaging elements respectively.

Furthermore, the imaging part **11402** is not necessarily required to be provided for the camera head **11102**. For example, the imaging part **11402** may be provided inside the lens barrel **11101** immediately after the objective lens.

The drive part **11403** includes an actuator, and moves the zoom lens and the focus lens of the lens unit **11401** by a predetermined distance along the optical axis in response to the control of the camera head control part **11405**. Thus, the magnification and the focus of the image captured by the imaging part **11402** can be appropriately adjusted.

The communication part **11404** includes a communication device configured to transmit and receive various information to and from the CCU **11201**. The communication part **11404** obtains the image signal from the imaging part **11402**,

and transmits the image signal to the CCU **11201** in the form of RAW data via the transmission cable **11400**.

Furthermore, the communication part **11404** receives a control signal for control of driving of the camera head **11102** from the CCU **11201**, and supplies the control signal to the camera head control part **11405**. The control signal includes information regarding the imaging condition, such as information specifying the frame rate of a captured image, information specifying the exposure value at the time of imaging, and/or information specifying the magnification and the focus of a captured image.

Note that the above-described imaging conditions such as the frame rate, the exposure value, the magnification, and the focus may be appropriately specified by the user, or may be automatically set by the control part **11413** of the CCU **11201** on the basis of the acquired image signal. In the latter case, a so-called auto exposure (AE) function, an auto focus (AF) function, and an auto white balance (AWB) function are installed in the endoscope **11100**.

The camera head control part **11405** receives the control signal from the CCU **11201** via the communication part **11404**, and controls driving of the camera head **11102** on the basis of the control signal.

The communication part **11411** includes a communication device configured to transmit and receive various information to and from the camera head **11102**. The communication part **11411** receives an image signal transmitted from the camera head **11102** via the transmission cable **11400**.

Furthermore, the communication part **11411** transmits a control signal for control of driving of the camera head **11102** to the camera head **11102**. The image signal and the control signal can be transmitted by electric communication, optical communication, or the like.

The image processing part **11412** performs various image processing on the image signal in the form of RAW data transmitted from the camera head **11102**.

The control part **11413** performs various control related to imaging of a surgical site or the like by the endoscope **11100** and to display of a captured image obtained by imaging of the surgical site or the like. For example, the control part **11413** generates a control signal for control of driving of the camera head **11102**.

Furthermore, the control part **11413** performs control so that the display device **11202** displays a captured image of a surgical site or the like on the basis of the image signal subjected to image processing by the image processing part **11412**. At this time, the control part **11413** may recognize various objects in the captured image using various image recognition technologies. For example, the control part **11413** can recognize a surgical tool such as forceps, a specific site of the living body, bleeding, mist at the time of using the energy treatment tool **11112**, and the like by detecting the shape of the edge, color, and the like of the object in the captured image. The control part **11413** may perform control using the recognition result so that when the display device **11202** displays the captured image, various surgery support information is superimposed on the image of the surgical site and displayed. The superimposed display of the surgery support information to the operator **11131** leads to reduction in the burden on the operator **11131** and reliable surgery operation by the operator **11131**.

The transmission cable **11400** connecting the camera head **11102** and the CCU **11201** is an electric signal cable for electric signal communication, an optical fiber for optical communication, or a composite cable thereof.

Here, in the illustrated example, communication is performed by wire using the transmission cable **11400**, but

communication between the camera head **11102** and the CCU **11201** may be performed by wireless.

An example of the endoscopic surgical system to which the technology according to the present disclosure can be applied has been described above. The technology according to the present disclosure can be applied to the endoscope **11100** and the imaging part **11402** of the camera head **11102** among the above-described configurations. Specifically, the solid-state imaging element **11** in FIGS. **2** and **3** can be applied to an imaging part **10402**. By applying the technology according to the present disclosure to the imaging part **10402**, it is possible to realize photoelectric conversion of blue light with high efficiency.

Note that, here, the endoscopic surgical system has been described as an example, but the technology according to the present disclosure may be applied to another system such as a microscopic surgical system.

Application Example to Mobile Body

The technology according to the present disclosure (present technology) can be applied to various products. For example, the technology according to the present disclosure may be realized as a device installed in any kind of mobile body such as an automobile, an electric vehicle, a hybrid electric vehicle, a motorcycle, a bicycle, a personal mobility, an airplane, a drone, a ship, or a robot.

FIG. **13** is a block diagram illustrating a schematic configuration example of a vehicle control system as an example of a mobile body control system to which the technology according to the present disclosure can be applied.

A vehicle control system **12000** includes a plurality of electronic control units connected via a communication network **12001**. In the example illustrated in FIG. **13**, the vehicle control system **12000** includes a drive system control unit **12010**, a body system control unit **12020**, a vehicle exterior information detection unit **12030**, a vehicle interior information detection unit **12040**, and an integrated control unit **12050**. Furthermore, a microcomputer **12051**, a sound/image output part **12052**, and an in-vehicle network interface (I/F) **12053** are illustrated as the functional configuration of the integrated control unit **12050**.

The drive system control unit **12010** controls the operation of devices related to the drive system of the vehicle according to various programs. For example, the drive system control unit **12010** functions as a control device of a driving force generation device configured to generate driving force of the vehicle, such as an internal combustion engine or a driving motor, a driving force transmission mechanism configured to transmit driving force to wheels, a steering mechanism configured to adjust the steering angle of the vehicle, a braking device configured to generate braking force of the vehicle, and the like.

The body system control unit **12020** controls the operation of various devices mounted on the vehicle body according to various programs. For example, the body system control unit **12020** functions as a control device of a keyless entry system, a smart key system, a power window device, or various lamps such as a headlamp, a back lamp, a brake lamp, a blinker, and a fog lamp. In this case, a radio wave transmitted from a portable device that substitutes for a key or signals of various switches can be input to the body system control unit **12020**. The body system control unit **12020** receives the input of the radio wave or the signals, and controls the door lock device, the power window device, the lamp, and the like of the vehicle.

The vehicle exterior information detection unit **12030** detects information outside the vehicle in which the vehicle control system **12000** is installed. For example, an imaging part **12031** is connected to the vehicle exterior information detection unit **12030**. The vehicle exterior information detection unit **12030** makes the imaging part **12031** capture an image outside the vehicle, and receives the captured image. The vehicle exterior information detection unit **12030** may perform object detection processing or distance detection processing for a target such as a person, a vehicle, an obstacle, a sign, or a character on a road surface on the basis of the received image.

The imaging part **12031** is an optical sensor that receives light and outputs an electric signal according to the amount of the received light. The imaging part **12031** can output the electric signal as an image or distance measurement information. Furthermore, the light received by the imaging part **12031** may be visible light or invisible light such as infrared rays.

The vehicle interior information detection unit **12040** detects information inside the vehicle. For example, a driver state detection part **12041** that detects the state of a driver is connected to the vehicle interior information detection unit **12040**. The driver state detection part **12041** includes, for example, a camera that images a driver, and the vehicle interior information detection unit **12040** may calculate the degree of fatigue or the degree of concentration of the driver or may determine whether or not the driver is dozing off on the basis of the detected information input from the driver state detection part **12041**.

The microcomputer **12051** can calculate the control target value of the driving force generation device, the steering mechanism, or the braking device on the basis of the information inside and outside the vehicle acquired by the vehicle exterior information detection unit **12030** or the vehicle interior information detection unit **12040**, and can output a control command to the drive system control unit **12010**. For example, the microcomputer **12051** can perform cooperative control for the purpose of realizing functions of an advanced driver assistance system (ADAS) that include collision avoidance or impact mitigation of the vehicle, following traveling based on the following distance, traveling while maintaining the vehicle speed, vehicle collision warning, vehicle lane departure warning, and the like.

Furthermore, the microcomputer **12051** controls the driving force generation device, the steering mechanism, the braking device, or the like on the basis of the information around the vehicle acquired by the vehicle exterior information detection unit **12030** or the vehicle interior information detection unit **12040**, and thus can perform cooperative control for the purpose of automatic driving or the like in which the vehicle autonomously travels without operation by the driver.

Furthermore, the microcomputer **12051** can output a control command to the body system control unit **12020** on the basis of the vehicle exterior information acquired by the vehicle exterior information detection unit **12030**. For example, the microcomputer **12051** can perform cooperative control for the purpose of preventing glare, such as switching from a high beam to a low beam by controlling the headlamp according to the position of the preceding vehicle or the oncoming vehicle detected by the vehicle exterior information detection unit **12030**.

The sound/image output part **12052** transmits an output signal of at least one of a sound or an image to an output device capable of visually or audibly notifying a vehicle occupant or a person outside the vehicle of information. In

the example in FIG. 13, an audio speaker **12061**, a display part **12062**, and an instrument panel **12063** are illustrated as the output device. The display part **12062** may include, for example, at least one of an on-board display or a head-up display.

FIG. 14 is a view illustrating an example of the installation position of the imaging part **12031**.

In FIG. 14, a vehicle **12100** includes imaging parts **12101**, **12102**, **12103**, **12104**, and **12105** as the imaging part **12031**.

