(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 300 807 A2

# (12) EUROPEAN PATENT APPLICATION

(21) Application number: 88306746.4

(22) Date of filing: 22.07.88

(51) Int. Cl.$^4$: G 03 G 5/082

(30) Priority: 24.07.87 JP 183480/87

(43) Date of publication of application:
25.01.89 Bulletin 89/04

(84) Designated Contracting States:
CH DE FR GB LI NL SE

(71) Applicant: **HITACHI, LTD.**
6, Kanda Surugadai 4-chome Chiyoda-ku
Tokyo (JP)

**Hitachi Chemical Co., Ltd.**
1-1, Nishi-shinjuku 2-chome Shinjuku-ku
Tokyo 160 (JP)

(72) Inventor: **Wakagi, Masatoshi**
Kowaryo 415 8-18, Kokubuncho-3-chome
Hitachi-shi (JP)

**Onuma, Shigeharu**
22-16 Higashionumacho-2-chome
Hitachi-shi (JP)

**Ishikawa, Fuminori**
17-2-504 Moriyamacho-3-chome
Hitachi-shi (JP)

**Ohno, Toshiyuki**
19-3-2-2, Ishinazakacho-1-chome
Hitachi-shi (JP)

**Tamahashi, Kunihiro**
681-6 Aoyagicho
Mito-shi (JP)

**Chigasaki, Mitsuo**
25-12 Suwacho-5-chome
Hitachi-shi (JP)

**Shimamura, Yasuo**
Yamazakiryo 212 2-9 Higashicho-4-chome
Hitachi-shi (JP)

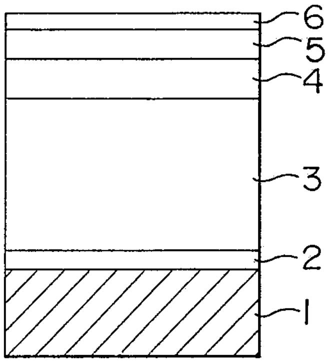
**Yamagishi, Chiaki**
Yamazakiryo 116 2-9 Higashicho-4-chome
Hitachi-shi (JP)

(74) Representative: **Paget, Hugh Charles Edward et al**
MEWBURN ELLIS & CO. 2/3 Cursitor Street
London EC4A 1BQ (GB)

## (54) Electrophotographic photosensitive member.

(57) An electrophotographic photosensitive member, comprises an electroconductive support (1), optionally a charge blocking layer (2), a photoconductive layer (3,4) made from hydrogen-containing amorphous silicon as a matrix and a charge injection blocking layer (5). To give the member high electrostatic charge acceptance and a good photosensitivity, the charge injection blocking layer (5) has a different conductivity type from that of the photoconductive layer (3,4) and a broader optical band gap than that of the photoconductive layer (3,4). A moisture and corona-resistant layer (6) is also provided.

FIG. 1



Bundesdruckerei Berlin

## Description

# ELECTROPHOTOGRAPHIC PHOTOSENSITIVE MEMBER

## BACKGROUND OF THE INVENTION

This invention relates to an electrophotographic photosensitive member, and particularly to an electrophotographic photosensitive member with excellent electrostatic charge acceptance for laser printers.

The conventional electrophotographic photosensitive member has a basic structure of a photoconductive layer and a surface protective layer, successively laid one upon another on an electroconductive support, where inorganic photoconductive materials such as Se, CdS, $As_2Se_3$, etc. or organic photoconductive materials such as $PVC_z$-TNF, etc. have been used in the photoconductive layer. These inorganic and organic photoconductive materials are not always satisfactory in heat resistance and durability. Heretofore, amorphous Si containing hydrogen, which will be hereinafter abbreviated to a-Si:H, has been proposed as a photoconductive material and has excellent heat resistance and a high hardness, and thus has excellent durability, but the volume resistivity of ordinary a-Si:H film is as low as about $10^{10}$ $\Omega$•cm, which is too low to obtain a satisfactory electrostatic charge acceptance. Thus, it has been proposed to dope the a-Si:H film with boron or to add carbon, nitrogen or oxygen to the a-Si:H film in order to increase the volume resistivity, or it has been proposed to add an element of Group III or V of the Periodic Table to the a-Si:H film in order to control the conduction type and increase the electrostatic charge acceptance [Japanese Patent Application Kokai (Laid-open) No. 58-88115]. In case of a photosensitive member for positive electrostatic charging, it has been proposed to locally increase the boron doping concentration in the photoconductive layer, that is, to make the boron doping concentration higher in the region near the substrate in order to suppress the charge injection from the substrate.

On the other hand, the surface protective layer provided on the surface of the photoconductive layer is a layer of high volume resistivity, which is directed to an increase in the moisture resistance and corona resistance as well as to a prevention of charge injection from the surface of the photosensitive member. When the thickness of the surface protective layer is increased to improve the electrostatic charging characteristics of the photosensitive member such as an electrostatic charge acceptance, dark decay, etc., the residual potential after light exposure will be increased. Thus, the thickness of the surface protective layer must take such a value as to satisfy the electrostatic charge acceptance and the dark decay as well as the residual potential.

It has been also proposed that the surface protective layer is in a double layer structure, that is, a moisture and corona-resistant layer as an upper layer and a charge injection blocking layer as a lower layer in order to increase the moisture resistance and corona resistance of the surface protective layer. The electrostatic charge acceptance and the dark decay, and the residual potential cannot be readily balanced owing to the influence of the charge injection blocking layer.

