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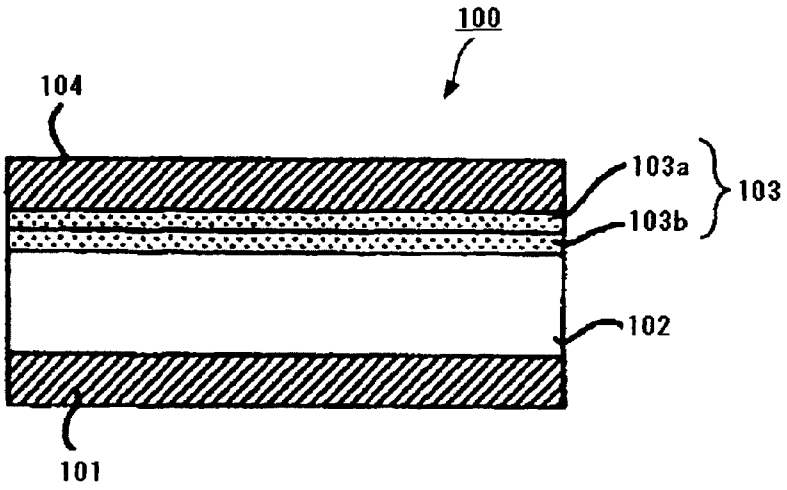
(54) **Title**: PHOTOELECTRIC CONVERSION DEVICE AND IMAGING DEVICE

FIG. 1



(57) **Abstract**: A photoelectric conversion device having an organic photoelectric conversion layer between a first electrode and a second electrode, wherein a material used for forming the organic photoelectric conversion layer has a purity of 96.5% or above as determined by liquid chromatography.

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DESCRIPTION

Title of Invention

PHOTOELECTRIC CONVERSION DEVICE AND IMAGING DEVICE

Technical Field

The present invention relates to a photoelectric conversion device and an imaging device which perform photoelectric conversion in their respective organic photoelectric conversion layers.

Background Art

Most of visible light sensors currently in use are devices which each are fabricated by forming a photoelectric conversion section including PN junctions in a surface part of a semiconductor substrate, such as a Si substrate. As to solid-state imaging devices, such a plane-type photoreceptors are prevailingly used that a plurality of photoelectric conversion sections is formed in the arrangement of a two-dimensional array in the surface part of a semiconductor substrate, each of the photoelectric conversion sections are utilized as a pixel and signals generated by photoelectric conversions in each pixel to the outside by means of a CCD-type or CMOS-type signal read-out circuit are read out.

It has been a general method for implementing a solid-state color imaging device to adopt a structure of disposing color filters capable of transmitting only light of certain wavelengths for color separation on the side of such a plane-type photoreceptor facing incident light, and more specifically, to adopt a well-known single-plate sensor, whose use in digital cameras and the like is prevalent at present, wherein color filters capable of transmitting blue light (B), green light (G) and red light (R), respectively, are placed regularly on each of pixels formed in the arrangement of a two-dimensional array.

However, the single-plate sensor of such a structure has a problem that light utilization efficiency is low because color filters transmit only light of wavelengths limited individually and light of the other wavelengths, which is not transmitted to color filters, cannot be utilized. Moreover, there has been a growing trend in recent years to increase the number of pixels mounted on one chip to ten million pixels or more, and thereby the pixel size has become smaller and the area of photodiode sections has been reduced. In addition thereto, it is required that the signal read-out circuit also be formed on the same semiconductor substrate. Therefore reductions in aperture ratio and light-collecting efficiency become problems.

As a method for solving these problems, it is thought up to stack photoelectric conversion sections capable of detecting different wavelengths of light in a direction

perpendicular to the surface of a semiconductor substrate. As an example of the imaging device of such a type, for cases where the detectable light is restricted to light in the visible region, the imaging device which utilizes the dependence of silicon's light absorption coefficient on wavelength and has a plurality of photoelectric conversion sections formed into a structure stacked in the depth direction of a semiconductor substrate, thereby achieving color separation according to differences among their respective depths, is disclosed in US Patent No. 5965875. In addition, the imaging device having an organic photoelectric conversion layer stacked above a semiconductor substrate is disclosed in JP-A-2003-332551. However, for cases where the differences in the depth direction of Si are utilized, wavelength ranges of light absorbed by the individual photoelectric conversion sections formed inside the Si substrate essentially overlap one another and spectral characteristics of such devices are unfavorable, therefore the devices have another problem of being inferior in color separation. Another technique of heightening the aperture ratio is known to consist in formation of a structure that a laminate of a photoelectric conversion film of amorphous silicon and an organic photoelectric conversion film is provided above a semiconductor substrate on which a signal read-out circuit is formed.

Hitherto, several examples have been known about each of organic photoelectric conversion film-utilized photoelectric conversion device, imaging device, light sensor and solar battery. Therein, a matter of particular concern is that the photoelectric conversion efficiency is insufficient and dark current is produced. As methods for improving the former point, introduction of a pn junction and introduction of a bulk heterostructure are disclosed, while introduction of a blocking layer or the like is disclosed as a method for improving the latter point. However, there is neither description of application of such disclosed methods to photoelectric conversion devices for use in imaging devices nor description suggestive of the application.

Although recent years have seen success in finding out compounds capable of developing high performance as materials for use in photoelectric conversion layers, processes from synthesis to making device are not set with sufficient consideration to develop performance of such compounds, therefore influence of impurities cannot be sufficiently excluded. Further, while the usefulness of an electron blocking layer is also disclosed in JP-A -2007-59517, it is not sufficiently paid attention, as in the above case, to process conditions and impurities' contribution.

On the other hand, in a field of OLED (which stands for Organic Light-Emitting Diode), it is disclosed e.g. in JP-A-2004-327455 and JP-A-2005-240011 that halide impurities and palladium impurities have influences upon the life time of OLED. However, there is no

description of impurities' influences in cases applied to photoelectric conversion devices. In addition, the OLED life time is shortened by decreasing amount of generated excitons and amount of luminescence with the passage of time. Impurities therefore result in contribution to acceleration of the decrease in amount of the light emission. On the other hand, as to the photoelectric conversion devices, photoelectric conversion performance itself of the device is changed, not their life time, by the presence of impurities. No light-emission process is included in their photoelectric conversion process and their excited states bring about charge separation at once. Therefore photoelectric conversion devices clearly differ from OLEDs in mechanism to develop their performance capabilities. Consequently, the phenomenon that the amount of luminescence in OLED decreases with the passage of time and the phenomenon that charge separation occurs in photoelectric conversion devices cannot be treated as equals.

In a field of organic thin-film solar battery, it is commonly known that ingredients conducted by sublimation purification results in improved electric-power generation. However, what kinds of impurities influence the electric power generation and what influences impurities exert on dark current and fast response of a photoelectric conversion device are unknown yet.

In order for organic photoelectric conversion devices to achieve high photoelectric-conversion efficiencies, low dark currents and fast responsiveness, it is desired that organic photoelectric conversion films used in the devices satisfy the following requirements.

1. For achievement of high efficiency and fast responsiveness, organic photoelectric conversion films are required to ensure that signal charges generated after dissociation of excitons can be transmitted to both electrodes without delay and loss. More specifically, the films are required to ensure a reduced number of carrier-trapping sites, high charge mobility and high charge-transporting capacity. Although it is known that impurities contained in an organic semiconducting material function as trap sites of electric charges to result in lowering of the mobility and the charge-transporting power, no concrete description of impurities can be found in hitherto known examples.

2. For achievement of high photoelectric conversion efficiency, it is desired that stabilization energy of excitons be small, therefore the excitons can be speedily dissociated by an externally applied electric field or an electric field generated internally by pn junctions or the like (exciton dissociation efficiency be high). It is known that mixing of impurities in organic dyes results in deactivation of excitons, and thereby the exciton dissociation efficiency is lowered. However, no concrete description of impurities can be found in hitherto known examples.

3. For minimizing the number of carriers generated inside the film under dark conditions, it is appropriate to select such a film structure and materials as to allow a low number of intermediate energy levels inside the film and a reduction in total content of impurities as one of causes for the intermediate energy levels. However, no concrete description of impurities can be found in hitherto known examples.

Summary of Invention

An object of the invention is to provide a photoelectric conversion device and an imaging device each having an organic photoelectric conversion layer which is made at low cost through the use of a material reduced in price by adjusting an impurity content of the organic photoelectric conversion layer to fall within a specified range, and thereby displaying a high degree of photoelectric conversion efficiency, a low dark-current characteristic and fast responsiveness.

Photoelectric conversion devices incorporating organic materials are affected by impurities, and the purity of materials used is therefore important. For instance, as to semiconductor wafers forming CCD- or CMOS-type image sensors currently in use, the degrees of purity of semiconductors as their materials are required to be 99.9999 or higher, and it is generally thought that the higher degrees of purity the materials have, the more favorable they become for use. However, the higher purity the materials used have, the larger sum the material costs amount to. Thus, a problem of raising fabrication costs of a device results.

Nevertheless, impurities which impact on the performance of a photoelectric conversion device are various according to the structure of a photoelectric conversion material used in the device. We have found that all the impurities contained in the material don't exert the same degree of influence upon the performance of the photoelectric conversion device, but impart different levels of performance to the photoelectric conversion device according to the structure of the material and the purpose that the material is used for (e.g. which layer the material is used in). And our research has revealed that, in the photoelectric conversion devices according to embodiments of the invention, the purity of materials to form their individual organic photoelectric conversion layers is not required to be higher than 99.9999, but may be at least 96.5%, and thereby it became possible to reduce material costs, thereby achieving the invention.

More specifically, the above described problems of the invention can be solved by the following embodiments of the invention.

<1> A photoelectric conversion device having an organic photoelectric conversion layer

between a first electrode and a second electrode, wherein a material used for forming the organic photoelectric conversion layer has a purity of 96.5% or above as determined by liquid chromatography.

<2> The photoelectric conversion device according to <1>, wherein the material used for forming the organic photoelectric conversion layer has an oxidized-compound impurity content of 9,000 ppm or below.

<3> The photoelectric conversion device according to <1> or <2>, wherein the material used for forming the organic photoelectric conversion layer is a material having been purified by solution refining.

<4> The photoelectric conversion device according to any of <1> to <3>, wherein the material used for forming the organic photoelectric conversion layer is a material having been purified by sublimation refining.

<5> The photoelectric conversion device according to <1> to <4>, wherein a charge blocking layer is provided between either of the electrodes and the organic photoelectric conversion layer.

<6> The photoelectric conversion device according to <5>, wherein the charge blocking layer is an electron blocking layer.

<7> The photoelectric conversion device according to <6>, wherein an electron blocking material used in the electron blocking layer has a purity of 96.7% or above as determined by liquid chromatography and a halide impurity content of 9,000 ppm or below.

<8> The photoelectric conversion device according to <6> or <7>, wherein an electron blocking material used in the electron blocking layer has a purity of 96.7% or above as determined by liquid chromatography and a heavy-metal impurity content of 4,000 ppm or below.

<9> The photoelectric conversion device according to any of <6> to <8>, wherein an electron blocking material used in the electron blocking layer is a material having been purified by solution refining.

<10> The photoelectric conversion device according to any of <6> to <8>, wherein an electron blocking material used in the electron blocking layer is a material having been purified by sublimation refining.

<11> The photoelectric conversion device according to any of <6> to <10>, wherein an electron blocking material used in the electron blocking layer is a triarylamine compound.

<12> The photoelectric conversion device according to any of <1> to <11>, wherein the material used for forming organic photoelectric conversion layer comprises a colorant having its absorption maximum wavelength in a visible wavelength region extending from 400 nm to

of 800 nm.

<13> The photoelectric conversion device according to any of <1> to <12>, wherein an electric field of 10^{-4} V/cm to 1×10^{7} V/cm is placed between the first electrode and the second electrode.

<14> The photoelectric conversion device according to any of <1> to <13>, wherein the organic photoelectric conversion layer comprises a fullerene.

<15> An imaging device having: the photoelectric conversion device according to any of <1> to <14>; and a semiconductor substrate, wherein the photoelectric conversion device is stacked on a surface of the semiconductor substrate.

In accordance with the invention, an organic photoelectric conversion layer ensuring high photoelectric conversion efficiency, low dark-current characteristics and fast responsiveness can be formed even by using a material with a purity of 96.5% which is a low purity material as compared with those currently used for photoelectric conversion devices, and it therefore becomes possible to reduce costs of fabricating photoelectric conversion devices and imaging devices.

Brief Description of Drawings

Fig. 1 is a cross-sectional view in schematic form depicting a photoelectric conversion device relating to a first embodiment of the invention.

Fig. 2 is a cross-sectional view in schematic form depicting an imaging device relating to a second embodiment of the invention.

Fig. 3 is a cross-sectional view in schematic form depicting the intermediate layer shown in Fig. 2.

Fig. 4 is a cross-sectional view in schematic form depicting an imaging device relating to a third embodiment of the invention.

Fig. 5 is a cross-sectional view in schematic form depicting an imaging device relating to a fourth embodiment of the invention

Fig. 6 is a cross-sectional view in schematic form depicting an imaging device relating to a fifth embodiment of the invention

Fig. 7 is a schematic diagram depicting a partial surface of an imaging device relating to a sixth embodiment of the invention

Fig. 8 is a schematic diagram depicting the vertical cross section which would appear if cut on the X-X line in Fig. 7

Fig. 9 is a diagram showing an example of a specific configuration of one of the

signal read-out sections depicted in Fig. 8

Description of Embodiments

Preferred embodiments of the invention are described below.

The devices relating to embodiments of the invention are photoelectric conversion devices which each include a conductive thin film, an organic photoelectric conversion film containing at least one material, and a transparent conductive thin film, and each device is characterized in that the material used for forming the device has a purity of 96.5% or higher as determined by HPLC (High-Performance Liquid Chromatography).

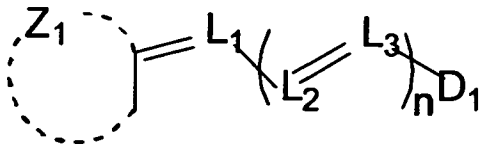
The photoelectric conversion devices according to embodiments of the invention are affected by impurities because they incorporate organic materials, and the purity of the used materials is therefore important to them. Since the purity of an organic material cannot be measured after the material is incorporated into a device, the purity which the material has before it is used for forming the device becomes important. The purity of at least 96.5% is adequate for organic materials used in the invention. Unless material costs amount to a large sum, however, purities of 99% or higher are especially beneficial. As a method for purity determination, the use of general-purpose HPLC (High-Performance Liquid Chromatography) is preferable. The value of purity can be determined as a percentage on the peak area of the whole chromatogram under the monitoring of absorbance at a wavelength where almost all organic materials absorb light, e. g., 254 nm.

The organic photoelectric conversion film is a film containing a photoelectric conversion material, and it is preferable to use an organic dye as the photoelectric conversion material because the material is required to fully absorb visible light involved in photoelectric conversion, it is more preferred that the organic dye has absorption maximum in the visible region of 400 nm to 800 nm. For checking on its absorption characteristic, it is appropriate that the organic dye be in a state of film, but it may be in a state of solution (e.g. chloroform solution) which can provide a nearly comparable result. The higher absorption constant is better, and more specifically, the value thereof is preferably 20,000 L/mol/cm or above, far preferably 40,000 L/mol/cm or above. For charge separation and signal readout, it is preferred that the organic dye have oxidation potential having constant value, and more specifically, the oxidation potential is preferably from 0.4 V to 1.0 V, particularly preferably from 0.5 V to 0.8 V, with respect to Ag/AgCl in an acetonitrile solution. Since the organic dye is used in a state of film, the film IP (Ionization Potential) thereof is preferably from 5.0 eV to 5.7 eV, particularly preferably from 5.2 eV to 6 eV.

As to a structure of the photoelectric conversion materials, the dyes disclosed in

JP-A-2006-86157, JP-A-2006-86160, JP-A-2006-100502, JP-A-2006-100508, JP-A-2006-100767, JP-A-2006-339424, JP-A-2008-244296 and JP-A-2009-088291 are exemplified. In particular, the compounds disclosed in JP-A-2000-297068 are usable.

As photoelectric conversion materials, compounds represented by the following formula (I) are suitable.



(I)

In the formula (I), Z_1 represents a condensed ring containing at least two carbon atoms and containing at least either a 5-membered ring or a 6-membered ring, or a combination thereof, each of L_1, L_2 and L_3 independently represents an unsubstituted methine group or a substituted methine group, D_1 represents an aryl group or a heteroaryl group, and n represents an integer equal to or greater than 0.

Z_1 represents a condensed ring containing at least two carbon atoms and containing at least either a 5-membered ring or a 6-membered ring, or a combination thereof. As the condensed ring having at least either a 5-membered ring or a 6-membered ring, or a combination thereof, those commonly used as acidic nuclei in merocyanine dyes are preferable, and examples thereof include the followings.

(a) 1,3-dicarbonyl nuclei, e.g. a 1,3-indanedione nucleus, 1,3-cyclohexanedione, 5,5-dimethyl-1,3-cyclohexanedione and 1,3-dioxane-4,6-dione.

(b) pyrazolinone nuclei, e.g. 1-phenyl-2-pyrazoline-5-one, 3-methyl-1-phenyl-2-pyrazoline-5-one and 1-(2-benzothiazolyl)-3-methyl-2-pyrazoline-5-one.

(c) isoxazolinone nuclei, e.g. 3-phenyl-2-isoxazoline-5-one and 3-methyl-2-isoxazoline-5-one.

(d) oxyindole nuclei, e.g. 1-alkyl-2,3-dihydro-2-oxyindole.

(e) 2,4,6-triketohexahydropyrimidine nuclei, e.g. barbituric acid or 2-thiobarbituric acid nucleus and derivatives thereof. Examples of the derivatives include mono-substituted barbituric or 2-thiobarbituric acids each of which has one alkyl group, such as one methyl or ethyl group, at the 1-position, and di-substituted barbituric or 2-thiobarbituric acids each of which has two alkyl groups, such as methyl, ethyl or butyl groups, at the 1- and 3-positions, or two aryl groups, such as phenyl, p-chlorophenyl or p-ethoxycarbonylphenyl groups, at the 1- and 3-positions, or one alkyl group such as ethyl and one aryl group such phenyl at the 1- and 3-positions, respectively, or two heterocyclic groups such as 2-pyridyl at the 1- and

3-positions.

(f) 2-thio-2,4-thiazolidinedione nuclei, e.g. rhodanine and derivatives thereof. Examples of the derivatives include 3-alkylrhodanines, such as 3-methylrhodanine, 3-ethylrhodanine, 3-allylrhodanine, 3-arylrhodanines, such as 3-phenylrhodanine, and rhodanines each of which is substituted by a heterocyclic group at the 3-position, such as 3-(2-pyridyl)rhodanine.

(g) 2-thio-2,4-oxazolidinediones (2-thio-2,4-(3H,5H)-oxazoledione nuclei), e.g. 3-ethyl-2-thio-2,4-oxazolidinedion.

(h) thianaphthenone nuclei, e.g. 3(2H)-thianaphthenone-1,1-dioxide.

(i) 2-thio-2,5-thiazolidinedione nuclei, e.g. 3-ethyl-2-thio-2,5-thiazolidinedione.

(j) 2,4-thiazolidinedione nuclei, e.g. 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione and 3-phenyl-2,4-thiazolidinedione.

(k) thiazoline-4-one nuclei, e.g. 4-thiazolinone and 2-ethyl-4-thiazolinone.

(l) 2,4-imidazolidinedione (hydantoin) nuclei, e.g. 2,4-imidazolidinedione and 3-ethyl-2,4-imidazolidinedione.

(m) 2-thio-2,4-imidazolidinedione (2-thiohydantoin) nuclei, e.g. 2-thio-2,4-imidazolidinedione and 3-ethyl-2-thio-2,4-imidazolidinedione.

(n) imidazoline-5-one nuclei, e.g. 2-propylmercapto-2-imidazoline-5-one.

(o) 3,5-pyrazolidinedione nuclei, e.g. 1,2-diphenyl-3,5-pyrazolidinedione and 1,2-dimethyl-3,5-pyrazolidinedione.

(p) benzothiophene-3-one nuclei, e.g. benzothiophene-3-one, oxobenzothiophene-3-one and dioxobenzothiophene-3-one.

(q) Indanone nuclei, e.g. 1-indanone, 3-phenyl-1-indanone, 3-methyl-1-indanone, 3,3-diphenyl-1-indanone and 3,3-dimethyl-1-indanone.

The ring formed from Z_1 is preferably a 1,3-dicarbonyl nucleus, a pyrazoline nucleus, a 2,4,6-triketohexahydropyrimidine nucleus (including a thioketone body, such as a barbituric acid nucleus or a 2-thiobarbituric acid nucleus), a 2-thio-2,4-thiazolidinedione nucleus, a 2-thio-2,4-oxazolidinedione nucleus, a 2-thio-2,5-thiazolidinedione nucleus, a 2,4-thiazolidinedione nucleus, a 2,4-imidazolidinedione nucleus, a 2-thio-2,4-imidazolidinedione nucleus, a 2-imidazoline-5-one nucleus, a 3,5-pyrazolidinedione nucleus or a benzothiophene-3-one nucleus, more preferably a 1,3-dicarbonyl nucleus, a 2,4,6-triketohexahydropyrimidine nucleus (including a thioketone body, such as a barbituric acid nucleus or a 2-thiobarbituric acid nucleus), a 3,5-pyrazolidinedione nucleus or a benzothiophene-3-one nucleus or an indanone nucleus, further preferably a 1,3-dicarbonyl nucleus or a 2,4,6-triketohexahydropyrimidine nucleus (including a thioketone body, such as a barbituric acid nucleus or a 2-thiobarbituric acid nucleus), particularly preferably a

1,3-indanedione nucleus, a barbituric acid nucleus, a 2-thiobarbituric acid nucleus or a derivative of each nucleus.

Each of L_1, L_2 and L_3 independently represents an unsubstituted methine group or a substituted methine group. L_1 to L_3 may combine with each other to form a ring, and the ring formed is preferably a cyclohexene ring, a cyclopentene ring, a benzene ring, a naphthalene ring, a thiophene ring or a pyran ring. Although the substituted methine group can have a substituent W as described hereinafter, the case where all of L_1, L_2 and L_3 are unsubstituted methine groups is preferred.

n represents an integer equal to or greater than 0, preferably an integer from 0 to 3, far preferably 0. An increase in the value of n makes it possible to shift the absorption wavelength region of the compound toward the longer wavelength side, but causes a decrease in thermal decomposition temperature of the compound. The case of n=0 is preferred in the sense that the compound can have an appropriate absorption in the visible region and can be prevented from thermal decomposition at the time of film formation by vapor deposition.

D_1 represents an aryl group or a heteroaryl group, preferably an aryl group. The group represented by D_1 is preferably a group containing $-NR^a(R^b)$, far preferably an aryl group substituted by $-NR^a(R^b)$. Each of R^a and R^b independently represents a hydrogen atom or a substituent.

The aryl group represented by D_1 is preferably an aryl group containing 6 to 30 carbon atoms, far preferably an aryl group containing 6 to 18 carbon atoms. Such an aryl group may have the substituent W as described hereinafter, and it is preferably an aryl group which contains 6 to 18 carbon atoms and may have an alkyl substituent containing 1 to 4 carbon atoms. Examples of the aryl group include a phenyl group, a naphthyl group, an anthracenyl group, a pyrenyl group, a phenanthrenyl group, a methylphenyl group and a dimethylphenyl group. Of these groups, a phenyl group and a naphthyl group are preferred over the others.

The heteroaryl group represented by D_1 is preferably a heteroaryl group containing 3 to 30 carbon atoms, far preferably a heteroaryl group containing 4 to 18 carbon atoms. Such a heteroaryl group may have the substituent W as described hereinafter, and it is preferably a heteroaryl group which contains 4 to 18 carbon atoms and may have an alkyl substituent containing 1 to 4 carbon atoms. Examples of a preferred heteroaryl structure include thiophene, furan, pyrrole, oxazole, diazole, thiazole, and benzo- or thieno-condensed ring derivatives of these heterocyclic compounds. Of these compounds, thiophene, benzothiophene, thienothiophene, dibenzothiophene and bithienothiophene are preferred over the others.

The substituent represented by each of R^a and R^b includes the substituent W as described hereinafter, and it is preferably an aliphatic hydrocarbon group (preferably an alkyl or alkenyl group which may have a substituent), an aryl group (preferably a phenyl group which may have a substituent) or a heterocyclic group.

The aryl group independently represented by each of R^a and R^b is preferably an aryl group containing 6 to 30 carbon atoms, far preferably an aryl group containing 6 to 18 carbon atoms. Such an aryl group may have a substituent, and it is preferably an aryl group which contains 6 to 18 carbon atoms and may have an alkyl substituent containing 1 to 4 carbon atoms or an aryl substituent containing 6 to 18 carbon atoms. Examples of the aryl group include a phenyl group, a naphthyl group, an anthracenyl group, a pyrenyl group, a phenanthrenyl group, a methylphenyl group, a dimethylphenyl group and a biphenyl group. Of these groups, a phenyl group, a naphthyl group and an anthracenyl group.