The imaging parts **12101**, **12102**, **12103**, **12104**, and **12105** are provided, for example, at positions such as the front nose, the side mirrors, the rear bumper, the back door, and the upper part of the windshield in the interior of the vehicle **12100**. The imaging part **12101** provided at the front nose and the imaging part **12105** provided at the upper part of the windshield in the interior of the vehicle mainly acquire images in front of the vehicle **12100**. The imaging parts **12102** and **12103** provided at the side mirrors mainly acquire images sideward from the vehicle **12100**. The imaging part **12104** provided at the rear bumper or the back door mainly acquires an image behind the vehicle **12100**. The images in front of the vehicle that are acquired by the imaging parts **12101** and **12105** are mainly used for detecting a preceding vehicle, a pedestrian, an obstacle, a traffic light, a traffic sign, a lane, or the like.

Note that FIG. 14 illustrates an example of the imaging ranges of the imaging parts **12101** to **12104**. An imaging range **12111** indicates the imaging range of the imaging part **12101** provided at the front nose, imaging ranges **12112** and **12113** respectively indicate the imaging ranges of the imaging parts **12102** and **12103** provided at the side mirrors, and an imaging range **12114** indicates the imaging range of the imaging part **12104** provided at the rear bumper or the back door. For example, it is possible to obtain an overhead view image of the vehicle **12100** viewed from above by superimposing image data captured by the imaging parts **12101** to **12104**.

At least one of the imaging part **12101**, **12102**, **12103**, or **12104** may have a function of acquiring distance information. For example, at least one of the imaging part **12101**, **12102**, **12103**, or **12104** may be a stereo camera including a plurality of imaging elements, or may be an imaging element having a pixel for phase difference detection.

For example, the microcomputer **12051** obtains the distance to each three-dimensional object in the imaging ranges **12111** to **12114** and the temporal change of the distance (relative speed with respect to the vehicle **12100**) on the basis of the distance information obtained from the imaging parts **12101** to **12104**, and thus can extract, as a preceding vehicle, a three-dimensional object that is, in particular, the closest to the vehicle **12100** on the traveling path of the vehicle **12100** and is traveling at a predetermined speed (of, for example, 0 km/h or more) in substantially the same direction as the vehicle **12100**. Moreover, the microcomputer **12051** can set, in advance, a following distance to be secured behind the preceding vehicle, and can perform automatic brake control (including following stop control), automatic acceleration control (including following start control), and the like. As described above, it is possible to perform cooperative control for the purpose of automatic driving or the like in which the vehicle autonomously travels without operation by the driver.

For example, the microcomputer **12051** can extract three-dimensional object data regarding three-dimensional objects in a state of being classified into a two-wheeled vehicle, an ordinary vehicle, a large vehicle, a pedestrian, and another three-dimensional object such as an utility pole on the basis

of the distance information obtained from the imaging parts **12101** to **12104**, and can use the three-dimensional object data for automatic obstacle avoidance. For example, the microcomputer **12051** identifies an obstacle around the vehicle **12100** as an obstacle that can be visually recognized by the driver of the vehicle **12100** or as an obstacle that is difficult to visually recognize. Then, the microcomputer **12051** determines the collision risk indicating a risk of collision with each obstacle, and when the collision risk is a set value or more and there is a possibility of collision, the microcomputer **12051** can perform driving assistance for collision avoidance by outputting an alarm to the driver via the audio speaker **12061** or the display part **12062** or performing forced deceleration or avoidance steering via the drive system control unit **12010**.

At least one of the imaging part **12101**, **12102**, **12103**, or **12104** may be an infrared camera that detects infrared rays. For example, the microcomputer **12051** can recognize a pedestrian by determining whether or not a pedestrian is present in the images captured by the imaging parts **12101** to **12104**. Such recognition of a pedestrian is performed by, for example, a procedure of extracting feature points in the images captured by the imaging parts **12101** to **12104** as infrared cameras, and a procedure of performing pattern matching processing on a series of feature points indicating the outline of an object to determine whether or not the object is a pedestrian. When the microcomputer **12051** determines that a pedestrian is present in the images captured by the imaging parts **12101** to **12104** and recognizes the pedestrian, the sound/image output part **12052** controls the display part **12062** so that a rectangular outline is superimposed on the image of the recognized pedestrian and displayed for emphasis. Furthermore, the sound/image output part **12052** may control the display part **12062** so that an icon or the like indicating the pedestrian is displayed at a desired position.

An example of the vehicle control system to which the technology according to the present disclosure can be applied has been described above. The technology according to the present disclosure can be applied to the imaging part **12031** among the above-described configurations. Specifically, the solid-state imaging element **11** in FIGS. **2** and **3** can be applied to the imaging part **12031**. By applying the technology according to the present disclosure to the imaging part **12031**, it is possible to realize photoelectric conversion of blue light with high efficiency.

Note that the present technology can also have the following configurations.

<1> A solid-state imaging element including

an organic photoelectric conversion element including at least two electrodes, in which

an organic photoelectric conversion layer is arranged between the two electrodes,

the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor,

the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light,

the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and

the third organic semiconductor includes a fullerene derivative.

<2> The solid-state imaging element according to the item <1>, in which

the organic photoelectric conversion layer strongly absorbs blue light that is light in a wavelength band in the vicinity of 400 to 500 nm, and weakly absorbs green light that is light in a wavelength band in the vicinity of 500 to 600 nm and red light that is light in a wavelength band in the vicinity of 600 to 700 nm.

<3> The solid-state imaging element according to the item <2>, in which

the organic photoelectric conversion layer has an absorption coefficient of the blue light of more than $40,000\text{ cm}^{-1}$, an absorption rate of the blue light of more than 80%, an absorption coefficient of the green light and the red light of less than $10,000\text{ cm}^{-1}$, and an absorption rate of the green light and the red light of less than 20%.

<4> The solid-state imaging element according to any one of the items <1> to <3>, in which

the first organic semiconductor strongly absorbs blue light that is light in a wavelength band in the vicinity of 400 to 500 nm, and weakly absorbs green light that is light in a wavelength band in the vicinity of 500 to 600 nm and red light that is light in a wavelength band in the vicinity of 600 to 700 nm.

<5> The solid-state imaging element according to the item <4>, in which

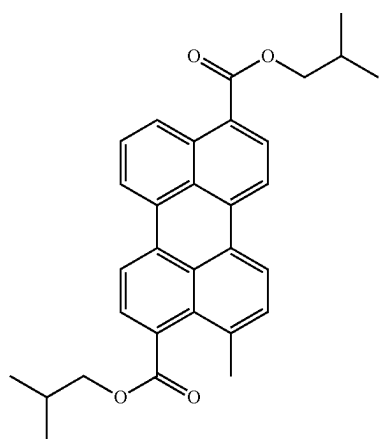
the first organic semiconductor has an absorption coefficient of the blue light of more than $40,000\text{ cm}^{-1}$ and an absorption coefficient of the green light and the red light of less than $10,000\text{ cm}^{-1}$.

<6> The solid-state imaging element according to the item <5>, in which

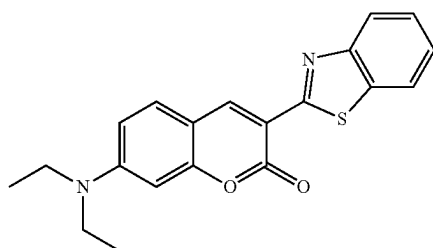
the first organic semiconductor includes dipyrromethane, azadipyrromethane, dipyrrolyl, azadipyrrolyl, coumarin, perylene, pyrene, naphthalenediimide, xanthene, xanthenoxanthene, phenoxazine, indigo, azo oxazine, benzodithiophene, naphthodithiophene, anthradithiophene, anthracene, tetracene, anthraquinone, tetraquinone, dinaphthothienothiophene, oligothiophene, cyanine, squalium, porphyrin, phthalocyanine, a substance represented by a chemical formula (2) described below, or a substance represented by a chemical formula (7) described below, or a derivative of dipyrromethane, azadipyrromethane, dipyrrolyl, azadipyrrolyl, coumarin, perylene, pyrene, naphthalenediimide, xanthene, xanthenoxanthene, phenoxazine, indigo, azo oxazine, benzodithiophene, naphthodithiophene, anthradithiophene, anthracene, tetracene, anthraquinone, tetraquinone, dinaphthothienothiophene, oligothiophene, cyanine, squalium, porphyrin, phthalocyanine, the substance represented by the chemical formula (2), or the substance represented by the chemical formula (7):

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Chemical Formula (2)



Chemical Formula (7)



[Chem. 46]

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<7> The solid-state imaging element according to any one of the items <1> to <6>, in which

the second organic semiconductor strongly absorbs blue light that is light in a wavelength band in the vicinity of 400 to 500 nm, and weakly absorbs green light that is light in a wavelength band in the vicinity of 500 to 600 nm and red light that is light in a wavelength band in the vicinity of 600 to 700 nm, the second organic semiconductor is a hole-transporting material, and the second organic semiconductor shows a peak of crystallinity by out-of-plane X-ray measurement.