An electrophotographic photosensitive member comprising a photoconductive layer of a-Si:H:B (4 ppm) of intrinsic conduction, a charge injection blocking layer of a-Si:H:B (100 ppm) of p-type conduction, and a moisture and corona-resistant layer of a-SiN, laid one upon another on an aluminum support is disclosed in J. Appl. Phys. Vol. 55, No. 8, 3197-3198 (1984), where the conduction type of the charge injection blocking layer is different from that of the photoconductive layer, but the optical band gap of the charge injection blocking layer is equal to that of the photoconductive layer, and the blocking ability of the charge injection blocking layer is small because of the equal optical band gaps, and thus the quantity of light into the photoconductive layer is smaller and the photosensitivity of the photosensitive member is lowered.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide an electrophotographic photosensitive member with excellent electrostatic charging characteristics, where the electrostatic charge acceptance and dark decay are increased, while suppressing a residual potential increase.

The present invention provides an electrophotographic photosensitive member, which comprises an electroconductive support, a photoconductive layer made from hydrogen-containing amorphous silicon as a matrix, a charge injection blocking layer having a different conduction type from that of the photoconductive layer and having a broader optical band gap than that of the photoconductive layer, and a moisture and corona-resistant layer, laid one upon another successively on the electroconductive support.

Different conduction type of the charge injection blocking layer from that of the photoconductive layer means that when the photoconductive layer is of p-type, the charge injection blocking layer is of n-type or intrinsic type, and when the photoconductive layer is of n-type, the charge injection blocking layer is of p-type or intrinsic type.

In order to improve the electrostatic charge acceptance and dark decay without increasing the residual potential, it is necessary to transfer the charges generated in the photoconductive layer by irradiation of light to the region near the surface of the photosensitive member. Thus, it is necessary that the charge injection blocking layer provided on the photoconductive layer has a high mobility of charges with a reversed polarity to the polarity of the charges on the surface of the photosensitive member. On the other hand, when the charges are injected from the surface of the photosensitive member, it is desirable that the charge injection blocking layer has a low mobility of such charges. That is, the charge injection blocking layer has a function to block the charges with the same polarity as that of charges on the surface of the photosensitive member.

For example, when the surface of the photosensitive member is plus (+) charged, the charge injection blocking layer on the photoconductive layer must be of n-type, whereas, when the surface of the photosensitive member is minus (-) charged, the charge injection blocking layer must be of p-type.

It is desirable that the photoconductive layer is of p-type in case of plus (+) charging, and of n-type in case of minus (-) charging, and thus the charge injection blocking layer provided on the photoconductive layer must have a different conductivity type from that of the photoconductive layer. That is, when the photoconductive layer is of p-type, the charge injection blocking layer provided thereon must have a conductivity type of n-type or intrinsic type, and when the photoconductive layer is of n-type, the charge injection blocking layer provided thereon must have a conductivity type of p-type or intrinsic type. When the photoconductive layer is of intrinsic conduction type, that is, when both plus (+) and minus (-) carriers have a high mobility, the charge injection blocking layer provided on the photoconductive layer must be of n-type in case of plus (+) charging and of p-type in case of minus (-) charging.

In order to allow light to go into the photocnductive layer, the charge injection blocking layer provided on the photoconductive layer must have a broader optical band gap than that of the photoconductive layer.

Thus, the charge injection blocking layer provided on the photoconductive layer must be a film capable of controlling the p-n conduction type and having a broader optical band gap.

As a result of extensive studies, the present inventors have found that a film of hydrogen-containing amorphous SiC (a-SiC:H) is preferable as the charge injection blocking layer. The a-SiC:H film has a broader band gap, i.e. 1.9 eV - 2.0 eV, than those of a-Si:H (optical band gap: 1.8 eV) or a-SiGe:H (hydrogen-containing amorphous SiGe; optical band gap: 1.5 eV), used as the photoconductive layer. The a-SiC:H film is of n-type, when not doped with an impurity such as B, and has a high electron mobility, but the hole mobility is not so high. The film, when doped with a small amount of boron, has a high hole mobility, but the electron mobility is decreased, and the conduction type of the film turns from n-type to p-type through the intrinsic type. That is, the conduction type of the electron injection blocking layer can be changed from the n-type to the p-type through the intrinsic type by doping with B.

On the other hand, when the film is doped with a small amount of phosphorus, the electron mobility of the film is increased; i.e. the n-type conduction of the film increases.

As the charge injection blocking layer provided on the electroconductive layer, a-SiC:X:H film where X is a halogen atom, (halogen and hydrogen containing amorphous SiC; optical band gap: 1.9 eV -2.0 eV) or a-SiN:X:H film, where X is a halogen atom (halogen and hydrogen containing amorphous SiN; optical band gap: 1.9 eV or more) can be used in place of the a-SiC:H film as the charge injection blocking layer provided on the photoconductive layer. The effect of halogen atom is an increase in the durability, that is, less susceptibility to optical fatigue.