The heterocyclic group independently represented by each of R^a and R^b is preferably a heterocyclic group containing 3 to 30 carbon atoms, far preferably a heterocyclic group containing 3 to 18 carbon atoms. Such a heterocyclic group may have a substituent, and it is preferably a heterocyclic group which contains 3 to 18 carbon atoms and may have an alkyl substituent containing 1 to 4 carbon atoms or an aryl substituent containing 6 to 18 carbon atoms. The heterocyclic group represented by each of R^a and R^b preferably has a condensed ring structure. Preferred examples of the condensed ring structure include condensed ring structures formed by combining the same or different rings selected from the group consisting of a furan ring, a thiophene ring, a selenophene ring, a silole ring, a pyridine ring, a pyrazine ring, a pyrimidine ring, an oxazole ring, a thiazole ring, a triazole ring, an oxadiazole ring and a thiadiazole ring, and more specifically, they include a quinoline ring, an isoquinoline ring, a benzothiophene ring, a dibenzothiophene ring, a thienothiophene ring, a bithienobenzene ring and a bithienothiphene ring.

It is preferable for the aryl group represented by each of D_1, R^a and R^b to have a condensed ring structure, preferably a condensed ring structure having a benzene ring, far preferably the ring structure of naphthalene, anthracene, pyrene or phenanthrene. Of these ring structures, the ring structures of naphthalene and anthracene are preferred over the others.

Examples of the substituent W include a halogen atom, an alkyl group (including a cycloalkyl group, a bicycloalkyl group and a tricycloalkyl group), an alkenyl group (including a cycloalkenyl group and a bicycloalkenyl group), an alkynyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxyl group, a nitro group, a carboxyl group, an alkoxy group, an aryloxy group, a silyloxy groujp, a heterocyclyloxy group, an acyloxy group, a carbgamoyloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an amino group

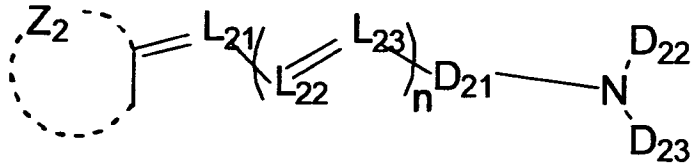
(containing an anilino group), an ammonio group, an acylamino group, an aminocarbonylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfamoylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a mercapto group, an alkylthio group, an arylthio group, a heterocyclylthio group, a sulfamoyl group, a sulfo group, an alkylsulfinyl group, an arylsulfinyl group, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an aryloxycarbonyl group, an alkoxycarbonyl group, a carbamoyl group, an arylazo group, a heterocyclylazo group, an imido group, a phosphino group, a phosphonyl group, a phosphinyloxy group, a phosphinylamino group, a phosphono group, a silyl group, a hydrazine group, a uredio group, a boronic acid group ($-B(OH)_2$), a phosphate group ($-OPO(OH)_2$), a sulfato group ($-OSO_3H$), and known other substituents.

When the substituent represented by each of R^a and R^b is an aliphatic hydrocarbon group (preferably an alkyl group or an alkenyl group), it may form a ring (preferably a 6-membered ring) by combining with a hydrogen atom or a substituent on the aromatic ring structure (preferably a benzene ring structure) of the aryl group substituted by $-NR^a(R^b)$.

R^a and R^b may combine with each other to form a ring (preferably a 5- or 6-membered ring, far preferably a 6-membered ring), or each of R^a and R^b may combine with a substituent in L (any of L_1, L_2 and L_3) to form a ring (preferably a 5- or 6-membered ring, far preferably a 6-membered ring).

The compounds represented by the formula (I) include the compounds disclosed in JP-A-2000-297068, and the compounds other than those disclosed in JP-A-2000-297068 can also be produced in accordance with the synthesis method disclosed therein.

It is preferable for the compounds represented by the formula (I) to be compounds represented by the following formula (II).



(II)

In the formula (II), Z_2, L_{21}, L_{22}, L_{23} and n have the same meanings as Z_1, L_1, L_2, L_3 and n in the formula (I), respectively, and their respective preferred examples are the same as those in the formula (I), D_{21} represents a substituted or unsubstituted arylene group, and each of D_{22} and D_{23} independently represents a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group.

The arylene group represented by D_{21} is preferably an arylene group containing 6 to 30 carbon atoms, far preferably an arylene group containing 6 to 18 carbon atoms. Such an arylene group may have the substituent W as mentioned above, and it is preferably an arylene

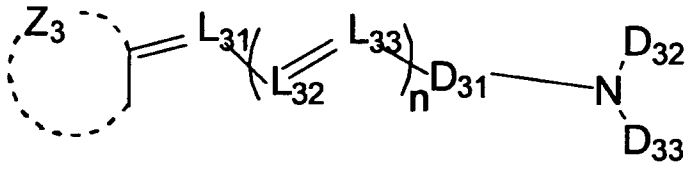
group which contains 6 to 18 carbon atoms and may have an alkyl substituent containing 1 to 4 carbon atoms. Examples of the arylene group include a phenylene group, a naphthylene group, an anthracenylene, a pyrenylene group, a phenanthrenylene group, a methylphenylene group and a dimethylphenylene group. Of these groups, a phenylene group and a naphthylene group are preferred over the others.

It is preferable for each of D_{22} and D_{23} to be independently a condensed aromatic ring group, specifically a group having a condensed aromatic ring structure formed by combining the same or different rings selected from the group consisting of a benzene ring, a furan ring, a thiophene ring, a selenophene ring, a silole ring, a pyridine ring, a pyrazine ring, a pyrimidine ring, an oxazole ring, a thiazole ring, a triazole ring, an oxadiazole ring and a thiadiazole ring, and more preferably, naphthalene ring, anthracene ring, pyrene ring, phenanthrene ring, quinoline ring, isoquinoline ring, benzothiophene ring, dibenzothiophene ring, thienothiophene ring, bithienobenzene ring or bithienothiophene ring.

It is preferable for the aryl group represented by each of D_{22} and D_{23} to have a condensed ring structure, preferably a condensed ring structure containing a benzene ring. Examples of preferred aryl group include the ring structure of phenyl ring, naphthalene ring, anthracene ring, pyrene ring or phenanthrene ring is preferably, particularly preferably the ring structure of naphthalene ring or anthracene ring.

For the heterocyclic group represented by each of D_{22} and D_{23}, it is preferable to have a condensed ring structure, preferably a condensed ring structure formed by combining the same or different rings selected from the group consisting of a furan ring, a thiophene ring, a selenophene ring, a silole ring, a pyridine ring, a pyrazine ring, a pyrimidine ring, an oxazole ring, a thiazole ring, a triazole ring, an oxadiazole ring and a thiadiazole ring, specifically, ring structure of quinoline ring, isoquinoline ring, benzothiophene ring, dibenzothiophene ring, thienothiophene ring, bithienobenzene ring or bithienothiophene ring.

Preferred examples of a photoelectric conversion material represented by the formula (I) are shown by the following formula (III), but these examples should not be construed as limiting the scope of the invention.

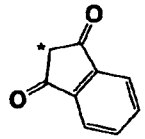
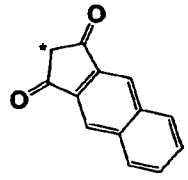
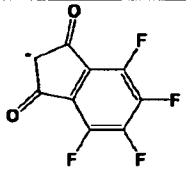
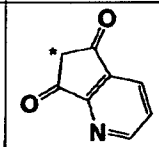
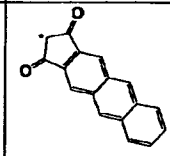
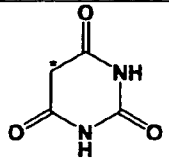
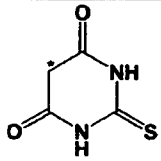
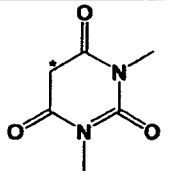
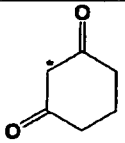
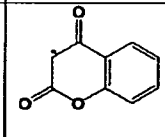
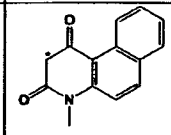
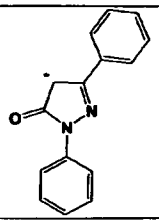


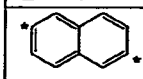
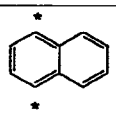
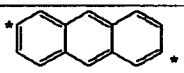
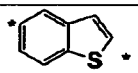
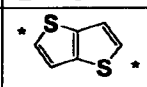
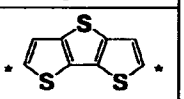
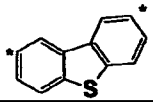
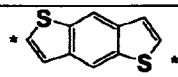
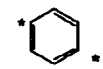
(III)

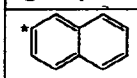
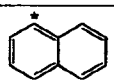
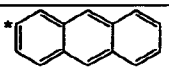
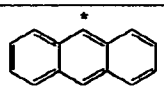
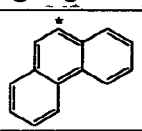
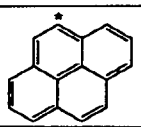
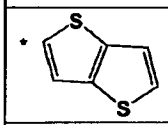
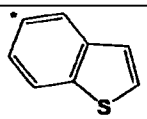
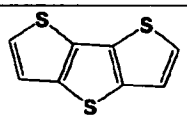
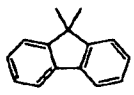
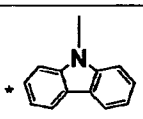
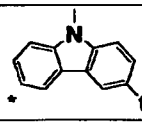
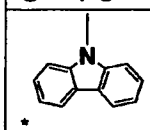
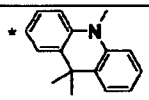
In the formula (III), Z_3 represents any of A-1 to A-12 in Table 1, L_{31} represents a methine group, and n represents 0. D_{31} is any of B-1 to B-9, and each of D_{32} and D_{33}

represents any of C-1 to C-15.

Table 1: (An asterisk (*) depicted in each of the rings in the table indicates a bonding position of each ring)

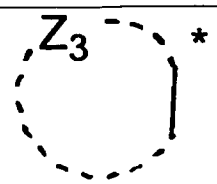
A−1	A−2	A−3	A−4	A−5	A−6
					
A−7	A−8	A−9	A−10	A−11	A−12
					

B−1	B−2	B−3	B−4	B−5	B−6
					
B−7	B−8	B−9	/	/	/
			/	/	/

C−1	C−2	C−3	C−4	C−5	C−6
					
C−7	C−8	C−9	C−10	C−11	C−12
					
C−13	C−14	C−15	/	/	/
			/	/	/

Far preferred examples of a photoelectric conversion material represented by the formula (I) are the following combinations of substituents, linkage groups and partial structures in the formula (III), but these combinations should not be construed as limiting the scope of the invention.

Table 2

Compound		L_{31}	n	D_{31}	D_{32}	D_{33}
1	A-1	CH	0	B-9	C-1	C-1
2	A-2	CH	0	B-9	C-15	C-15
3	A-3	CH	0	B-9	C-15	C-15
4	A-4	CH	0	B-9	C-15	C-15
5	A-5	CH	0	B-9	C-15	C-15
6	A-10	CH	0	B-9	C-15	C-15
7	A-11	CH	0	B-9	C-15	C-15
8	A-6	CH	0	B-1	C-15	C-15
9	A-7	CH	0	B-1	C-15	C-15
10	A-8	CH	0	B-1	C-15	C-15
11	A-9	CH	0	B-1	C-15	C-15
12	A-12	CH	0	B-1	C-15	C-15
13	A-2	CH	0	B-2	C-15	C-15
14	A-2	CH	0	B-3	C-15	C-15
15	A-2	CH	0	B-4	C-15	C-15
16	A-2	CH	0	B-5	C-15	C-15
17	A-2	CH	0	B-6	C-15	C-15
18	A-2	CH	0	B-7	C-15	C-15
19	A-2	CH	0	B-8	C-15	C-15
20	A-2	CH	0	B-1	C-1	C-1
22	A-2	CH	0	B-1	C-1	C-3
23	A-2	CH	0	B-9	C-15	C-4
24	A-2	CH	0	B-9	C-15	C-5
25	A-2	CH	0	B-9	C-15	C-6
26	A-2	CH	0	B-9	C-7	C-7
27	A-2	CH	0	B-9	C-8	C-8
28	A-2	CH	0	B-1	C-10	C-10
29	A-2	CH	0	B-9	C-11	C-11
30	A-2	CH	0	B-9	C-12	C-12

Additionally, A-1 to A-12, B-1 to B-9 and C-1 to C-15 in Table 2 have the same meanings as those shown in Table 1, respectively.

As to the content of impurities in each of these materials, it is preferably 10,000 ppm or below, and the lower the better. As to the purity of an objective material, the higher the better, and more specifically, it is preferably 99% or higher, far preferably 99.5% or higher.

As previously mentioned, impurities affecting the performance of a photoelectric conversion device vary according to structure of a photoelectric conversion material used. However, it does not mean that all impurities contained in a photoelectric conversion material exert the same degree of influence upon performance of the photoelectric conversion device obtained, but the levels of impact of the impurities on the photoelectric conversion device differ according to the structure of the material and the purpose that the material is used for (e.g. which layer the material is used in).

Examples of impurities in a photoelectric conversion material used for an organic photoelectric conversion film include raw materials, reaction reagents, solvents, reactive intermediates and a wide variety of decomposed products from side reactions. When there occurs oxidation reaction as side reaction, oxidized-compound impurities are formed; when there occurs reduction reaction as side reaction, reduction impurities are produced; when there occurs decomposition reaction as side reaction, decomposition impurities are produced; while when there occurs isomerization reaction as side reaction, isomerization impurities are produced. Among these varieties of impurities, oxidized-compound impurities in particular are found to be of great influence upon the performance of the photoelectric conversion device.

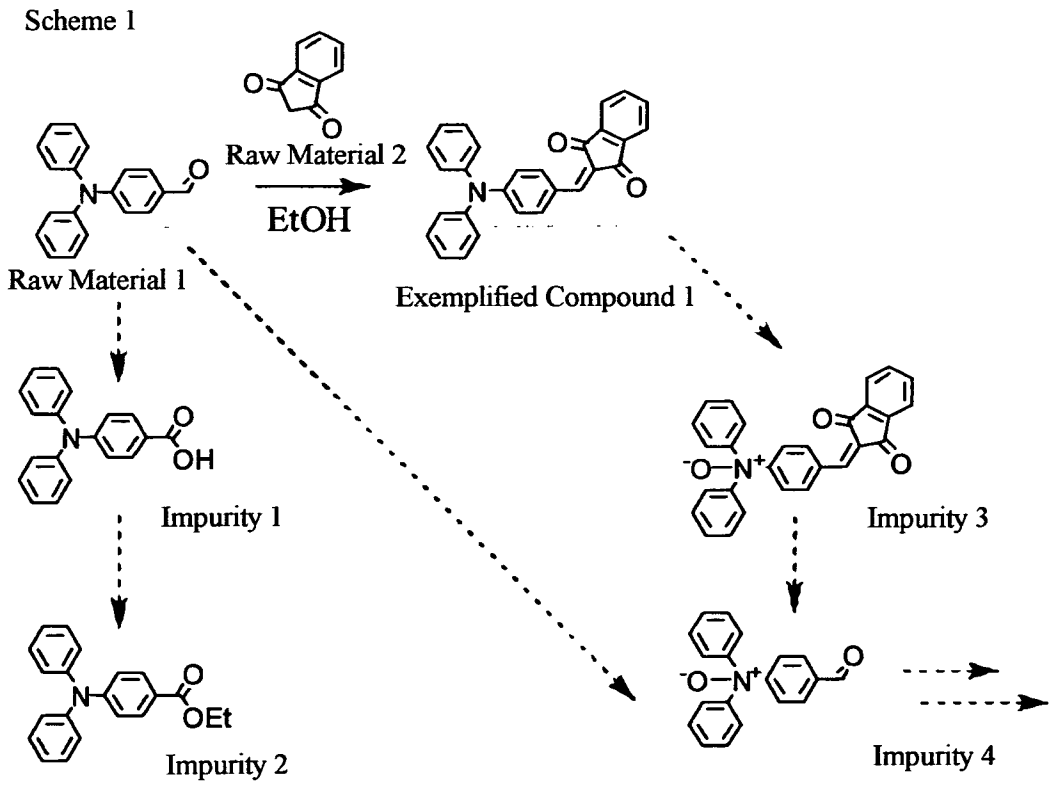
In the case of taking the synthesis route as shown in the following scheme 1, the oxidized-compound impurities include oxidized compounds of the raw materials used and oxidized compounds of the synthesis product. As for these oxidized-compound impurities, the lesser the quantity thereof, the better performance is achieved.

In the invention, the purity of a material used for forming an organic photoelectric conversion layer is 96.5% or higher as determined through the use of liquid chromatography, and the content of oxidized-compound impurities is preferably 9,000 ppm or below, far preferably 3,000 ppm or below, further preferably 1,000 ppm or below. As far as the content of oxidized-compound impurities falls within the range specified above, photoelectric conversion devices delivering higher performance can be fabricated. In particular, cases where the content of oxidized-compound impurities is 9,000 ppm or below and the purity of a material used for forming an organic photoelectric conversion layer is in a range of 96.5% to

99.9% as determined by liquid chromatography are preferable because high-performance photoelectric conversion devices can be fabricated and costs for purifying the material can be reduced.

The lower limit of a content of oxidized-compound impurities is zero, and it is preferable for the content to be brought as close to zero as possible. As to the devices according to embodiments of the invention, however, such a low content of impurities is not required. For instance, the experimental examples described later revealed that no degradation in device performance was caused so long as oxidized-compound impurities have a total content of 9,000 ppm or below. In view of the experimental results, it is supposed that a reason why the influence of impurities upon the present photoelectric conversion devices is lesser than that upon organic electroluminescence devices in spite of their almost equal driving voltage lies in that the electric current flowing under driving of the photoelectric conversion devices is at most 1/10 the electric current flowing under driving of organic electroluminescence devices and, even when their organic films have some defects of impurity origin, influence of electric resistance resulting from the defects is therefore slight.

Scheme 1

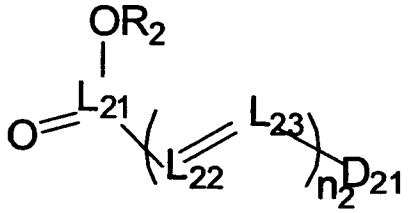


An explanation of Scheme 1 is given below. While exemplified compound 1 can be synthesized using the raw material 1, the raw material 1 is converted into the impurity 1 when undergoes oxidation and, depending on reaction conditions, part of the impurity 1 is further

converted into the impurity 2. On the other hand, when another part of the raw material 1 undergoes oxidation, the raw material 1 is converted into the impurity 4, and when the similar reaction is caused in the exemplified compound 1, the exemplified compound 1 is converted into impurity 3.

The term "oxidized-compound impurities" used herein is explained below.

Specific structures of oxidized-compound impurities include structures represented by the following formula (AI). When complex reactions occur, a further increase in number of impurity compounds is also possible.



(AI)

In the formula (AI), L_{21}, L_{22}, L_{23}, D_{21} and n_2 have the same meanings as L_1, L_2, L_3, D_1 and n in the formula (I), respectively, and examples of the former ones each are also the same as those of the latter one corresponding to each former one. R_2 represents a hydrogen atom or an alkyl group containing 1 to 3 carbon atoms.

Concrete structures of oxidized-compound impurities are e.g. the structures of the impurities 1 to 4 in the scheme 1. Structural changes in a photoelectric conversion material to be used involve structural changes of the exemplified compound 1 and the raw materials 1 and 2, and the impurities 1 to 4 responding to those structural changes are produced.

Examples of a method for reducing the content of those oxidized-compound impurities include a wide variety of methods.

Where methods of production are concerned, the use of higher-purity reactive raw materials and reagents is the more appropriate for reduction of impurity contents in the product obtained. Raw materials to be used can be purified by sublimation refining, distillation refining, solution refining or the like, and the raw material purity is preferably 99% or higher.

At the time of preparation for reaction and during progress of reaction, it is appropriate that the interior of a reaction vessel be kept full of an inert gas atmosphere. For creation of such a condition, it is appropriate to start a reaction operation after replacement of the atmosphere inside the reaction vessel with an inert gas and, under progress of the reaction, to keep the inside pressure of the reaction vessel slightly higher than atmospheric pressure by use of the inert gas. Thereby, oxidized-compound impurities of raw materials used and the reaction product can be inhibited from forming. In order to create an inert atmosphere,

nitrogen gas or an argon gas is preferably used. Further, it is appropriate for prevention of side reactions caused by light, such as oxidation reaction, isomerization reaction and reduction reaction, to carry out the synthesis reaction under conditions of shielding light by a metal film, a metal plate, a black cloth or the like.

For reduction in impurity content, it is appropriate that photoelectric conversion materials be purified in a refining process. In the refining process, any of a sublimation refining method, a solution refining method (recrystallization, reprecipitation or purification using a adsorbent) and a zone melting method can be preferably used, and adoption of combinations of these methods are preferable by far. Alternatively, one and the same method may be carried out over two or more times. The sublimation refining, as usually carried out, can be performed by heating and gasifying a raw material in a boat under high vacuum of 1 Pa or below in the inert gas atmosphere, and further by solidifying or, in some cases, liquefying the gasified material in a collection section adjusted to a lower temperature. The boat used is a boat made of quartz glass, Pyrex (trademark) glass or metal. The temperature of the heating section is preferably from 200°C to 400°C, and the temperature of the collection section is preferably lower than that of the heating section by 20°C to 100 °C.

As the solution refining method, though a recrystallization method, a reprecipitation method or the refining method using an adsorbent are usable, recrystallization and reprecipitation methods are preferable from the viewpoint of costs. In this specification, the refining method is categorized as a recrystallization method when the solid obtained is in a crystal state, while it is categorized as a reprecipitation method when the solid obtained in an amorphous state. However, the operations in both methods are the same. In these methods, solids are obtained by dissolution in hot solvents and subsequent cooling (more specifically, by preparing solutions of concentrations close to saturation at temperatures near their boiling points, filtering the solutions in hot conditions and then cooling the filtrates to room temperature or below), or by dissolution in good solvents, filtration and then addition of poor solvents. Further, the yield ratios therein can be enhanced by carrying out selective vaporization of the good solvents to some extent under reduced pressure and heightening proportions of the poor solvents. It is preferable for these operations to be basically carried out under an inert atmosphere, but they may also be carried out under conditions opened to the air as needs come up.

The refining method utilizing an absorbent is a method of dissolving a sample in a solvent and then inducing adsorption of impurities by an adsorbent (e.g. silica gel, alumina or activated carbon), and adopts the form of chromatography using a column for the purpose of

achieving high purity. In order to carry out the method at low price, on the other hand, the process of adding an adsorbent to a sample solution, filtering the sample solution and then washing the filtrate may be adopted.

As an alternative to the recrystallization method or the reprecipitation method, it is also useful to stir a sample without completely dissolving the sample under reflux with heating.

As one among solution refining methods, which is exceptional, it is also possible to adopt a method of decomposing impurities by reactions. More specifically, there are cases where impurities can be lessened by setting up conditions appropriate to occurrence of reduction when the impurities are those produced by oxidation or conditions appropriate to occurrence of condensation reaction when the impurities are those produced by hydrolysis.

The zone melting method is typical of silicon refining methods, and it is also applicable to purification of organic materials. More specifically, it is a method of eliminating impurities in a process that a material to be purified is charged into a tubular vessel, the material is melted in an area near to one end of the vessel, and then the melted portion of the material is made to move to the other end, thereby concentrating impurities into the melted portion.

In each of embodiments of the invention, it is preferable for each photoelectric conversion device to have a charge blocking layer between an electrode and an organic photoelectric conversion layer. The charge blocking layer may be either of hole blocking and electron blocking layers.

In each of embodiments of the invention, it is appropriate for dark current suppression that either hole blocking layer or electron blocking layer be provided. In the hole blocking layer provided for prevention of hole injection from an electrode, the electron-transporting materials as disclosed in JP-A-2007-59515 can be used. Not only structures but also preferred characteristics of compounds suitable for the materials are also described in JP-A-2007-59515, and information about them are known publicly.

It is advantageous for an electron-blocking material for use in the electron blocking layer to exhibit its absorption maximum at a wavelength of 400 nm or shorter, preferably 380 nm or shorter, in order not to obstruct absorption of light by the photoelectric conversion layer. As long as the material has a small absorption constant, it doesn't matter even if the absorption maximum of the material falls outside the above range. Such being the case, the absorption constant of the material is preferably 5,000 L/mol/cm or below, far preferably 2,000 L/mol/cm or below. From the necessity for transport of signal charges from the photoelectric conversion layer, the electron-blocking material is required to have a lower oxidation potential

and a smaller IP value relative to those of the photoelectric conversion layer. These values that the electron-blocking material has by itself are similar to those already described in regard to photoelectric conversion materials.