<8> The solid-state imaging element according to the item <7>, in which

the second organic semiconductor has an absorption coefficient of the blue light of more than $40,000 \text{ cm}^{-1}$ and an absorption coefficient of the green light and the red light of less than $10,000 \text{ cm}^{-1}$, the second organic semiconductor has a hole mobility of $1\text{E-}6 \text{ cm}^2/\text{Vs}$ or more, the second organic semiconductor is a hole-transporting material having an HOMO energy level of 5.3 to 6.2 eV, and the organic photoelectric conversion layer has a peak of crystallinity by out-of-plane X-ray measurement at a position equivalent to a position of a peak of crystallinity by out-of-plane X-ray measurement of a single film of the second organic semiconductor.

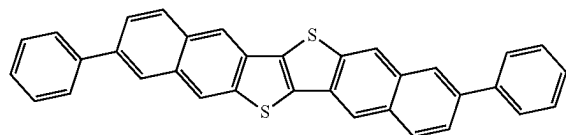
<9> The solid-state imaging element according to the item <8>, in which

the second organic semiconductor includes a substance represented by any one of a chemical formula (3), a chemical formula (6), and chemical formulae (8) to (26) described below,

X in the chemical formula (26) is oxygen, sulfur, or selenium, and at least one of R1, R2, R3, or R4 is a substituent other than hydrogen:

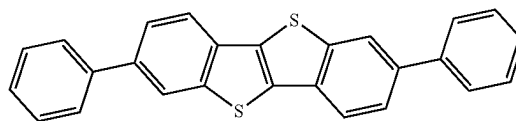
[Chem. 48]

Chemical Formula (3)



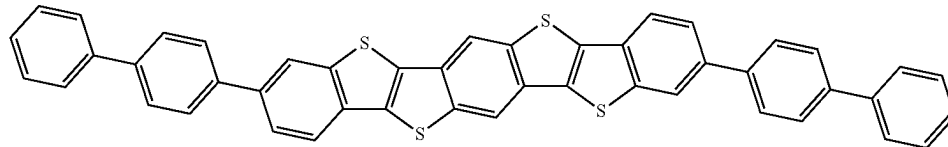
[Chem. 49]

Chemical Formula (6)



[Chem. 50]

Chemical Formula (8)

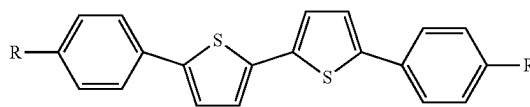
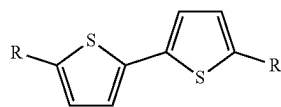


[Chem. 51]

[Chem. 52]

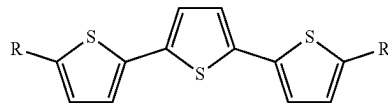
Chemical Formula (9)

Chemical Formula (10)



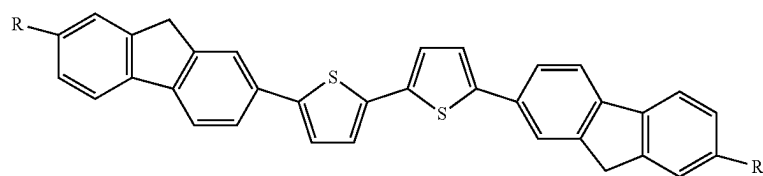
[Chem. 53]

Chemical Formula (11)



-continued

[Chem. 54]

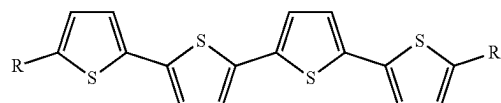


Chemical Formula (12)

[Chem. 55]

[Chem. 56]

Chemical Formula (13)

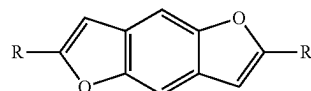


Chemical Formula (14)

[Chem. 57]

[Chem. 58]

Chemical Formula (15)

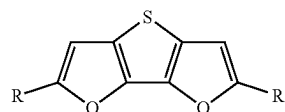


Chemical Formula (16)

[Chem. 59]

[Chem. 60]

Chemical Formula (17)

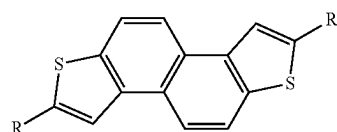


Chemical Formula (18)

[Chem. 61]

[Chem. 62]

Chemical Formula (19)

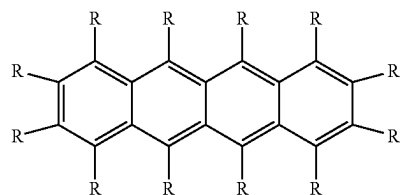


Chemical Formula (20)

[Chem. 63]

[Chem. 64]

Chemical Formula (21)

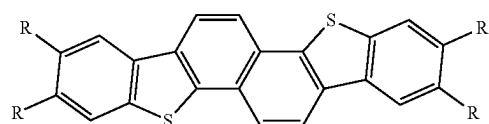


Chemical Formula (22)

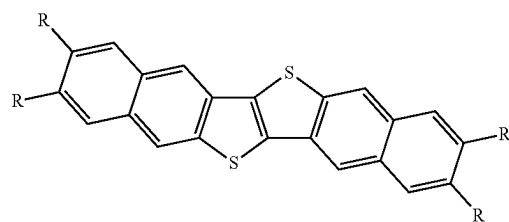
[Chem. 65]

[Chem. 66]

Chemical Formula (23)



Chemical Formula (24)



53

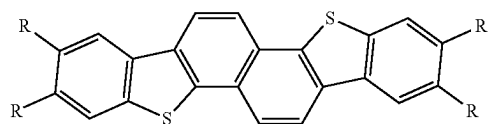
54

-continued

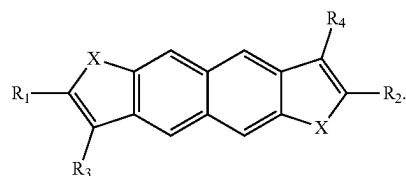
[Chem. 67]

[Chem. 68]

Chemical Formula (25)



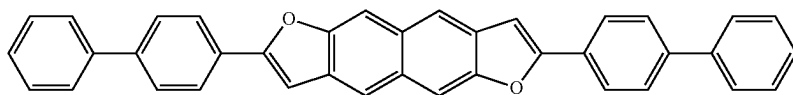
Chemical Formula (26)



<10> The solid-state imaging element according to the item <9>, in which¹⁵
 the substance represented by the chemical formula (26) includes a substance represented by any one of chemical formulae (27) to (44) described below:

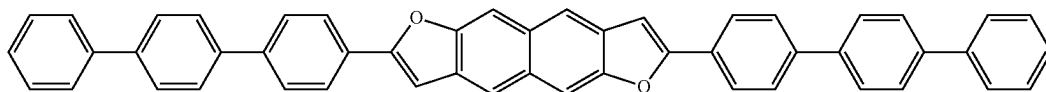
[Chem. 69]

Chemical Formula (27)



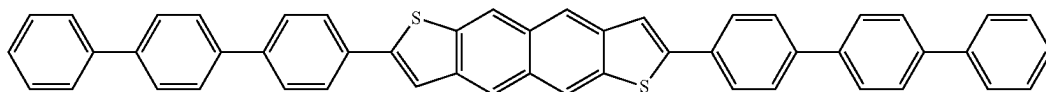
[Chem. 70]

Chemical Formula (28)



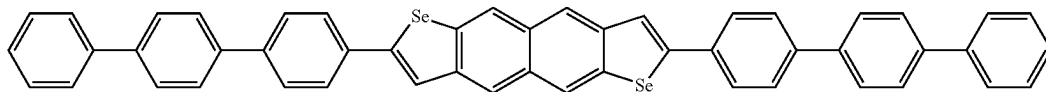
[Chem. 71]

Chemical Formula (29)



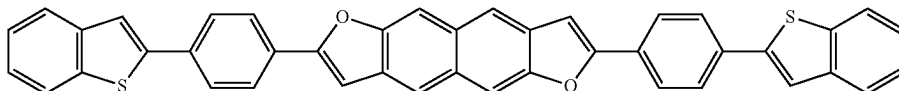
[Chem. 72]

Chemical Formula (30)



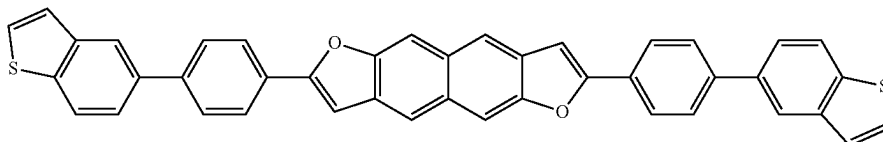
[Chem. 73]

Chemical Formula (31)



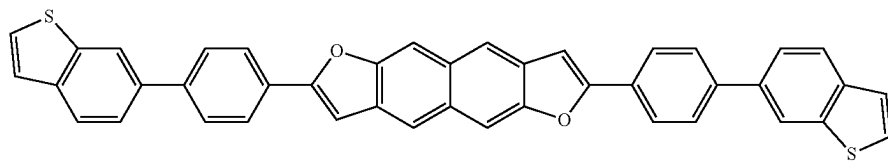
[Chem. 74]