By providing a charge injection blocking layer having a different conduction type from that of a photoconductive layer on the photoconductive layer, injection of charges from the surface of the photosensitive member can be suppressed, and the charges can be readily transferred from the photo conductive layer, and thus an electrophotographic photosensitive member with a lower residual potential and better dark decay and charge acceptance can be obtained. By using a charge injection blocking layer having a broader optical band gap than that of the photoconductive layer, the photoconductive layer can be thoroughly irradiated with light, and a higher photosensitivity can be obtained.

In order to improve the moisture and corona resistance of an electrophotographic layer, an a-SiC:H film having a higher carbon content or an a-C film is desirably provided as a moisture and corona-resistant layer on the surface of the charge injection blocking layer.

Furthermore, a charge blocking layer can be provided between the support and the photoconductive layer. The charge blocking layer can be made of the same material as used in the charge injection blocking layer.

Films of the charge blocking layer, photoconductive layer, charge injection blocking layers and the moisture and corona blocking layer can be formed on the electroconductive support one upon another successively by CVD including plasma CVD, photo CVD, thermal CVD and ECR microwave CVD, by sputtering or by vapor deposition, and the individual films can be also formed by any combination of these forming procedures.

The individual layers desirably have a thickness as given below:

The charge blocking layer : 0.5 - 3μm
The photoconductive layer : 20 - 50 μm
The charge injection blocking layer: 0.5 - 3 μm
The moisture and corona-resistant layer: 0.2 - 1 μm

Furthermore, the photoconductive layer can be of a double structure of different materials, i.e. a lower photoconductive layer of e.g. a-Si:H film and an upper photoconductive layer of e.g. a-SiGe:H film.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1, 4 and 7 are cross-sectional profiles of the present electrophotographic photosensitive members.

Figs. 2 and 5 are diagrams showing a relationship between the thickness of charge injection blocking layer and dark decay of the photosensitive member.

Figs. 3 and 6 are diagrams showing a

relationship between the thickness of charge injection blocking layer, and the electrostatic charge acceptance or the residual potential of the photosensitive member.

## PREFERRED EMBODIMENTS OF THE INVENTION

The present invention will be described in detail below, referring to Examples and the drawings, which are not limitative of the present invention.

### Example 1

An electrophotographic photosensitive member having a cross-sectional profile as shown in Fig. 1 was prepared.

As aluminum drum whose outer surface was polished to the mirror surface degree was fixed as an electroconductive support 1 in a vacuum chamber, which was evacuated to about 1x10$^{-6}$ Torr. Then, a gas mixture of monosilane ($SiH_4$), ethylene ($C_2H_4$) and hydrogen ($H_2$) was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, ($SiH_4$ + $C_2H_4$)/($H_2$ + $SiH_4$ + $C_2H_4$), of 0.6 and a gas ratio, $C_2H_4$/($SiH_4$ + $C_2H_4$), of 0.05. Diborane ($B_2H_6$) was introduced thereto to make a gas ratio, $B_2H_6$/($SiH_4$ + $C_2H_4$), of 1x10$^{-4}$. The aluminum drum 1 was kept at 250°C and an a-SiC:H film was formed to a thickness of 1 μm as a charge blocking layer 2 on the aluminum drum 1 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

Successively, a gas mixture of $SiH_4$, $H_2$ and $B_2H_6$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $SiH_4$/($SiH_4$ + $H_2$), of 0.6 and a gas ratio, $B_2H_6$/$SiH_4$, of 3x10$^{-6}$. The aluminum drum 1 was kept at 250°C, and an a-Si:H film was formed to a thickness of 20 μm as a lower photoconductive layer 3 on the charge blocking layer 2 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

Then, a gas mixture of $SiH_4$, $GeH_4$ and $H_2$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, ($SiH_4$ + $GeH_4$)/($H_2$ + $SiH_4$ + $GeH_4$), of 0.6 and a gas ratio, $GeH_4$/($SiH_4$ + $GeH_4$), of 0.2. Furthermore, $B_2H_6$ was introduced thereto to make a gas ratio, $B_2H_6$/($SiH_4$ + $GeH_2$), of 1x10$^{-6}$. The aluminum drum 1 was kept at 250°C, and an a-SiGe:H film was formed to a thickness of 1 μm as an upper photoconductive layer 4 on the lower photoconductive layer 3 by high frequency glow discharge at 13.56 MHz and a power of 300 W (optical band gap: 1.5 eV; conduction type: p-type).

Then, a gas mixture of $SiH_4$, $C_2H_4$ and $H_2$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, ($SiH_4$ + $C_2H_4$)/($H_2$ + $SiH_4$ + $C_2H_4$), of 0.6 and a gas ratio, $C_2H_4$/($SiH_4$ + $C_2H_4$), of 0.05, and an a-SiC:H film was formed to a thickness of 0 to 3 μm as a charge injection blocking layer 5 on the upper photoconductive layer 4 by high frequency glow discharge at 13.56 MHz and a power of 300 W (optical band gap: 1.9 eV; conduction type: n-type).

Then, the same gas mixture as used in forming the charge injection blocking layer 5 was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, ($SiH_4$ + $C_2H_4$)/($H_2$ + $SiH_4$ + $C_2H_4$), of 0.6 and a gas ratio, $C_2H_4$/($SiH_4$ + $C_2H_4$), of 0.6, and an a-SiC:H film was formed to a thickness of 0.4 μm as a moisture and corona-resistant layer 6 on the charge injection blocking layer 5 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

In Fig. 2, a relationship between the thickness of the charge injection blocking layer 5 (μm) on the abscissa and the dark decay (3-second value) of the photosensitive member on the ordinate is shown. By providing the charge injection blocking layer 5 in the electrophotographic photosensitive member, the dark decay can be improved. Better electrostatic charge acceptance and the residual potential of the photosensitive member can be also obtained thereby, as shown in Fig. 3.