As for examples of the electron-blocking material, aromatic hydrocarbon compounds or complex compounds are usable as long as they satisfy the characteristics specified above. Of such compounds, triarylamine compounds are preferable to others, and the hole-transporting materials described in Chem. Rev. 2007, 107, 953 and those disclosed in JP-A-2007-59517 can be used to particular advantage. Further, known other materials or novel ones may be used.

Impurity contents in these materials are preferably 10,000 ppm or below, and the lower the better. In addition, the higher the object material content, the better the performance attained. The object material content is preferably from 96.7 to 99.9%, far preferably from 99.5 to 99.9%.

Examples of impurities in an electron-blocking material for use in the electron blocking layer include raw materials, reaction reagents, solvents, reactive intermediates and a wide variety of decomposed products from side reactions. When there occurs oxidation reaction as side reaction, oxidized-compound impurities are formed; when there occurs reduction reaction as side reaction, reduction impurities are produced; when there occurs decomposition reaction as side reaction, decomposition impurities are produced; while when there occurs isomerization reaction as side reaction, isomerization impurities are produced. Among these varieties of impurities, halides formed as the reactive intermediates and heavy metals derived from reaction reagents in particular are found to be of great influence upon the performance of the photoelectric conversion device.

(Electron Blocking Layer)

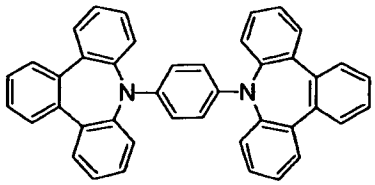
In the electron blocking layer, an electron donating organic material can be used. Examples of a usable electron-donating low-molecular material include aromatic diamine compounds such as N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) and 4,4'-bis[N-(naphthyl)-N-phenyl-amino]biphenyl (α-NPD), oxazole, oxadiazole, triazole, imidazole, imdazolone, stilbene derivatives, pyrazoline derivatives, tetrahydroimidazole, polyarylalkanes, butadiene, 4,4',4"-tris(N-(3-methylphneyl)N-phenylamino)triphenylamine (m-MTDATA), porphyrin compounds such as porphin, tetraphenylporphin copper, phthalocyanine, copper phthalocyanine and taitanium phthalocyanine oxide, triazole derivatives, oxadiazole derivatives, imidazole derivatives, polyarylalkane derivatives, pyrazoline derivatives, pyrazolone derivatives, phenylenediamine derivatives, arylamine

derivatives, amino-substituted chalcone derivatives, oxazole derivatives, styrylanthracene derivatives, fluorenone derivatives, hydrazone derivatives and silazane derivatives. And examples of a usable electron-donating high-molecular material include phenylenevinylene polymer, fluorene polymer, carbazole polymer, indole polymer, pyrene polymer, pyrrole polymer, picoline polymer, thiophene polymer, acetylene polymer, diacetylene polymer and derivatives of these polymers. In addition, compounds having a sufficient hole-transporting property can be used in the electron blocking layer even when they have no electron-donating property.

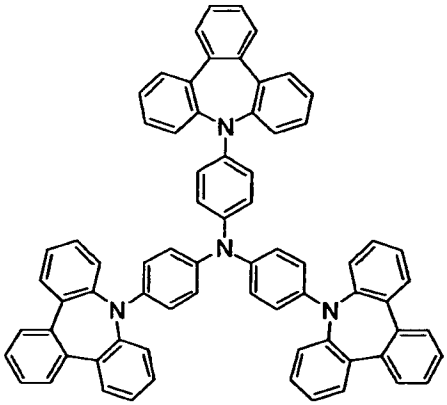
The thickness of the electron blocking layer is preferably from 10 nm to 200 nm, far preferably from 30 nm to 150 nm, particularly preferably from 50 nm to 100 nm. This is because reduction in effect of suppressing dark current occurs when the layer is too thin, while the lowering of photoelectric conversion efficiency occurs when the layer is too thick.

In the concrete, examples of an electron-blocking material include the following materials symbolized as EB-1 to EB-5, TPD and m-MTDATA, respectively.

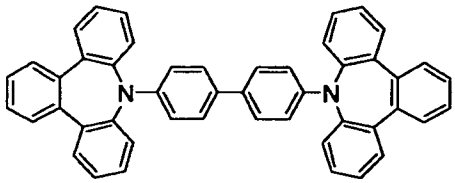
EB-1 : Ea=1.9, Ip=4.9



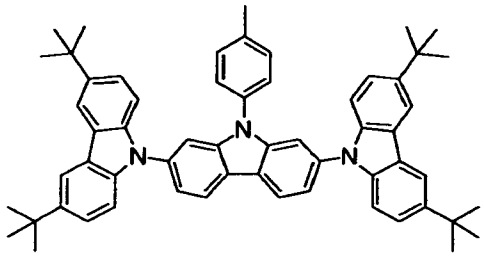
EB-2 : Ea=1.7, Ip=4.7



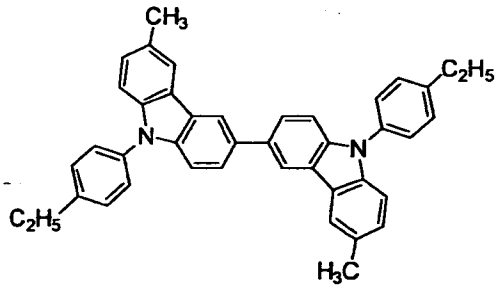
EB-3 : Ea=1.9, Ip=5.2



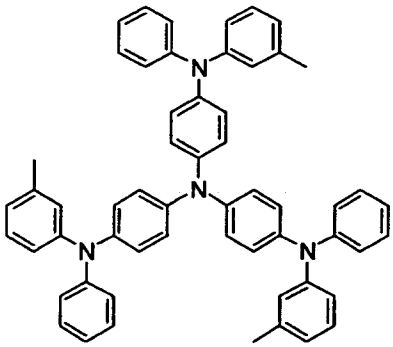
EB-4 : Ea=2.1, Ip=5.4



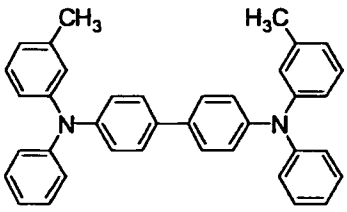
EB-5 : Ea=2.1, Ip=5.8



m-MTDATA : Ea=1.9, Ip=5.1



TPD : Ea=2.3, Ip=5.5



A selection of materials practically usable in the electron blocking layer is limited by materials for the electrode adjacent to the electron blocking layer and materials for the photoelectric conversion layer adjacent to the electron blocking layer. Materials suitable for use in the electron blocking layer are those having electron affinity (Ea) greater than work functions (Wf) of materials for the electrode adjacent to the electron blocking layer by at least 1.3 eV and ionization potentials (Ip) equal to or smaller than those of materials for the

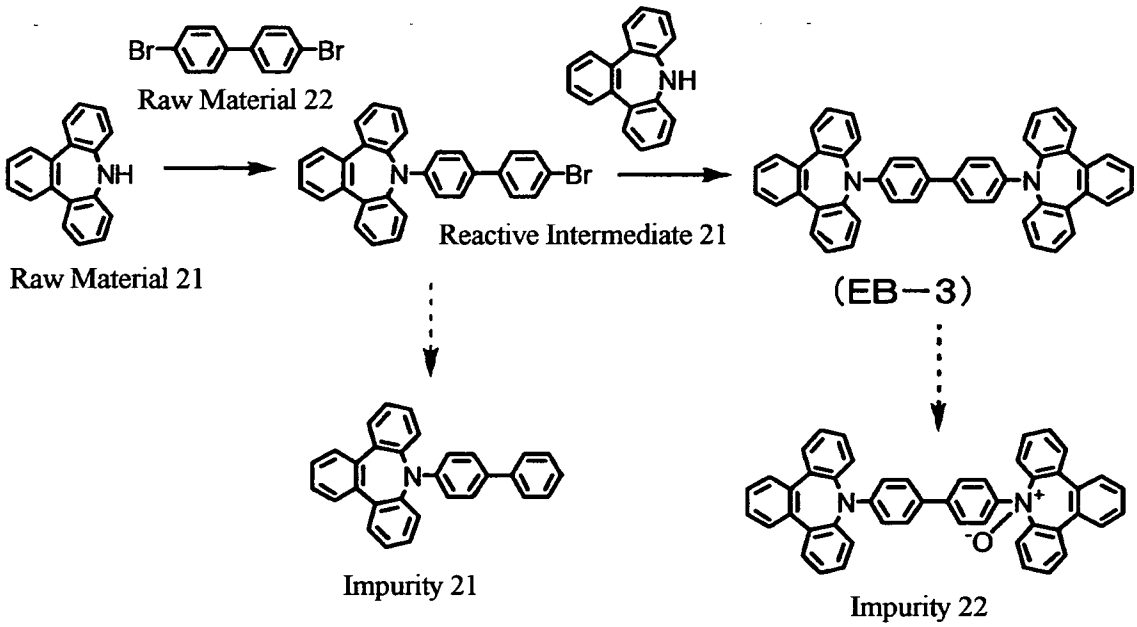
photoelectric conversion layer adjacent to the electron blocking layer.

(Halide Impurity)

The halide impurity content in the electron blocking layer is preferably 9,000 ppm or below, particularly preferably 4,000 ppm or below. The lower limit of the halide impurity content is zero, and it is preferable for the content to be brought as close to zero as possible. In particular, the cases where the halide impurity content is 9,000 ppm or below and the purity of a material used for formation of the organic photoelectric conversion layer is from 96.5% to 99.9% as determined by liquid chromatography are preferable, because they allows fabrication of high-performance photoelectric conversion devices and reduction in costs for purification of materials.

The halogen in a halide depends on a raw material used, and examples of a halide include a fluoride, a chloride, a bromide, an iodide and a perfluoroalkylsulfonate. From the viewpoint of synthesis yield, a bromide or an iodide is generally chosen as raw material. When the compound intended as a reaction product is an arylamine, the halide as raw material is the arylhalide. By way of explanation, the case of the following scheme 2 is taken. In this case, compounds referred to as the halides are 4.4'-dibromobiphenyl as a raw material and the compound described as a reactive intermediate. And there may further occur reduction of the reactive intermediate and thereby conversion into its hydride.

Scheme 2



Halide impurities in the cases of using EB-1 to EB-5, TPD and m-MTDATA as electron-blocking materials, respectively, are illustrated below, but impurities in the invention should not be construed as being limited to the following.

Table 3

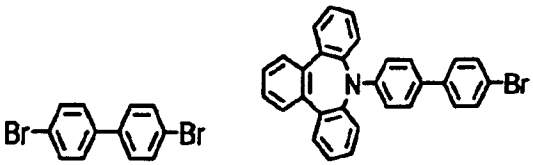
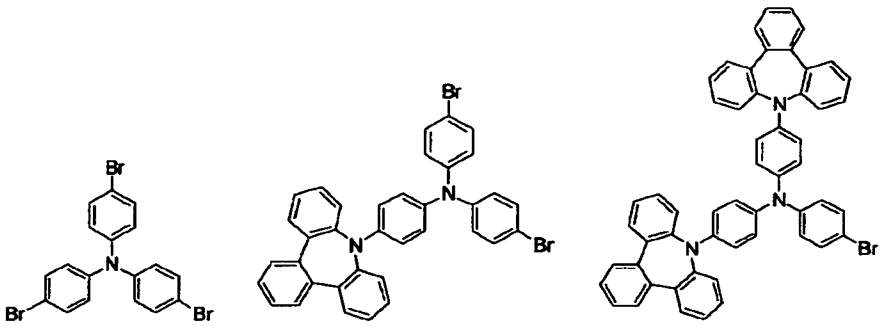
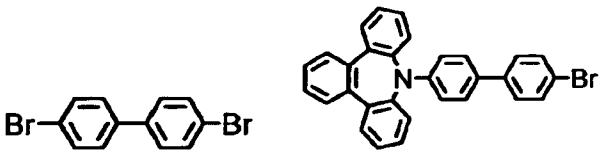
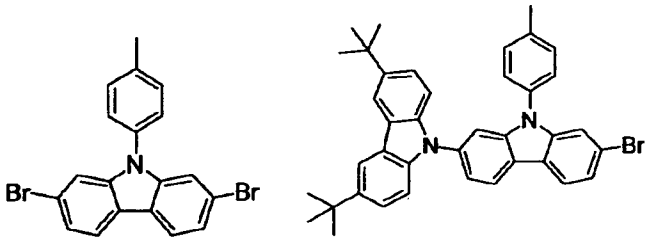
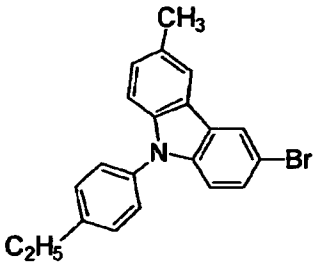
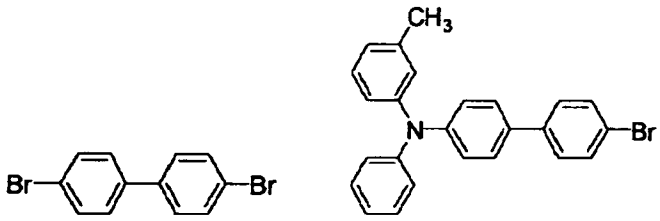
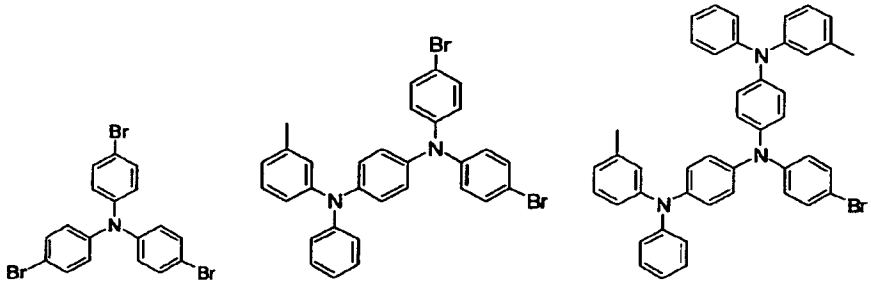
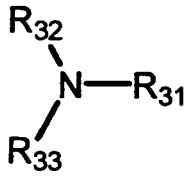
Electron-blocking Material	Halide Impurity
EB-1	
EB-2	
EB-3	
EB-4	
EB-5	

Table 3 (Continued)

Electron-blocking Material	Halide Impurity
TPD	
m-MTDATA	

The halide impurities are therefore compounds represented by the following formula (AII).



(AII)

In the formula (AII), each of R_{31}, R_{32} and R_{33} represents an aryl group containing 6 to 30 carbon atoms or a heteroaryl group containing 4 to 30 carbon atoms, and at least one of R_{31}, R_{32} and R_{33} has a halogen substituent.

The aryl group which each of R_{31}, R_{32} and R_{33} independently represents is preferably an aryl group containing 6 to 18 carbon atoms. The aryl group may have a substituent, and it is preferably an aryl group which contains 6 to 18 carbon atoms and may have as a substituent an alkyl group containing 1 to 4 carbon atoms (such as a methyl group, an ethyl group, a n-propyl group, an isopropyl group, a t-butyl group or a n-butyl group), an aryl group containing 6 to 18 carbon atoms (such as a phenyl group or a naphthyl group) or a heteroaryl group containing 4 to 18 carbon atom (such as 9H-9-aza-tricyclobenzo[a,c,e]cyclohentene). Examples of the aryl group represented by each of R_{31}, R_{32} and R_{33} wherein 6 to 30 carbon atoms are contained include a phenyl group, a naphthyl group, an anthryl group, a phenanthryl group and a fluorenyl group. Of these groups, a phenyl group is preferred over the others. Examples of a substituent suitable for such an aryl group include

9H-9-aza-tricyclobenzo[a,c,e]cycloheptene, a methyl group and an ethyl group.

Examples of a heteroaryl group represented by each of R_{31}, R_{32} and R_{33} wherein 4 to 30 carbon atoms are contained include a pyrazyl group, a pyrimidinyl group, a pyridazinyl group, a triazinyl group, a quinolinyl group, a quinoxalinyl group, a cinnolinyl group, an isoquinolinyl group, a pteridinyl group, an acridinyl group, a phenazinyl group, a phenanthrolinyl group, a tetrazolyl group, a pyrazolyl group, an imidazolyl group, a thiazolyl group, an oxazolyl group, an indazolyl group, a benzimidazolyl group, a benzotriazolyl group, a benzoxazolyl group, a benzothiazolyl group and a carbamoyl group.

R_{31}, R_{32} and R_{33} may be the same or different from one another, and any adjacent two of them may combine with each other to form an aryl ring or a heteroaryl ring.

Examples of an aryl ring formed by combining any adjacent two of R_{31}, R_{32} and R_{33} include acenes such as a benzene ring, a naphthalene ring, an anthracene ring, a phenanthrene ring, a pyrene ring and a naphthacene ring.

Examples of a heteroaryl ring formed by combining any adjacent two of R_{31}, R_{32} and R_{33} include a thiophene ring, a pyrrole ring, a furan ring, a thiazole ring, a diazole ring, an oxazole ring and benzene-condensed derivatives of these rings. Each of the substituents as recited above may further has another substituent. Examples of a ring structure in a case where a nitrogen-containing heterocyclic ring is formed by combining any adjacent two of R_{31}, R_{32} and R_{33} include a carbazole ring, an acridan ring, an azepine ring, a phenoxazine ring, a phenothiazine ring and benzene-condensed derivatives of these rings.

A halogen atom substituted to R_{31}, R_{32} and R_{33} is a fluorine atom, a chlorine atom, a bromine atom or an iodine atom, preferably a bromine atom or an iodine atom. The number of halogen substituents is preferably 1 or 2.

Specific structures of halide impurities are e.g. the raw material 22 and the reactive intermediate 21 in the scheme 2. When the structures of materials used are modified, exemplified compound 2 and the raw materials 1 and 2 have modified structures, and raw materials and a reactive intermediate which have structures responding to the modifications made become halide impurities.

(Heavy Metal Impurity)

When the synthesis of an intended material requires a heavy metal catalyst, the heavy metal impurity content of the material is preferably 4,000 ppm or below, far preferably 1,000 ppm or below. The heave metal catalyst is preferably a copper catalyst or a palladium catalyst from the viewpoint of yield. When a copper catalyst is used, the heavy metal impurities therefore include copper, copper(I) oxide, copper(II) oxide and copper salts (such as copper carbonate, copper chloride, copper bromide and copper iodide). When a palladium

catalyst is used, the heavy metal impurities therefore include palladium, palladium(II) oxide and palladium(II) salts (such as palladium acetate, palladium carbonate, palladium chloride, palladium bromide and palladium iodide). When palladium is used as a catalyst, trialkyl phosphines or triaryl phosphines are used as ligands for activation of the catalyst. Complexes formed from these ligands and palladium(0) are also included in examples of impurities. Special cases where the material used for formation of an organic photoelectric conversion layer has a heavy-metal catalyst content of 4,000 ppm or below and a purity of 96.5% to 99.9% as determined by liquid chromatography are preferred because high-performance photoelectric conversion devices can be fabricated, and besides, costs of purifying materials can be reduced.

It is also advantageous for electron-blocking materials to be purified, and details of their purification are similar to the details on the case of purifying photoelectric conversion materials.

There are cases where water and solvents are contained in photoelectric conversion materials as well as electron-blocking materials. The solvents are those used in reactions and refining processes. Examples of such solvents include alcohol compounds (such as methanol, ethanol and propanol), acetonitrile, acetone, ethyl acetate, toluene, xylene, hexane, N,N-dimethylformamide, N,N-diethylacetamide, N-methylpyrrolidone and diethyl ether. It is preferred that these impurities have been removed by airflow drying, reduced-pressure drying, heat drying or the like before the refining process is completed.

In order to avoid increases in impurities during the storage, it is preferred that photoelectric conversion materials as well as electron blocking materials are stored in the presence of a light shield under an inert gas atmosphere. As to the temperature, room temperature presents no problem, but lower temperatures are preferred.

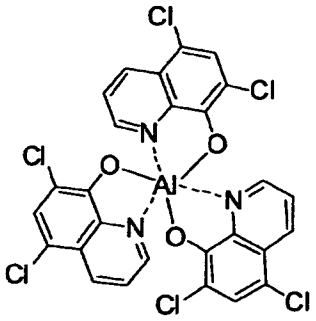
(Hole Blocking Layer)

In a hole blocking layer, an electron accepting organic material can be used. Examples of a compound usable as the electron accepting material include an oxadiazole derivative such as 1,3-bis(4-tert-butylphenyl-1,3,4-oxadiazolyl)phenylene (OXD-7), an anthraquinodimethane derivative, a diphenylquinone derivative, bathocuproin, bathophenanthroline and their derivatives, triazole compounds, tris(8-hydroxyquinolinato)aluminum complexes, bis(4-methyl-8-quinolinato)aluminum complexes, distyrylarylene derivatives and silole compounds. In addition, it is possible to use materials which have sufficient electron-transporting properties though they are not electron-accepting organic materials. For instance, porphyrin compounds, styryl compounds such as DMC (4-dicyanomethylene-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran), and

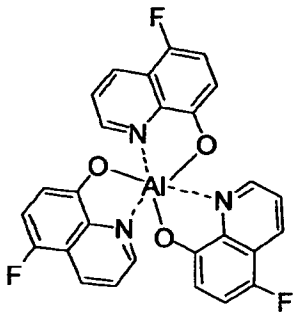
4H-pyran compounds.

To be more specific, the following compounds as disclosed e.g. in JP-A-2008-72090 are preferably used. "HB" in HB-1 to HB-5 is an abbreviation for hole blocking.

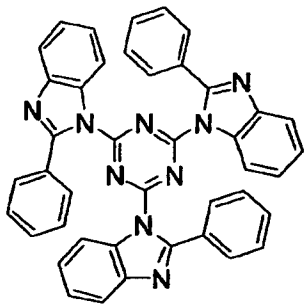
HB-1 : Ea=3.5, Ip=6.2



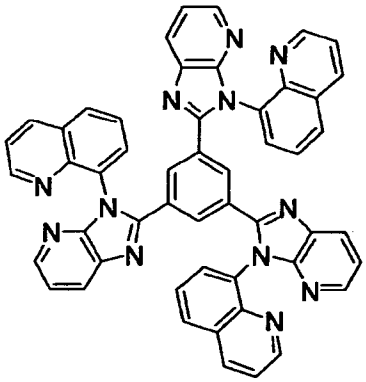
HB-2 : Ea=3.3, Ip=6.0



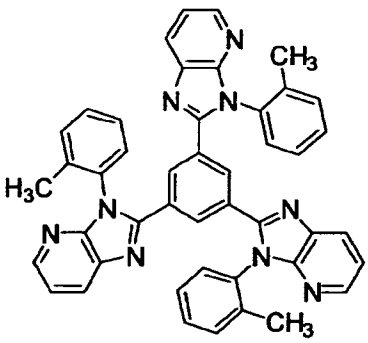
HB-3 : Ea=3.7, Ip=7.2



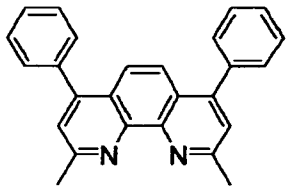
HB-4 : Ea=3.6, Ip=7.6



HB-5 : Ea=3.6, Ip=7.6



BCP : Ea=3.2, Ip=6.7



In the present embodiments, those containing fullerenes in photoelectric conversion layers are preferable. As for fullerenes also, high-purity fullerenes in which mixing of impurities is reduced are preferred. The purity of fullerenes is preferably 99% or higher, far preferably 99.5% or higher. In the case of C_{60} fullerene, examples of impurities contained in the fullerene include allotropes other than C_{60} (such as C_{70}, C_{74}, C_{76} and C_{78}), oxides (such as $C_{60}O$, $C_{60}O_2$ and $C_{60}O_3$) and fullerene hydroxides.

In the next place, effects brought about by providing a charge blocking layer in a multilayer form, other than the effect on intermediate levels, are explained. Although the above-mentioned technique of shifting intermediate levels present in each layer by forming the layer in a multilayer form makes it possible to reduce dark current by "inhibiting the transport of injected charges", formation of multilayer charge blocking layer has another effect of reducing dark current by "controlling the injection of charges from an electrode".

In controlling the injection of charges from an electrode, it is important to heighten an energy barrier between the electrode and a layer adjoining it and to make the charge blocking

layer homogeneous so that the electrode is not brought into contact with a layer (a photoelectric conversion layer) underneath the blocking layer.

The former is a solution of providing an energy barrier against injection, and the latter is a solution from the standpoint of physical structure, whereby it is prevented from occurring that an electrode material intrudes into fine defects of the blocking layer and comes into contact with a photoelectric conversion layer, thereby forming leak spots.