Chemical Formula (32)



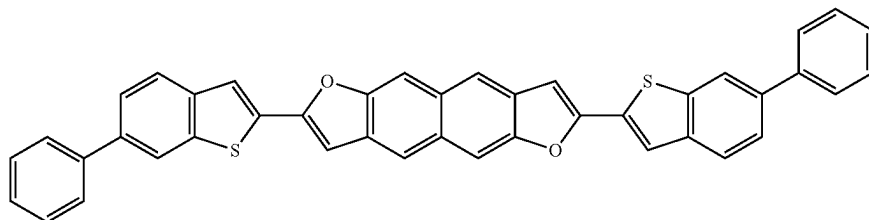
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[Chem. 75]



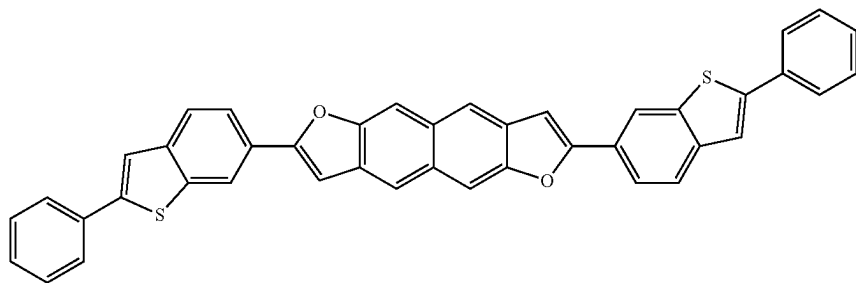
Chemical Formula (33)

[Chem. 76]



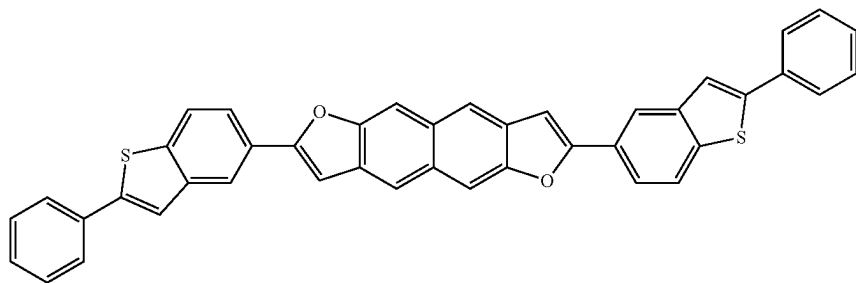
Chemical Formula (34)

[Chem. 77]



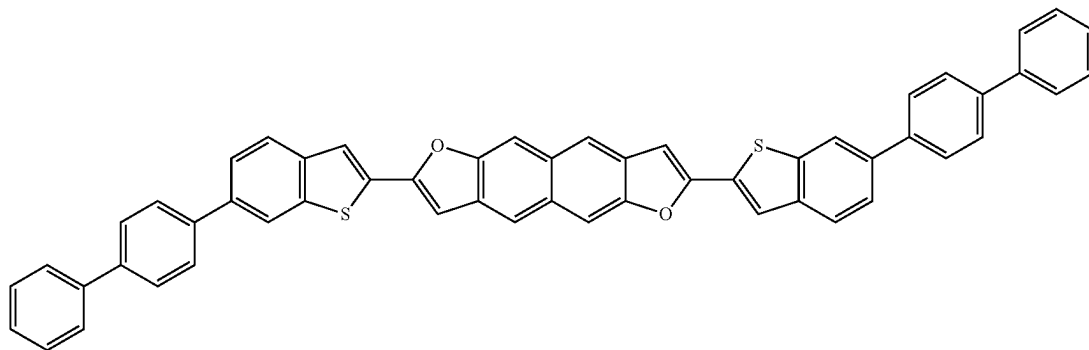
Chemical Formula (35)

[Chem. 78]



Chemical Formula (36)

[Chem. 79]

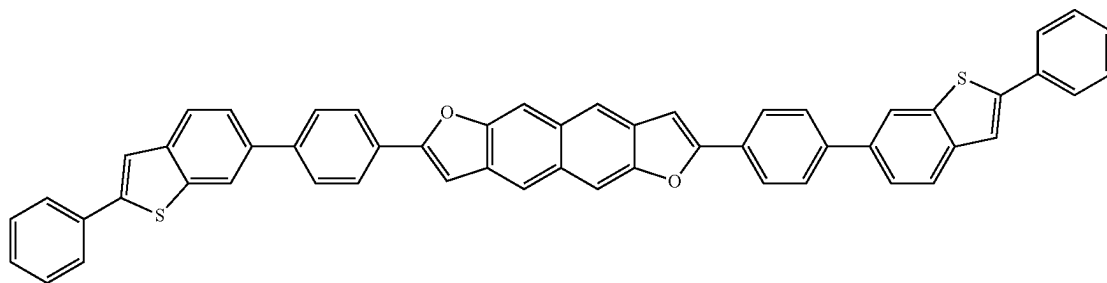


Chemical Formula (37)

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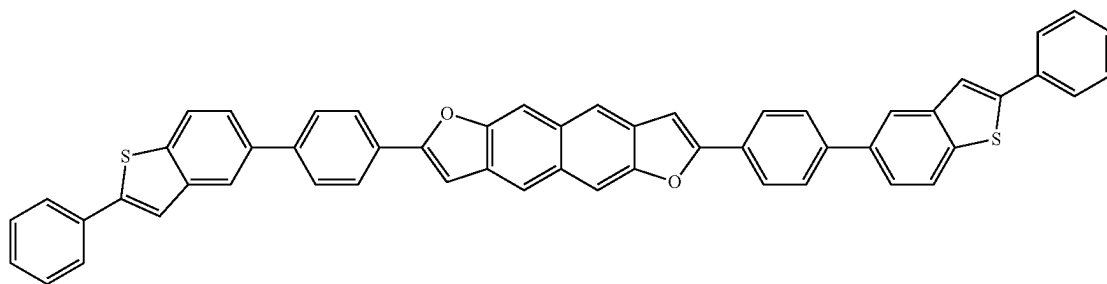
[Chem. 80]

Chemical Formula (38)



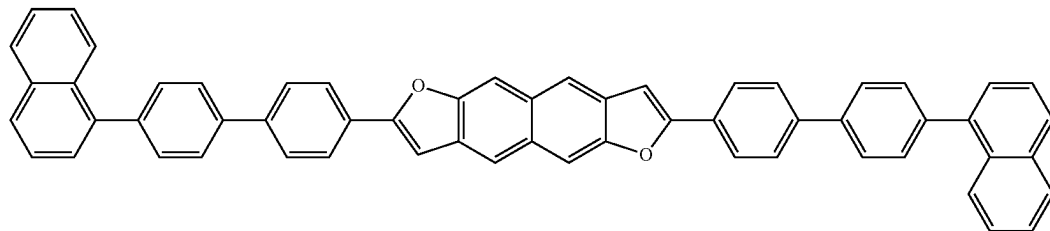
[Chem. 81]

Chemical Formula (39)



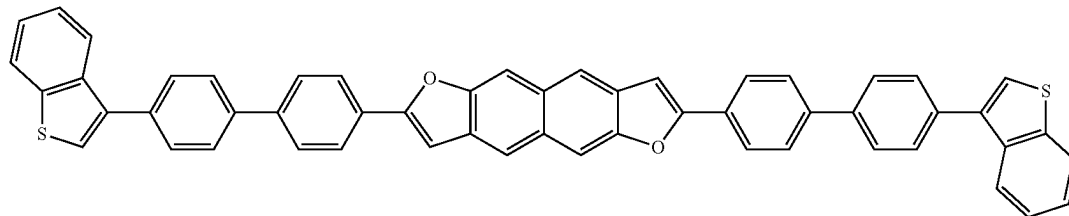
[Chem. 82]

Chemical Formula (40)



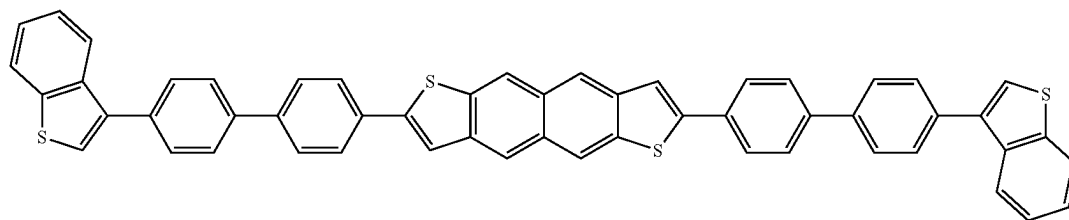
[Chem. 83]

Chemical Formula (41)



[Chem. 84]

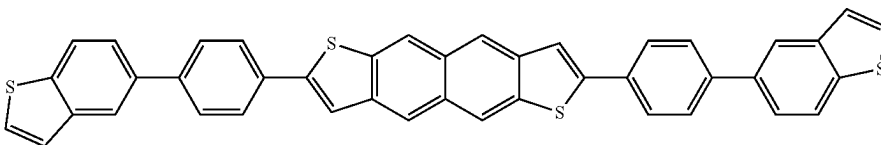
Chemical Formula (42)