### Example 2

An electrophotographic photosensitive member having a cross-sectional profile as shown in Fig. 4 was prepared.

An aluminum drum whose outer surface was polished to the mirror surface degree was fixed as an electroconductive support 1 in a vacuum chamber, which was evacuated to about 1x10$^{-6}$ Torr. Then, a gas mixture of monosilane ($SiH_4$), ethylene ($C_2H_4$) and hydrogen ($H_2$) was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, ($SiH_4$ + $C_2H_4$)/($H_2$ + $SiH_4$ + $C_2H_4$), of 0.6 and a gas ratio, $C_2H_4$/ ($SiH_4$ + $C_2H_4$), of 0.05. Diborane ($B_2H_6$) was introduced thereto to make a gas ratio, $B_2H_6$/($SiH_4$ + $C_2H_4$), of 1x10$^{-4}$. The aluminum drum1 was kept at 250°C and an a-SiC:H film was formed to a thickness of 1 μm as a charge blocking layer 2 on the aluminum drum 1 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

Successively, the gas ratio, $B_2H_6$/($SiH_4$ + $C_2H_4$), was changed to 3 x 10$^{-6}$, and an a-SiC:H film was formed to a thickness of 20 μm as a lower photoconductive layer 7 on the charge blocking layer 2 under the same high frequency glow discharge conditions as above.

Then, a gas mixture of $SiH_4$, $GeH_4$ and $H_2$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, ($SiH_4$ + $GeH_4$)/($H_2$ + $SiH_4$ +$GeH_4$), of 0.6 and a gas ratio, $GeH_4$/($SiH_4$ + $GeH_4$), of 0.2. $B_2H_6$ was introduced thereto to make a gas ratio, $B_2H_6$/($SiH_4$ + $GeH_4$), of 1x10$^{-6}$. The aluminum drum 1 was kept at 250°C, and an a-SiGe:H film was formed to a thickness of 1 μm as an upper photoconductive layer 4 on the lower photoconductive layer 7 by high frequency glow discharge at 13.56 MHz and a power of 300 W (optical band gap: 1.5 eV; conduction type: p-type).

Then, a gas mixture of $SiH_4$, $C_2H_4$ and $H_2$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, ($SiH_4$ + $C_2H_4$)/ ($H_2$ + $SiH_4$ + $C_2H_4$), of 0.6 and a gas ratio, $C_2H_4$/($SiH_4$ + $C_2H_4$) of 0.05, and an a-SiC:H film was formed to a thickness of 0 to 3 μm as a charge injection blocking layer 5 on the upper photoconductive layer 4 by high frequency glow discharge at 13.56 MHz and a power of 300 W (optical band gap: 1.9 eV; conduction type: n-type).

Then, the same gas mixture as used in forming the charge injection blocking layer 5 was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $(SiH_4 + C_2H_4)/(H2 + SiH_4 + C_2H_4)$, of 0.6 and a gas ratio, $C_2H_4/(SiH_4 + C_2H_4)$, of 0.6 and an a-SiC:H film was formed to a thickness of 0.4 µm as a moisture and corona-resistant layer 6 on the charge injection blocking layer 5 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

In Fig. 5, a relationship between the thickness of the charge injection blocking layer 5 (µm) on the abscissa and the dark decay (3-second value) of the photosensitive member on the ordinate is shown. By providing the charge injection blocking layer 5 in the electrophotographic photosensitive member, the dark decay can be improved. Better electrostatic charge acceptance and the residual potential of the photosensitive member can be also obtained thereby, as shown in Fig. 6.

Example 3

An electrophotographic photosensitive member having a cross-sectional profile as shown in Fig. 7 was prepared.

An aluminum drum whose outer surface was polished to the mirror surface degree was fixed as an electroconductive support 1 in a vacuum chamber, which was evacuated to about $1x10^{-6}$ Torr. Then, a gas mixture of monosilane ($SiH_4$), ethylene ($C_2H_4$) and hydrogen ($H_2$) was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $(SiH_4 + C_2H_4)/(H_2 + SiH_4 + C_2H_4)$, of 0.6 and a gas ratio, $C_2H_4/(SiH_4 + C_2H_4)$, of 0.05. Diborane ($B_2H_6$) was introduced thereto to make a gas ratio, $B_2H_6/(SiH_4 + C_2H_4)$ of $1x10^{-4}$. The aluminum drum 1 was kept at 250° C and and a-SiC:H film was formed to a thickness of 1 µm as a charge blocking layer 2 on the aluminum drum 1 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

Successively, a gas mixture of $SiH_4$, $H_2$ and $B_2H_6$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $SiH_4/(SiH_4 + H_2)$, of 0.6 and a gas ratio, $B_2H_6/SiH_4$, of $3x10^{-6}$. The aluminum drum 1 was kept at 250° C, and an a-Si:H film was formed to a thickness of 20 µm as a photoconductive layer 3 on the charge blocking layer 2 by high frequency glow discharge at 13.56 MHz and a power of 300 W. (optical band gap: 1.8 eV; conduction type: p-type).