When the charge blocking layer is designed to have a multilayered structure, the functions thereof can be assigned to its multiple constituent layers, and more specifically, one constituent layer adjoining an electrode can be adjusted to differ from the electrode in energy barrier, while another constituent layer not adjoining the electrode can be adjusted to have a charge-transporting property and homogeneity, whereby occurrence of leak spots can be prevented.

By using an inorganic material layer including an inorganic material as the charge blocking layer adjoining an electrode and an organic material layer including an organic material as the charge blocking layer provided underneath the inorganic material layer (between the inorganic material layer and the photoelectric conversion layer), more pronounced suppression of dark current becomes possible, and besides, inhibition of readout of signal charges can be avoided. In Fig. 1, for example, a first layer 103a on the side of an electrode 104 is assigned as an inorganic material layer, and a second layer 103b as an organic material layer.

For an inorganic material forming the inorganic material layer, any of Si, Mo, Ce, Li, Hf, Ta, Al, Ti, Zn, W and Zr can be preferably used. As for the inorganic material, the use of an oxide is preferable, and SiO in particular is suitable as the oxide.

For prevention of charge injection from the electrode, the inorganic material layer is required to have such ionization energy Ip as to create an energy barrier between the ionization energy and a work function of the adjacent electrode, and it is advantageous for the layer to have a greater Ip. However, when the inorganic material layer alone constitutes the charge blocking layer, reduction in layer thickness brings about leak spots in between the electrode and the photoelectric conversion layer, and fails to have sufficient effect on prevention of injection, while increase in layer thickness diminishes charge transporting property and makes it difficult to read out signal charges.

In addition to the inorganic material layer, it therefore becomes important to provide an organic material layer underneath the inorganic material layer. The organic material layer is preferably a layer having not only a charge transporting property enough to transport signal charges generated in the photoelectric conversion layer but also homogeneity, and an organic

material used therein is preferably a material reduced in carriers as a cause of dark current originating in the material.

By providing such an organic material layer, the charge blocking layer can be made homogeneous and thick without attended by an increase in the dark current originating in the charge blocking layer and a reduction in photoelectric conversion efficiency and, by combining these effects with the effect of the inorganic material layer, suppression of dark current becomes possible.

Then, structures of devices according to embodiments of the invention are illustrated by reference to drawings.

Figure 1 is a schematic cross-sectional diagram of a photoelectric conversion device relating to a first embodiment of the invention. The photoelectric conversion device 100 according to this embodiment is configured so that a photoelectric conversion layer 102 is stacked on a first electrode film 101, a charge blocking layer 103 is stacked on the photoelectric conversion layer 102, and further a second electrode film 104 is stacked on the charge blocking layer 103.

The device can be designed to allow incidence of light from the side of the first electrode film 101, or it can be designed to allow incidence of light from the side of the second electrode film 104. In the case of incidence of light from the side of the second electrode film 104, the second electrode film 104 is the upper electrode, and the lower electrode 101 is stacked on a substrate not depicted in the drawing. In the present embodiment, the charge blocking layer 103 has a double-layer structure made up of a first charge blocking layer 103a and a second charge blocking layer 103b.

Because there is the necessity for making incident light reach into the photoelectric conversion layer 102, it is appropriate that the upper electrode 104 is formed from a highly transparent material. As for the highly transparent electrode, transparent conductive oxides (TCO) are given as examples thereof. Likewise, the lower electrode 101 is preferably formed from a highly transparent material because there may be cases where transmission of light in the downward direction is required as seen in the structures of imaging devices mentioned hereafter.

The charge blocking layer 103 is a layer for inhibiting the charge transfer from the electrode 104 to the photoelectric conversion layer 102 from occurring when a voltage is applied between the electrodes 101 and 104. When the charge blocking layer 103 has a single-layer structure, there exist intermediate levels (such as an impurity level) in the material itself, constituting the charge blocking layer 103, and charge (electron, hole) transfer occurs via these intermediate levels to result in an increase of dark current. For the purpose of

preventing this phenomenon, the charge blocking layer 103 in this embodiment is designed to have a double-layer structure, not a single-layer structure.

By creating an interface between the first layer 103a and the second layer 103b which constitute the charge blocking layer 103, discontinuity is generated in the intermediate levels existing in each of the layers 103a and 103b, and thereby carriers are made difficult to move via intermediate levels or the like. It is therefore thought that control of dark current becomes possible. However, when the layer 103a and the layer 103b are formed from the same material, there may be a case where the intermediate levels existing in the layer 103a are exactly the same as those existing in the layer 103b. For further heightening dark-current control effect, it is appropriate that materials forming the layer 103a and 103b, respectively, are made different from each other.

Although the case of providing a charge blocking layer between the photoelectric conversion layer 102 and the upper electrode 104 is illustrated in Fig. 1, another charge blocking layer may be provided between the photoelectric conversion layer 102 and the lower electrode 101. Herein, one charge blocking layer is designed as an electron blocking layer and the other is designed as a hole blocking layer. As in the explanation about the charge blocking layer, it is appropriate that a double-layer structure be given to each of the electron blocking layer and the hole blocking layer. Alternatively, it is also appropriate that a multilayer structure including three or more layers may be given to each layer and materials forming the multiple layers are made to differ from one another.

Figure 2 is a schematic cross-sectional diagram showing a one-pixel portion of imaging device relating to a second embodiment of the invention, and Fig. 3 is a schematic cross-sectional diagram of the intermediate layer shown in Fig. 2. The imaging device 200 is a device having on one and the same plane a large number of pixels, each of which is shown in Fig. 2, arranged in the form of an array, and signals emitted from each individual pixel can produce one pixel data of image data.

One pixel of the imaging device shown in Fig. 2 is equipped with an n-type silicon substrate 1, a transparent insulating film 7 formed on the n-type silicon substrate 1, the following photoelectric conversion section formed on the insulating film 7, a light-shielding film 14 which is provided on the photoelectric conversion section and has an aperture, and a transparent insulating film 15 laminated on the light-shielding film 14.

The photoelectric conversion section is made up of a first electrode film 11, an intermediate layer 12 formed on the first electrode film 11 and a second electrode film 13 formed on the intermediate layer 12. By laminating the light-shielding film 14, which has the aperture, on the photoelectric conversion section, a limit is imposed on a light-receiving area

of the intermediate 12. In this photoelectric conversion section, the structure of the photoelectric conversion device illustrated in Fig. 1 can be adopted.

The intermediate layer 12, as shown in Fig. 3, is configured to stack on the first electrode film 11 an undercoat layer-cum-electron blocking layer 122, a photoelectric conversion layer 123 and a hole blocking layer-cum-buffer layer 124 in order of mention. Each of the electron blocking layer 122 and the hole blocking layer-cum-buffer layer 124 has a multilayer structure as mentioned above.

The photoelectric conversion layer 123 is made up so as to contain materials having properties of generating charges including electrons and holes in response to light incident from an upward direction of the second electrode film 13 and, what's more, imparting smaller mobility to electrons than to holes, and besides, generating greater numbers of electrons and holes in the vicinity of the second electrode film 13 than in the vicinity of the first electrode film 11. Representative examples of photoelectric conversion materials having such properties include organic materials. In the makeup shown in Fig. 2, materials generating electrons and holes in response to absorption of green light are used. Because the photoelectric conversion layer 123 can be shared among all the pixels, it may be a film of single-sheet form, and needn't be divided on a pixel basis.

The photoelectric conversion layer 123 can be preferably implemented by combined use of the materials as described above. When organic materials other than those recited above are included in constituent materials of the photoelectric conversion layer 123, it is appropriate that at least either organic p-type semiconductor or organic n-type semiconductor is included. As each of the organic p-type semiconductor and the organic n-type semiconductor, any of quinacridone derivatives, naphthalene derivatives, anthracene derivatives, phenanthrene derivatives, tetracene derivatives, perylene derivatives and fluoranthene derivatives can be used to particular advantage.

Organic p-type semiconductors (compounds) are organic semiconductors (compounds) having donor nature, and refer to organic compounds having the property of easily donating electrons, typified mainly by hole transporting organic compounds. More specifically, when two organic materials are used in a state of being in contact with each other, the organic compound having donor nature refers to the organic compound lower in ionization potential than the other. Therefore any of organic compounds are usable as an organic compound having donor nature as long as they have the property of donating electrons. Examples of organic compounds usable as those having electron donating properties include triarylamine compounds, benzidine compounds, pyrazoline compounds, styrylamine compounds, hydrazone compounds, triphenylmethane compounds, carbazole compounds,

polysilane compounds, thiophene compounds, phthalocyanine compounds, cyanine compounds, merocyanine compounds, oxonol compounds, polyamine compounds, indole compounds, pyrrole compounds, pyrazole compounds, polyarylene compounds, condensed aromatic carbon ring compounds (such as naphthalene derivatives, anthracene derivatives, phenanthrene derivatives, tetracene derivatives, pyrene derivatives, perylene derivatives and fluoranthene derivatives), and metal complexes whose ligands are nitrogen-containing heterocyclic compound. However, the organic compounds usable as those having electron donating properties are not limited to the compounds recited above but, as mentioned above, as long as organic compounds are lower in ionization potential than the organic compounds used as n-type compounds (having acceptor nature), they may be used as organic semiconductors having donor nature.

Organic n-type semiconductors (compounds) are organic semiconductors (compounds) having acceptor nature, and refer to organic compounds having the property of easily accepting electrons, typified mainly by electron transporting organic compounds. More specifically, when two organic materials are used in a state of being in contact with each other, the organic compound having acceptor nature refers to the organic compound greater in electron affinity than the other. Therefore any of organic compounds are usable as an organic compound having acceptor nature as long as they have the property of accepting electrons. Examples of organic compounds usable as those having electron accepting properties include condensed aromatic carbon ring compounds (such as naphthalene derivatives, anthracene derivatives, phenanthrene derivatives, tetracene derivatives, pyrene derivatives, perylene derivatives and fluoranthene derivatives), nitrogen-, oxygen- or/and sulfur-containing 5- to 7-membered heterocyclic compounds (such as pyridine, pyrazine, pyrimidine, pyridazine, triazine, quinoline, quinoxaline, quinazoline, phthalazine, cinnoline, isoquinoline, pteridine, acridine, phenazine, phenanthroline, tetrazole, pyrazole, imidazole, thiazole, oxazole, indazole, benzimidazole, benzotriazole, benzoxazole, benzothiazole, carbazole, purine, triazolopyridazine, triazolopyrimidine, tetrazaindene, oxadiazole, imidazopyridine, pyralidine, pyrrolopyridine, thiadiazolopyridine, dibenzazepine and tribenzoazepine), polyarylene compounds, fluorene compounds, cyclopentadiene compounds, silyl compounds and metal complexes whose ligands are nitrogen-containing heterocyclic compounds. However, the organic compounds usable as those having electron accepting properties are not limited to the compounds recited above but, as mentioned above, as long as organic compounds are greater in electron affinity than the organic compounds used as those having donor nature, they may be used as organic semiconductors having acceptor nature.

It is also possible to use n-type organic dyes or p-type organic dyes. Although any

dyes may be used as such dyes, examples of preferred dyes include cyanine dyes, styryl dyes, hemicyanine dyes, merocyanine dyes (including zero-methine merocyanine (simple merocyanine)), trinuclear merocyanine dyes, tetranuclear merocyanine dyes rhodacyanine dyes, complex cyanine dyes, complex merocyanine dyes, allopolar dyes, oxonol dyes, hemioxonol dyes, squarylium dyes, croconium dyes, azamethine dyes, coumarin dyes, arylidene dyes, anthraquinone dyes, triphenylmethane dyes, azo dyes, azomethine dyes, spiro compounds, metallocene dyes, fluorenone dyes, fulgide dyes, perylene dyes, phenazine dyes, phenothiazine dyes, quinone dyes, indigo dyes, diphenylmethane dyes, polyene dyes, acridine dyes, acridinone dyes, diphenylamine dyes, quinacridone dyes, quinophthalone dyes, phenoxazine dyes, phthaloperylene dyes, porphyrin dyes, chlorophyll dyes, phthalocyanine dyes, metal complex dyes, and condensed aromatic carbon ring series dyes (such as naphthalene derivatives, anthracene derivatives, phenanthrene derivatives, tetracene derivatives, pyrene derivatives, perylene derivatives and fluoranthene derivatives).

In an embodiment of the invention, the intermediate layer 12 has a p-type semiconductor layer and an n-type semiconductor layer, and it is a preferred case that at least either p-type semiconductor or n-type semiconductor is an organic semiconductor, and what's more, a photoelectric conversion layer with a bulk heterojunction structure incorporating the p-type semiconductor and the n-type semiconductor is sandwiched in between those semiconductor layers. In this case, the bulk heterojunction structure is incorporated into the intermediate layer 12, and thereby a defect that carrier diffusion length of the photoelectric conversion layer 123 is short can be compensated so that photoelectric conversion efficiency of the photoelectric conversion layer 123 is enhanced.

In addition, the photoelectric conversion layer included in the intermediate layer 12 has a layer of a p-type semiconductor and a layer of an n-type semiconductor layer, preferably a mixed-and-dispersed layer (of bulk heterojunction structure). Herein, the case of containing an orientation-controlled organic compound in at least either p-type semiconductor or n-type semiconductor is preferred, and the case of containing an orientation-controlled (controllable) organic compound in each of the p-type semiconductor and the n-type semiconductor is far preferred. As such an organic compound, a compound having π-conjugate electrons is preferably used. And it is preferable that the plane of these π-electrons is not oriented perpendicularly to the substrate (electrode substrate). As for the orientation angle of the plane, the closer to parallel to the substrate the more favorable. More specifically, the angle which the π-electron plane forms with the substrate is preferably from 0° to 80°, far preferably from 0° to 60°, further preferably from 0° to 40°, still further

preferably from 0° to 20°, particularly preferably from 0° to 10°, optimally 0° (namely parallel to the substrate). It is appropriate that the layer of an orientation-controlled organic compound be contained in even a portion of the whole intermediate layer 12, and more specifically, the proportion of the orientation-controlled organic compound portion to the whole intermediate layer 12 is preferably 10% or above, far preferably 30% or above, further preferably 50% or above, still further preferably 70% or above, particularly preferably 90% or above, optimally 100%. By controlling the orientation of an organic compound contained in the intermediate layer 12 so as to satisfy the above conditions, a defect that carrier diffusion length of the photoelectric conversion layer is short can be compensated so that photoelectric conversion efficiency of the photoelectric conversion layer is enhanced.

Among the cases where the orientations of organic compounds are controlled, the case where a heterojuction face (e.g. a pn-junction face) is not parallel to a substrate (an electrode substrate) is far preferred. As for the orientation angle of the heterojunction face, it is not parallel to the substrate, but the closer to the vertical the more favorable. More specifically, the angle which the heterojunction face forms with the substrate is preferably from 10° to 90°, far preferably from 30° to 90°, further preferably from 50° to 90°, still further preferably from 70° to 90°, particularly preferably from80° to 90°, optimally 90° (namely vertical to the substrate). It is appropriate that the organic compound layers under the hererojuction-face control be contained in even a portion of the whole intermediate layer 12, and more specifically, the proportion of the orientation-controlled portion to the whole intermediate layer 12 is preferably 10% or above, far preferably 30% or above, further preferably 50% or above, still further preferably 70% or above, particularly preferably 90% or above, optimally 100%. In such a case, the area of the heterojuction face in the intermediate layer 12 increases, and thereby an increase in the quantity of carriers, such as electrons, holes and electron-hole pairs, generating at the interface is brought about, and enhancement of photoelectric conversion efficiency becomes possible. Thus, the photoelectric conversion layer in which orientations of both the heterojunction face of organic compounds and the π-electron plane are so controlled as mentioned above can ensure enhancement of photoelectric conversion efficiency in particular. Detailed explanation of those conditions can be found in JP-A-2006-086493 (Japanese Patent Application No. 2004-079931). As to the absorption of light, the greater the organic layer thickness is the better. However, in view of the proportion which does not contribute charge separation, the thickness of the organic layer is preferably from 30 nm to 300 nm, far preferably from 50 nm to 250 nm, particularly preferably from 80 nm to 200 nm.

The intermediate layer 12 including those organic layers can be provided in the form of film by use of a dry method or a wet method for film formation. Examples of a dry method for film formation include a vacuum evaporation method, a sputtering method, an ion plating method, a physical vapor deposition method such as MBE, and a CVD method such as plasma polymerization. Examples of a wet method for film formation include a cast method, a spin coating method, a dipping method and a LB method.

When a polymer compound is used as at least one among p-type semiconductors (compounds) or n-type semiconductors (compounds), the polymer compound is preferably formed into film by use of a wet film-forming method which allows easy film formation. When a dry film-forming method, such as a vapor deposition method, is adopted, polymer compounds are difficult to use because there is the fear of decomposition. Instead of polymers, their olygomers can be used to advantage. When low molecular compounds are used, dry film-forming methods are preferably used. A vacuum evaporation method in particular can be used to advantage. Basic factors of the vacuum evaporation method include the method used for heating a compound, e.g. which method, a resistance heating evaporation method or an electron-beam heating evaporation method, is used, the shape of an evaporation source used, e.g. the shape of a crucible or a boat, the degree of vacuum, the evaporation temperature, the base temperature, the evaporation speed, and so on. In order to make uniform evaporation possible, it is preferred that the evaporation be carried out under rotation of the base. As for the degree of vacuum, the higher the degree, the better the result obtained. More specifically, it is appropriate that the vacuum evaporation be carried out in a vacuum of 10^{-4} Torr or below, preferably 10^{-6} Torr or below, particularly preferably 10^{-8} Torr or below, and the compound to undergo evaporation is kept from direct contact with oxygen and moisture of the outside air. It is preferred that the compound is evaporated in vacuum throughout evaporation steps is conducted in vacuum, so as not to be in contact with oxygen and moisture of the outside air. The conditions for vacuum evaporation are required to be strictly controlled because they have influences upon e.g. the crystallinity, amorphousness, density and compactness of the organic film formed. Further, the PI or PID control of the evaporation speed by use of a film-thickness monitor such as a quartz resonator or an interferometer is preferably adopted. In the case of evaporating two or more kinds of compounds at the same time, a coevaporation method, a flash evaporation method or the like can be adopted.

When the photoelectric conversion layer 123 containing organic materials gets light incident from an upward direction of the second electrode 13 in the device structure illustrated above, absorption of the light thereby generally generates a great many electrons and holes in

the vicinity of the second electrode 13 and not-so-many electrons and holes in the vicinity of the first electrode 11. This is because most of light having wavelengths in the vicinity of the absorption peak of the photoelectric conversion layer 123 is absorbed in the vicinity of the second electrode 13 and the absorbance of light decreases with an increase in distance from the vicinity of the second electrode 13. Thus, unless electrons or holes generating in the vicinity of the second electrode 13 are transferred to the silicon substrate with efficiency, reduction in the photoelectric conversion efficiency is caused to result in desensitization of the device obtained. In addition, signals from the wavelengths of light absorbed strongly in the neighborhood of the second electrode 13 are decreased to result in an extension of the spectral sensitivity range, or the so-called broadening.

Further, it is a general trend in the photoelectric conversion layer 123 containing organic materials that the mobility of electrons is considerably smaller than that of holes. Furthermore, it has already turned out that the mobility of electrons in the photoelectric conversion layer 123 containing organic materials were susceptible to oxygen and exposure of the photoelectric conversion layer 123 to the air further lowered the mobility of electrons. On account of this fact, when it is intended to move electrons into the silicon substrate 1, as long as the electrons generating in the vicinity of the second electrode 13 have a long travel distance in the photoelectric conversion layer 123, it occurs that part of electrons are deactivated during their travel and cannot be collected into the electrode, and thereby desensitization and broadening of the spectral sensitivity range are caused.

For prevention of the desensitization and the broadening of the spectral sensitivity range, it is effective that electrons or holes generating in the vicinoty of the second electrode 13 are made to travel to the silicon substrate 1 with efficiency. In order to achieve efficient travel of electrons or holes, management of electrons or holes generating in the photoelectric conversion layer 123 becomes an issue.

The imaging device 200 shown in Fig. 2 incorporates the photoelectric conversion layer 123 having the properties specified above, and therefore allows an increase in external quantum efficiency, as mentioned above, by collecting holes into the first electrode film 11 opposite to the electrode on the incident light side and utilizing them, as a result, enhancing the sensitivity and narrowing the spectral sensitivity range become possible. In the imaging device 200, a voltage is therefore applied between the first electrode film 11 and the second electrode film 13 so that the electrons generating in the photoelectric conversion layer 123 are transferred to the second electrode film 13 and the holes generating in the photoelectric conversion layer 123 are transferred to the first electrode film 11.

One function of the undercoat-cum-electron blocking layer 122 is lessening asperities

on the first electrode film 11. When the first electrode film 11 has asperities on the surface or dust adhering to the surface and thereonto a low molecular organic compound is evaporated and made into the photoelectric conversion layer 123, fine cracks tends to be produced in portions of the photoelectric conversion layer 123 which are in contact with the asperities or dust. In other words, only portions where the photoelectric conversion layer 123 is reduced in thickness tend to be produced. Herein, when the second electrode film 13 is further formed on the photoelectric conversion layer, the crack portions are covered with the second electrode film 13 and bring about proximity to the first electrode film 11. Thus DC short and an increase in leak current tend to occur. When TCO in particular is used as the second electrode film 13, such a tendency becomes pronounced. Therefore the undercoat-cum-electron blocking layer 122 is in advance provided on the first electrode film 11, and thereby influences of the asperities are lessened and the foregoing phenomena can be inhibited from occurring.

It is important for the undercoat-cum-electron blocking layer to be a homogeneous-and-smooth film. Examples of a material suitable for formation of a smooth film in particular include organic high polymer materials such as polyaniline, polythiphene, polypyrrole, polycarbazole, PTPDES and PTPDEK, and the film can be formed also by a spin coating method.

The electron blocking layer 122 is provided for the purpose of reducing dark current produced by injection of electrons from the first electrode film 11, and inhibits injection of electrons from the first electrode film 11 into the photoelectric conversion layer 123.

The hole blocking-cum-buffer layer 125 is provided as a hole blocking layer for the purpose of reducing dark current produced by injection of holes from the second electrode film 13, and not only performs a function of inhibiting the injection of holes from the second electrode film 13 into the photoelectric conversion layer 123, but also in some cases performs a function of lessening damage inflicted on the photoelectric conversion layer 123 at the time of formation of the second electrode film 13.

When the second electrode film 13 is formed as an upper layer of the photoelectric conversion layer 123, there may be cases where high-energy particles present in apparatus used for formation of the second electrode film 13, such as sputtered particles, secondary electrons, Ar particles and oxygen anions, in the case of adopting e.g. a sputtering method, come into collision with the photoelectric conversion layer 123, and thereby the photoelectric conversion layer 123 alters its quality and performance degradation, such as an increase in leak current and a drop in sensitivity, are caused. As a method for preventing such cases, a method of providing a buffer layer 125 on the photoelectric conversion layer 123 can be

preferably adopted.

Getting back to Fig. 2, a p-type semiconductor region (hereafter abbreviated as a p region) 4, an n-type semiconductor region (hereafter abbreviated as an n region) 3 and a p region 2 are formed in an n-type silicon substrate 1 in the order of increasing depth. In the portion of the surface part of the p region 4 which is shielded from light by a light-shielding film 14, a high-density p region (referred to as a p^+ region) 6 is formed, and the p^+ region 6 is surrounded by an n region 5.

The depth of the pn-junction face between the p region 4 and the n region 3 from the surface of the n-type silicon substrate 1 is adjusted to a depth (about 0.2 μm) allowing absorption of blue light. Therefore the p region 4 and the n region 3 absorb blue light and produce holes responsive to the light absorbed, and forms a photodiode (B photodiode) accumulating the holes. Holes produced in the B photodiode are stored in the p region 4.

The depth of the pn-junction face between the p region 2 and the silicon substrate 1 from the surface of the n-type silicon substrate is adjusted to a depth (about 2 μm) allowing absorption of red light. Therefore the p region 2 and the n-type silicon substrate 1 absorb red light and produce holes responsive to the light absorbed, and forms a photodiode (R photodiode) accumulating the holes. Holes produced in the R photodiode are accumulated in the p region 2.

The p^+ region 6 is connected electrically to the first electrode film 11 via a connection section 9 formed in an aperture bored in the insulating film 7, and accumulates holes collected in the first electrode film11 via the connection section 9. The connection section 9 is electrically insulated from its surroundings other than the first electrode film 11 and the p^+ region 6 by an insulating film 8.