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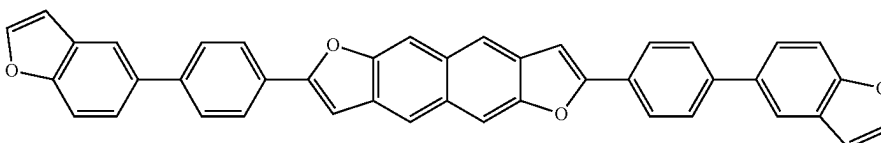
[Chem. 85]

Chemical Formula (43)



[Chem. 86]

Chemical Formula (44)

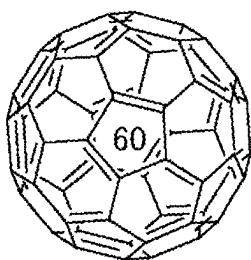


<11> The solid-state imaging element according to any one of the items <1> to <9>, in which

the third organic semiconductor includes a substance represented by a chemical formula (4) or a chemical formula (45) described below:

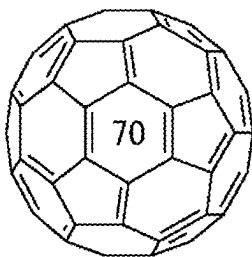
[Chem. 87]

Chemical Formula (4)



[Chem. 88]

Chemical Formula (45)



<12> The solid-state imaging element according to any one of the items <1> to <11>, in which

the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at a predetermined ratio to form each of the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor at a predetermined film formation rate so that the organic photoelectric conversion layer is formed.

<13> The solid-state imaging element according to the item <12>, in which

the third organic semiconductor is included at a ratio of approximately 20% of the organic photoelectric conversion

layer, the first organic semiconductor and the second organic semiconductor are mixed at a ratio of approximately 70% to approximately 80% of the organic photoelectric conversion layer, and the first organic semiconductor and the second organic semiconductor are mixed at approximately 3:5 to approximately 5:3.

<14> A method for manufacturing a solid-state imaging element, the method including:

a first step of forming a first electrode;
a second step of forming an organic photoelectric conversion layer over the first electrode; and

a third step of forming a second electrode over the organic photoelectric conversion layer, in which

the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor,

the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light,

the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and

the third organic semiconductor includes a fullerene derivative.

<15> A photoelectric conversion element including an organic photoelectric conversion element including at least two electrodes, in which

an organic photoelectric conversion layer is arranged between the two electrodes,

the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor,

the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light,

the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and

the third organic semiconductor includes a fullerene derivative.

<16> An imaging device including an organic photoelectric conversion element including at least two electrodes, in which

an organic photoelectric conversion layer is arranged between the two electrodes,

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the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor,

the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light,

the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and

the third organic semiconductor includes a fullerene derivative.

<17> An electronic apparatus including

an organic photoelectric conversion element including at least two electrodes, in which

an organic photoelectric conversion layer is arranged between the two electrodes,

the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor,

the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light,

the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and

the third organic semiconductor includes a fullerene derivative.

REFERENCE SIGNS LIST

11 Solid-state imaging element

21 to 23 Photoelectric conversion element (photoelectric conversion film)

31 Photoelectric conversion element (photodiode)

41 First electrode

42 Charge storage electrode

43 Insulating layer

44 Semiconductor layer

45 Hole blocking layer

46 Photoelectric conversion layer

47 Work function adjustment layer

48 Second electrode

50 Evaluation element

51 First electrode

52 Hole blocking layer

53 Photoelectric conversion material layer

54 Second electrode

55 Substrate

The invention claimed is:

1. A solid-state imaging element comprising an organic photoelectric conversion element including at least two electrodes, wherein

an organic photoelectric conversion layer is arranged between the two electrodes,

the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor,

the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light,

the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and

the third organic semiconductor includes a fullerene derivative,

wherein the second organic semiconductor strongly absorbs blue light that is light in a wavelength band in

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a vicinity of 400 to 500 nm, and weakly absorbs green light that is light in a wavelength band in a vicinity of 500 to 600 nm and red light that is light in a wavelength band in a vicinity of 600 to 700 nm, the second organic semiconductor is a hole-transporting material, and the second organic semiconductor shows a peak of crystallinity by out-of-plane X-ray measurement, and

wherein the second organic semiconductor has an absorption coefficient of the blue light of more than 40,000 cm^{-1} and an absorption coefficient of the green light and the red light of less than 10,000 cm^{-1} , the second organic semiconductor has a hole mobility of $1\text{E-}6$ cm^2/Vs or more, the second organic semiconductor is a hole-transporting material having an HOMO energy level of 5.3 to 6.2 eV, and the organic photoelectric conversion layer has a peak of crystallinity by out-of-plane X-ray measurement at a position equivalent to a position of a peak of crystallinity by out-of-plane X-ray measurement of a single film of the second organic semiconductor.

2. The solid-state imaging element according to claim 1, wherein

the organic photoelectric conversion layer strongly absorbs blue light that is light in a wavelength band in a vicinity of 400 to 500 nm, and weakly absorbs green light that is light in a wavelength band in a vicinity of 500 to 600 nm and red light that is light in a wavelength band in a vicinity of 600 to 700 nm.

3. The solid-state imaging element according to claim 2, wherein

the organic photoelectric conversion layer has an absorption coefficient of the blue light of more than 40,000 cm^{-1} , an absorption rate of the blue light of more than 80%, an absorption coefficient of the green light and the red light of less than 10,000 cm^{-1} , and an absorption rate of the green light and the red light of less than 20%.

4. The solid-state imaging element according to claim 1, wherein

the first organic semiconductor strongly absorbs blue light that is light in a wavelength band in a vicinity of 400 to 500 nm, and weakly absorbs green light that is light in a wavelength band in a vicinity of 500 to 600 nm and red light that is light in a wavelength band in a vicinity of 600 to 700 nm.

5. The solid-state imaging element according to claim 4, wherein

the first organic semiconductor has an absorption coefficient of the blue light of more than 40,000 cm^{-1} and an absorption coefficient of the green light and the red light of less than 10,000 cm^{-1} .

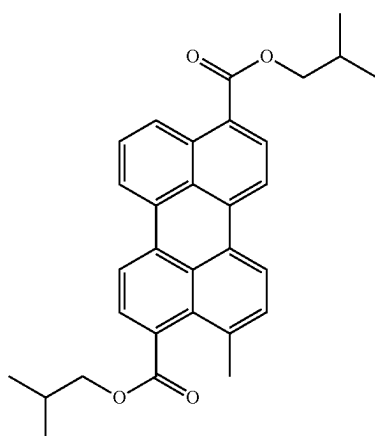
6. The solid-state imaging element according to claim 5, wherein

the first organic semiconductor includes dipyrromethane, azadipyrromethane, dipyridyl, azadipyridyl, coumarin, perylene, pyrene, naphthalenediimide, xanthene, xanthoxanthene, phenoxazine, indigo, azo oxazine, benzodithiophene, naphthodithiophene, anthradithiophene, anthracene, tetracene, anthraquinone, tetraquinone, dinaphthothienothiophene, oligothiophene, cyanine, squalium, porphyrin, phthalocyanine, a substance represented by a chemical formula (2) described below, or a substance represented by a chemical formula (7) described below,

or a derivative of dipyrromethane, azadipyrromethane, dipyridyl, azadipyridyl, coumarin, perylene, pyrene, naphthalenediimide, xanthene, xanthoxanthene, phenoxazine, indigo, azo oxazine, benzodithiophene,

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naphthodithiophene, anthradithiophene, anthracene, tetracene, anthraquinone, tetraquinone, dinaphthothienothiophene, oligothiophene, cyanine, squalium, porphyrin, phthalocyanine, the substance represented by the chemical formula (2), or the substance represented by the chemical formula (7):



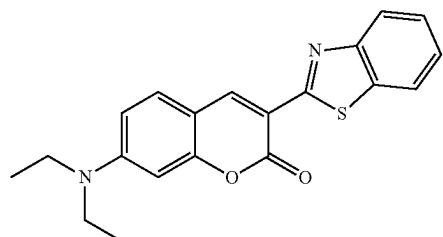
Chemical Formula (2)

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64

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Chemical Formula (7)

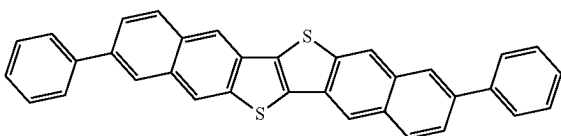


7. The solid-state imaging element according to claim 1, wherein

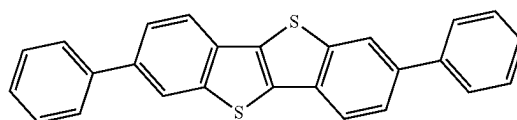
the second organic semiconductor includes a substance represented by any one of a chemical formula (3), a chemical formula (6), and chemical formulae (8) to (26) described below,