Then, a gas mixture of $SiH_4$, $C_2H_4$ and $H_2$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $(SiH_4 + C_2H_4)/(H_2 + SiH_4 + C_2H_4)$, of 0.6 and a gas ratio, $C_2H_4/(SiH_4 + C_2H_4)$, of 0.05, and an a-Sic:H film was formed to a thickness of 0.5 to 2 µm as a charge injection blocking layer 5 on the photoconductive layer 3 by high frequency glow discharge at 13.56 MHz and a power of 300 W (optical band gap: 1.9 eV; conduction type: n-type)

Then, the same gas mixture as used in forming the charge injection blocking layer 5 was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $(SiH_4 + C_2H_4)/(H_2 + SiH_4 + C_2H_4)$, of 0.6 and a gas ratio, $C_2H_4/(SiH_4 + C_2H_4)$, of 0.6, and an a-SiC:H film was formed to a thickness of 0.4 µm as a moisture and corona-resistant layer 6 on the charge injection blocking layer 5 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

The thus prepared photosensitive member has a good electrostatic charge acceptance as in Examples 1 and 2.

Example 4

An electrophotographic photosensitive member having a cross-sectional profile as shown in Fig. 7 was prepared.

An aluminum drum whose outer surface was polished to the mirror surface degree was fixed as an electroconductive support 1 in a vacuum chamber, which was evacuated to about $1x10^{-6}$ Torr. Then, a gas mixture of monosilane ($SiH_4$), ethylene ($C_2H_4$) and hydrogen ($H_2$) was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $(SiH_4 + C_2H_4)/(H_2 + SiH_4 + C_2H_4)$, of 0.6 and a gas ratio, $C_2H_4/(SiH_4 + C_2H_4)$, of 0.05. Phosphine ($PH_3$) was introduced thereto to make a gas ratio, $PH_3/(SiH_4 + C_2H_4)$ of $1x10^{-4}$. The aluminum drum 1 was kept at 250° C and an a-SiC:H film was formed to a thickness of 1 µm as a charge blocking layer 2 on the aluminum drum 1 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

Successively, a gas mixture of $SiH_4$, $H_2$ and $B_2H_6$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $SiH_4/(SiH_4 + H_2)$, of 0.6 and a gas ratio, $B_2H_6/SiH_4$, of $0.5x10^{-6}$. The aluminum drum 1 was kept at 250° C, and an a-Si:H film was formed to a thickness of 20 µm as a photoconductive layer 3 on the charge blocking layer 2 by high frequency glow discharge at 13.56 MHz and a power of 300 W. (optical band gap; 1.8 eV; conduction type: n-type).

Then, a gas mixture of $SiH_4 + C_2H_4$ and $H_2$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $(SiH_4 + C_2H_4)/(H_2 + SiH_4 + C_2H_4)$, of 0.6 and a gas ratio, $C_2H_4/(SiH_4 + C_2H_4)$, of 0.05. Diborane ($B_2H_6$) was introduced thereto to make a gas ratio, $B_2H_6/(SiH_4 + C_2H_4)$, of $3 x 10^{-6}$, and an a-SiC:H film was formed to a thickness of 0.5 to 2 µm as a charge injection blocking layer 5 on the photoconductive layer 3 by high frequency glow discharge at 13.56 MHz and a power of 300 W (optical band gap: 1.9 eV; conduction type: p-type).

Then, the same gas mixture as used in forming the charge injection blocking layer 5 was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $(SiH_4 + C_2H_4)/(H_2 + SiH_4 + C_2H_4)$, of 0.6 and a gas ratio, $C_2H_4/(SiH_4 + C_2H_4)$, of 0.6, and an a-SiC:H film was formed to a thickness of 0.4 µm as a moisture and corona-resistant layer 6 on the charge injection blocking layer 5 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

The thus prepared photosensitive member has a good electrostatic charge acceptance as in Examples 1 and 2.

Example 5

An electrophotographic photosensitive member having a cross-sectional profile as shown in Fig. 1 was prepared.

An aluminum drum whose outer surface was polished to the nirror surface degree was fixed as an electroconductive support 1 in a vacuum chamber, which was evacuated to about $1x10^{-6}$ Torr. Then, a gas mixture of monosilane ($SiH_4$), ethylene ($C_2H_4$) and hydrogen ($H_2$) was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $(SiH_4 + C_2H_4)/(H_2 + SiH_4 + C_2H_4)$, of 0.6 and a gas ratio, $C_2H_4/(SiH_4 + C_2H_4)$, of 0.05. Phosphine ($PH_3$) was introduced thereto to make a gas ratio, $PH_3/(SiH_4 + C_2H_4)$ of $1x10^{-4}$. The aluminum drum 1 was kept at 250° C and an a-SiC:H film was formed to a thickness of 1 μm as a charge blocking layer 2 on the aluminum drum 1 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

Successively, a gas mixture of $SiH_4$, $H_2$ and $B_2H_6$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $SiH_4/(SiH_4 + H_2)$, of 0.6 and a gas ratio, $B_2H_6/SiH_4$, of $0.5x10^{-6}$. The aluminum drum 1 was kept at 250° C, and an a-Si:H film was formed to a thickness of 20 μm as a lower photoconductive layer 3 on the charge blocking layer 2 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

Then, a gas mixture of $SiH_4$, $GeH_4$ and $H_2$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $(SiH_4 + GeH_4)/(H_2 + SiH_4 + GeH_4)$, of 0.6 and a gas ratio, $GeH_4/(SiH_4 + GeH_4)$, of 0.2. The aluminum drum 1 was kept at 250° C, and an a-SiGe:H film was formed to a thickness of 1 μm as an upper photoconductive layer 4 on the lower photoconductive layer 3 by high frequency glow discharge at 13.56 MHz and a power of 300 W (optical band gap: 1.5 eV; conduction type: n-type).