The holes accumulated in the p region 2 are converted into signals responsive to the amount of their charges by means of a MOS circuit (not shown in the diagram) made up of p-channel MOS transistors formed in the n-type silicon substrate 1, the holes accumulated in the p region 4 are converted into signals responsive to the amount of their charges by means of a MOS circuit (not shown in the diagram) made up of p-channel MOS transistors formed in the n region 3, the electrons accumulated in the p^+ region 6 are converted into signals responsive to the amount of their charges by means of a MOS circuit (not shown in the diagram) made up of p-channel MOS transistors formed in the n region 5, and these signals are output to the outside of the imaging device 200. These MOS circuits make up a signal read-out section. Additionally, each MOS circuit is connected to a signal read-out pad (not shown in the diagram) by wiring 10. Additionally, the p region 2 and the p region 4 are

provided with extraction electrodes. When specified reset potentials are given to these electrodes, each region is brought into a depleted state and the capacitance of each pn-junction is minimized. Thus the capacitance generating on the junction faces can be made minuscule.

By designing the device to have such makeup, it becomes possible to perform photoelectric conversion of G light in e.g. the photoelectric conversion layer 123, and further to perform photoelectric conversions of B light and R light in the B photodiode and the R photodiode, respectively, formed in the n-type silicon substrate. In addition, the device can deliver excellent color separation between B light and G light and that between G light and R light because G light is absorbed first in the upper part of the device. This is a far superior point as compared with a solid-state imaging device of the type that three photodiodes (PDs) are stacked on top of each other inside the silicon substrate and all separations between B light, G light and R light are performed inside the silicon substrate. In the following explanation, the sections performing photoelectric conversion (the B photodiode and the R photodiode) which are formed from inorganic materials inside the n-type silicon substrate 1 of the solid-state imaging device 200 are also referred to as inorganic layers.

Alternatively, between the n-type silicon substrate 1 and the first electrode film 11 (e.g. in between the insulating film 7 and the n-type silicon substrate 1), it is possible to form an inorganic photoelectric conversion section made up of inorganic materials allowing absorption of light having passed through the photoelectric conversion layer 123, production of charges responsive to the light and accumulation of these charges. In this case, it is essential only that a MOS circuit for readout of signals responsive to charges accumulated in the charge accumulation region of the inorganic photoelectric conversion section be provided inside the n-type silicon substrate 1 and wiring 10 be connected to this MOS circuit too.

The first electrode film 11 has a function of collecting holes which have generated in the photoelectric conversion layer 123 and have accomplished the travel to the electrode film 11. The first electrode film 11 is divided on a pixel basis, and thereby image data can be produced. According to the makeup shown in Fig. 2, photoelectric conversion is also performed in the n-type silicon substrate 1, and it is therefore appropriate that the first electrode film 11 has a visible-light transmittance of 60% or above, preferably 90% or above. In the case of a device having such makeup that no photoelectric conversion region is present in the lower part of the first electrode film 11, the first electrode film 11 may be low in transparency. Any of ITO, IZO, ZnO_2, SnO_2, TiO_2, FTO, Al, Ag and Au can be used optimally for the first electrode film 11. Details of the first electrode film 11 are described later.

The second electrode film 13 has a function of discharging electrons which have

generated in the photoelectric conversion layer 123 and have accomplished the travel to the electrode film 13. The second electrode film 13 can be shared among all the pixels. In the imaging device 200, the second electrode film 13 is therefore a film of single-sheet form to be shared among all the pixels. Because it is necessary to allow the incident light to reach into the photoelectric conversion layer 123, the second electrode film 13 is required to be formed by use of a material highly pervious to visible light. It is therefore appropriate that he visible-light transmittance of the second electrode film 13 be 60% or above, preferably 90% or above. A material used optimally for the second electrode film 13 may be any of ITO, IZO, ZnO_2, SnO_2, TiO_2, FTO, Al, Ag and Au. Details of the second electrode film 13 are described later.

As to the inorganic layers, pn junctions or pin junctions formed from crystal silicon, amorphous silicon and compound semiconductors including GaAs are generally used. In these cases, the spectrum range detected by each of light-receptive sections stacked on top of each other becomes broad because color separation is done according to the traveling depth of light inside the silicon substrate. However, by the use of the photoelectric conversion layer 123 as an upper layer as shown in Fig. 2, namely by detecting the light having passed through the photoelectric conversion layer 123 in the depth direction of the silicon substrate, color separation can be significantly improved. In the special case as shown in Fig. 2, where G light is detected by the photoelectric conversion layer 123, the light having passed through the photoelectric conversion layer 123 includes B light and R light, and separation of light in the depth direction of the silicon substrate is therefore required to be done only between B light and R light. Thus, improved color separation is achieved. Even when the photoelectric conversion layer 123 detects either B light or R light, color separation can be markedly improved by properly selecting the depth of each pn junction face in the silicon substrate.

Viewed from the light incidence side, the configuration of inorganic layers is preferably npn or pnpn. And the pnpn junction is far preferred because keeping the surface at a high potential in particular by forming a p layer in the surface allows trapping holes and dark current generating in the vicinity of the surface, and thereby dark current can be reduced.

Although Fig. 2 shows a structure that one photoelectric conversion section is laid above the n-type silicon substrate 1, the device can also have a structure that two or more photoelectric conversion sections are stacked on top of each other in layers above the n-type silicon substrate 1. Explanation of the structure having two or more photoelectric conversion sections stacked on top of each other in layers is given in the description of another embodiment of the invention. In such a case, the light detected by the inorganic layer may be light of one color, and satisfactory color separation can be achieved. In another case where it

is intended to detect light of four colors by one pixel of the imaging device 200, it is possible to conceive e.g. (1) a structure that light of one color is detected by one photoelectric conversion section and light of three colors is detected by three inorganic layers, (2) a structure that two photoelectric conversion sections are stacked on top of each other in two layers and detect light of two colors, while inorganic layers detect light of the other two colors, and (3) a structure that three photoelectric conversion sections are stacked on top of each other in three layers and detect light of three colors, while an inorganic layer detects light of the other color. On the other hand, the imaging device 200 may have a structure allowing detection of light of one color alone by one pixel. The structure in this case corresponds to one which has neither the p region 2, nor the n region 3, nor the p region 4 in the diagram shown in Fig. 2.

Now, the inorganic layers are described in more detail. Examples of a suitable structure of inorganic layers include not only the structures of photoreceptors of photoconductive type, p-n junction type, Shottky junction type, PIN junction type and MSM (metal-semiconductor-metal) type but also the structure of a photoreceptor of phototransistor type. As shown in Fig. 2, it is particularly suitable to use inorganic layers formed by alternately stacking first and second conductive regions in layers, wherein the first conductive region is opposite in conductive type to the second one, inside the single semiconductor substrate and creating each junction face between the first and second conductive regions at a depth suitable for photoelectric conversion of light with wavelengths included mainly in any of different wavelength bands. As the single semiconductor substrate, single-crystal silicon is suitable, and color separation can be achieved by utilizing the absorption wavelength characteristic depending on the depth direction of a silicon plate.

As inorganic semiconductors, those of InGaN type, InAlN type, InAlP type or InGaAlP type can also be used. The semiconductors of InGaN type are designed to have their respective absorption maxima within the wavelength range of blue light by changing their In contents as appropriate. In other words, their compositions are expressed in the formula of $In_xGa_{1-x}N$ ($0 \leq X < 1$). These compound semiconductors are produced by using a metal-organic chemical-vapor deposition method (MOCVD method). The nitride semiconductors of InAlN type which incorporate Al belonging to the same group 13 as Ga can also be utilized as shortwave photoreceptors as in the case of the semiconductors of InGaN type. Alternatively, it is possible to use InAlP and InGaAlP having a lattice match to a GaAs substrate.

Each inorganic semiconductor may be formed into an embedded structure. The term "embedded structure" refers to the structure that both ends of a shortwave photoreceptor

portion are covered with a semiconductor different from those used in the shortwave photoreceptor. The semiconductor covering the both ends is preferably a semiconductor having a band-gap wavelength equal to or shorter than the band-gap wavelength of the shortwave photoreceptor.

Materials which can be used for the first electrode film 11 and the second electrode film 13 are e.g. metals, alloys, metal oxides, electrically conductive compounds, or various mixtures of these substances. Examples of a usable metallic substance include arbitrary combinations of elements chosen from Li, Na, Mg, K, Ca, Rb, Sr, Cs, Ba, Fr, Ra, Sc, Ti, Y, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, Sb, Bi, Se, Te, Po, Br, I, At, B, C, N, F, O, S and N. Examples of a metallic substance especially suitable for use include Al, Pt, W, Au, Ag, Ta, Cu, Cr, Mo, Ti, Ni, Pd and Zn.

The first electrode film 11 extracts holes from a hole-transportable photoelectric conversion layer included in the intermediate layer 12 or a hole transporting layer and collects them, and therefore it is selected with consideration given to adhesion to adjacent layers such as the hole-transportable photoelectric conversion layer and the hole transporting layer, electron affinity, ionization potential, stability and so on. On the other hand, the second electrode film 13 extracts electrons from an electron-transportable photoelectric conversion layer included in the intermediate layer 12 or an electron transporting layer and discharges them, and therefore it is selected with consideration given to adhesion to adjacent layers such as the electron-transportable photoelectric conversion layer and the electron transporting layer, electron affinity, ionization potential, stability and so on. Examples of materials for such films include conductive metal oxides such as tin oxide, zinc oxide, indium oxide and indium tin oxide (ITO), metals such as gold, silver, chromium and nickel, mixtures or laminates of these metals and conductive metal oxides, inorganic conductive substances such as copper iodide and copper sulfide, organic conductive materials such as polyaniline, polythiophene and polypyrrole, silicon compounds, and laminates of silicon compounds and ITO. Of these materials, conductive metal oxides are preferable to the others, and ITO and IZO in particular are used to advantage in terms of productivity, high conductivity and transparency.

For making electrodes, various methods are adopted according to materials used. In the case of ITO, for example, film formation can be performed using an electron-beam method, a sputtering method, a resistance-heating evaporation method, a chemical reaction method (sol-gel method), or a method of coating a dispersion of indium tin oxide. In the case of ITO, it is possible to give UV-ozone treatment or plasma treatment to the ITO film formed.

Conditions at the time of formation of a transparent electrode film are mentioned

below. The temperature of a silicon substrate at the time of formation of a transparent electrode film is preferably 500°C or below, far preferably 300°C or below, further preferably 200°C or below, still further preferably 150°C or below. In addition, introduction of gas may be carried out during the formation of a transparent electrode film. The species of the gas introduced is not limited to particular ones, but any of Ar, He, oxygen, nitrogen and the like may be introduced. Alternatively, a mixture of these gases may be used. In the case of an oxide material in particular, the film formed often develops oxygen defects, and therefore introduction of oxygen is appropriate.

The suitable range of surface resistance of a transparent electrode film differs according to whether the transparent electrode film is used for the first electrode film 11 or the second electrode film 13. When the signal read-out section has a CMOS structure, the surface resistance of the transparent electrode film is preferably 10,000 Ω/□ or below, far preferably 1,000 Ω/□ or below. Even when the signal read-out section has a CCD structure, the surface resistance is preferably 1,000 Ω/□ or below, far preferably 100 Ω/□ or below. On the other hand, the surface resistance of a transparent electrode film used as the second electrode film 13 is preferably 1,000,000 Ω/□ or below, far preferably 100,000 Ω/□ or below.

The material especially suitable as the material of a transparent electrode film is any of ITO, IZO, SnO_2, ATO (antimony-doped tin oxide), ZnO, AZO (Al-doped zinc oxide), GZO (gallium-doped zinc oxide), TiO_2 and FTO (fluorine-doped tin oxide).

The light transmittance of a transparent electrode film is preferably 60% or above, far preferably 80% or above, further preferably 90% or above, still further preferably 95% or above, at the absorption peak wavelength of a photoelectric conversion film incorporated into the photoelectric conversion section including the transparent electrode film.

When more than one intermediate layer 12 is stacked, a first electrode film 11 and a second electrode film 13 included in each intermediate layer 12 are required to allow passage of light with wavelengths other than those of light detected by the photoelectric conversion layer included in the intermediate layer concerned, irrespective of whether the photoelectric conversion layer lies at the position near to or far from the light incidence side, and therefore it is appropriate to use materials capable of transmitting 90% or more, preferably 95%or more of visible light incident thereon as the materials for the electrode films.

The second electrode film 13 is preferably formed under a plasma-free condition. By forming the second electrode film 13 under a plasma-free condition, plasma's influences upon the substrate can be reduced, and thereby photoelectric conversion characteristics can be made better. The term "plasma-free condition" as used herein means a condition that no

plasma generates during formation of the second electrode film 13 or a condition that the distance between the plasma source and the substrate is 2 cm or above, preferably 10 cm or above, far preferably 20 cm or above, and thereby the quantity of plasma reaching to the substrate is reduced.

As to the apparatus generating no plasma during formation of the second electrode film 13, there are e.g. electron-beam evaporation apparatus (EB evaporation apparatus) and pulse-laser evaporation apparatus. Examples of the electron-beam evaporation apparatus and the pulse-laser evaporation apparatus which can be used include those described e.g. in a book issued under the editorship of Sawada Yutaka, entitled "Toumei Dendoumaku no Shin-Tenkai" (by CMC publishing Co. Ltd. in 1999), a book issued under the editorship of Sawada Yutaka, entitled "Toumei Dendoumaku no Shin-Tenkai II" (by CMC Publishing Co., Ltd. in 2002), a book edited by Nippon Gakujutsu Shinkoukai (Japan Society for the Promotion of Science), entitled "Toumei Dendoumaku no Gijutsu" (and published by Ohmsha Ltd. in 1999), and references appended to those books. Hereafter, the method of forming a transparent electrode film by means of EB evaporation apparatus is referred to as the EV evaporation method, and the method of forming a transparent electrode film by means of pulse-laser evaporation apparatus is referred to as the pulse-laser evaporation method.

As the apparatus capable of achieving a condition that the distance between a plasma source and a substrate is 2 cm or above and the quantity of plasma reaching to the substrate is reduced (hereinafter referred to as plasma-free film-forming apparatus), it is possible to think of e.g. sputtering apparatus of opposed-target type and arc plasma evaporation apparatus. Examples of such apparatus include those described e.g. in a book issued under the editorship of Sawada Yutaka, entitled "Toumei Dendoumaku no Shin-Tenkai" (by CMC Publishing Co. Ltd. in 1999), a book issued under the editorship of Sawada Yutaka, entitled "Toumei Dendoumaku no Shin-Tenkai II" (by CMC publishing Co., Ltd. in 2002), a book edited by Nippon Gakujutsu Shinkoukai (Japan Society for the Promotion of Science), entitled "Toumei Dendoumaku no Gijutsu" (and published by Ohmsha Ltd. in 1999), and references appended to those books.

When a transparent conductive film such as a TCO film is used as the second electrode film 13, there may be cases where DC short or an increase in leak current occurs. It is thought to be one of causes for such cases that fine cracks brought in the photoelectric conversion layer 123 are covered by a dense film such as TCO film to result in an increase of conduction between the second electrode film 13 and the first electrode film 11 provided on opposite sides of the photoelectric conversion layer. Therefore, in an electrode such as Al film which is inferior to TCO in film quality, it is not easy to cause an increase in leak current.

By controlling the thickness of the second electrode film 13 with respect to the thickness of the photoelectric conversion layer 123 (or the depth of cracks), an increase in leak current can be greatly suppressed. It is appropriate that the thickness of the second electrode film 13 be adjusted to at most one-fifth, preferably one-tenth, of the thickness of the photoelectric conversion layer 123.

Although a steep increase in resistance is generally caused by a reduction in thickness of a conductive film beyond a certain range, preferred sheet resistance in the solid-state imaging device 200 according to an embodiment of the invention may fall within a range of 100 Ω/□ to 10,000 Ω/□, and therefore the device has a lot of latitude in reducing the film thickness. And the thinner the thickness of a transparent conductive film, the smaller the quantity of light absorbed by the film, generally resulting in a light-transmittance increase. The light-transmittance increase is highly advantageous because it can bring about an increase in light absorption by the photoelectric conversion layer 123 and an increase in photoelectric conversion power. Considering the leak-current reduction, the film-resistance increase and the transmittance increase which are associated with the film-thickness reduction, the thickness of a transparent conductive film is preferably from 5 nm to 100 nm, far preferably from 5 nm to 20 nm.

The materials suitable for transparent electrode films are materials which can be formed into films by means of plasma-free film-forming apparatus, EB evaporation apparatus or pulse-laser evaporation apparatus. Such materials are preferably metals, alloys, metal oxides, metal nitrides, metal borides, organic conductive compounds or mixtures of two or more thereof. Examples of these materials include conductive metal oxides such as tin oxide, zinc oxide, indium oxide, indium zinc oxide (IZO), indium tin oxide (ITO) and indium wolfram oxide (IWO), metal nitride such as titanium nitride, metals such as gold, platinum, silver, chromium, nickel and aluminum, mixtures or laminates of these metals and conductive metal oxides, inorganic conductive substances such as copper iodide and copper sulfide, organic conductive materials such as polyaniline, polythiophene and polypyrrole, and laminates of these conductive materials and ITO. In addition, the materials described in detail in a book issued under the editorship of Sawada Yutaka, entitled "Toumei Dendoumaku no Shin-Tenkai" (by CMC Publishing Co. Ltd. in 1999), a book issued under the editorship of Sawada Yutaka, entitled "Toumei Dendoumaku no Shin-Tenkai II" (by CMC publishing Co., Ltd. in 2002), a book edited by Nippon Gakujutsu Shinkoukai (Japan Society for the Promotion of Science), entitled "Toumei Dendoumaku no Gijutsu" (and published by Ohmsha Ltd. in 1999), and so on may also be used.

Figure 4 is a schematic cross-sectional diagram of an imaging device relating to a third embodiment of the invention. While the imaging device according to the embodiment shown in Fig. 2 is configured to have two photodiodes stacked on top of each other in layers inside the silicon substrate, the imaging device according to this embodiment differs in a point that it is configured to have two photodiodes juxtaposed in a state of keeping them separated in a horizontal direction parallel to the surface of a semiconductor substrate.

One pixel of this imaging device 300 is configured to include an n-type silicon substrate 17 and a photoelectric conversion section composed of a first electrode film 30 formed above the n-type silicon substrate 17, an intermediate layer 31 formed on the first electrode film 30 and a second electrode film 32 formed on the intermediate layer 31. On the photoelectric conversion section, a light-shielding film 34 having apertures is formed, and thereby the light-receiving region of the intermediate layer 31 is limited. Further, a transparent insulating film 33 is formed on the light-shielding film 34.

Compositions of the first electrode film 30, the intermediate layer 31 and the second electrode film 32 are the same as those of the first electrode film 11, the intermediate layer 12 and the second electrode film 13, respectively, which are described in explanations of Fig. 1.

In surface portions of the n-type silicon substrate 17 which are situated underneath apertures of the light-shielding film 34, a photodiode made up of an n region 19 and a p region 18 and a photodiode made up of an n region 21 and a p region 20 are formed side by side. Any direction on the surface of the n-type silicon substrate 17 is perpendicular to the incoming direction of incident light.

A color filter 28 pervious to B light is formed above the photodiode made up of the n region 19 and the p region 18 via a transparent insulating film 24, and thereon the first electrode film 30 is formed. And a color filter 29 pervious to R light is formed above the photodiode made up of the n region 21 and the p region 20 via the transparent insulating film 24, and thereon the first electrode film 30 is formed. The periphery of the color filter 28 and that of the color filter 29 are covered with a transparent insulating film 25.

The photodiode made up of the n region 19 and the p region 18 absorbs B light having passed through the color filter 28, and produces holes responsive to the absorbed B light. The holes produced are accumulated in the p region 18. On the other hand, the photodiode made up of the n region 21 and the p region 20 absorbs R light having passed through the color filter 29, and produces holes responsive to the absorbed R light. The holes produced are accumulated in the p region 20.

In a portion of the n-type silicon substrate 17 surface which is shaded from light with the light-shielding film 34, a p^+ region 23 is formed, and the the p+ region is surrounded by an

n region 22. The p^+ region 23 is connected electrically to the first electrode film 30 via a connection section 27 formed in an aperture bored in the insulating films 24 and 25, and accumulates holes collected in the first electrode film30 via the connection section 27. The connection section 27 is electrically insulated from its surroundings other than the first electrode film 30 and the p^+ region 23 by an insulating film 26.

The holes accumulated in the p region 18 are converted into signals responsive to the amount of their charges by means of a MOS circuit (not shown in the diagram) made up of p-channel MOS transistors formed in the n-type silicon substrate 17, the holes accumulated in the p region 20 are converted into signals responsive to the amount of their charges by means of a MOS circuit (not shown in the diagram) made up of p-channel MOS transistors formed in the n-type silicon substrate 17, the holes accumulated in the p^+ region 23 are converted into signals responsive to the amount of their charges by means of a MOS circuit (not shown in the diagram) made up of p-channel MOS transistors formed in the n region 22, and all of these signals are output to the outside of the imaging device 300. Those MOS circuits make up a signal read-out section. Each MOS circuit is connected to a signal read-out pad (not shown in the diagram) by wiring 35.

Alternatively, the signal read-out section may be made up of CCDs and amplifiers, not MOS circuits. To be more specific, the signal read-out section may be configured to read holes accumulated in the p region 18, the p region 20 and the p^+ region 23 into CCDs formed inside the n-type silicon substrate, transfer the holes to amplifiers with the CCDs, and output signals responsive to the holes from the amplifiers. The signal read-out section may have either CCD structure or CMOS structure, but the CMOS structure is preferred in terms of power consumption, high-speed readout, pixel addition, partial readout and so on.

Although color separation between R light and B light is performed by the color filters 28 and 29 in the device shown in Fig. 4, the device needn't be provided with the color filters 28 and 29, but may be configured to adjust appropriately the depth of a pn-junction face between the p region 20 and the n region 21 and that between the p region 18 and the n region 19 and absorb R light and B light by the photodiodes, respectively. In this case, it is possible to form between the n-type silicon substrate 17 and the first electrode film 30 (e.g. in between the insulating film 24 and the n-type silicon substrate 17) an inorganic photoelectric conversion section made up of inorganic materials allowing absorption of light having passed through the intermediate layer 31, production of charges responsive to the light and accumulation of the charges. In this case, it is essential only that a MOS circuit for readout of signals responsive to charges accumulated in the charge accumulation region of the inorganic photoelectric conversion section is provided inside the n-type silicon substrate 17

and wiring 35 be connected to this MOS circuit also.

In another case, the device may have a structure that one photodiode is provided inside the n-type silicon substrate 17 and two or more photoelectric conversion sections are stacked on top of each other in layers above the n-type silicon substrate 17. In still another case, the device may have a structure that two or more photodiodes are provided inside the n-type silicon substrate 17, and besides, two or more photoelectric conversion sections are stacked on top of each other in layers above the n-type silicon substrate 17. On the other hand, unless formation of color images is required, the device may have a structure that one photodiode is provided inside the n-type silicon substrate 17 and only one photoelectric conversion section is stacked in a layer.

Figure 5 is a schematic cross-sectional diagram showing a one-pixel portion of imaging device relating to a fourth embodiment of the invention. While the photodiodes for photoelectric conversion are provided inside the semiconductor substrate according to the embodiments explained using Fig. 2 and Fig. 4, the device in the present embodiment has a structure that only a signal read-out circuit is provided inside the semiconductor substrate and three photoelectric conversion layers, namely a photoelectric conversion layer for detection of R light, a photoelectric conversion layer for detection of G light and a photoelectric conversion layer for detection of B light, are stacked on top of each other above the semiconductor substrate.

More specifically, the imaging device 400 shown in Fig. 5 has a structure that, above a silicon substrate 41, a R photoelectric conversion section including: a first electrode film 56; an intermediate layer 57 stacked on the first electrode film 56; and a second electrode film 58 stacked on the intermediate layer 57, a B photoelectric conversion section including: a first electrode film 60; an intermediate layer 61 stacked on the first electrode film 60; and a second electrode film 62 stacked on the intermediate layer 61 in a layer, and a G photoelectric conversion section including: a first electrode film 64; an intermediate layer 65 stacked on the first electrode film 64; and a second electrode film 66 stacked on the intermediate layer 65 in a layer, are stacked in order of mention in a state that each first electrode film faces on the side of the silicon substrate 41.

On the silicon substrate 41, a transparent insulating film 48 is formed, and thereon the R photoelectric conversion section is formed. Further thereon, a transparent insulating film 59 is formed. Still further thereon, the B photoelectric conversion section is formed. On this section, a transparent insulating film 63 is formed. On the film 63, the G photoelectric conversion section is formed, and thereon a light-shielding film 68 having apertures is formed. On the light-shielding film 68, a transparent insulating film 67 is formed.

Compositions of the first electrode film 64, the intermediate layer 65 and the second electrode film 66 included in the G photoelectric conversion section are the same as those of the first electrode film 11, the intermediate layer 12 and the second electrode film 13, respectively, which are described in the explanations of Fig. 2. Likewise, compositions of the first electrode film 60, the intermediate layer 61 and the second electrode film 62 included in the B photoelectric conversion section are the same as those of the first electrode film 11, the intermediate layer 12 and the second electrode film 13, respectively, which are described in the explanations of Fig. 2, and compositions of the first electrode film 56, the intermediate layer 57 and the second electrode film 58 included in the R photoelectric conversion section are the same as those of the first electrode film 11, the intermediate layer 12 and the second electrode film 13, respectively, which are described in the explanations of Fig. 2.