X in the chemical formula (26) is oxygen, sulfur, or selenium, and at least one of R1, R2, R3, or R4 is a substituent other than hydrogen:

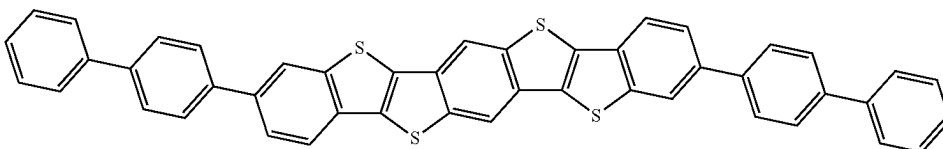
Chemical Formula (3)



Chemical Formula (6)

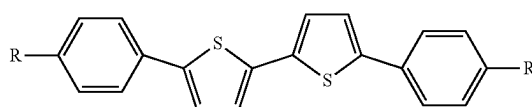
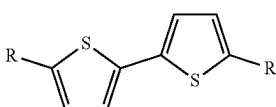


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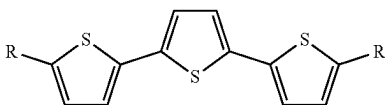


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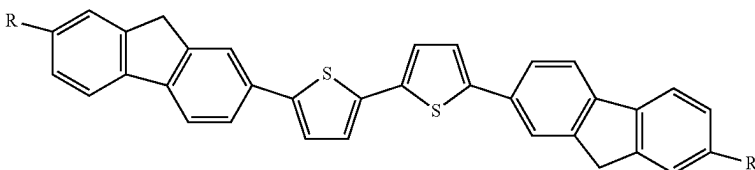
Chemical Formula (10)



Chemical Formula (11)

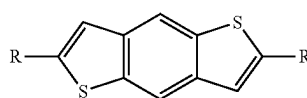
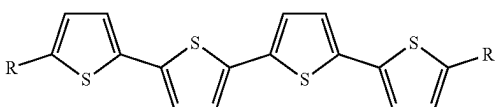


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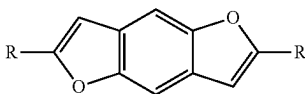


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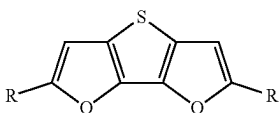
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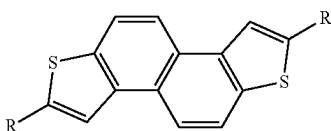
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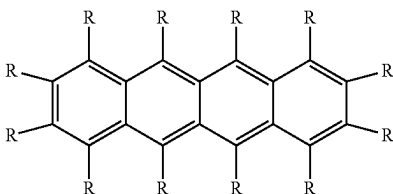
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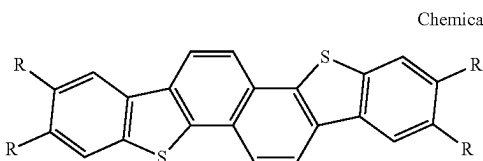
Chemical Formula (17)



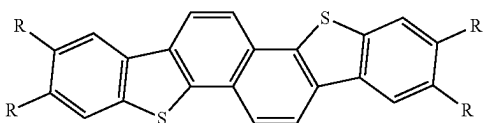
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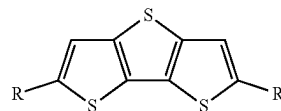
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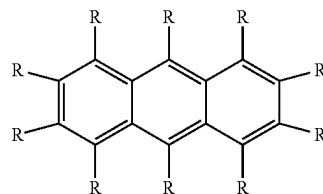
Chemical Formula (23)



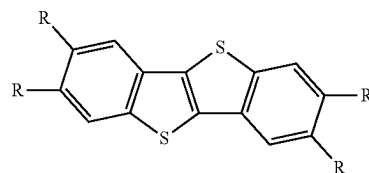
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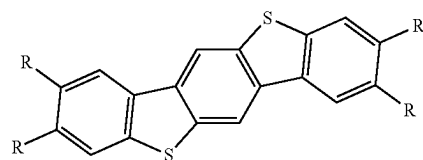
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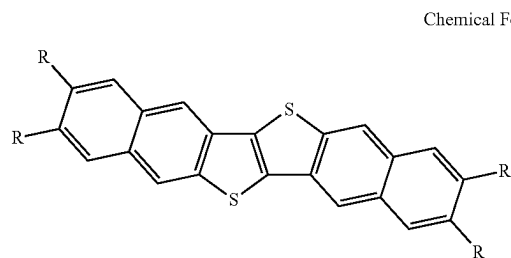
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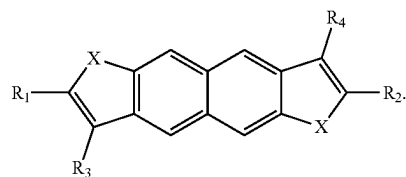
Chemical Formula (20)



Chemical Formula (22)

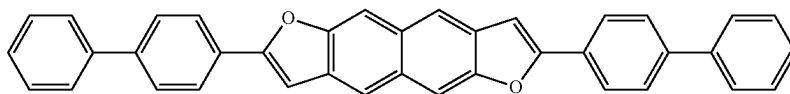


Chemical Formula (24)



Chemical Formula (26)

8. The solid-state imaging element according to claim 7, 55
wherein
the substance represented by the chemical formula (26)
includes a substance represented by any one of chemical
formulae (27) to (44) described below:



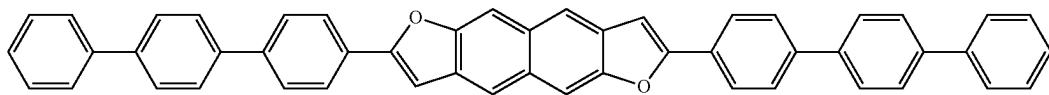
Chemical Formula (27)

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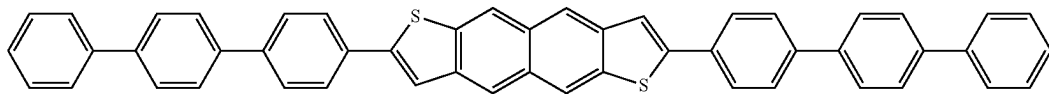
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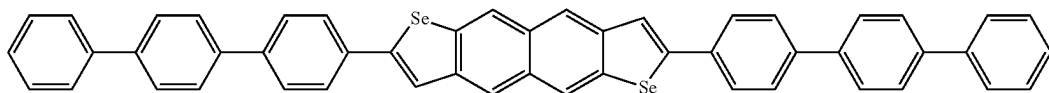
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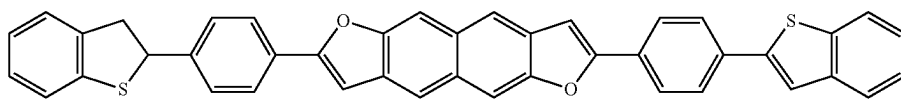
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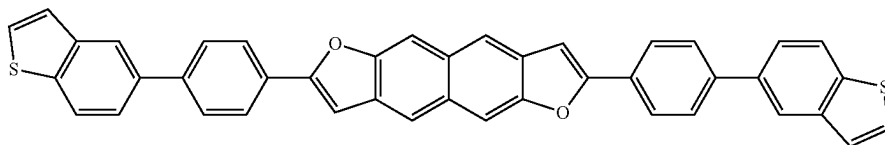
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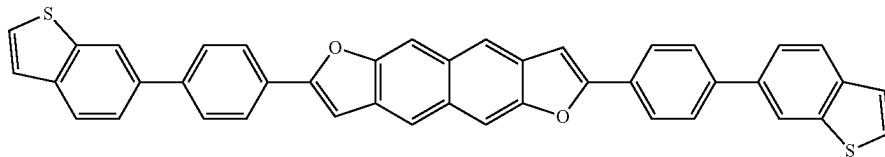
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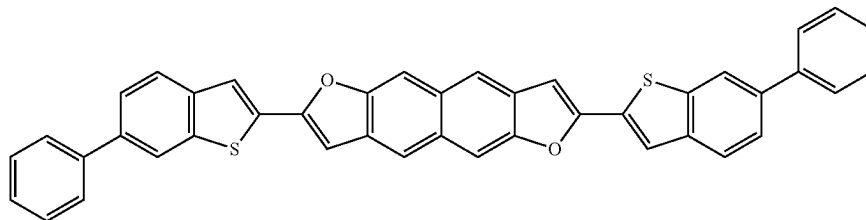
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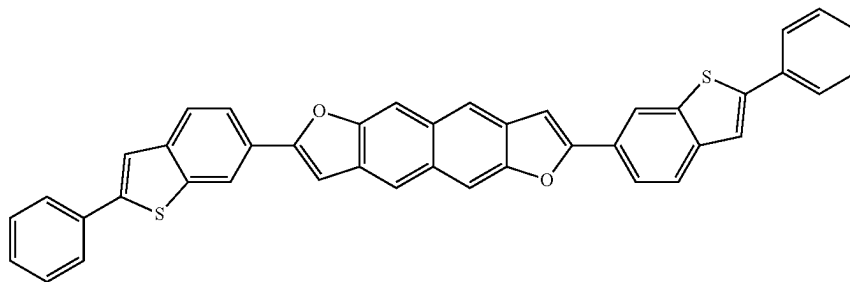
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Chemical Formula (34)