Then, a gas mixture of $SiH_4$, $C_2H_4$ and $H_2$ was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $(SiH_4 + C_2H_4)/(H_2 + SiH_4 + C_2H_4)$, of 0.6 and a gas ratio, $C_2H_4/(SiH_4 + C_2H_4)$, of 0.05. Diborane ($B_2H_6$) was introduced thereto to make a gas ratio, $B_2H_6/(SiH_4 + C_2H_4)$ of $3 \times 10^{-6}$, and an a-SiC:H film was formed to a thickness of 0.5 to 2 μm as a charge injection blocking layer 5 on the upper photoconductive layer4 by high frequency glow discharge at 13.56 MHz and a power of 300 W (optical band gap: 1.9 eV; conduction type: p-type).

Then, the same gas mixture as used in forming the charge injection blocking layer 5 was introduced at a pressure of 0.5 Torr into the vacuum chamber in a gas ratio, $(SiH_4 + C_2H_4)/(H_2 + SiH_4 + C_2H_4)$, of 0.6 and a gas ratio, $C_2H_4/(SiH_4 + C_2H_4)$, of 0.6, and an a-SiC:H film was formed to a thickness of 0.4 μm as a moisture and corona-resistant layer 6 on the charge injection blocking layer 5 by high frequency glow discharge at 13.56 MHz and a power of 300 W.

The thus prepared photosensitive member had a good electrostatic charge acceptance as in Example 1.

According to the present invention, an electrophotographic photosensitive member with excellent electrostatic charge acceptance and photosensitivity can be provided by providing on a photoconductive layer a charge injection blocking layer having a different conduction type and a broader band gap from and than those of the photoconductive layer.

**Claims**

1. An electrophotographic photosensitive member, which comprises an electroconductive support, a photoconductive layer made from hydrogen-containing amorphous silicon as a matrix, a charge injection blocking layer having a different conduction type from that of the photoconductive layer and a broader optical band gap than that of the photoconductive layer and a moisture and corona-resistant layer, laid one upon another successively on the electroconductive support.

2. An electrophotographic photosensitive member, which comprise an electroconductive support, a charge blocking layer, a photoconductive layer made from hydrogen-containing amorphous silicon as a matrix, a charge injection blocking layer having a different conduction type from that of the photoconductive layer and a broader optical band gap than that of the photoconductive layer and a moisture and corona-resistant layer, laid one upon another successively on the electroconductive support.

3. An electrophotographic photosensitive member according to Claim 1 or 2, wherein the photoconductive layer is of p-type, and the charge injection blocking layer is of n-type or intrinsic type.

4.An electrophotographic photosensitive member according to Claim 1 or 2, wherein the photoconductive layer is of n-type and the charge injection blocking layer is of p-type or intrinsic type.

5. An electrophotographic photosensitive member according to any one of claims 1 to 4 wherein the charge injection blocking layer is made from a film of a-SiC:H, a-SiC:X:H, or a-SiN:X:H wherein X represents an halogen atom.

6. An electrophotographic photosensitive member according to any one of claims 1 to 5 wherein the photoconductive layer is made of a single film of a-Si:H or a-SiGe, or a double film of a-Si:H or a-SiC:H and a SiGe:H.

7. An electrophotographic photosensitive member according to any one of claims 1 to 6 wherein the photoconductive layer has an optical band gap of 1.5 to 1,8 eV and the charge injection blocking layer has an optical band gap of 1.9 to 2.9 eV.

8. An electrophotographic photosensitive

member according to any one of claims 1 to 7 wherein the moisture and corona-resistant layer is made from a film of a-SiC:H having a high carbon content.

9. An electrophotographic photosensitive member according to Claim 2, wherein the charge blocking layer is made from the same film as that for the charge injection blocking layer.

10. An electrophotographic photosensitive member according to Claim 1, wherein the photoconductive layer has a thickness of 20 to 50 µm, the charge injection blocking layer has a thickness of 0.5 to 3 µm, and the moisture and corona-resistant layer has a thickness of 0.2 to 1 µm.

11.An electrophotographic photosensitive member according to Claim 2, wherein the charge blocking layer has a thickness of 0.5 to 3 µm, the photoconductive layer has a thickness of 20 to 50 µm, the charge injection blocking layer has a thickness of 0.5 to 3 µm, and the moisture and corona-resistant layer has a thickness of 0.2 to 1 µm.

12. An electrophotographic photosensitive member according to any one of claims 1 to 11 wherein the individual layers are formed by CVD, sputtering or vapor deposition alone or in their combination.