However, a photoelectric conversion layer incorporated into the B photoelectric conversion section uses a material capable of absorbing blue light and producing electrons and holes responsive to the light absorbed thereby, and a photoelectric conversion layer incorporated into the R photoelectric conversion section uses a material capable of absorbing red light and producing electrons and holes responsive to the light absorbed thereby.

As to electron and hole blocking layers incorporated into each of the intermediate layers 61 and 57, it is appropriate that ingredients and a composition of each blocking layer be selected properly so as not to create an energy barrier to transport of signal charges in relations between HOMO and LUMO energy levels of a photoelectric conversion film in each intermediate layer and HOMO and LUMO energy levels of each blocking layer adjoining the photoelectric conversion film in each intermediate layer.

In a portion of the silicon substrate 41 surface which is shaded from light with the light-shielding film 68, p^+ regions 43, 45 and 47 are formed, and they surrounded by n regions 42, 44 and 46, respectively. The p^+ region 43 is connected electrically to the first electrode film 56 via a connection section 54 formed in an aperture bored in the insulating films 48, and accumulates holes collected in the first electrode film56 via the connection section 54. The connection section 54 is electrically insulated from its surroundings other than the first electrode film 56 and the p^+ region 43 by an insulating film 51.

The p^+ region 45 is connected electrically to the first electrode film 60 via a connection section 53 formed in an aperture bored in the insulating films 48, the R photoelectric conversion section and the insulating film 59, and accumulates holes collected in the first electrode film 60 via the connection section 53. The connection section 53 is electrically insulated from its surroundings other than the first electrode film 60 and the p^+ region 45 by an insulating film 50.

The p^+ region 47 is connected electrically to the first electrode film 64 via a connection section 52 formed in an aperture bored in the insulating films 48, the R photoelectric conversion section, the insulating film 59, the B photoelectric conversion section and the insulating film 63, and accumulates holes collected in the first electrode film 64 via the connection section 52. The connection section 52 is electrically insulated from its surroundings other than the first electrode film 64 and the p^+ region 47 by an insulating film 49.

The holes accumulated in the p^+ region 43 are converted into signals responsive to the amount of their charges by means of a MOS circuit (not shown in the diagram) made up of p-channel MOS transistors formed in the n region 42, the holes accumulated in the p^+ region 45 are converted into signals responsive to the amount of their charges by means of a MOS circuit (not shown in the diagram) made up of p-channel MOS transistors formed in the n region 44, the holes accumulated in the p^+ region 47 are converted into signals responsive to the amount of their charges by means of a MOS circuit (not shown in the diagram) made up of p-channel MOS transistors formed in the n region 46, and all of these signals are output to the outside of the imaging device 400. Those MOS circuits make up a signal read-out section. Each MOS circuit is connected to a signal read-out pad (not shown in the diagram) by wiring 55. Alternatively, the signal read-out section may be made up of CCDs and amplifiers as mentioned above.

On the other hand, it is also possible to form between the n-type silicon substrate 41 and the first electrode film 56 (e.g. in between the insulating film 48 and the silicon substrate 41) an inorganic photoelectric conversion section made up of inorganic materials allowing reception of light having passed through the intermediate layers 57, 61 and 65, production of charges in response to the received light and accumulation of these charges. In this case, it is essential only that a MOS circuit for readout of signals responsive to charges accumulated in the charge accumulation region of the inorganic photoelectric conversion section is provided inside the silicon substrate 41 and wiring 55 is connected to this MOS circuit.

In the above explanations, the term "B light-absorbing photoelectric conversion layer" refers to the layer which can absorb at least light of wavelengths in a range of 400 nm to 500 nm and preferably has an absorption factor of 50% or above at the peak wavelength in such a wavelength range, the term "G light-absorbing photoelectric conversion layer" refers to the layer which can absorb at least light of wavelengths in a range of 500 nm to 600 nm and preferably has an absorption factor of 50% or above at the peak wavelength in such a wavelength range, and the term "R light-absorbing photoelectric conversion layer" refers to the layer which can absorb at least light of wavelengths in a range of 600 nm to 700 nm and

preferably has an absorption factor of 50% or above at the peak wavelength in such a wavelength range.

In the present embodiment, three photoelectric conversion layers are provided. The colors of light detected by these photoelectric conversion layers, respectively, are in no particular order. Viewed from the incident light side (upper layer side), a pattern of detecting the colors in order of BGR, BRG, GBR, GRB, RBG or RGB is thinkable. Of these patterns, those in which G detection occurs in the uppermost layer are preferable to the others. In the embodiment shown in Fig. 4, on the other hand, it is possible to adopt a combination of the upper layer of an R layer and the lower layer formed by juxtaposing B and G layers on the same plane, a combination of the upper layer of a B layer and the lower layer formed by juxtaposing G and R layers on the same plane, or a combination of the upper layer of a G layer and the lower layer formed by juxtaposing B and R layers on the same plane. Of these combinations, a combination of the upper layer of a G layer and the lower layer formed by juxtaposing B and R layers on the same plane is preferable to the others.

Figure 6 is a schematic cross-sectional diagram of an imaging device 500 in a fifth embodiment of the invention. In Fig. 6, the cross-sectional view of two pixel portions in a pixel region where light is detected and charges are accumulated, the wiring connected to electrodes in the pixel region and the cross-sectional view of a peripheral circuit region wherein a bonding pad connected to such wiring is formed are illustrated together.

In a surface part of the n-type silicon substrate 413 in the pixel region, a p region 421 is formed, and an n region 422 is formed in a surface part of the p-region 421. In a surface part of the n region 422, a p region 423 is formed. Further, n regions each of which is numbered "424" are formed in a surface part of the p region 423.

The p region 421 accumulates holes of the red (R) component photoelectrically converted by the pn junction with the n-type silicon substrate 413. A change caused in potential of the p region 421 by accumulation of holes of the R component is read into a signal read-out pad 427 from a MOS transistor 426 forming inside the n-type silicon substrate 413 via metal wiring 419 connecting them.

The p region 423 accumulates holes of the blue (B) component photoelectrically converted by the pn junction with the n region 422. A change caused in potential of the p region 423 by accumulation of holes of the B component is read into the signal read-out pad 427 from a MOS transistor 426' formed inside the n region 422 via the metal wiring 419 connecting them.

Inside the n region 424 is formed a hole accumulation region 425 including a p region accumulating holes of the green (G) component generating in the photoelectric conversion

layer 123 stacked above the n-type silicon substrate 413. A change caused in potential of the hole accumulation region 425 by accumulation of holes of the G component is read into the signal read-out pad 427 from a MOS transistor 426" formed inside the n region 424 via the metal wiring 419 connecting them. In ordinary cases, a different signal read-out pad 427 is provided for each of transistors from which the three color components are read, respectively.

The p regions, the n regions, the transistors, the metal wiring and so on being schematically illustrated herein, their respective structures and so on are not limited to those illustrated ones, but optimal ones may be chosen as appropriate. Because B light and R light are separated according to the depth of the silicon substrate, selections of the depths of pn junctions below the silicon substrate surface, concentrations of impurities as dopants and so on are of importance. To a CMOS circuit functioning as a signal read-out section, technologies used for ordinary CMOS image sensors can be applied. Not only low-noise read-out column amplifiers and CDS circuits but also circuit structures allowing reduction in number of transistors in each pixel region can be applied.

On the n-type silicon substrate 413, a transparent insulating film 412 containing silicon oxide, silicon nitride or the like as a main ingredient is formed. On the insulating film 412, a transparent insulating film 411 containing silicon oxide, silicon nitride or the like as a main ingredient is formed. As for the insulating film 412, the thinner its thickness, the better the result obtained. Specifically, the suitable thickness is 5 μm or below, preferably 3 μm or below, far preferably 2 μm or below, further preferably 1 μm or below.

Inside insulating films 411 and 412, a plug 415 is formed which contains e.g. tungsten as a main ingredient and electrically connects the first electrode film 414 to the p region 425 as a hole accumulation region. The plug 415 is in a state of junctional connection via a pad 416 at the interface between the insulating film 411 and the insulating film 412. The pad 416 used therein is preferably one which contains aluminum as a main ingredient. Inside the insulating film 412, the metal wiring 419, gate electrodes of the transistors 426, 426' and 426", and so on are formed too. It is preferable that barrier layers including the metal wiring are provided. The plug 415 is provided on a pixel basis.

Inside the insulating film 411, a light-shielding film 417 is provided for the purpose of prevention of noises resulting from generation of charges by the pn junction between the n region 424 and the p region 425. As the light-shielding film 417, a film containing tungsten, aluminum or the like as a main ingredient is generally used. Inside the insulating film 411, a bonding pad 420 (a pad for power supply from the outside) and a signal read-out pad 427 are formed, and metal wiring (not shown in the diagram) for electrical connection between the

bonding pad 420 and a first electrode film 414 described later is also formed.

A first transparent electrode film 414 is formed on the plug 415 provided for each pixel inside the insulating film 411. The first electrode film is divided according to the number of pixels, and the size of each divided film determines the area of light reception. From the bonding pad 420, a bias is applied to the first electrode 414 via the wiring. It is advantageous to design a structure that holes can be accumulated in the hole accumulation region 425 by giving the first electrode film 414 a negative bias with respect to a second electrode film 405 described later.

On the first electrode film 414, an intermediate layer 12 having the same structure as shown in Fig. 2 is formed, and on this layer a second electrode film 405 is formed.

On the second electrode film 405 is formed a protective film 404 which has a function of protecting the intermediate layer 12 and contains silicon nitride or the like as a main ingredient. In the protective film 404, an aperture is made at a location underneath which the first electrode film 414 is absent in the pixel region. Another aperture is formed in the insulating film 411 and the protective film 404 at a location above a portion of the bonding pad 420. And wiring 418 including aluminum or the like and electrically connecting portions of the second electrode film 405 and the bonding pad 420 which are exposed by those two apertures, through which an electric potential is applied to the second electrode film 405, is formed in the interior of the apertures and on the protective film 404. As a material for the wiring 418, an aluminum-containing alloy such as Al-Si or Al-Cu can also be used.

On the wiring 418 is formed a protective film 403 containing silicon nitride or the like as a main component and allowing protection of the wiring 418, on the protective film 403 is formed an infrared protection multilayer dielectric film 402, and on the infrared protection multilayer dielectric film 402 is formed an antireflective film 401.

The first electrode film 414 performs the same function as the first electrode film 11 shown in Fig. 2 does. And the second electrode film 405 performs the same function as the second electrode film 13 shown in Fig. 2 does.

By making up the device as mentioned above, color imaging through the detection of light of BGR three colors by each pixel becomes possible. According to the makeup shown in Fig. 6, R and B are used as common values in two pixels, and the value of B alone is used in isolation. Because the sensitivity of G becomes important in the formation of images, even such makeup allows formation of color images of good quality.

The imaging devices illustrated above can be applied to digital cameras, video cameras, facsimiles, scanners, copiers and other imaging devices. Further, they are usable as photosensors including biosensors and chemical sensors.

Examples of materials for the insulating films in the explanations for the embodiments of the invention include metal oxides, such as SiOx, SiNx, BSG, PSG, BPSG, Al_2O_3, MgO, GeO, NiO, CaO, BaO, Fe_2O_3, Y_2O_3 and TiO_2, and Metal fluorides such as MgF_2, LiF, AlF_3 and CaF_2. Of these materials, SiOx, SiNx, BSG, PSG and BPSG are preferred over the others.

In each of the embodiments of the invention as shown in Fig. 2, Fig. 4, Fig. 5 and Fig. 6, signal readout, other than that from the photoelectric conversion layer, may be performed using either holes or electrons. More specifically, as mentioned above, the device may be made up so that holes are accumulated in an inorganic photoelectric conversion section provided between the semiconductor substrate and the photoelectric conversion section stacked above the semiconductor substrate or a photodiode formed inside the semiconductor substrate and signals responsive to these holes are read out by the signal read-out section, or it may be made up so that electrons are accumulated in an inorganic photoelectric conversion section and a photodiode formed inside the semiconductor substrate and signals responsive to these electrons are read out by the signal read-out section.

In each of the embodiments of the invention as shown in Fig. 2, Fig. 4, Fig. 5 and Fig. 6, though one which has the structure shown in Fig. 3 is used as the photoelectric conversion section provided above the silicon substrate, it is also possible to use one which has the structure shown in Fig. 1. According to the structure shown in Fig. 3, both electrons and holes can be blocked, and therefore the effect of suppressing dark current becomes high. When the electrode placed on the side opposite to the light incidence side is used as an electrode for collecting electrons, it is essential only that the connection section 9 in Fig. 2 is connected to the second electrode 13 or the connection section 27 in Fig. 4 is connected to the second electrode 13.

Each of the imaging devices 200, 300, 400 and 500 illustrated as embodiments of the invention is configured so that a large number of pixels are arranged in the form of an array on the same plane, and color signals of RGB can be obtained from each pixel therein. Hence each of these pixels can be regarded as a photoelectric conversion device for converting light of RGB into electric signals. Thus each of the imaging devices illustrated as embodiments of the invention can be said to have a structure that each of photoelectric conversion devices as shown in Fig. 2 to Fig. 6 are arranged in large numbers in the form of an array on the same plane.

Fig. 7 and Fig. 8 are explanatory diagrams of an imaging device relating to the sixth embodiment of the invention. Fig. 7 is a schematic diagram depicting a partial surface of the imaging device, and Fig. 8 is a schematic diagram depicting the vertical cross section which

would appear if cut on the X-X line in Fig. 7.

In the imaging device 600 according to an embodiment of the invention, a p well layer 602 is formed on a n-type silicon substrate 601. Hereafter, the combination of the n-type silicon substrate 601 and the p well layer 602 is referred to as the semiconductor substrate. In the row direction and the column direction orthogonal thereto on the same plane above the semiconductor substrate, each of three kinds of color filters, namely color filters 613r pervious mainly to R light, color filters 613g pervious mainly to G light and color filters 613b pervious mainly to B light, are arranged in large numbers.

Materials known to be pervious to R light can be used in the color filter 613r, materials known to be pervious to G light can be used in the color filter 613g, and materials known to be pervious to B light can be used in the color filter 613b.

As an arranging pattern of the color filters 613r, 613g and 613b, arranging patterns of color filters used in known single-plate solid-state imaging devices (such as Bayer pattern, a vertical stripe pattern and a lateral stripe pattern) can be adopted.

A transparent electrode 611r is formed above an n region 604r, a transparent electrode 611g is formed above an n region 604g, and a transparent electrode 611b is formed above an n region 604b. The transparent electrodes 611r, 611g and 611b are kept separated from each other in correspondence with color filters 613f, 613g and 613b, respectively. Each of the transparent electrodes 611r, 611g and 611b has the same function as the lower electrode 11 in Fig. 1 has.

On each of the transparent electrodes 611r, 611g and 611b, a photoelectric conversion film 612 of one-sheet structure is formed and shared with the color filters 613r, 613g and 613b.

On the photoelectric conversion film 612, an upper electrode 613 of one-sheet structure is formed and shared with the color filters 613r, 613g and 613b.

A photoelectric conversion element corresponding to the color filter 613r is formed of the transparent electrode 611r, a portion of the upper electrode 613 which is opposite the electrode 611r and a portion of the photoelectric conversion film 612 which is sandwiched between them. Hereafter, such a photoelectric conversion element is referred to as an R photoelectric conversion device since the element is one which is formed on the semiconductor substrate.

A photoelectric conversion element corresponding to the color filter 613g is formed of the transparent electrode 611g, a portion of the upper electrode 613 which is opposite the electrode 611g and a portion of the photoelectric conversion film 612 which is sandwiched between them. Hereafter, such a photoelectric conversion element is referred to as a G

photoelectric conversion device

A photoelectric conversion element corresponding to the color filter 613b is formed of the transparent electrode 611b, a portion of the upper electrode 613 which is opposite the electrode 611b and a portion of the photoelectric conversion film 612 which is sandwiched between them. Hereafter, such a photoelectric conversion element is referred to as a B photoelectric conversion device.

In an n region inside the p well layer 602, a high-density n-type impurity region (hereafter referred to as "n^+ region") 604r for accumulating charges generated in the photoelectric conversion film 612 of the R photoelectric conversion device is formed. Additionally, it is preferable that a light-shielding film is provided on the n^+ region 604r for the purpose of protecting the n^+ region 604r from light.

In an n region inside the p well layer 602 is formed an n^+ region 604g for accumulating charges generated in the photoelectric conversion film 612 of the G photoelectric conversion device. Additionally, it is preferable that a light-shielding film is provided on the n^+ region 604g for the purpose of protecting the n^+ region 604g from light.

In an n region inside the p well layer 602 is formed an n^+ region 604b for accumulating charges generated in the photoelectric conversion film 612 of the B photoelectric conversion device. Additionally, it is preferable that a light-shielding film is provided on the n^+ region 604b for the purpose of protecting the n^+ region 604b from light.

A contact section 606r including a metal such as aluminum is formed on the n^+ region 604r, and on the contact section 606r the transparent electrode 611r is formed. The n^+ region 604r and the transparent electrode 611r are electrically connected together by the contact section 606r. The contact section 606r is embedded in an insulating layer 605 transparent to visible rays and infrared rays.

A contact section 606g including a metal such as aluminum is formed on the n^+ region 604g, and on the contact section 606g the transparent electrode 611g is formed. The n^+ region 604g and the transparent electrode 611g are electrically connected together by the contact section 606g. The contact section 606g is embedded in the insulating layer 605.

A contact section 606b including a metal such as aluminum is formed on the n^+ region 604b, and on the contact section 606b the transparent electrode 611b is formed. The n^+ region 604b and the transparent electrode 611b are electrically connected together by the contact section 606b. The contact section 606b is embedded in the insulating layer 605.

In a region of the p well layer 602, other than the regions in which the n^+ regions 604r, 604g and 604b are formed, a signal read-out section 605r for reading out each of signals responsive to charges generated in the R photoelectric conversion device and accumulated in

the n^+ region 604r, a signal read-out section 605g for reading out each of signals responsive to charges generated in the G photoelectric conversion device and accumulated in the n^+ region 604g and a signal read-out section 605b for reading out each of signals responsive to charges generated in the B photoelectric conversion device and accumulated in the n^+ region 604b are formed. Each of the signal read-out sections 605r, 605g and 605b can adopt the known makeup using CCD or MOS circuitry. Additionally, it is preferable that a light-shielding film is provided on the signal read-out sections 605r, 605g and 605b for the purpose of protecting these sections from light.

Figure 9 is a diagram showing an example of a specific configuration of the signal read-out section 605r shown in Fig. 8. In Fig. 9, the same constituent members as in Fig. 7 and Fig. 8 are marked with the same reference numerals as in these diagrams. Additionally, since the signal read-out sections 605r, 605g and 605b have the same makeup, explanations of the signal read-out sections 605g and 605b are omitted.

The signal read-out section 605r is equipped with a reset transistor 543 whose drain is connected to the n^+ region 604f and whose source is connected to a power supply Vn, an output transistor 542 whose gate is connected to the drain of the reset transistor 543 and whose source is connected to a power supply Vcc, a row selection transistor 541 whose source is connected to the drain of the output transistor 542 and whose drain is connected to a signal output line 545, a reset transistor 546 whose drain is connected to the n region 603r and whose source is connected to a power supply Vn, an output transistor 547 whose gate is connected to the drain of the reset transistor 546 and whose source is connected to a power supply Vcc, and a row selection transistor 548 whose source is connected to the drain of the output transistor 547 and whose drain is connected to a signal output line 549.

By applying a bias voltage between the transparent electrode 611r and the upper electrode 613, charges are generated in response to light incident on the photoelectric conversion film 612, and these charges move to the n^+ region 604r via the transparent electrode 611r. The charges accumulated in the n^+ region 604r are converted into signals responsive to their amount by the output transistor 542. And by switching the row selection transistor 541 to the on position, the signals are output to the signal output line 545. After output of the signals, charges in the n+ region 604r are reset by the reset transistor 543.

Thus the signal read-out section 605r can be made up of the known MOS circuit including 3 transistors.

Resuming explanations of Fig. 8, a protective layer of double-layer structure, 615 and 616, is formed on the photoelectric conversion layer 612 for the purpose of protecting the photoelectric conversion element, and on the protective layer 616 the color filters 613r, 613g

and 613r are formed.

This imaging device 600 is made by passing through the process of forming the photoelectric conversion film 612 first, then the color filters 613r, 613g and 613b and so on. The process of forming the color filters 613r, 613g and 613b includes a photolithographing step and a baking step. When an organic material is used for the photoelectric conversion film 612 and the photolithographing and baking steps are carried out in a state that the photoelectric conversion film 612 is exposed, properties of the photoelectric conversion film 612 suffer degradation. For the purpose of preventing degradation caused in properties of the photoelectric conversion film 612 by the process of production, the protective layers 615 and 616 are provided.

The protective film 615 is preferably an inorganic layer including an inorganic material and being formed by an ALCVD method. The ALCVD method is an atomic-layer CVD method and allows formation of a dense inorganic layer. Therefore the layer formed can be an effective protective layer for the photoelectric conversion layer 612. The ALCVD method is also known as an ALE method or an ALD method. The composition of an inorganic layer formed by the ALCVD method is preferably Al_2O_3, SiO_2, TiO_2, ZrO_2, MgO, HfO_2 or Ta_2O_5, far preferably Al_2O_3 or SiO_2, especially preferably Al_2O_3.

The protective layer 616 is formed on the protective layer 615 for the purpose of further enhancing the capability of protecting the photoelectric conversion film 612, and it is preferably an organic layer including an organic polymer. The organic polymer is preferably palyrene, far preferably palyrene C. Alternatively, the protective film 616 may be omitted, or the arranging order of the protective film 615 and the protective film 616 may be inverted. The structure shown in Fig. 8 can bring about particularly high effect upon protection of the photoelectric conversion film 612.

When a specified bias voltage is applied between the transparent electrode 611r and the upper electrode 613, charges generated in the photoelectric conversion film 612 incorporated into the R photoelectric conversion device are moved to the n^+ region 604r via the transparent electrode 611r and the contact section 606r, and accumulated in this region. And signals responsive to the charges accumulated in the n^+ region 604r are read out by the signal read-out section 605r, and output to the outside of the imaging device 600.

Likewise, when a specified bias voltage is applied between the transparent electrode 611g and the upper electrode 613, charges generated in the photoelectric conversion film 612 incorporated into the G photoelectric conversion device are moved to the n^+ region 604g via the transparent electrode 611g and the contact section 606g, and accumulated in this region. And signals responsive to the charges accumulated in the n+ region 604g are read out by the

signal read-out section 605g, and output to the outside of the imaging device 600.

Similarly to the above, when a specified bias voltage is applied between the transparent electrode 611b and the upper electrode 613, charges generated in the photoelectric conversion film 612 incorporated into the B photoelectric conversion device are moved to the n^+ region 604b via the transparent electrode 611b and the contact section 606b, and accumulated in this region. And signals responsive to the charges accumulated in the n+ region 604b are read out by the signal read-out section 605b, and output to the outside of the imaging device 600.

In this manner, the signals of the R component responsive to charges generated in the R photoelectric conversion device, the signals of the G component responsive to charges generated in the G photoelectric conversion device and the signals of the B component responsive to charges generated in the B photoelectric conversion device are output from the imaging device 600 to the outside. Thus color images can be obtained. In this mode, the photoelectric conversion section can be made thin, and thereby the resolution can be enhanced and false colors can be reduced. In addition, the aperture rate can be made high regardless of the lower circuitry formed in the semiconductor substrate, and thereby the sensitivity can be achieved, and besides, omission of microlenses becomes possible to have an effect on reduction in parts count.

In accordance with each embodiment of the invention, the organic photoelectric conversion film has its maximum absorption wavelength in a high region of green light and, though it is required to absorb light in the whole visible region, the materials recited above are able to well meet the requirement.

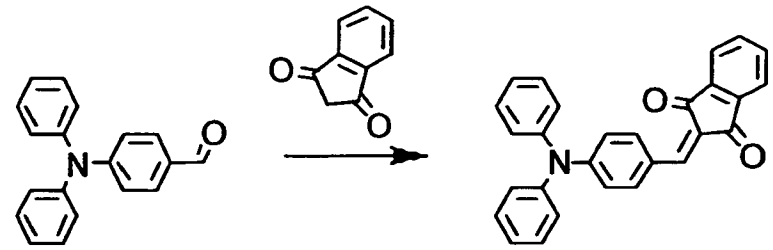
While the embodiments of the invention by using the photoelectric conversion devices according to embodiments of the invention in imaging devices are described above, the present photoelectric conversion devices can deliver high performance even when they are used as solar cells, because they have high photoelectric conversion efficiency.

The invention will now be illustrated in more detail by reference to the following examples, but these examples should not be construed as limiting the scope of the invention in any way.