Chemical Formula (35)

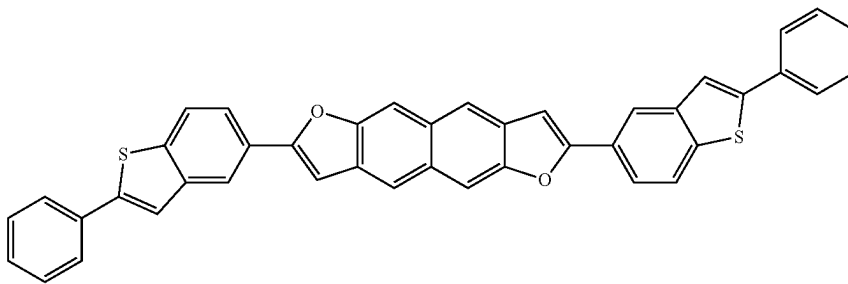


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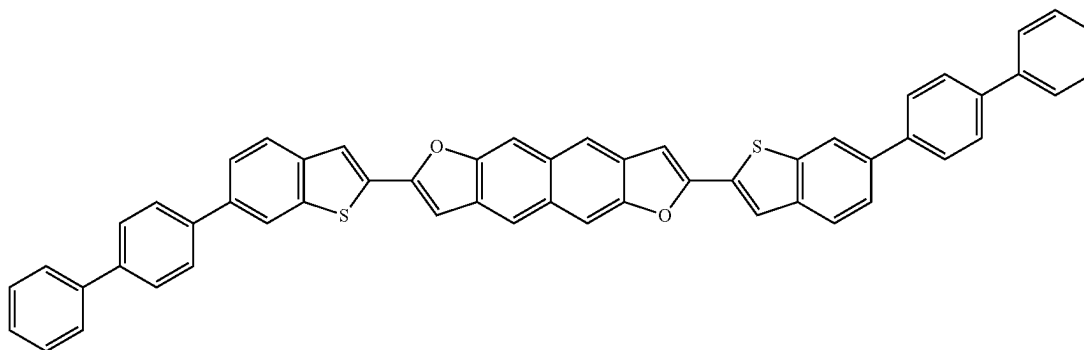
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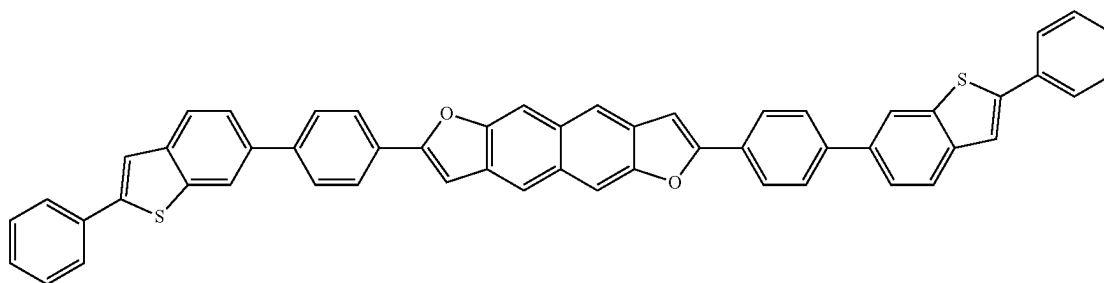
Chemical Formula (36)



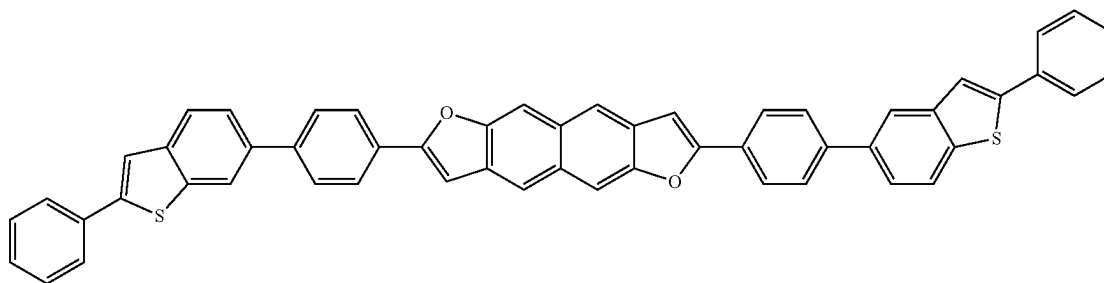
Chemical Formula (37)



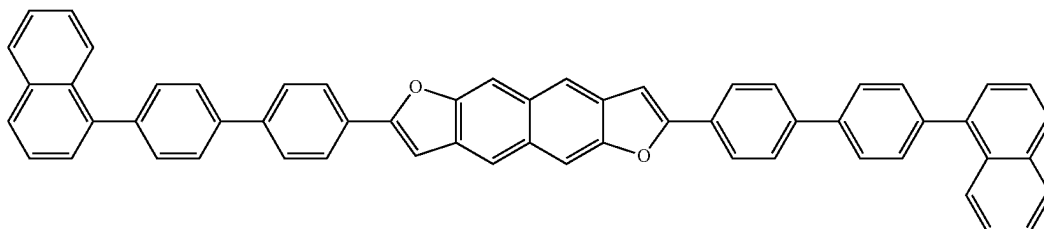
Chemical Formula (38)



Chemical Formula (39)



Chemical Formula (40)

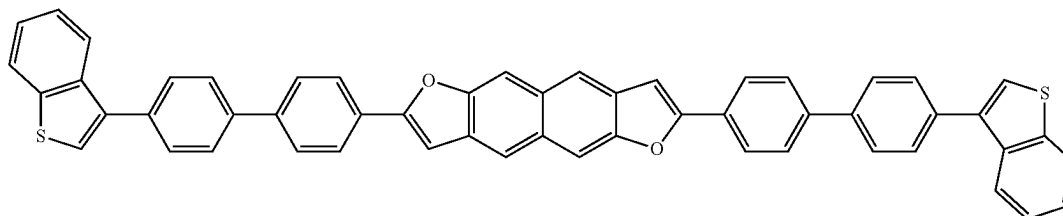


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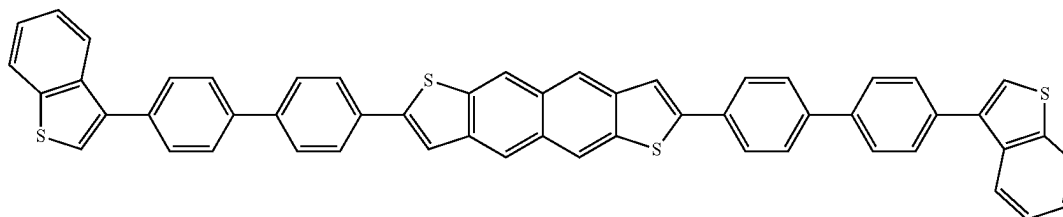
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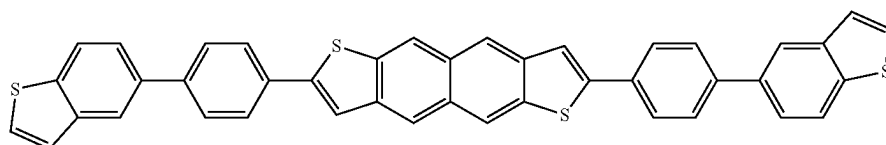
Chemical Formula (41)



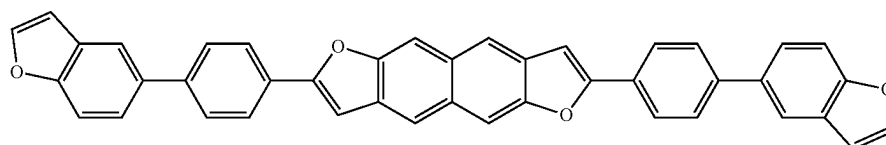
Chemical Formula (42)



Chemical Formula (43)



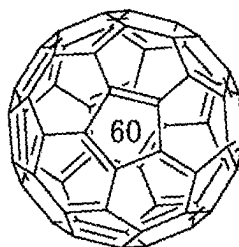
Chemical Formula (44)



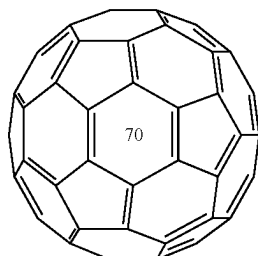
9. The solid-state imaging element according to claim 1, wherein

the third organic semiconductor includes a substance represented by a chemical formula (4) or a chemical formula (45) described below:

[Chem. 42]



[Chem. 43]



10. A solid-state imaging element comprising:
 an organic photoelectric conversion element including at least two electrodes, wherein
 an organic photoelectric conversion layer is arranged between the two electrodes,
 the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor,
 the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light,
 the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and
 the third organic semiconductor includes a fullerene derivative,
 wherein the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at a predetermined ratio to form each of the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor at a predetermined film formation rate so that the organic photoelectric conversion layer is formed, and
 wherein the third organic semiconductor is included at a ratio of approximately 20% of the organic photoelectric conversion layer, the first organic semiconductor and the second organic semiconductor are mixed at a ratio of approximately 70% to approximately 80% of the organic photoelectric conversion layer, and the first organic semiconductor and the second organic semiconductor are mixed at approximately 3:5 to approximately 5:3.