13. An electrophotographic photsensitive member according to any one of claims 1 to 12 wherein the conduction type of the photoconductive layer and the charge injection blocking layer is controlled by doping with boron or phosphorus.

FIG. 1

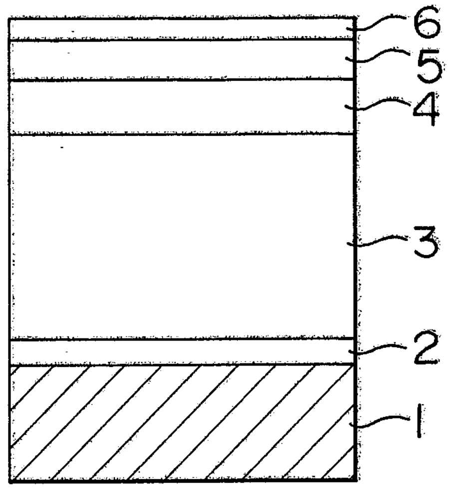

6
5
4
3
2
1

FIG. 2

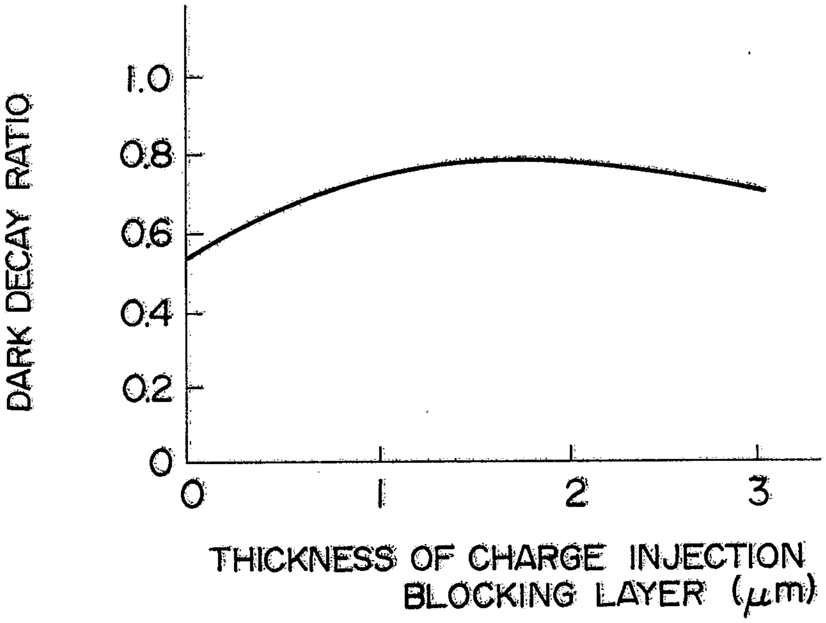

DARK DECAY RATIO
1.0
0.8
0.6
0.4
0.2
0
0
1
2
3
THICKNESS OF CHARGE INJECTION BLOCKING LAYER (μm)

FIG. 3

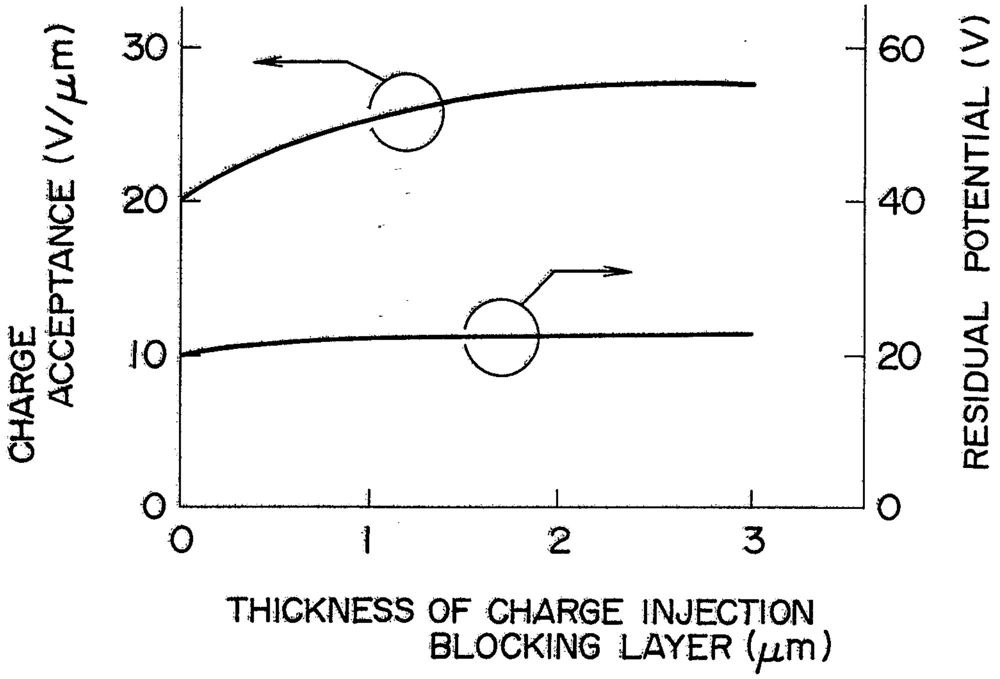

CHARGE ACCEPTANCE (V/$\mu$m)
30
20
10
0
RESIDUAL POTENTIAL (V)
60
40
20
0
0
1
2
3
THICKNESS OF CHARGE INJECTION BLOCKING LAYER ($\mu$m)