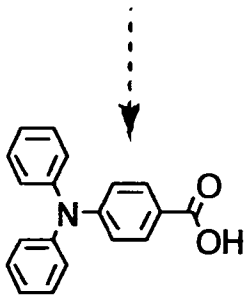
Examples

<Sample a1>

Exemplified Compound 1 illustrated above was synthesized in the following manner. The essential part of Scheme 1 already explained is noted again as the following reaction scheme.



Exemplified Compound 1



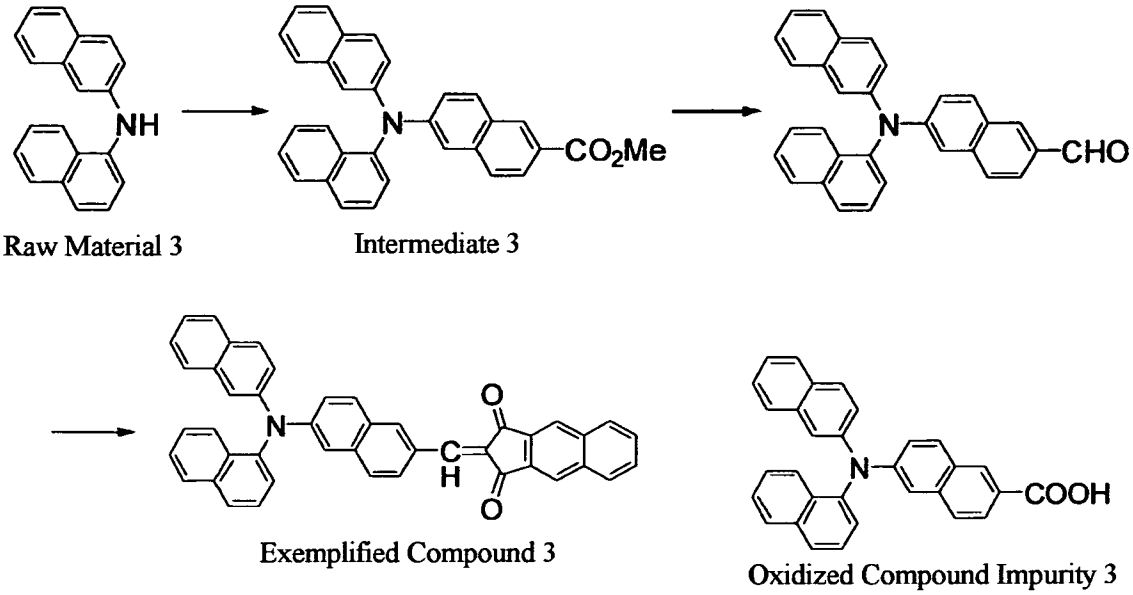
Oxidized-Compound Impurity 1

After the air in a reaction vessel is replaced with nitrogen gas, 2.7 g of 4-(N,N-diphenylamino)benzaldehyde (manufactured by Tokyo Chemical Industry Co., Ltd.) and 1.5 g of 1,3-indanedione (manufactured by Tokyo Chemical Industry Co., Ltd.) are placed as raw materials into the reaction vessel, 50 ml of ethanol is further added into the reaction vessel, and 1.0 ml of piperidine is added thereto. Then the reaction vessel is shaded from light under an atmosphere of nitrogen and the reaction solution is heated for 3 hours under reflux. After conclusion of the reaction, the resulting solution is cooled to room temperature, and crystals thus produced are filtered off and washed with 50 ml of ethanol. In a solution refining process, these crystals are dissolved again in 170 ml of methylene chloride, and passed through a filter. Further, 170 ml of methanol is added to the filtrate obtained, and the resulting mixture is concentrated under reduced pressure until the total volume thereof is reduced by about 1/2. The crystals thus obtained are filtered off, washed by 50 ml of methanol, dried under an atmosphere of nitrogen, further dried by heating (at 100°C) in a vacuum (0.2 Torr). Thus 3.3 g of exemplified compound 1 is obtained as recrystallized matter. This recrystallized matter is subjected to sublimation refining by means of a sublimation refining instrument (TRS-1, a product of ULVAC-RIKO, Inc.).

The sublimation refining is performed in a stream of argon under conditions that the boat temperature is 200°C or above, the collection section is controlled to 200°C or below and the in-system pressure is 0.1 Pa. The crystal yield after the sublimation refining is 88%. The sublimed crystal thus obtained is taken out of the sublimation tube inside a globe box with a nitrogen atmosphere and transferred to a brown glass vial. Further, the vial is closed with a cap, and stored in a light cut-off condition under an atmosphere of nitrogen. The thus

obtained sample is referred to as Sample a1.

<Sample a3> Synthesis of Exemplified Compound 3



Raw Material 3 Intermediate 3

Exemplified Compound 3 Oxidized Compound Impurity 3

To 10 ml of dehydrated xylene, 4.4 g of the raw material 3, 4 g of methyl 6-bromo-2-naphthoate (manufactured by Wako Pure Chemical Industries, Ltd.), 0.2 g of palladium acetate, 0.6 g of triphenyl phosphine and 10 g of cesium carbonate are added. The resulting mixture is refluxed for 7 hours in a stream of nitrogen. The reaction mixture is filtered under suction, the filtrate is concentrated under reduced pressure, and then the concentrated matter is purified by silica-gel column chromatography using toluene. Then the solvent is distilled away, and thereby 6.4 g of the intermediate 3 is obtained.

To 30 ml of dehydrated toluene, 24 ml of SMEAH (a toluene solution (about 70%) of bis(2-methoxyethoxy)aluminum sodium hydride, a product of Wako Pure Chemical Industries, Ltd.) is added. The resulting solution is cooled so as to have an internal temperature of 0°C with an ice bath, and thereto a solution containing 10 ml of 1-methylpiperadine in 17 ml of dehydrated toluene is added dropwise. A 6 g portion of the intermediate 3 is dissolved in 50 ml of dehydrated toluene, and the resulting solution is cooled to have an internal temperature of -40°C with a dry ice bath, and thereto the SMEAH toluene solution prepared a little while ago is added dropwise. The resulting reaction solution is stirred for 8 hours in a stream of nitrogen, and thereto concentrated hydrochloric acid is added until the pH reached 1. Thereto, water and ethyl acetate are further added, and an oil layer separated is washed with an aqueous solution of sodium hydrogen carbonate. Further, the oil layer is dried with magnesium sulfate, and then filtered. From the filtrate, the solvent is distilled away by means of an evaporator. To one-third of the residue, 1.3 g of benz[f]indane-1,3-dione synthesized in conformity to the descriptions in J. Med. Chem., vol. 16, pp. 1334-1339 (1973) and 50 ml of

acetonitrile are added. The resulting mixture is refluxed for 12 hours in a stream of nitrogen, and then allowed to stand for cooling. Thereafter, suction filtration is carried out, and the solid matter obtained is added to chloroform and heated for 2 hours under reflux in an atmosphere of nitrogen. By cooling to room temperature, crystals are obtained. The crystals obtained are filtered under suction, washed with acetonitrile, and dried under vacuum. Thus, 2.5 g of exemplified compound 3 is obtained. This sample is subjected to the same sublimation refining as Sample a1, thereby giving Sample a3 though the yield was 3%

In Sample a1 and Sample a3, the oxidized-compound impurity 1 and the oxidized-compound impurity 3 illustrated above are detected as impurities, respectively, by means of HPLC, and their contents are 870 ppm or below. Therein, the content which exemplified compound 1 had and that which exemplified compound 3 has are in a range of 99.9% to 99.5%. The analytical values according to HPLC are expressed in terms of relative area ratios between peaks in the chromatogram obtained by using a THF-water mixture solvent as a moving bed and monitoring absorbance at 254 nm.

When the water contents in these samples are determined by the Karl Fischer technique and the solvent contents are determined from reductions in weight by drying (as values obtained by subtracting their respective water contents from the percentages of weights reduced by heating at 100°C under vacuum), they are all 0.1% or below. Even when solution refining is carried out two or more times and sublimation refining is also carried out two or more times, similar results are obtained.

<Sample a2 and Sample a4>

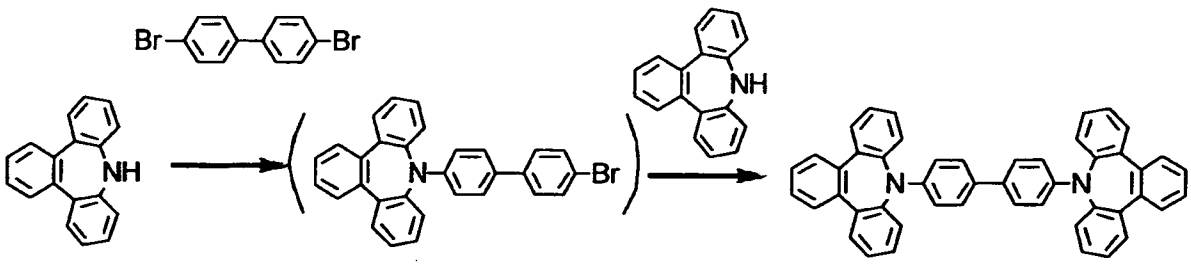
Sample a2 and Sample a4 are obtained by omitting the sublimation refining process in Examples of Sample a1 and Sample a3 syntheses, respectively. The content of the oxidized-compound impurity 1 in Sample a2 and that of the oxidized-compound impurity 3 in Sample a4 are in a range of 1,100 ppm to 2,800 ppm, and the contents which exemplified compounds 1 and 3 has in those samples, respectively, are in a range of 99.1% to 97.3%. The water contents and solvent contents are all 0.1 % or below.

<Comparative Sample a1 and Comparative Sample a3>

Comparative Sample a1 and Comparative Sample a3 are obtained by further omitting the solution refining process in Examples of Sample a2 and Sample a4 syntheses, respectively. The content of the oxidized-compound impurity 1 in Comparative Sample a1 and that of the oxidized-compound impurity 3 in Comparative Sample a3 are each 3,200 ppm or above, and the contents which exemplified compounds 1 and 3 had in those samples, respectively, are each 96.3% or below.

<Sample b1>

Exemplified compound 2 in Scheme 2 explained hereinbefore is synthesized in the following manner. The essential part of Scheme 2 is noted below.

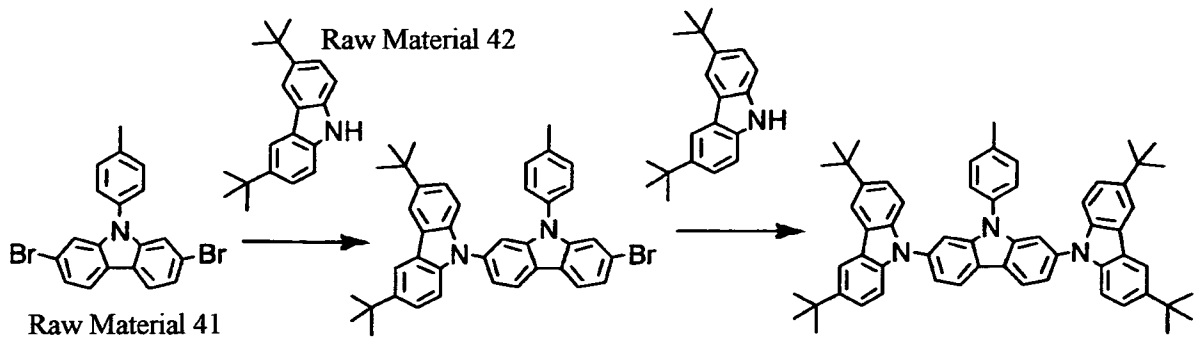


Halide Impurity 2 Exemplified Compound 2

After the air in a reaction vessel is replaced with nitrogen gas, 2.4 g of 9H-trisbenzo[b, d,f]azepine (synthesized according to the description in J. Org. Chem., 56, 3906 (1991)) and 2.4 g of 4,4'-dibromobiphenyl (manufactured by Tokyo Chemical Industry Co., Ltd.) are placed as raw materials into the reaction vessel, and further 1.5 g of t-butoxysodium (manufactured by Wako Pure Chemical Industries, Ltd.), 100 mg of palladium acetate (manufactured by Wako Pure Chemical Industries, Ltd.), 450 mg of triphenyl phosphine (manufactured by Wako Pure Chemical Industries, Ltd.) and 50 ml of toluene are added into the reaction vessel. Then the reaction vessel is shaded from light under an atmosphere of nitrogen and the reaction solution is heated for 8 hours under reflux. After conclusion of the reaction, the resulting solution is cooled to room temperature, and thereto 50 ml of methanol is added. Crystals thus produced are filtered off and washed with 50 ml of methanol. In a solution refining process, these crystals are dissolved again in 100 ml of methylene chloride, and passed through a filter. Further, 100 ml of methanol is added to the filtrate obtained, and the resulting mixture is concentrated under reduced pressure until the total volume thereof is reduced by about 1/2. The crystals thus obtained are filtered off, washed by 50 ml of methanol, dried under an atmosphere of nitrogen, further dried by heating (at 100°C) under vacuum (0.2 Torr). Thus 5.0 g of exemplified compound 2 is obtained as recrystallized matter. This recrystallized matter is subjected to sublimation refining by means of a sublimation refining instrument (TRS-1, a product of ULVAC-RIKO, Inc.). The sublimation refining is performed in a stream of argon under conditions that the boat temperature is 300°C or above, the collection section is controlled to 200°C or below and the in-system pressure is 0.1 Pa. The crystal yield after the sublimation refining is 85%. The thus obtained sample is referred to as Sample b1. The sublimed solid obtained is taken out of the sublimation tube inside a globe box with a nitrogen atmosphere and transferred to a brown glass vial. Further, the vial is closed with a cap, and stored in a light cut-off condition under an atmosphere of

nitrogen.

[Sample b3]



After the air in a reaction vessel is replaced with nitrogen gas, raw materials, namely 1 g of Material 41 (synthesized according to the descriptions in Journal of Materials Chemistry, vol. 15, pp. 4753-4760 (2005)) and 1.5 g of Raw Material 42 (synthesized according to the descriptions in Organic Letters, vol. 9, pp. 797-800 (2007)), 100 mg of palladium acetate, 300 mg of triphenyl phosphine, 2.5 g of cesium carbonate and 50 ml of dehydrated toluene (manufactured by Wako Pure Chemical Industries, Ltd.) are placed into the reaction vessel, and the reaction vessel is shaded from light under an atmosphere of nitrogen. Under these conditions, 12-hour heating under reflux is carried out. After conclusion of the reaction, the reaction solution is cooled to room temperature, and thereto 50 ml of methanol is added. Thus, crystals separated out, filtered off, and then washed with 50 ml of methanol. In a solution refining process, these crystals are dissolved again in 10 ml of methylene chloride, and passed through a filter. By adding 100 ml of acetonitrile to the filtrate, crystals separated out, filtered off, washed with 50 ml of isopropanol, dried in a stream of nitrogen gas, and further dried by heating (at 100°C) under vacuum (0.2 Torr). Thus, 1.2 g of exemplified compound 4 is obtained as recrystallized matter. This recrystallized matter is subjected to the same sublimation refining as Sample b1, and thereby Sample b3 is obtained.

In Sample b1 and Sample b3, the halide impurity 1 and the halide impurity 4 illustrate above are detected as impurities, respectively, by means of HPLC, and their contents are 3,900 ppm or below. Therein, the content which exemplified compound 2 had and that which exemplified compound 4 has are in a range of 99.9% to 99.2%. In addition, when the content of palladium as a catalytic metal is determined by ICP method, the metal impurity content is found to be 960 ppm or below.

When the water contents in these samples are determined by the Karl Fischer technique and the solvent contents are determined from reductions in weight by drying (as values obtained by subtracting their respective water contents from the percentages of weights

reduced by heating at 100°C under vacuum), they are all 0.1% or below. Even when solution refining is carried out two or more times and sublimation refining is also carried out two or more times, similar results are obtained.

<Sample b2 and Sample b4>

Sample b2 and Sample b4 are obtained by omitting the sublimation refining process in Examples of Sample b1 and Sample b3 syntheses, respectively. The content of the halide impurity 2 in Sample b2 and that of the halide impurity 4 in Sample b4 are in a range of 4,100 ppm to 8,700 ppm, the contents which exemplified compounds 2 and 4 has in those samples, respectively, are in a range of 98.8% to 96.7%, and the palladium contents as metal impurity contents are in a range of 1,200 ppm to 3,600 ppm. The water contents and solvent contents are all 0.1 % or below.

<Comparative Sample b1 and Comparative Sample b3>

Comparative Sample b1 and Comparative Sample b3 are obtained by further omitting the solution refining process in Examples of Sample b2 and Sample b4 syntheses, respectively. The content of the halide impurity 2 in Comparative Sample b1 and that of the halide impurity 4 in Comparative Sample b3 are each 9,000 ppm or above, the contents which exemplified compounds 2 and 4 had in those samples, respectively, are each 95.0% or below, and the palladium contents are 4,000 ppm or above.

<<Example 1>>

In accordance with the embodiment of the invention, which is shown in Fig. 2, an imaging device is fabricated as follows. After amorphous ITO film is formed in a thickness of 30 nm on a CMOS substrate by use of a sputtering method, the film is made into pixel electrodes by undergoing such photolithographic patterning that one pixel is present on each of photodiodes (PDs) on the CMOS substrate. On the pixel electrodes, an electron blocking layer is formed in a thickness of 100 nm by vacuum heating evaporation of Sample b1. On the electron blocking layer, a photoelectric conversion layer is formed by vacuum heating coevaporation of Sample a1 and fullerene (C_{60}) in amounts of 100 nm and 300 nm, respectively, in single-layer thickness terms. Further, as the upper transparent electrode on the photoelectric conversion layer, amorphous ITO is formed into film with a thickness of 5 nm by sputtering. In addition, on the upper electrode, SiO film as a protective layer is formed by heating evaporation, and on the SiO film an Al_2O_3 layer is further formed by the ALCVD method. The vacuum evaporation for forming the photoelectric conversion layer is carried out under a condition that the degree of vacuum is 4×10^{-4} Pa or below.

Prior to testing of the imaging device, a voltage providing a dark current of 500

pA/cm^2 is checked within a range of electric-field conditions from 10^{-4} V/cm to 1×10^7 V/cm and, at this voltage, measurements of the photoelectric conversion device's external quantum efficiency at the maximum sensitivity wavelength, dark current and response speed (start-up time from 0 to 98% signal intensity) are made.

<<Examples 2 to 8 and Comparative Examples 1 to 4>>

Devices of Examples 2 to 8 and those of Comparative Examples 1 to 4 are each fabricated in the same manner as the device of Example 1, except that Sample a1 and Sample b1 used in Example 1 are replaced with those shown in the following Table 4, respectively.

In Table 4, the external quantum efficiency at the maximum sensitivity wavelength, the dark current and the response speed (start-up time from 0 to 98% signal intensity) which each of the photoelectric conversion devices in Examples 1 to 8 and Comparative Examples 1n to 4 has are shown as relative values wherein those of the photoelectric conversion device in Example 1 is considered as 1.0, respectively. As for the external quantum efficiency, greater values thereof mean that the devices have the better characteristics. As for the dark current and the response speed, on the other hand, smaller values thereof mean that the devices have the better characteristics.

Table 4

	Sample used in Electron Blocking Layer	Sample used in Photoelectric Conversion Layer	External Quantum Efficiency (relative value)	Dark Current (relative value)	Response Speed (relative value)
Example 1	b1	a1	1.0	1.0	1.0
Example 2	b1	a2	0.9	1.0	1.5
Example 3	b1	a3	1.1	1.0	1.1
Example 4	b1	a4	1.0	1.0	1.5
Example 5	b2	a1	1.0	1.5	2.0
Example 6	b2	a2	0.9	2.0	2.7
Example 7	b3	a1	1.0	0.5	0.5
Example 8	b4	a1	1.0	0.5	1.0
Comparative Example 1	b1	Comparative Sample a1	0.7	1.2	30
Comparative Example 2	b1	Comparative Sample a3	0.7	1.5	50
Comparative Example 3	Comparative Sample b1	a1	0.8	70	90
Comparative Example 4	Comparative Sample b3	a1	0.7	100	130

Here the contents which exemplified compounds 1-4 has in samples, respectively, and so on are summarized in the following Table 5.

Table 5

Sample	Oxidized-Compound Impurity or Halide Impurity		Exemplified Compound		Content of Palladium
Sample a1	1	870 ppm or below	1	99.5 - 99.9 %	-
Sample a2	1	1,100 -2,800 ppm	1	99.1 – 97.3 %	-
Comparative Sample a1	1	3,200 ppm or above	1	96.3% or below	-
Sample b1	2	3,900 ppm or below	2	99.2% or above	960 ppm or below
Sample b2	2	4,100 – 8,700 ppm	2	98.8 – 96.7 %	1,200 – 3,600 ppm
Comparative Sample b1	2	9,000 ppm or above	2	95.0% or below	4,000 ppm or above
Sample a3	3	8,70 ppm or below	3	99.5 – 99.9 %	-
Sample a4	3	1,100 – 2,800 ppm	3	99.1 – 97.3 %	-
Comparative Sample a3	3	3,200 ppm or above	3	96.3% or below	-
Sample b3	4	3,900 ppm or below	4	99.2% or above	960 ppm or below
Sample b4	4	4,100 – 8,700 ppm	4	98.8 – 96.7 %	1,200 – 3,600 ppm
Comparative Sample b3	4	9,000 ppm or above	4	95.0% or below	4,000 ppm or above

It can be seen from Table 4 that each of the devices fabricated in Examples 1 to 8 using varying combinations of one of Samples a1 to a4 and one of Samples b1 to b4 achieved high external quantum efficiency, low dark current and fast response speed, but the device fabricated in Comparative Example 1 using Comparative Sample a1 and the device fabricated in Comparative Example 2 using Comparative Sample a3 are vastly inferior in external quantum efficiency and response speed, and the device fabricated in Comparative Example 3 using Comparative Sample b1 and the device fabricated in Comparative Example 4 using Comparative Sample b3 are vastly inferior in dark current and response speed.

Thus these tests revealed that imaging devices delivering high external quantum efficiency, low dark current and fast response speed can be obtained as long as they incorporate exemplified compounds 1-4 having contents of at least 96.5% and they don't necessarily require organic materials having ultrahigh purities of 99.99% or above. Ingredients of these effects are thought to be reductions in oxidized-compound impurity content, halide impurity content and metal impurity content.

In accordance with the invention, as long as the purity of a material used for forming an organic photoelectric conversion layer is at least 96.5%, it becomes possible to fabricate photoelectric conversion devices and imaging devices each having high external quantum

efficiency, low dark current and fast response speed, and these devices can circumvent the use of expensive high-purity materials and thereby allow reduction in fabrication costs.

Industrial Applicability

The photoelectric conversion devices and imaging devices according to embodiments of the invention can be applied to imaging devices such as digital cameras, video cameras, facsimiles, scanners and copiers. The present devices can also be utilized as photosensors including biosensors and chemical sensors.

Although the invention has been described in detail and by reference to specific embodiments, it is apparent to those skilled in the art that it is possible to add various alterations and modifications insofar as the alterations and modifications do not depart from the spirit and the scope of the invention.

This application is based on a Japanese patent application filed on March 8, 2010 (Japanese Patent Application No. 2010-051075), and the contents thereof are incorporated herein by reference.

CLAIMS

1. A photoelectric conversion device comprising an organic photoelectric conversion layer between a first electrode and a second electrode,

wherein a material used for forming the organic photoelectric conversion layer has a purity of 96.5% or above as determined by liquid chromatography.

2. The photoelectric conversion device according to claim 1,

wherein the material used for forming the organic photoelectric conversion layer has an oxidized-compound impurity content of 9,000 ppm or below.

3. The photoelectric conversion device according to claim 1 or 2,

wherein the material used for forming the organic photoelectric conversion layer is a material having been purified by solution refining.

4. The photoelectric conversion device according to any of claims 1 to 3,

wherein the material used for forming the organic photoelectric conversion layer is a material having been purified by sublimation refining.

5. The photoelectric conversion device according to claims 1 to 4,

wherein a charge blocking layer is provided between either of the electrodes and the organic photoelectric conversion layer.

6. The photoelectric conversion device according to claim 5,

wherein the charge blocking layer is an electron blocking layer.

7. The photoelectric conversion device according to claim 6,

wherein an electron blocking material used in the electron blocking layer has a purity of 96.7% or above as determined by liquid chromatography and a halide impurity content of 9,000 ppm or below.

8. The photoelectric conversion device according to claim 6 or 7,

wherein an electron blocking material used in the electron blocking layer has a purity of 96.7% or above as determined by liquid chromatography and a heavy-metal impurity content of 4,000 ppm or below.

9. The photoelectric conversion device according to any of claims 6 to 8, wherein an electron blocking material used in the electron blocking layer is a material having been purified by solution refining.

10. The photoelectric conversion device according to any of claims 6 to 8, wherein an electron blocking material used in the electron blocking layer is a material having been purified by sublimation refining.

11. The photoelectric conversion device according to any of claims 6 to 10, wherein an electron blocking material used in the electron blocking layer is a triarylamine compound.