11. A photoelectric conversion element comprising:
 an organic photoelectric conversion element including at
 least two electrodes, wherein
 an organic photoelectric conversion layer is arranged
 between the two electrodes, 5
 the organic photoelectric conversion layer includes at
 least a first organic semiconductor, a second organic
 semiconductor, and a third organic semiconductor,
 the first organic semiconductor includes a semiconductor
 having a characteristic of absorbing blue light, 10
 the second organic semiconductor includes a semicon-
 ductor having a characteristic of absorbing blue light
 and a characteristic as a hole-transporting material
 having crystallinity, and
 the third organic semiconductor includes a fullerene 15
 derivative,
 wherein the second organic semiconductor strongly
 absorbs blue light that is light in a wavelength band in
 a vicinity of 400 to 500 nm, and weakly absorbs green
 light that is light in a wavelength band in a vicinity of 20
 500 to 600 nm and red light that is light in a wavelength
 band in a vicinity of 600 to 700 nm, the second organic
 semiconductor is a hole-transporting material, and the
 second organic semiconductor shows a peak of crys-
 tallinity by out-of-plane X-ray measurement, and 25
 wherein the second organic semiconductor has an absorp-
 tion coefficient of the blue light of more than 40,000
 cm^{-1} and an absorption coefficient of the green light
 and the red light of less than 10,000 cm^{-1} , the second
 organic semiconductor has a hole mobility of $1\text{E-}6$ 30
 cm^{-2}/Vs or more, the second organic semiconductor is
 a hole-transporting material having an HOMO energy
 level of 5.3 to 6.2 eV, and the organic photoelectric
 conversion layer has a peak of crystallinity by out-of-
 plane X-ray measurement at a position equivalent to a 35
 position of a peak of crystallinity by out-of-plane X-ray
 measurement of a single film of the second organic
 semiconductor.

12. An imaging device comprising:
 an organic photoelectric conversion element including at 40
 least two electrodes, wherein
 an organic photoelectric conversion layer is arranged
 between the two electrodes,
 the organic photoelectric conversion layer includes at
 least a first organic semiconductor, a second organic 45
 semiconductor, and a third organic semiconductor,
 the first organic semiconductor includes a semiconductor
 having a characteristic of absorbing blue light,
 the second organic semiconductor includes a semicon-
 ductor having a characteristic of absorbing blue light 50
 and a characteristic as a hole-transporting material
 having crystallinity, and
 the third organic semiconductor includes a fullerene
 derivative,
 wherein the second organic semiconductor strongly 55
 absorbs blue light that is light in a wavelength band in
 a vicinity of 400 to 500 nm, and weakly absorbs green
 light that is light in a wavelength band in a vicinity of
 500 to 600 nm and red light that is light in a wavelength
 band in a vicinity of 600 to 700 nm, the second organic 60
 semiconductor is a hole-transporting material, and the
 second organic semiconductor shows a peak of crys-
 tallinity by out-of-plane X-ray measurement, and
 wherein the second organic semiconductor has an absorp-
 tion coefficient of the blue light of more than 40,000 65
 cm^{-1} and an absorption coefficient of the green light
 and the red light of less than 10,000 cm^{-1} , the second

organic semiconductor has a hole mobility of $1\text{E-}6$
 cm^{-2}/Vs or more, the second organic semiconductor is
 a hole-transporting material having an HOMO energy
 level of 5.3 to 6.2 eV, and the organic photoelectric
 conversion layer has a peak of crystallinity by out-of-
 plane X-ray measurement at a position equivalent to a
 position of a peak of crystallinity by out-of-plane X-ray
 measurement of a single film of the second organic
 semiconductor.

13. An electronic apparatus comprising:
 an organic photoelectric conversion element including at
 least two electrodes, wherein
 an organic photoelectric conversion layer is arranged
 between the two electrodes,
 the organic photoelectric conversion layer includes at
 least a first organic semiconductor, a second organic
 semiconductor, and a third organic semiconductor,
 the first organic semiconductor includes a semiconductor
 having a characteristic of absorbing blue light,
 the second organic semiconductor includes a semicon-
 ductor having a characteristic of absorbing blue light
 and a characteristic as a hole-transporting material
 having crystallinity, and
 the third organic semiconductor includes a fullerene
 derivative,
 wherein the second organic semiconductor strongly
 absorbs blue light that is light in a wavelength band in
 a vicinity of 400 to 500 nm, and weakly absorbs green
 light that is light in a wavelength band in a vicinity of
 500 to 600 nm and red light that is light in a wavelength
 band in a vicinity of 600 to 700 nm, the second organic
 semiconductor is a hole-transporting material, and the
 second organic semiconductor shows a peak of crys-
 tallinity by out-of-plane X-ray measurement, and
 wherein the second organic semiconductor has an absorp-
 tion coefficient of the blue light of more than 40,000
 cm^{-1} and an absorption coefficient of the green light
 and the red light of less than 10,000 cm^{-1} , the second
 organic semiconductor has a hole mobility of $1\text{E-}6$
 cm^{-2}/Vs or more, the second organic semiconductor is
 a hole-transporting material having an HOMO energy
 level of 5.3 to 6.2 eV, and the organic photoelectric
 conversion layer has a peak of crystallinity by out-of-
 plane X-ray measurement at a position equivalent to a
 position of a peak of crystallinity by out-of-plane X-ray
 measurement of a single film of the second organic
 semiconductor.

14. A photoelectric conversion element comprising:
 an organic photoelectric conversion element including at
 least two electrodes, wherein
 an organic photoelectric conversion layer is arranged
 between the two electrodes,
 the organic photoelectric conversion layer includes at
 least a first organic semiconductor, a second organic
 semiconductor, and a third organic semiconductor,
 the first organic semiconductor includes a semiconductor
 having a characteristic of absorbing blue light,
 the second organic semiconductor includes a semicon-
 ductor having a characteristic of absorbing blue light
 and a characteristic as a hole-transporting material
 having crystallinity, and
 the third organic semiconductor includes a fullerene
 derivative,
 wherein the first organic semiconductor, the second
 organic semiconductor, and the third organic semicon-
 ductor are mixed at a predetermined ratio to form each
 of the first organic semiconductor, the second organic

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semiconductor, and the third organic semiconductor at a predetermined film formation rate so that the organic photoelectric conversion layer is formed, and wherein the third organic semiconductor is included at a ratio of approximately 20% of the organic photoelectric conversion layer, the first organic semiconductor and the second organic semiconductor are mixed at a ratio of approximately 70% to approximately 80% of the organic photoelectric conversion layer, and the first organic semiconductor and the second organic semiconductor are mixed at approximately 3:5 to approximately 5:3.

15. An imaging device comprising:
 an organic photoelectric conversion element including at least two electrodes, wherein
 an organic photoelectric conversion layer is arranged between the two electrodes,
 the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor,
 the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light,
 the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and
 the third organic semiconductor includes a fullerene derivative,
 wherein the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at a predetermined ratio to form each of the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor at a predetermined film formation rate so that the organic photoelectric conversion layer is formed, and
 wherein the third organic semiconductor is included at a ratio of approximately 20% of the organic photoelectric conversion layer, the first organic semiconductor and the second organic semiconductor are mixed at a ratio

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of approximately 70% to approximately 80% of the organic photoelectric conversion layer, and the first organic semiconductor and the second organic semiconductor are mixed at approximately 3:5 to approximately 5:3.

16. An electronic apparatus comprising:
 an organic photoelectric conversion element including at least two electrodes, wherein
 an organic photoelectric conversion layer is arranged between the two electrodes,
 the organic photoelectric conversion layer includes at least a first organic semiconductor, a second organic semiconductor, and a third organic semiconductor,
 the first organic semiconductor includes a semiconductor having a characteristic of absorbing blue light,
 the second organic semiconductor includes a semiconductor having a characteristic of absorbing blue light and a characteristic as a hole-transporting material having crystallinity, and
 the third organic semiconductor includes a fullerene derivative,
 wherein the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor are mixed at a predetermined ratio to form each of the first organic semiconductor, the second organic semiconductor, and the third organic semiconductor at a predetermined film formation rate so that the organic photoelectric conversion layer is formed, and
 wherein the third organic semiconductor is included at a ratio of approximately 20% of the organic photoelectric conversion layer, the first organic semiconductor and the second organic semiconductor are mixed at a ratio of approximately 70% to approximately 80% of the organic photoelectric conversion layer, and the first organic semiconductor and the second organic semiconductor are mixed at approximately 3:5 to approximately 5:3.

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