FIG. 4

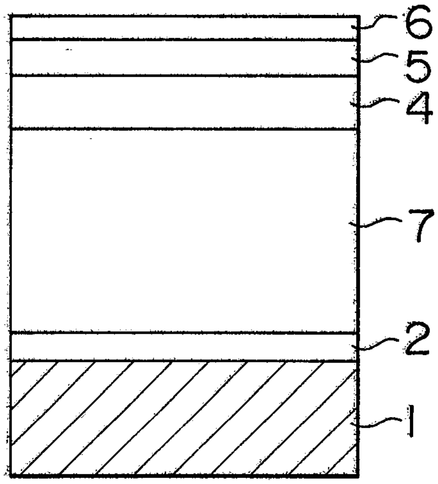

6
5
4
7
2
1

FIG. 5

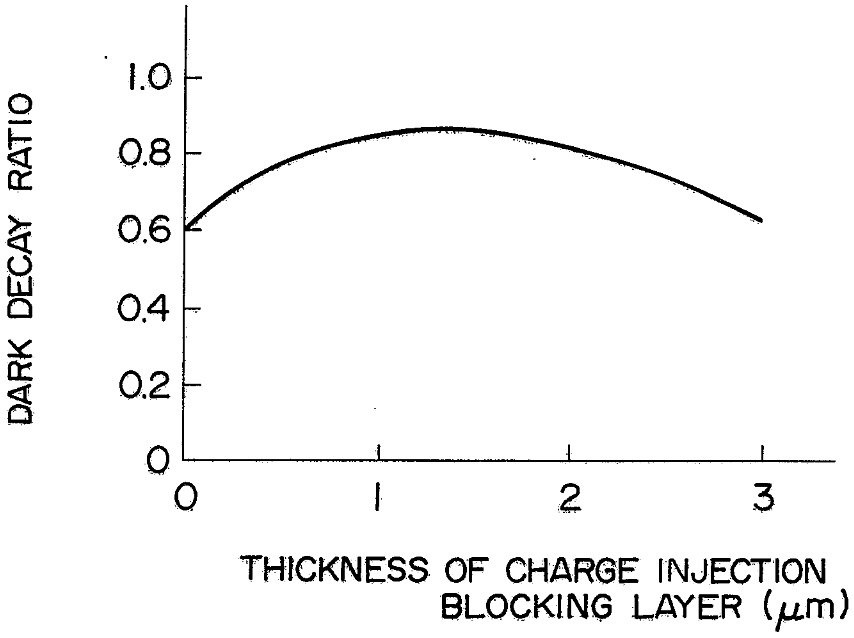

DARK DECAY RATIO
1.0
0.8
0.6
0.4
0.2
0
0
1
2
3
THICKNESS OF CHARGE INJECTION BLOCKING LAYER (μm)

FIG. 6

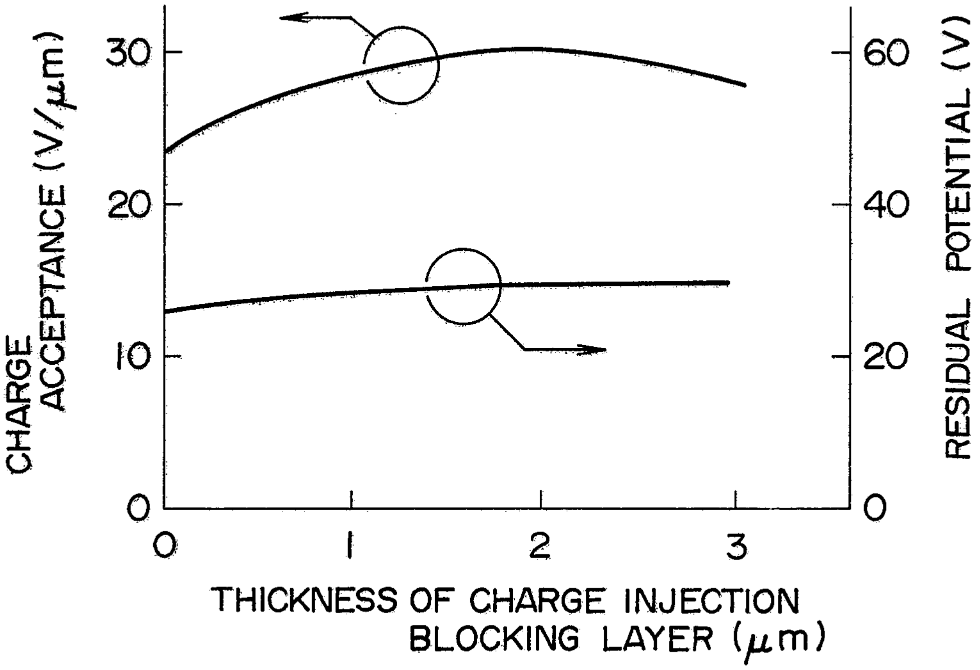

CHARGE ACCEPTANCE (V/μm)
30
20
10
0
RESIDUAL POTENTIAL (V)
60
40
20
0
0
1
2
3
THICKNESS OF CHARGE INJECTION BLOCKING LAYER (μm)

FIG. 7