12. The photoelectric conversion device according to any of claims 1 to 11, wherein the material used for forming organic photoelectric conversion layer comprises a colorant having its absorption maximum wavelength in a visible wavelength region extending from 400 nm to of 800 nm.

13. The photoelectric conversion device according to any of claims 1 to 12, wherein an electric field of 10^{-4} V/cm to 1×10^{7} V/cm is placed between the first electrode and the second electrode.

14. The photoelectric conversion device according to any of claims 1 to 13, wherein the organic photoelectric conversion layer comprises a fullerene.

15. An imaging device comprising:
the photoelectric conversion device according to any of claims 1 to 14; and
a semiconductor substrate,
wherein the photoelectric conversion device is stacked on a surface of the semiconductor substrate.

FIG. 1

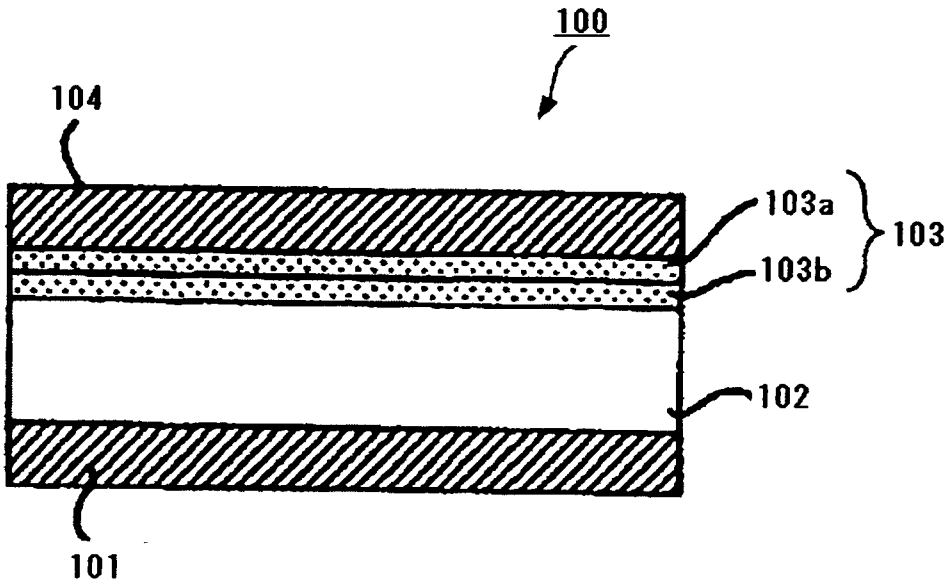


FIG. 2

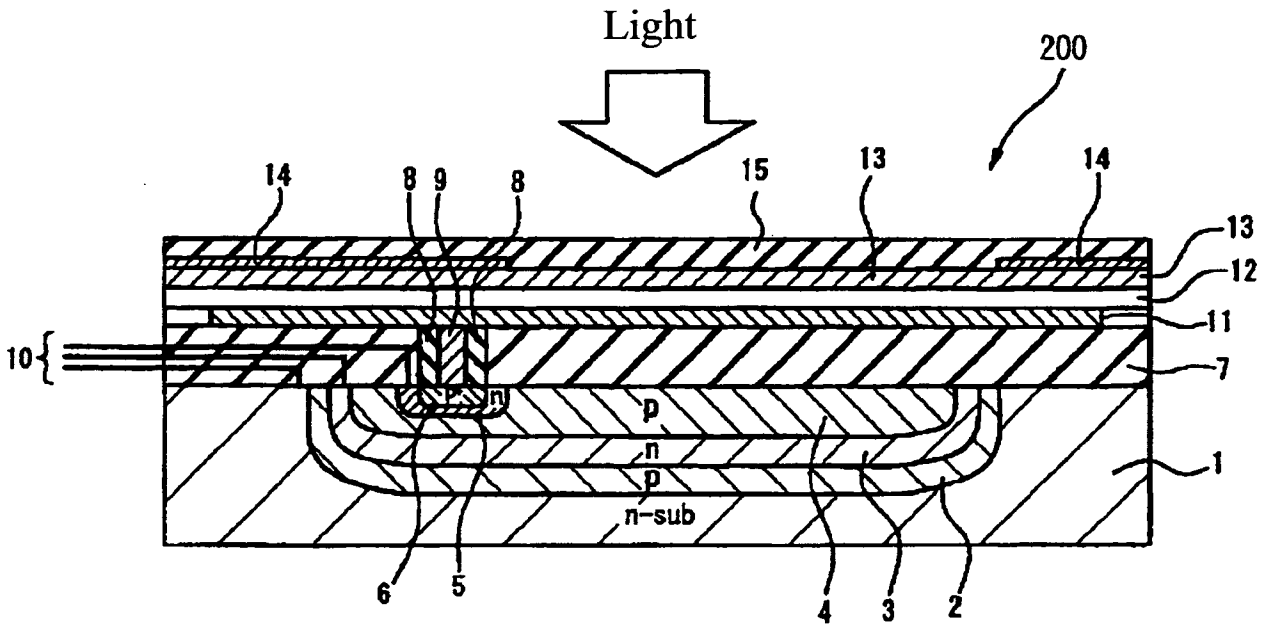


FIG. 3

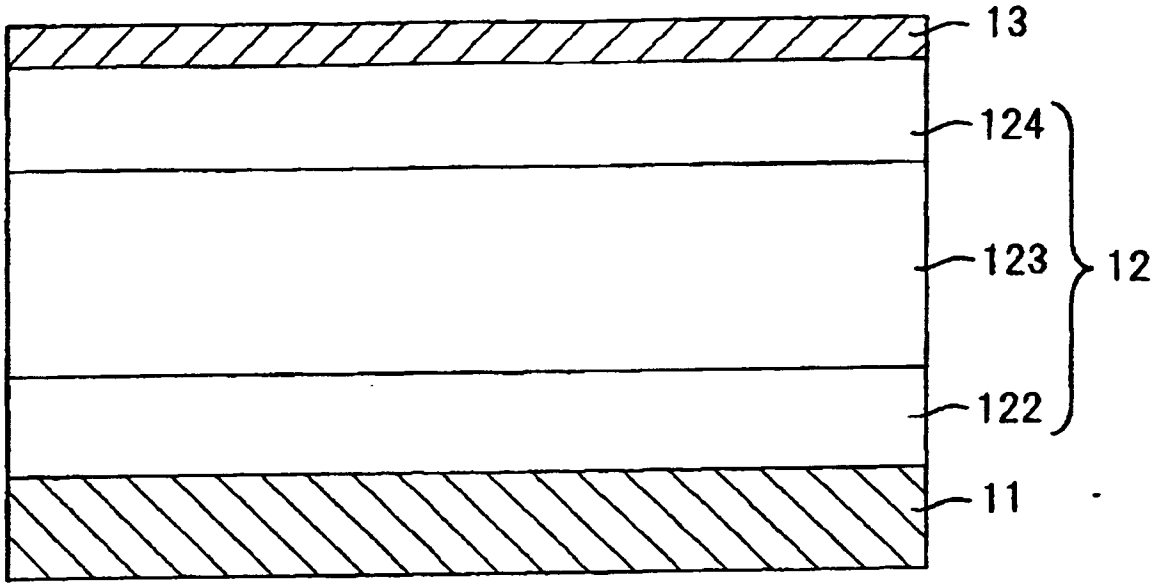


FIG. 4

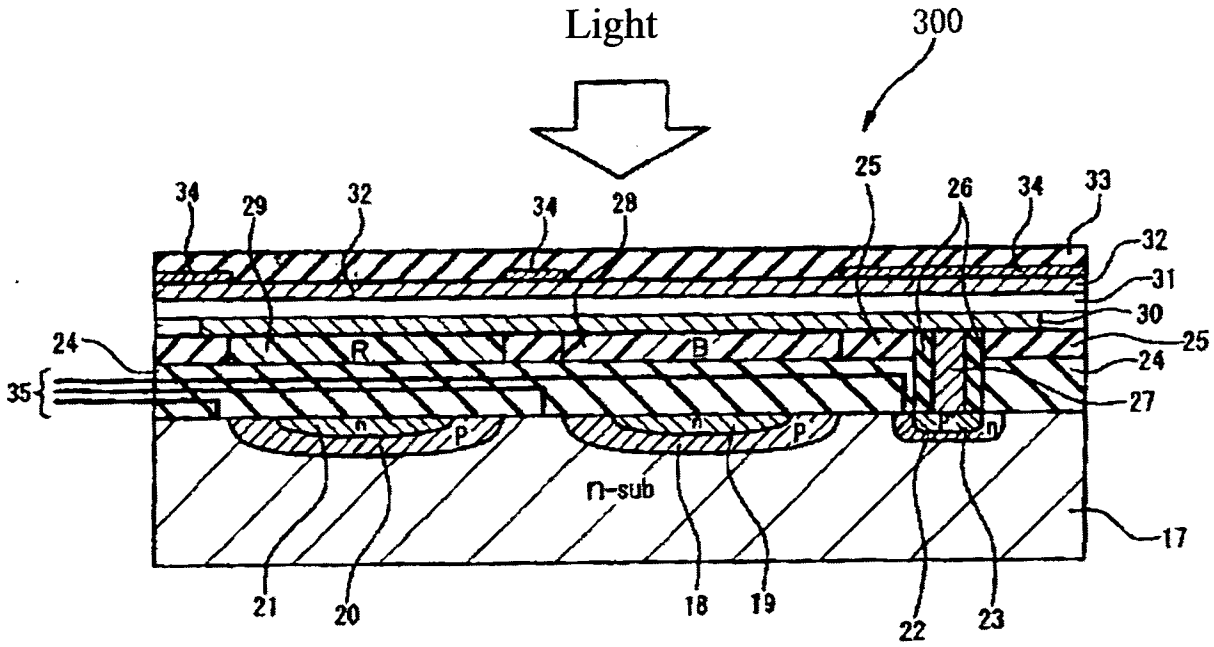

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FIG. 5

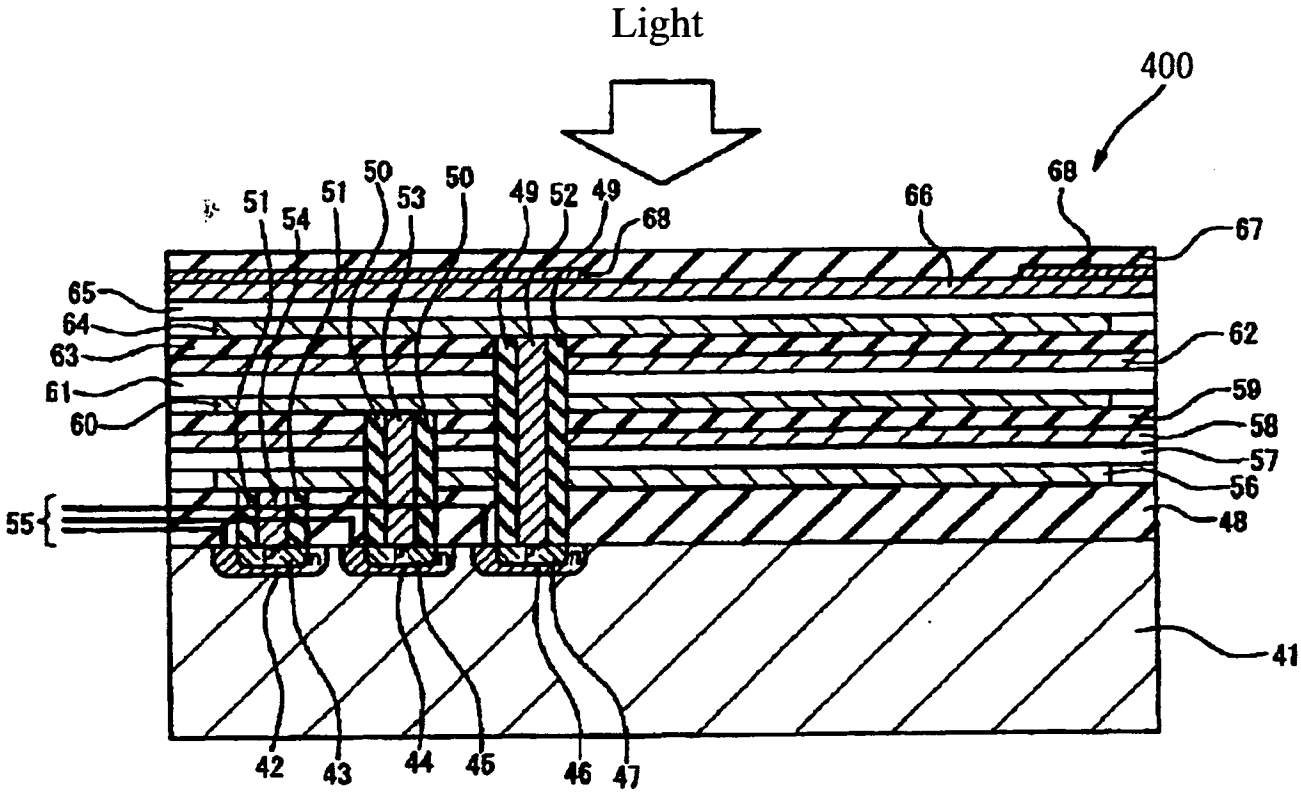
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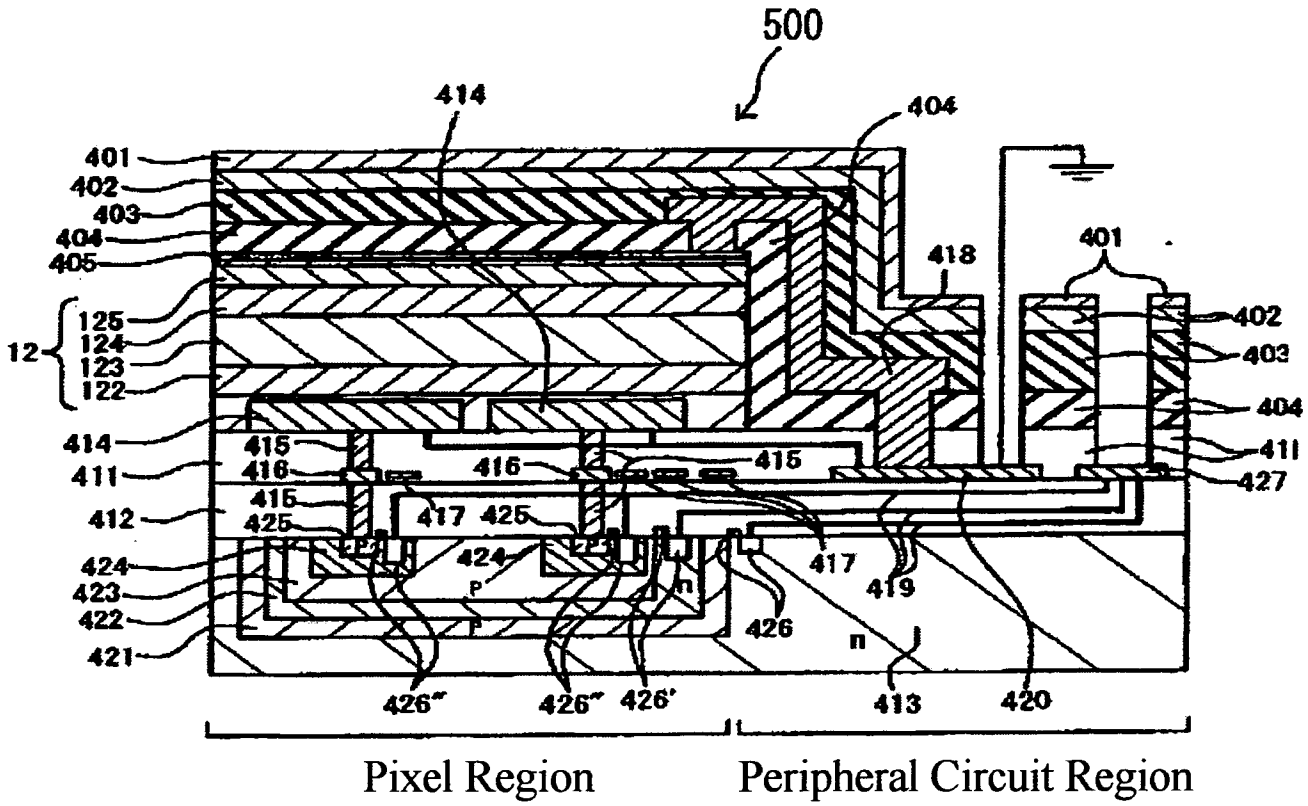
FIG. 6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Pixel Region
Peripheral Circuit Region

FIG. 7

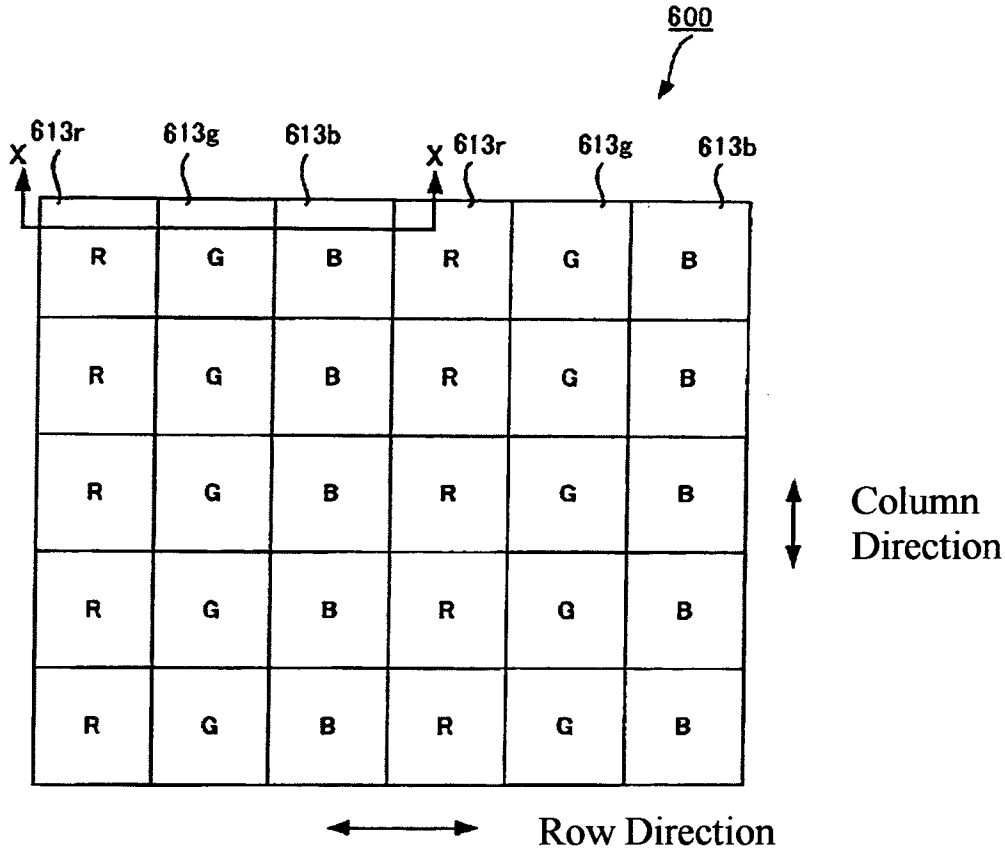
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FIG. 8

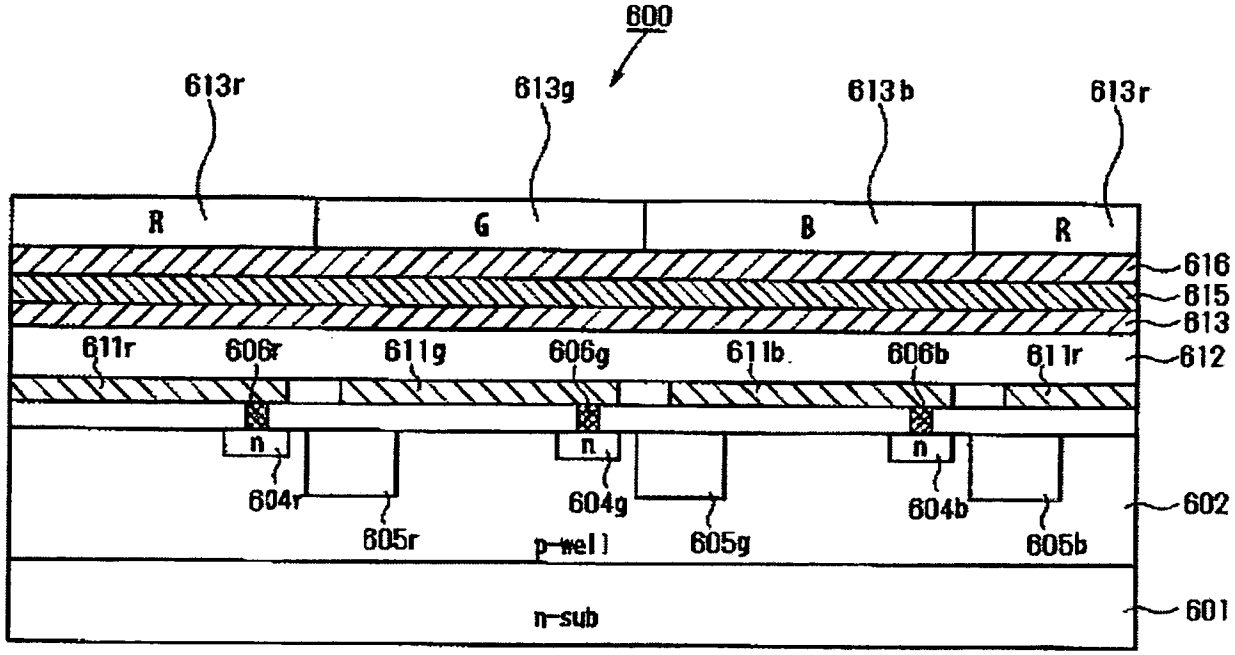
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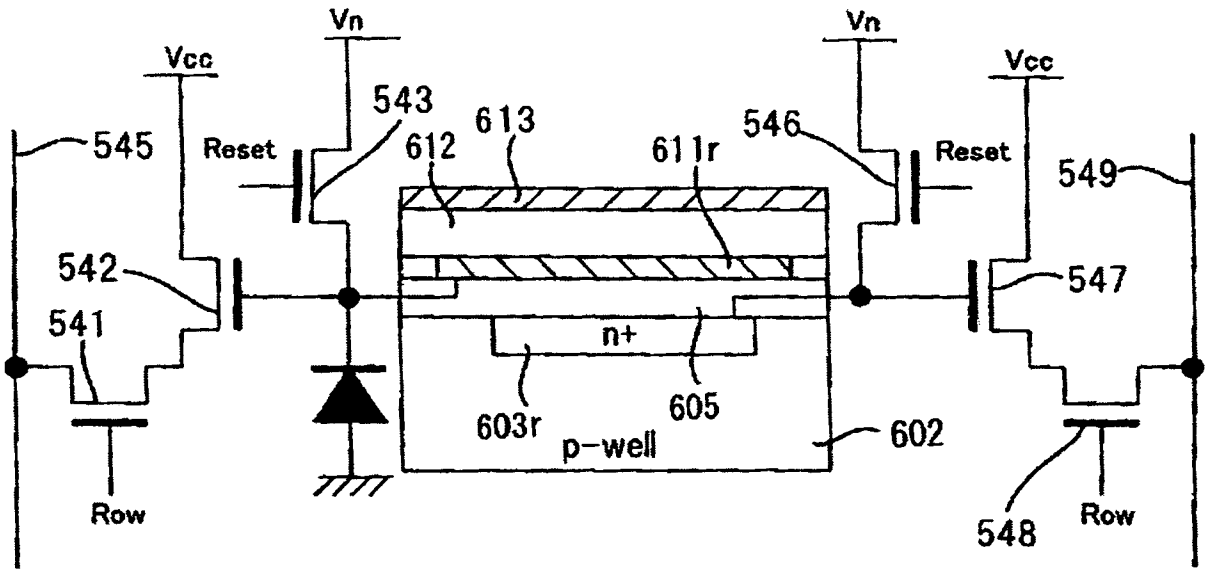
FIG. 9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Row

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/054837

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. H01L31/10(2006.01)i, H01L27/14(2006.01)i, H01L27/146(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. H01L31/10, H01L27/14, H01L27/146

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2011
Registered utility model specifications of Japan 1996-2011
Published registered utility model applications of Japan 1994-2011

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2009-54606 A (Fujifilm Corporation) 2009.03.12, [0098],[0108],[0113],[0114],[0117]-[0121] & US 2009/0054641 A1	1-15
A	JP 2009-215260 A (Fujifilm Corporation) 2009.09.24, [0014] & US 2009/0229670 A1	1-15
A	JP 2010-3901 A (Fujifilm Corporation) 2010.01.07, [0102] & US 2009/0315136 A1	1-15

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22.03.2011	29.03.2011

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